PATTERN FORMATION IN LIQUID CRYSTALS: THE SAFFMAN-TAYLOR INSTABILITY AND THE DYNAMICS OF PHASE SEPARATION

A dissertation submitted
to Kent State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

by
Roland Ennis
May 2004
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Preface

Notation

Einstein summation convention

We imply summation when an indexed quantity – subscript, superscript or mixed
is labeled by greek indices and the same index appears twice in the same tensor
or product. We do not imply summation over latin indices or when the same index
appear twice in two terms separated by a plus or minus sign. The summation is taken
over the whole range of available values for the respective index pair. An example
for this notation is given by

\[ A_{\alpha \beta \alpha ii} + B_{\alpha \beta j kj} = \sum_{k,l} A_{kllki}i + \sum_{l} B_{l l j kj}. \] (1)

Tensor indices can be written both latin and greek and mixed. We will use greek
indices exclusively to imply summation. This representation has several advantages:
1) The free indices can be identified quickly in lengthy expressions involving many
indices. 2) It permits the representation of diagonal elements of a tensor. 3) A latin
index can appear in the same expression more than twice without causing ambiguity.
We will sometimes use greek letters to denote quantities (e.g., inverse temperature
\( \beta \), polarizability \( \alpha \)) that are not indices. An expression may contain a pair of \( \beta \)'s
and also the inverse temperature:

\[ \sum_{k,l} \frac{\partial^4 \beta F}{\partial x_k \partial x_k \partial x_l \partial x_l} = \beta F_{\alpha \alpha \beta \beta}. \] (2)
Partial derivatives: comma notation

Partial derivatives are represented by a comma followed by the variable

\[ \frac{\partial f}{\partial S} = f_S. \]  \hspace{1cm} (3)

If the partial derivative is with respect to a spatial coordinate, the comma is followed by the index of the basis coordinate:

\[ \frac{\partial f}{\partial x_k} = f_k. \]  \hspace{1cm} (4)

In cases where the spatial derivative is the only index we sometimes omit the comma, provided that this causes no ambiguity

\[ f_k = f_k. \]  \hspace{1cm} (5)

Similarly, if the derivative applies to a tensor enclosed by brackets we omit the comma. For example

\[ \frac{\partial \langle \sigma_{ij} \rangle}{\partial x_k} = \langle \sigma_{ij} \rangle_k \]  \hspace{1cm} (6)

\[ \frac{\partial (Q_{ij} - \langle \sigma_{ij} \rangle)}{\partial x_k} = (Q_{ij} - \langle \sigma_{ij} \rangle)_k \]  \hspace{1cm} (7)

Evaluation at a point

The spatial argument of a function can be written alternatively by writing the coordinate after a vertical bar.

\[ Q_{ij}(r) \equiv Q_{ij|r} \]  \hspace{1cm} (8)
Example

As an example for the notation we write the Taylor expansion of the tensor $Q_{ij}$ about a location $\mathbf{r}$:

$$Q_{ij}(\mathbf{r} + \mathbf{h}) \simeq Q_{ij} + Q_{ij,\alpha\beta}r_\alpha r_\beta + \frac{1}{2}Q_{ij,\alpha\beta\gamma\delta}r_\alpha r_\beta r_\gamma r_\delta,$$  \hspace{1cm} (9)

where $r = |\mathbf{h}|$ and $r_k \equiv \mathbf{h} \cdot \mathbf{e}_k / |\mathbf{h}|$, and $\mathbf{e}_k$ is the $k^{th}$ basis vector of an orthonormal basis.

Functional arguments

Functional arguments are put in square brackets, indicating dependence on a continuous field, or in curly braces, indicating dependence on a discrete set of locations, e.g.

$$f[\mathbf{h}] = f \left( \int h(\mathbf{r}) \, d^3\mathbf{r} \right)$$ \hspace{1cm} (10a)

$$f\{h\} = f(h(\mathbf{r}_1), ..., h(\mathbf{r}_n))$$ \hspace{1cm} (10b)

If the functional also has non-functional arguments, these are put in round parentheses following the functional-argument list, e.g.,

$$f[\mathbf{h}, H](y, z) = (z + y)^3 \int h(\mathbf{r}) \, H(\mathbf{r} - \mathbf{r}') \, d^3\mathbf{r} \, d^3\mathbf{r}'$$ \hspace{1cm} (11)

Dyads

Two tensors of rank $p$ and $q$, respectively can be set adjacently in an expression, without any summation over indices. The resulting product is a tensor of rank $p + q$.  

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E.g., for two tensors $T_{ijkl}$ and $U_{lm}^1$

$$(TU)_{ijklmn} = T_{ijkl}U_{mn}.$$  \hfill (12)

We always mean a dyadic product when we write two adjacent tensors of arbitrary rank. A scalar product is indicated by a dot-product. Thus $\mathbf{v} \mathbf{w}$ is always a second rank tensor, while $\mathbf{v} \cdot \mathbf{w}$ is a scalar.

---

$^1$In mathematical literature, this dyadic product is sometimes written as a tensor product $\mathbf{T} \otimes \mathbf{U}$. 

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List of symbols

The following lists does not necessarily contain all symbols appearing in this dissertation. The list of standard symbols contains symbols that are in widespread use and are not usually replaced by different symbols. The list of commonly used symbols are standard symbols that may be represented differently elsewhere. The list of standard symbols in liquid crystal literature are just that. The list of non-standard symbols contains symbols that are introduced in this dissertation for notational convenience. Another set of symbols, used in the description of the generalized forces on density and nematic order parameter, is given in Table 6.4, page 136.
Standard symbols

\( k_B \) \quad \text{Boltzmann constant, } 1.38 \cdot 10^{-23} \text{J/K}

\( \varepsilon_0 \) \quad \text{vacuum permittivity, } 8.85 \cdot 10^{-12} \text{As/Vm}

\( h \) \quad \text{Planck constant, } 6.63 \cdot 10^{-34} \text{Js}

\( T \) \quad \text{absolute temperature}

\( \beta \) \quad \text{“inverse temperature”, } (k_B T)^{-1}

\( \delta_{ij} \) \quad 2nd rank identity tensor, Kronecker delta

\( \delta (r - r') \) \quad \text{Dirac’s delta function}

\( \mathbf{I} \) \quad \text{identity matrix or tensor}

\( \int_{\partial \Omega} \) \quad \text{integral over boundary of region } \Omega

\( \int \, d^d \mathbf{r} \) \quad \text{integral over all space, } d \text{ dimensions}

\( f^{(n)} \) \quad n^{th} \text{ total derivative, } d^n f / dx^n; \text{ also the } n^{th} \text{ component of a tuple}

\( \delta F / \delta y \) \quad \text{functional derivative}

\( \hat{e}_k \) \quad \text{cartesian unit vector}

\( P_2 (x) \) \quad \text{second Legendre polynomial, } \frac{3}{2} x^2 - \frac{1}{2}

\( g (r_1, r_2) \) \quad \text{pair distribution function}

\( \rho \) \quad \text{(number) density}

\( \mathbf{j} \) \quad \text{number current}

\( f \in C^\infty \) \quad f \text{ is an arbitrary number of times continuously differentiable.}

\( f \in C_0^\infty \) \quad f \in C^\infty \text{ and vanishes outside a bounded region.}
Commonly used symbols

\( y_{,k} \) \hspace{1cm} partial derivative (contravariant), \( \partial y / \partial x_k \)

\( f,g \) \hspace{1cm} partial derivative, \( \partial f / \partial g \)

\( Z \) \hspace{1cm} partition function, sum of states

\( \phi \) \hspace{1cm} volume fraction

\( \text{Tr} \ f \ (\sigma) \) \hspace{1cm} trace, sum over all states of \( \sigma \)

Standard symbols in liquid crystal literature

\( \hat{n}, n_i \) \hspace{1cm} molecular long axis; also used for the nematic director

\( \hat{l}, l_i \) \hspace{1cm} alternative symbol for the molecular long axis

\( \hat{\mathbf{N}}, N_i \) \hspace{1cm} nematic director = average of mol. long axis

\( \sigma, \sigma_{ij} \) \hspace{1cm} molecular orientation, \( \frac{3}{2} n_i n_j - \frac{1}{2} \delta_{ij} \)

\( Q, Q_{ij} \) \hspace{1cm} nematic tensor order parameter, \( \sigma_{ij} \)

\( \hat{L}, \hat{M}, \hat{N} \) \hspace{1cm} eigenvectors of \( Q_{ij} \),

\[
Q_{ij} = -L_i L_j (S - P) / 2 - M_i M_j (S + P) / 2 + N_i N_j S
\]

\( S \) \hspace{1cm} scalar order parameter, \( \frac{3}{2} (\hat{\mathbf{N}} \cdot \hat{n})^2 - \frac{1}{2} \), largest eigenvalue of \( Q_{ij} \)

\( P \) \hspace{1cm} biaxiality parameter of \( Q_{ij} \)

\( \alpha_{ij} \) \hspace{1cm} molecular polarizability
Non-standard symbols

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<td>( y ) is a continuous functional argument of ( f )</td>
<td>xiv</td>
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<tr>
<td>( f {y } )</td>
<td>( y ) is a discrete functional argument of ( f )</td>
<td>xiv</td>
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<td>( \mathbf{r}_{12} )</td>
<td>( \mathbf{r}_2 - \mathbf{r}_1 )</td>
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<tr>
<td>( r )</td>
<td>magnitude of ( \mathbf{r}_{12},</td>
<td>\mathbf{r}_{12}</td>
</tr>
<tr>
<td>( r_k )</td>
<td>( k^{\text{th}} ) component of direction of ( \mathbf{r}<em>{12}, \mathbf{r}</em>{12} \cdot \mathbf{\hat{e}}_k/</td>
<td>\mathbf{r}_{12}</td>
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<td>( \langle \xi \rangle_H )</td>
<td>canonical average of ( \xi ) in the local field ( \mathbf{H} )</td>
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<td>( P_{ijkl} )</td>
<td>traceless, symmetric projector, ( (\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il})/2 - \delta_{ij}\delta_{kl}/3 )</td>
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<td>( T_{ij} )</td>
<td>dipole tensor, ( (3r_i r_j - \delta_{ij})/4\pi\varepsilon_0 r^3 )</td>
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<td>( J_{ijkl} )</td>
<td>orientational part of the Van-der-Waals kernel, ( (3r_i r_k - \delta_{ik})(3r_j r_l - \delta_{jl}) )</td>
<td>83</td>
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<td>( K_{ijkl} )</td>
<td>traceless, symmetric part of ( J_{ijkl}, P_{ij\alpha\beta}J_{\alpha\beta kl} )</td>
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<tr>
<td>( [A_{ij}]^# )</td>
<td>traceless, symmetric part of ( A_{ij}, P_{ij\alpha\beta}A_{\beta\alpha} )</td>
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Part I

Phase Separation in Nematic Mixtures
Chapter 1

Overview

This chapter gives a bird’s eye view of the contents of the first part of this dissertation. The first part is devoted to phase separation of mixtures of nematic liquid crystals and/or isotropic fluids. In chapter two we introduce the technological system that we are interested in, polymer dispersed liquid crystals, whose theoretical understanding requires an understanding of phase separation in mixtures of liquid crystals. We point out the shortcomings of previous theoretical/numerical work and introduce the approach that we are going to use in describing phase separation in nematic mixtures. In chapter three we introduce functional derivatives for those, who are not familiar with them and describe how we enforce constraints on the generalized force on the nematic order parameter. In chapter four we describe the free energy of elastic deformations in liquid crystals. We discuss the notorious “$K_{13}$-problem,” which states that a local description of the free energy by means of a gradient expansion that includes all symmetry allowed-terms, will not lead to a well-posed minimization problem for the free energy. The conclusion of this chapter leads us to suggest a non-local mean field description circumventing this problem. In the fifth chapter we develop such a procedure based on mean field theory, and show that this procedure leads to a well-posed minimization problem. The resulting procedure is suitable for dynamic systems. In the sixth chapter we apply this procedure to a system of par-
ticles that pair-wise interact by London forces alone. Including the pair-distribution function in the single particle potential permits a description of steric interactions within the same framework. We derive the generalized forces on nematic order parameters and densities in a $n$-ary mixture in fully non-local form and proceed to apply various simplifications, in particular to isotropic pair-distribution functions. We then perform gradient expansion on the generalized forces, and summarize the results in tabular form. We discuss the results in the limit for a binary mixture of one nematic and one isotropic component. In chapter seven we derive the dynamic equations that we are using for numerical simulation. In chapter eight we discuss why one needs to include thermal fluctuation to the simulation and derive the Langevin equation for a nematic tensor order parameter. In chapter nine we describe the nematic order parameter diagram and the phase diagram, respectively, and show the diagrams corresponding to the generalized forces that we are using. In chapter 10 we develop a procedure for efficient evaluation of the canonical average of the molecular orientation and of the free energy, both of which are used in the simulation. We also describe how we characterize the growth of length scales in the system. In chapter 11 we discuss some issues occurring in numerical simulation, which lead to constraints for choosing length and time scales. In chapter 12 we present the results of numerical simulations for various systems: binary isotropic mixtures, nematic liquid crystal enclosed in a spherical cavity, deformation modes in a strongly deformed hybrid cell, and for a binary mixture of a nematic and an isotropic fluid.
Chapter 2

Introduction

This work is about phase separation in liquid crystals. It was motivated by the desire to model the creation of Polymer Dispersed Liquid Crystals (PDLCs). In some sense, PDLC’s are a form of self-assembled liquid crystal displays. If the liquid crystal is in the minority phase, phase separation leads to the formation of small droplets of liquid crystal embedded in a polymer matrix. The equilibrium configuration of the director field depends on the character and strength of the forces acting on the director at the liquid crystal/polymer interface. Figure 2.1 shows configurations for strong anchoring of the director parallel to the interface, negligible anchoring and intermediate and strong anchoring, respectively of the director perpendicular to the interface. These configurations are called “bipolar,” “constant” or “homogenous,” “axial” and “radial,” respectively. Except for the radial configuration, the director field has, in a spherical droplet, a single axis of continuous rotational symmetry.

The rotational symmetry axes of the droplets are randomly oriented throughout the polymer matrix (figure 2.2, right). Incident light is scattered because of the refractive-index mismatch at the polymer/liquid-crystal interface. Application of an external field re-orient the droplet axes, and if the refractive index of the polymer matrix is carefully chosen, the index mismatch can be minimized for some directions of the incident light, minimizing scattering. A special PDLC device is a
Figure 2.1: Director configuration in a spherical droplet for various preferred alignments at the liquid crystal/polymer interface. From left to right: bipolar configuration for strong anchoring parallel to the surface, constant director for negligible anchoring, axial (with ring defect) and radial configuration for respectively intermediate and strong anchoring perpendicular to the surface.

holographic PDLC [1][2][3] (figure 2.3), in which the droplets are not distributed randomly throughout the polymer matrix, but periodically along at least one dimension. Such a device is a diffraction grating which can be switched on and off, permitting, for example, beam steering. Other devices that are assembled by phase separation, with liquid crystal in the majority phase, are polymer stabilized liquid crystals and polymer stabilized cholesteric texture.

Phase separation in liquid crystals is technologically important, and researchers have put forth various models. This dissertation addresses some of the shortcomings of these models. On the other hand, anybody who deals with problems of comparable complexity has to make approximations and so will we: while the above-mentioned devices employ polymers, we will not address the physics of polymers at all. (The physics of polymers will add a large number of degrees of freedom, like internal con-
Figure 2.2: Working principle of a PDLC device. Left: droplets are randomly oriented. The refractive index does not match for most droplets and incident light is strongly scattered, including back scattering. The device appears opaque. Right: applied voltage aligns droplets. The refractive index of the polymer matrix is matched to reduce scattering in this state and the device is transparent.

Figure 2.3: In a holographic PDLC device the droplets are not randomly oriented but periodic along at least one direction, forming a grating.
configuration energy of polymer chains, elasticity of the polymer matrix, polydispersity of molecular volumes and chemical reactions, to name a few.) Our goal is to find a satisfactory approach of describing the dynamics of a system consisting of nematic order-parameter and concentration fields. When performing numerical integration of the dynamic equations we will further simplify by assuming an isotropic pair-distribution function and a binary incompressible mixture, with only one material exhibiting a nematic phase.

2.1 Previous work and its shortcomings

Researchers often employ a Landau-Ginzburg expansion of the free energy density to model the physical system, i.e., a power series in the fields and their gradients of the system. The homogenous terms are expanded to the lowest power necessary to describe salient details of the system, which in most cases is a fourth order power series, while the gradient terms are typically taken to be quadratic in the field and its gradients. Most researchers modeling phase separation in liquid crystals use such an approach, e.g., [4][5][6]. Both the power series expansion of the homogenous terms (which is called “Landau-expansion”) and the squared gradient terms have significant drawbacks. The first, because a truncated power series is only a good approximation close to some selected point. Unfortunately, in a phase-separating liquid-crystal system we do not have the liberty to determine what this point should be: we show next that the local concentration effectively rescales the temperature, and therefore the state of the local subsystem may be very far from the point of expansion.
The free energy density $\mathcal{F}$, for a homogenous system of a uniaxial nematic liquid crystal in Maier-Saupe mean field theory [7][8][9] is given by this equation\(^1\):

\[\beta \mathcal{F} = -\ln \int_0^1 \exp \left(5T^* \frac{\phi}{T} \left( S P_2(x) - \frac{1}{2} S^2 \right) \right) dx,\]  

(2.1)

where $P_2(x) \equiv (3x^2 - 1)/2$ is the second Legendre polynomial. The scalar nematic order parameter $S$ is defined as the average of the second Legendre polynomial of the projection $\mathbf{n} \cdot \mathbf{N}$ of the molecular long axis $\mathbf{n}$ onto its average direction $\mathbf{N}$ as measured over some short time interval, $S \equiv \overline{P_2(\mathbf{n} \cdot \mathbf{N})}$. The overbar denotes an “out-of-equilibrium” average, where the underlying probability distribution is unknown. The Boltzmann-weighted average will instead be denoted with pointed brackets, as in $\langle P_2 \rangle$. The temperature is $T$ and $\beta \equiv (k_B T)^{-1}$ is “inverse temperature.” The volume fraction of liquid crystal is $\phi$. (In a pure liquid crystal, ignoring free volume, $\phi = 1$, of course. Equation (2.1) is the contribution of nematic order to the free energy, in both pure liquid crystal and mixtures.) The nematic pseudo-critical temperature $T^*$ is defined as the temperature at which the free energy density (2.1) has two global minima. At all other temperatures $\mathcal{F}$ has only one global minimum, which is at $S = 0$ (the isotropic phase) for temperatures $T > T^*$ and at some $S \neq 0$ (the nematic phase) otherwise. The temperature in (2.1) only occurs as a product $T\phi^{-1}$, thus, given a system temperature $T$, a region in space described by a local volume fraction $\phi(\mathbf{r})$ can equivalently be described by a local temperature $T_{\text{eff}}(\mathbf{r}) \equiv T/\phi(\mathbf{r})$.

\(^1\)This can be found for example, in slightly different form, in the textbook by Plischke and Bergerson [10].
Expanding (2.1) in $S = 0$ yields\(^2\)

$$\beta F \simeq \frac{5}{2} \left( \frac{T}{T^* \phi} - 1 \right) \left( \frac{T^* \phi}{T} S \right)^2 - \frac{25}{21} \left( \frac{T^* \phi}{T} S \right)^3 + \frac{25}{28} \left( \frac{T^* \phi}{T} S \right)^4. \quad (2.2)$$

Figure 2.4 illustrates that (2.2) does not yield the correct behavior of the nematic order parameter for a varying effective temperature. The first image shows the correct phase behavior, as predicted from (2.1). The second image shows the phase diagram for a free energy of the form (2.2). It is even qualitatively incorrect: the equilibrium order parameter should always be decreasing with increasing effective temperature. The third image shows the same expansion, but here we did remove the concentration/temperature dependence from the coefficients in the power series: we simply set $T^* \phi / T = 1$ everywhere it occurs in a product with $S$ in (2.2), i.e., except for the first parenteses. This diagram shows the correct monotonicity, but the nematic-isotropic transition temperature is quite different from the original phase diagram. Also, the nematic order-parameter attains really large values, even larger than one, which is incompatible with its definition. We should remark at this point that, of course one can take a different point of expansion, which may adjust better to the phase-diagram of the Maier-Saupe free energy, but this lacks theoretical foundation, other than that it is a good fit. Of course, a Landau expansion is a good first approximation, useful if not much is yet known about the system under consideration. It also lends itself to efficient numerical evaluation, but we show in chapter 10.2 that, at least for liquid-crystal binary mixtures, the generalized force

\(^2\)It is interesting to note that the next highest order in this expansion that yields a positive definite free energy is $S^{10}$.
Figure 2.4: Nematic phase diagrams. Each solution of $\frac{d\mathcal{F}}{dS} = 0$ is labeled s(table), m(eta-stable) and u(eta-stable). Top left: the phase diagram for the Maier-Saupe free energy. Top right: phase diagram for the free energy density expanded in $S = 0$. Bottom: phase diagram for the same Landau expansion, but only the quadratic term is taken to be temperature dependent. The Phase diagram for the Landau expansion exhibits the wrong qualitative behavior - the equilibrium order parameter does not decrease monotonously with temperature. The qualitative behavior is better for constant coefficients but this is poorly justified in a phase-separating system.
on the nematic order-parameter using the true mean field potential can be evaluated relatively efficiently.

The next problem, of the squared gradient term, is dealt with in detail in chapter 4. When using such a term, then as Nehring and Saupe have argued [11] second derivative terms should also be added, because they have the same symmetry and magnitude. Unfortunately, the inclusion of second-derivative terms will make the minimization problem of the free energy ill-posed. This was pointed out by Oldano and Barbero [12], and this problem is known in the field of liquid crystal research as the "$K_{13}$-problem." We will show an approach that circumvents this problem by realizing that it is not really the free energy that matters but only the generalized forces. The basic idea is to evaluate these generalized forces on the total free energy, i.e., without any gradient approximation, and only subsequently performing a gradient expansion, if so desired.

Most numerical work on phase separation in liquid crystals was carried out in two dimensions. For most problems the numerical evaluation of the dynamic equations is too expensive to be carried out in three-dimensional space, at least it was until the recent arrival of cheap and powerful computers. However, simulations on inhomogenous systems containing liquid crystals should best be carried out in three dimensions, because the topology of director configurations will be quite different from two dimensions. For example, in three dimensions the nematic order-parameter field for a liquid crystal enclosed by a spherical capsule with homeotropic boundary conditions can form a biaxial torus [13][14]. Obviously, such a configuration is not
possible in two dimensions\textsuperscript{3}. Another issue about using two dimensions is that using a two-dimensional order parameter tensor changes the character of the isotropic-nematic phase-transition from first to second order. The work by Lapeña, Glotzer, Langer and Liu\textsuperscript{[5]} uses such an approach.

Some work uses a scalar nematic order parameter field\textsuperscript{[4]}. While such may show the correct phase behavior (i.e., a field of droplets of the right concentration), the dynamics will likely not be described correctly as it will involve collective motion of defects that can only be captured by the presence of a director field. Also, a question of interest is how the director affects the shape of the droplets. Again, a scalar nematic order parameter can only lead to spherical droplets.

\textbf{2.2 Summary}

This dissertation will describe the dynamic equations of nematic order-parameter and concentration fields in mixtures of low-molecular weight molecules. Instead of using a Landau-expansion we use a fully non-local free-energy. Instead of a squared-gradient approach to elastic deformations we will develop a mean-field based approach that postpones any gradient expansion until after the generalized forces are determined, effectively circumventing the so-called \textquoteleft{}K\textsubscript{15}-problem." We are describing the nematic order-parameter field by the traceless, symmetric Q-tensor and perform all numerical simulations in three spatial dimensions.

\textsuperscript{3}If the system is a cylindrical extension of a two-dimensional field into three dimensions, this configuration will not be a minimum free-energy state.
Chapter 3

Background

3.1 Functional derivatives

This chapter will motivate and define functional derivatives because this work makes heavy use of them, and the reader may not be familiar with them.

A functional takes a function as an argument and maps it to a real number. One such functional is the integral over a function, for example

\[ f[y](x) = \int y(x_1, x) \, dx_1. \] (3.1)

We use square brackets \([y]\) to denote a functional dependence on the argument, i.e., \(f[y](x)\) indicates that \(f\) is a functional of \(y\) and a function of \(x\). In discussions we will write \(y\) without the argument when we mean the whole function, while \(y(x)\) is the function evaluated at a specific point \(x\). We interchangeably call a functional argument a “field” or a “function.” The class of functions that \(f\) can take as an argument will generally be restricted to functions that lead to a well-defined finite value of \(f\). A common functional in statistical mechanics is the integral over the locally defined free-energy density \(\mathcal{F}\), which in return is a function of an order parameter \(y\) and its
first derivative at the location $x^1$.

$$F[y] : y \in \mathcal{D}_y \to \mathbb{R}$$

$$F[y] = \int \mathcal{F}(x, y(x), y'(x)) \, dx,$$ (3.2a)

with the total free energy $F$, the functional that maps the field $y$ to a real number. The domain $\mathcal{D}_y$ of the functional denotes the set of admissible fields $y$. (The field $y'$ is known if $y$ is known, thus we do not need to write $\mathcal{D}_{y,y'}$.)

### 3.1.1 Generalized force and the Euler-Lagrange equation

For a static problem one may seek the field $y$ that minimizes the functional (3.2b). This will be described in detail in the chapter on elasticity and surface gradients (chapter 4, page 27). A necessary condition for a minimum of the total free energy is that $y$ is a solution to the Euler-Lagrange equation, which can be derived as follows. Given that $\bar{y}$ minimizes the functional, consider a small, arbitrary displacement $\varepsilon(x) = y(x) - \bar{y}(x)$, leading to a displacement $\delta F$ of the functional, to first order in $\varepsilon$:

$$\delta F \simeq F[\bar{y} + \varepsilon] - F[\bar{y}] = \int_{x_0}^{x_1} \left( \frac{\partial \mathcal{F}}{\partial y_{|x,\bar{y}(x),\bar{y}'(x)}} \varepsilon(x) + \frac{\partial \mathcal{F}}{\partial y'_{|x,\bar{y}(x),\bar{y}'(x)}} \varepsilon'(x) \right) \, dx. \tag{3.3}$$

(In the following will normally not use the asymptotic equals symbol when writing a functional displacement. Since $\delta F$ always represents a power series expansion in the variation $\varepsilon$, the presence of higher order terms in $\varepsilon$ is tacitly implied. Explicitly carrying this symbol would distract from additional approximations that we will

---

1We are considering a one-dimensional problem, but generalization to three dimensions (volume densities and volume integrals) is straight-forward.
make.) Integrating by parts the term with \( \varepsilon' \), we can write

\[
\delta F = \int_{x_0}^{x_1} \left( \frac{\partial F}{\partial y} - \frac{d}{dx} \frac{\partial F}{\partial y'} \right) \varepsilon dx + \left[ \frac{\partial F}{\partial y'} \varepsilon \right]_{x_0}^{x_1},
\]  

(3.4)

and because \( \bar{y} \) minimizes \( F \), the differential \( \delta F \) must vanish identically. Since this must be true for any variation \( \varepsilon \), this implies that \( \bar{y} \) is a solution of the Euler-Lagrange equation

\[
\frac{\partial F}{\partial y} - \frac{d}{dx} \frac{\partial F}{\partial y'} = 0.
\]  

(3.5)

The reverse is not true: the Euler-Lagrange equation does not imply that \( \bar{y} \) corresponds to a minimum of the free energy; it is only a necessary condition, implying that \( \mathcal{F} \) is stationary for the given field \( \bar{y} \). A candidate for a minimum can be verified by expanding \( \mathcal{F} \) to second order in \( \varepsilon \) and checking if an arbitrary but small displacement always leads to positive \( \delta F \). This form of the Euler-Lagrange equation only holds if \( \varepsilon \) is not subject to constraint. We treat some constrained displacements below in section 3.1.4.

### 3.1.2 Functional derivatives

We now define functional derivatives. We will define them as response to a local perturbation in the field. Consider the case that the system is not in equilibrium and therefore the free energy \( F[y] > F[\bar{y}] \). A displacement from this field is given by

\[
\delta F = \int_{x_0}^{x_1} G(x, y, y') \varepsilon(x) dx + [H(x, y) \varepsilon(x)]_{x_0}^{x_1}
\]  

(3.6)

\[2\] It is shown in the chapter on surface gradients that \( H \) should typically not depend on \( y' \).
where we define
\[
G(x, y, y') = \frac{\partial F}{\partial y} - \frac{d}{dx} \frac{\partial F}{\partial y'} \quad (3.7a)
\]
\[
H(x, y) = \frac{\partial F}{\partial y'}. \quad (3.7b)
\]

Now we partition the interval \([x_L, x_R]\) into \(n\) small disjoint intervals, \([x_L, x_R] = [x_0, x_1] \cup \ldots \cup [x_{n-1}, x_n = x_R]\). For simplicity and without loss of generality we take a constant interval length \(\Delta\). We assume that the displacement does not vary too wildly: given a small \(\Delta\), the displacement is approximated to be constant on any interval of this length. This yields a partitioning of \(\varepsilon(x)\) given by
\[
\varepsilon(x) \simeq \varepsilon_{local}(x_0; x) \frac{\Delta}{2} + \Delta \sum_{k=1}^{n-1} \varepsilon_{local}(x_k; x) + \varepsilon_{local}(x_n; x) \frac{\Delta}{2}, \quad (3.8)
\]
with the local displacements defined as
\[
\varepsilon_{local}(x_k; x) = \begin{cases} 
\frac{\varepsilon(x_k)}{\Delta} & \text{for } x \in \left[ x_k - \frac{\Delta}{2}, x_k + \frac{\Delta}{2} \right] \text{ and } k \in \{1, \ldots, n-1\} \\
\frac{\varepsilon(x_0)}{\Delta/2} & \text{for } x \in \left[ x_0, x_0 + \frac{\Delta}{2} \right] \text{ and } k = 0 \\
\frac{\varepsilon(x_n)}{\Delta/2} & \text{for } x \in \left[ x_n - \frac{\Delta}{2}, x_n \right] \text{ and } k = n \\
0 & \text{otherwise}
\end{cases} \quad (3.9)
\]
i.e., \(\varepsilon(x_k; x)\) is a constant within the respective interval in (3.9) and zero outside of it. (We cannot use a local displacement without the other intervals, because this would introduce discontinuities and we could not have done the partial integration to arrive at (3.4).) The change in free energy due to the displacement on the \(k\)th interval is given by
\[
\delta F[\varepsilon_{local}^k] \simeq \int G(x) \varepsilon_{local}(x_k; x) \, dx \quad (3.10)
\]
\[
= \frac{\varepsilon(x_k)}{\Delta} \int_{-\Delta/2}^{\Delta/2} G(x) \, dx, \quad (3.11)
\]
and if the integrand $G(x)$ is of sufficiently weak variation, for small enough $\Delta$

$$\delta F \left[ \varepsilon_{k}^{k} \right] \simeq \varepsilon (x_{k}) G(x_{k}).$$

We define the functional derivative as the change of $F$ in response to the local change in $y$:

$$\frac{\delta F}{\delta y (x^{*})} \equiv \lim_{\varepsilon (x^{*}) \to 0} \lim_{\Delta \to 0} \frac{\delta F}{\varepsilon (x^{*})} = G (x^{*}). \quad (3.12)$$

(We write $x^{*}$ instead of $x_{k}$ because the limit $\Delta \to 0$ changes the index $k$ for which $x^{*} \in [x_{k-1}, x_{k+1}]$.) The partitioning in the limit $\Delta \to 0$ can be written using Dirac’s delta function

$$\varepsilon (x) = \int \varepsilon_{\text{local}} (x'; x) \, dx' = \int \varepsilon (x') \delta (x - x') \, dx', \quad (3.13)$$

where the local displacement is now

$$\varepsilon_{\text{local}} (x; x^{*}) = \varepsilon (x) \delta (x^{*} - x) \quad (3.14)$$

leading to the definition of the functional derivative

$$\frac{\delta F}{\delta y (x^{*})} \equiv \lim_{\varepsilon (x^{*}) \to 0} \frac{\delta F}{\varepsilon (x^{*})} = \lim_{\varepsilon (x^{*}) \to 0} \frac{F \left[ y (x') + \varepsilon (x') \delta (x^{*} - x') \right] - F \left[ y (x') \right]}{\varepsilon (x^{*})}. \quad (3.15)$$

We note that we can also define functional derivative procedurally: first the displacement of $F$ would be transformed into a form

$$\delta F = \int G_{\varepsilon} (x) \varepsilon (x) \, dx, \quad (3.16a)$$

and then the functional derivative is defined as

$$\frac{\delta F}{\delta y (x^{*})} \equiv \lim_{\varepsilon (x^{*}) \to 0} G_{\varepsilon} (x^{*}). \quad (3.16b)$$
We assume that for all intents and purposes in this dissertation both definitions are equivalent. Some researchers, e.g.,[15], define the functional derivative operator in (3.16b) such that it is dimensionless: assume that the functional $F$ can be written in a form

$$F = \int \mathcal{F}[y](x) \, dx,$$

e.g., $\mathcal{F}$ is a free energy density and $F$ the total free energy (note that $\mathcal{F}$ itself may be a functional of $y$). If $F$ can be written this way then one can define a dimensionless functional derivative operator as

$$\frac{\delta \mathcal{F}}{\delta y(x^*)} \equiv \lim_{\epsilon(x^*) \to 0} G_\epsilon(x^*), \quad (3.17)$$

which is the same as (3.16b), except for the dimension of the functional derivative. Since apparently Eq. (3.15) is more commonly used [16][17], we will use definition (3.16b), where the functional derivative has the dimension of Dirac’s delta function (inverse length or volume, respectively) and not (3.17).

### 3.1.3 Example

The following example will occur again in a later chapter, but with $S$ replaced by a traceless symmetric tensor $Q_{ij}$ and in three dimensions. Consider the following free energy

$$F = \int \mathcal{F}[S](x) \, dx \quad (3.18)$$

with

$$\mathcal{F}[S](x) \equiv -\ln \int_\Omega \exp \left( \left( \sigma - \frac{1}{2} S(x) \right) Y[S](x) \right) \, d^3 \sigma, \quad (3.19)$$
where the integral is over the unit sphere and \( \sigma \equiv (3\cos^2\theta - 1)/2 \) and \( d^2\sigma \equiv d\phi d\cos\theta \). The functional \( Y [S] (x) \) is defined by

\[
Y [S] (x) \equiv \int w (|x - x'|) S (x') \, dx',
\]

(3.20)

and \( w (|x - x'|) \) is some function that falls off rapidly with increasing distance \( |x - x'| \).

We evaluate \( F [S + \varepsilon] \) for a small displacement \( \varepsilon \). First expand all sub-functionals to first order in the displacement \( \varepsilon \) of \( S \):

\[
Y [S + \varepsilon] (x) = Y [S] (x) + \eta [\varepsilon] (x)
\]

(3.21a)

with

\[
\eta [\varepsilon] (x) \equiv \int w (|x - x'|) \varepsilon (x') \, dx'.
\]

(3.21b)

To save some writing we occasionally omit arguments of functions or functionals. The complete form is then to be taken from the corresponding definition. Equation (3.19) for a displaced order-parameter field yields now (\( \eta \) is an infinitesimal displacement like \( \varepsilon \))

\[
F [S + \varepsilon] (x) = -\ln \int \exp \left( \left( \sigma - \frac{1}{2} (S (x) + \varepsilon (x)) \right) (Y (x) + \eta (x)) \right) d^2\sigma
\]

(3.22a)

\[
\simeq -\ln \int \exp \left( \left( \sigma - \frac{1}{2} S \right) Y + \sigma \eta - \frac{1}{2} S \eta - \frac{1}{2} \varepsilon Y + O (\varepsilon \eta) \right) d^2\sigma
\]

(3.22b)

\[
= -\left[ \ln \int \exp \left( \left( \sigma - \frac{1}{2} S \right) Y \right) \, d^2\sigma \right] \left( 1 + \langle \sigma \rangle_Y \eta - \frac{1}{2} S \eta - \frac{1}{2} \varepsilon Y + O (\varepsilon \eta) \right)
\]

(3.22c)

\[
= F [S] (x) - \langle \sigma \rangle_{Y (x)} \eta (x) + \frac{1}{2} S (x) \eta (x) + \frac{1}{2} \varepsilon (x) Y (x),
\]

(3.22d)

where the pointed brackets \( \langle \cdot \rangle \) denote the following average:

\[
\langle \sigma \rangle_{Y (x)} \equiv \frac{\int \sigma \exp (\sigma Y (x)) \, d^2\sigma}{\int \exp (\sigma Y (x)) \, d^2\sigma}.
\]

(3.23)
Then the displacement of the total free energy is given by

$$F [S + \varepsilon] - F [S]$$

$$= \int \left( \frac{S (x) \eta (x) + \varepsilon (x) Y (x)}{2} - \langle \sigma \rangle_{Y (x)} \eta (x) \right) d^d x$$

$$= \int \int S (x) w (|x - x'|) \varepsilon (x') d^d x' + \frac{1}{2} \int S (x') w (|x - x'|) \varepsilon (x) d^d x' d^d x$$

$$- \int \int \langle \sigma \rangle w (|x - x'|) \varepsilon (x') d^d x' d^d x.$$  \hspace{1cm} (3.24b)

We are free to relabel the differential \(dx\) and \(dx'\) in the second term in the sum, yielding

$$F [S + \varepsilon] - F [S] = \int \left\{ \int (S (x) - \langle \sigma \rangle (x)) w (|x - x'|) d^d x \right\} \varepsilon (x') d^d x'$$

$$= \int G (x') \varepsilon (x') d^d x'.$$  \hspace{1cm} (3.25b)

Following our procedure, we identify \(G (x')\) with the functional derivative of \(F\) at \(x'\):

$$\frac{\delta F}{\delta S} [S] (x_0) = G (x_0) = \int (S (x) - \langle \sigma \rangle (x)) w (|x - x_0|) dx.$$  \hspace{1cm} (3.26)

3.1.4 Tensors and constraints

We show how certain constraints on the functional derivative are enforced for the case of tensor-valued arguments. Consider a functional on a tensor \(T_{ijk...}\)

$$F [T + \varepsilon] = F [T] + \int G_{\alpha \beta \gamma...} [T] (x) \varepsilon_{\alpha \beta \gamma...} (x) dx$$  \hspace{1cm} (3.27)

If the functional is a scalar and \(\varepsilon_{ijk...}\) a tensor-valued displacement, then by the quotient rule, \(G_{ijk...}\) must be a tensor of the same rank as \(\varepsilon_{ijk...}\). We call \(G_{ijk...}\) the
tensor valued functional derivative of $F$ with respect to the tensor $T_{ijk...}$ and write

$$G_{ijk...}[T](x) = \frac{\delta F}{\delta T_{ijk...}(x)}.$$  \hfill (3.28)

A functional derivative may be subject to constraints. Sometimes we may be able to write the constrained displacement $\varepsilon^*$ as a linear projection from the unconstrained displacement onto the space of constrained displacements:

$$\varepsilon^*_{ijk...} = P_{ijk...\alpha\beta...\gamma...} \varepsilon_{\alpha\beta...\gamma...},$$  \hfill (3.29)

where $P_{ijk...}$ is some projection operator. Examples are: a) the tensor $T$ is a symmetric traceless tensor, e.g., the nematic tensor order parameter $Q$. Therefore, the displaced tensor $Q' = Q + \varepsilon$ must be symmetric and traceless, which holds true if and only if the displacement $\varepsilon$ itself is symmetric and traceless. The respective projector that maps arbitrary displacements to traceless, symmetric ones is given by

$$P_{ijkl} = \frac{\delta_{ik} + \delta_{jl}}{2} - \frac{1}{3} \delta_{ij} \delta_{ik}.$$  \hfill (3.30)

b) The tensor $T$ is a unit vector (e.g., the nematic director $\hat{n}$) \footnote{Kelly and Palffy-Muhoray [18] pointed out that the monograph by deGennes [19] contains an error in this regard.}; therefore, the displacement must be orthogonal to $\hat{n}$, and the respective projector is given by

$$P_{ij} = \delta_{ij} - n_i n_j.$$  \hfill (3.31)
This can be seen when normalizing the new director $\hat{n}' = \hat{n} + \varepsilon$, where $\varepsilon$ is an arbitrary displacement of the director:

\[
\hat{n}' = \frac{\hat{n}''}{|\hat{n}''|} = \frac{\hat{n} + \varepsilon}{|\hat{n} + \varepsilon|} \simeq (\hat{n} + \varepsilon) (1 - \hat{n} \cdot \varepsilon) \quad (3.32a)
\]

\[
n'_i = (n_i + \varepsilon_i) (1 - n_\alpha \varepsilon_\alpha) + O(\varepsilon^2) \quad (3.32b)
\]

\[
= n_i + \varepsilon_i - n_i n_\alpha \varepsilon_\alpha + O(\varepsilon^2) = n_i + (\delta_\alpha - n_i n_\alpha) \varepsilon_\alpha \quad (3.32c)
\]

\[
= n_i + P_{i\alpha} \varepsilon_\alpha. \quad (3.32d)
\]

The displacement of the free energy due to a constrained tensor displacement is given by

\[
\delta F = F[\mathbf{T} + \varepsilon] - F[\mathbf{T}] = \int G_{\alpha\beta\gamma\ldots}(x) P_{\alpha\beta\gamma\ldots\mu\nu\ldots\varepsilon_{\mu\nu\ldots}}(x) \, dx. \quad (3.33)
\]

We can either associate the projection operator with the functional derivative $G_{ijk\ldots}$ or with the displacement $\varepsilon_{ijk\ldots}$. In the first case we define the functional derivative such that the displacement is arbitrary and the functional derivative is constrained, as follows:

\[
\frac{\delta F}{\delta T_{ijk\ldots}} \equiv G_{\alpha\beta\gamma\ldots} P_{\alpha\beta\gamma\ldots ijk\ldots} \leftrightarrow \varepsilon_{ijk\ldots} \text{ free} \quad (3.34)
\]

or, in the second case we define alternatively the functional derivative such that the displacement is constrained and the functional derivative unconstrained, as follows:

\[
\frac{\delta F}{\delta Q_{ijk\ldots}} \equiv G_{ijk\ldots} \leftrightarrow \varepsilon^{\ast}_{ijk\ldots} \equiv P_{\alpha\beta\gamma\ldots\alpha\beta\gamma\ldots} \varepsilon_{\alpha\beta\gamma\ldots} \text{ constrained.} \quad (3.35)
\]

A third alternative exists because projectors are idempotent ($P_{\alpha\beta\gamma\ldots i\beta\gamma\ldots i\ldots\mu\nu\ldots m\ldots n\ldots} = P_{\alpha\beta\gamma\ldots i\beta\gamma\ldots i\ldots\mu\nu\ldots m\ldots n\ldots}$):

\[
\delta F = F[\mathbf{T} + \varepsilon] - F[\mathbf{T}] = \int (G_{\alpha\beta\gamma\ldots}(x) P_{\alpha\beta\gamma\ldots\mu\nu\ldots}(x) (P_{\mu\nu\ldots\zeta\mu\nu\ldots\varepsilon_{\zeta\mu\nu\ldots}}(x)) \, dx, \quad (3.36)
\]
and we may define both the functional derivative and the displacement as constrained:

\[
\frac{\delta F}{\delta Q_{i\beta\gamma...}} \equiv G_{\alpha\beta\gamma...} P_{\alpha\beta\gamma...} \varepsilon_{ijk...} = P_{i\beta\gamma...} \varepsilon_{\alpha\beta\gamma...} \text{ constrained.} \tag{3.37}
\]

We generalize Eq. (3.15) and write either the functional derivative for an arbitrary displacement

\[
\frac{\delta F}{\delta T(x_0)} = \left( \lim_{|\varepsilon(x_0)| \to 0} \frac{F[T(x') + \varepsilon(x') \delta(x_0 - x')] - F[T]}{\varepsilon(x_0)} \right)^* \tag{3.38}
\]

where the star denotes projection:

\[
A_{\alpha\beta\gamma...}^* = P_{i\beta\gamma...} A_{\alpha\beta\gamma...} \tag{3.39}
\]

and $|\varepsilon|$ is a suitable tensor norm (e.g., the maximum norm). Alternatively, we can write the functional derivative for a constrained displacement

\[
\frac{\delta F}{\delta T(x_0)} = \lim_{|\varepsilon^*(x_0)| \to 0} \frac{F[T + \varepsilon^*(x_0) \delta(x_0)] - F[T]}{\varepsilon^*(x_0)} \tag{3.40}
\]

### 3.1.5 Arithmetic rules

In this section we use the identity

\[
\delta F \equiv \int \frac{\delta F}{\delta y(x)} \delta y(x) \, dx. \tag{3.41}
\]

### Functional derivative of a function

The displacement of the function is given by

\[
\delta f(x) = \frac{f(x + \varepsilon) - f(x)}{\varepsilon} \tag{3.42}
\]
which can be written as an integral using Dirac’s delta function

\[
\delta f = \int \frac{f(x+\varepsilon) - f(x)}{\varepsilon} \delta(x' - x) \, dx',
\]

(3.43)

where the integral extends over an interval that contains \( x \), and \( x \) does not coincide with an interval end. This yields by identification

\[
\frac{\delta f(x)}{\delta x'} = \lim_{\varepsilon \to 0} \frac{f(x+\varepsilon) - f(x)}{\varepsilon} \delta(x' - x) = f'_x \delta(x' - x).
\]

(3.44)

Specifically for \( f(x) = x \) this yields

\[
\frac{\delta x}{\delta x'} = \delta(x' - x).
\]

(3.45)

**Chain rule**

The chain rule is slightly different from the one on non-functionals, because integrals are involved. The displacement \( \delta F \) is given by Eq. (3.41)

\[
\delta F[y[z]] = \int \frac{\delta F}{\delta y(x')} \delta y(x') \, dx',
\]

(3.46)

but the displacement \( \delta y \) itself can be written using eqn. 3.41

\[
\delta y(x') = \int \frac{\delta y(x')}{\delta z(x)} \delta z(x) \, dx
\]

(3.47)

thus,

\[
\delta F = \int \frac{\delta F}{\delta y(x')} \left\{ \int \frac{\delta y(x')}{\delta z(x)} \delta z(x) \, dx \right\} \, dx'.
\]

(3.48)

We assume that the intervals are independent, then

\[
\delta F = \int \left\{ \int \frac{\delta F}{\delta y(x')} \frac{\delta y}{\delta z(x')} \, dx' \right\} \delta z(x) \, dx
\]

(3.49)

thus

\[
\frac{\delta F}{\delta z(x)} = \int \frac{\delta F}{\delta y(x')} \frac{\delta y(x')}{\delta z(x)} \, dx'.
\]

(3.50)
Example

We take the same example as in section 3.1.3

\[ F = - \int \ln Z[S](x) \, dx, \quad (3.51) \]

with

\[ Z[S] \equiv \int_{\Omega} \exp \left( \left( \sigma - \frac{1}{2} S(x) \right) Y[S](x) \right) \, d^3 \sigma, \quad (3.52) \]

where the integral is over the unit sphere and \( \sigma \equiv P_2(\cos \theta) \) and \( d^3 \sigma \equiv d\phi d\cos \theta. \)

The functional \( Y[S](x) \) is defined by

\[ Y[S](x) \equiv \int w(|x - x'|) S(x') \, dx'. \quad (3.53) \]

Then

\[ -\delta F = \int \delta \ln Z \, dx = \int \frac{\delta \ln Z(x)}{\delta Z(x')} \delta Z(x') \, dx' \, dx \quad (3.54a) \]

\[ = \int \frac{1}{Z(x)} \delta(x' - x) \delta Z(x') \, dx' \, dx = \int \frac{\delta Z(x)}{Z(x)} \, dx \quad (3.54b) \]

and

\[ \delta Z(x) = \int \left( \frac{\delta Z(x)}{\delta S(x')} \right)_{|Y \text{ fixed}} \delta S(x') \, dx' \]

\[ + \int \left( \frac{\delta Z}{\delta Y(x'')} \right)_{|S \text{ fixed}} \left( \int \frac{\delta Y(x'')}{\delta S(x')} \frac{\delta S(x')}{\delta S(x')} \, dx' \right) \, dx'' \quad (3.55a) \]

\[ = \int \left( \frac{\partial Z}{\partial S} \right)_{|x} \delta(x' - x) \delta S(x') \, dx' \]

\[ + \int \left( \frac{\partial Z}{\partial Y} \right)_{|x} \delta(x'' - x) \frac{\delta Y(x'')}{\delta S(x')} \, dx'' \delta S(x') \, dx' \quad (3.55b) \]

\[ \frac{\delta Z(x)}{Z(x)} = \int \left\{ \left( \frac{1}{Z} \frac{\delta Z}{\partial S} \right)_{|x} \delta(x' - x) + \left( \frac{1}{Z} \frac{\delta Z}{\partial Y} \right)_{|x} \frac{\delta Y(x)}{\delta S(x')} \right\} \delta S(x') \, dx', \quad (3.55c) \]
yielding

\[
\frac{\delta F}{\delta S(x')} = \int \left\{ \left( \frac{1}{Z} \frac{\partial Z}{\partial S} \right)_{x'} \delta(x' - x) + \left( \frac{1}{Z} \frac{\partial Z}{\partial Y} \right)_{x} \frac{\delta Y(x)}{\delta S(x')} \right\} dx,
\]  \hspace{1cm} (3.56)

where

\[
\delta Y = \int w(|x - x'|) \delta S(x') \, dx'
\]  \hspace{1cm} (3.57a)

\[
\frac{\delta Y(x)}{\delta S(x')} = w(|x - x'|)
\]  \hspace{1cm} (3.57b)

and therefore

\[
\frac{\delta F}{\delta S(x')} = \left( \frac{1}{Z} \frac{\partial Z}{\partial S} \right)_{x'} + \int \left( \frac{1}{Z} \frac{\partial Z}{\partial Y} \right)_{x} w(|x - x'|) \, dx
\]  \hspace{1cm} (3.58a)

\[
= -\frac{1}{2} Y[S](x') + \int \left( \langle \sigma \rangle_{x'} - \frac{1}{2} S(x) \right) w(|x - x'|) \, dx
\]  \hspace{1cm} (3.58b)

\[
= -\frac{1}{2} \int w(|x' - x|) S(x) \, dx + \int \left( \langle \sigma \rangle_{x} - \frac{1}{2} S(x) \right) w(|x - x'|) \, dx
\]  \hspace{1cm} (3.58c)

\[
= \int \left( \langle \sigma \rangle_{x} - S(x) \right) w(|x - x'|) \, dx,
\]  \hspace{1cm} (3.58d)

which is the same result as before, Eq. (3.26).
Chapter 4

Curvature elasticity, surface gradients and the $K_{13}$-problem

In condensed matter systems one is often interested in the minimum free-energy state of a system that has elastic deformations. A common approach is to write down the free energy density as an expansion in the order parameter and add terms quadratic in the gradient of the order parameter. Symmetry would require then the addition of second derivative terms to the free energy, too. This was proposed by Nehring and Saupe [11], possibly for the first time. Unfortunately, including second derivative terms makes the problem ill posed, as was shown by Oldano and Barbero [12].

This chapter illustrates that this problem is intrinsic in deriving the bulk free energy density from symmetry considerations and that it cannot be solved by resorting to higher order terms in the expansion. First we will introduce the problem as it occurs in nematic liquid crystals, where Nehring and Saupe had argued that second derivative terms have to be added to the Frank-Oseen free energy density, because they have the same symmetry and are of the same order in the gradient as the terms in the Frank-Oseen free energy density. Oldano and Barbero then disputed this claim by showing that such a free energy cannot be minimized. We will study the cause of this using a simplified expression for the free energy density. Then we will show a solvability condition for the minimization of a free energy based on a density $\mathcal{F}(x, y, ...y^{(n)})$. Finally we will demonstrate that second derivative terms naturally
appear when deriving the free energy density from a molecular pair interaction, showing that one cannot simply forbid second derivative terms in the enumeration of symmetry-allowed terms.

4.1 Curvature elastic free energy density for liquid crystals

The elastic free energy density for nematic and cholesteric liquid crystals was given by Oseen [20]:

\[ F = \frac{K_{11}}{2} (\nabla \cdot \hat{n})^2 + \frac{K_{22}}{2} (\hat{n} \cdot \nabla \times \hat{n} + q_0)^2 + \frac{K_{33}}{2} (\hat{n} \times \nabla \times \hat{n})^2, \quad (4.1) \]

where \( \hat{n} \) is the nematic director, and \( q_0 \) the cholesteric pitch. (The pitch \( q_0 \neq 0 \) only if the nematic liquid crystal is intrinsically chiral, i.e., “cholesteric.” The ground state of the bulk then exhibits twist deformation, explained below, and \( q_0 \) gives the number of times the director makes a full rotation per distance travelled along the gradient.) The terms in Oseen’s free energy, (let’s denote them \( F_{11}, F_{22} \) and \( F_{33} \)) are called “splay-,” “twist-” and “bend” elastic-free-energy, respectively, after the deformations that leave the respective term unharmed while “killing” all the others.

These normal mode deformations, shown in fig. 4.1, can be found as follows. Assume a system that locally only varies along one direction, \( \hat{d} \). At location \( \mathbf{r} \) the director is \( \hat{n}(\mathbf{r}) = \hat{n}_0 \), at location \( \mathbf{r} + t\hat{d} \), it is \( \hat{n}' = \hat{n}(\mathbf{r} + t\hat{d}) = \hat{n}_0 + \delta \hat{n} \). Given sufficiently small \( t \) (and \( \mathbf{r} \) sufficiently far from any singularity in the director field) the displacement \( \delta \hat{n} \) is small. In addition \( |\hat{n}'| = 1 \), therefore \( \delta \hat{n} \) is perpendicular to \( \hat{n}_0 \). We can thus

\[ 1\] According to Nehring and Saupe[11], Oseen had included second derivative terms in earlier articles, but later omitted them on ground that they do not enter the Euler-Lagrange equations.
define an orthogonal basis \( \{ \hat{n}, \delta \hat{n}, \hat{n} \times \delta \hat{n} \} \). The three normal modes are determined by the relation of \( \hat{d} \) to this basis: \( \hat{d} \) along \( \delta \hat{n} \) (splay, \( F_{11} \neq 0 \)), along \( \hat{n} \times \delta \hat{n} \) (twist, \( F_{22} \neq 0 \)) and along \( \hat{n} \) (bend, \( F_{33} \neq 0 \)), respectively.

Frank [21] later added a term to Eq. (4.1) that he coined “saddle-splay”

\[
K_{24} \nabla \cdot (\hat{n} (\nabla \cdot \hat{n}) - (\hat{n} \cdot \nabla) \hat{n}) = K_{24} (n_{\alpha,\alpha} n_{\beta,\beta} - n_{\alpha,\beta} n_{\beta,\alpha}) .
\]  

(4.2)

Nehring and Saupe [11] revisited the problem and argued that Frank’s and Oseen’s theories only considered squares of gradient terms, but that symmetry also require the inclusion of terms that are second gradients. They identified an additional term that should be added to Frank’s free energy:

\[
K_{13} \nabla \cdot ((\hat{n} \cdot \nabla) \hat{n}) = K_{13} (n_{\alpha,\alpha} n_{\beta,\beta}) = K_{13} (n_{\alpha,\beta} n_{\beta,\alpha} + n_{\alpha} n_{\beta,\alpha \beta}) .
\]  

(4.3)

Both the \( K_{24} \)-term and the \( K_{13} \)-term are a divergence of a vector field. It is customary to perform a partial integration on such terms to convert them into surface free energy density terms. For sufficiently large systems it is then argued that these terms will be negligible compared to the bulk free energy and therefore can be omitted (thermodynamic limit). Nehring and Saupe pointed out that this is not permissible in the case of liquid crystals, since the boundary conditions determine the director field even deep within the bulk: Consider a system with infinite extent in two dimensions, \( x \) and \( y \), and boundary conditions that induce a preferred alignment of the director at the surface, located at \( z = L \) and \( z = -L \), of \( \hat{n} (-L) = \hat{n} (L) = \hat{x} \). Then, in a non-chiral nematic liquid crystal \( (q_0 = 0) \), \( \hat{n} = \hat{x} \) everywhere, because the bulk elastic free energy is invariant with respect to rotation of the whole system about any
Figure 4.1: Local deformation and integral curves for the “splay,” “twist” and “bend” normal modes.

axis perpendicular to \( \hat{x} \) and \( \hat{y} \). It is only the boundary conditions, however weak, that select a specific orientation of the director. Therefore the thermodynamic limit cannot be invoked to remove surface energy densities from the problem.

The critical difference between \( K_{24} \) and \( K_{13} \) is that the \( K_{13} \) term contains higher than first order partial derivatives. Oldano and Barbero [12] have shown that the free energy cannot be minimized when the \( K_{13} \) term suggested by Nehring and Saupe is added to Frank’s free energy: the boundary value problem is ill-posed.

4.2 A simple example

To keep things simple we consider a one dimensional system and a prototype free energy with order parmeter \( y(x) \) of the form

\[
F = \int_{x_0}^{x_1} \left( F^h(y^2) + \frac{k_1}{2} (y')^2 - \frac{k_2}{2} y y'' \right) dx + \left[ G(x,y,y') \right]_{x_0}^{x_1},
\] (4.4)
where $\mathcal{F}^h$ is the homogenos part of the free energy density, i.e., it does not depend on any gradients of $y$. This free energy density has a similar symmetry as Nehring and Saupe's version of Oseen's free energy density: It is even in the order parameter, and has two derivatives per term (assuming $q_0 = 0$). We assume that $k_1$ and $k_2$ do not vary in space, although in reality this will happen in a region sufficiently close to the surface. This assumption is only relevant if $k_2$ were to vanish at the surface, because this would indeed make the problem well-posed. However, when we derive the free energy we do not find that this is the case (see section 4.4.1). Both the $k_1$ and the $k_2$ term behave identically under symmetry operations and have the same magnitude under deformations. The latter can be verified by inserting a pure sinusoidal deformation $y = y_0 \sin(qx)$ into Eq. (4.4), resulting in $(y')^2 = q^2 \cos^2 qx$ and $-y y'' = q^2 \sin^2 qx$. The change in the free energy 4.4 due to a displacement $\varepsilon(x)$ of the order parameter field $y(x)$ is given by

$$
\delta F = \int_{x_0}^{x_1} \left( \mathcal{F}^h_{yy} \varepsilon + k_1 y' \varepsilon' - \frac{k_2}{2} y'' \varepsilon - \frac{k_2}{2} y \varepsilon'' \right) dx + \left[ G_{yy} \varepsilon + G_{y} \varepsilon' \right]_{x_0}^{x_1}.
$$

(4.5)

Partial integration in order to remove the $\varepsilon'$ and $\varepsilon''$ terms from the integral yields

$$
\delta F = \int_{x_0}^{x_1} \left( \mathcal{F}^h_{yy} - (k_1 + k_2) y'' \right) \varepsilon dx + \left[ G_{yy} + \left( k_1 + \frac{k_2}{2} \right) y' \right] \varepsilon + \left( G_{y} - \frac{k_2}{2} y \right) \varepsilon' \right]_{x_0}^{x_1}.
$$

(4.6)

A necessary condition for a minimum is that $\delta F = 0$ for any permitted displacement $\varepsilon$. Assuming that $\varepsilon$ is not subject to constraints\(^2\), expect maybe at the boundaries.

\(^2\)We show in section 3.1.4 that one can often write $(\delta F/\delta y) \varepsilon^*$, where $\varepsilon^*$ is a constrained variation, as $(\delta F/\delta y)^* \varepsilon$, where $\varepsilon$ is an arbitrary variation and $(\delta F/\delta y)^*$ is a constrained functional derivative.
the term in the integral must vanish independently of \( \varepsilon \), leading to the Euler-Lagrange equation for this system:

\[
\mathcal{F}^h_{,y} - (k_1 + k_2) y'' = 0.
\]  

(4.7)

Solving this second order ordinary differential equation (o.d.e.) results in two constants of integration. The boundary conditions are

\[
[g_1 (y, y') \varepsilon + g_2 (y) \varepsilon \frac{\partial}{\partial x}]_{x_0} = 0,
\]  

(4.8a)

with

\[
g_1 \equiv \mathcal{G}_{,y} + \left( k_1 + \frac{k_2}{2} \right) y'.
\]  

(4.8b)

and

\[
g_2 \equiv \mathcal{G}_{,y} + \frac{k_2}{2} y .
\]  

(4.8c)

If \( \varepsilon \) is arbitrary, including at the boundaries, all terms must vanish independently, leading to four equations,

\[
g_1 (y (x_0), y' (x_0)) = g_1 (y (x_1), y' (x_1))
\]

\[
= g_2 (y (x_0), y' (x_0)) = g_2 (y (x_1), y' (x_1)) = 0.
\]

(4.9)

If these equations are linearly independent, they fully determine the four constants \( y_0, y'_0, y_1, \) and \( y'_1 \). We denote these constants \( \hat{y}_0, \hat{y}'_0, \hat{y}_1, \) and \( \hat{y}'_1 \) to mark that they are determined by the system given in Eq. (4.9). We may use two of these, say \( y_0 \) and \( y'_0 \) to determine the two constants of integration in the solution to Eq. (4.7), which in turn completely defines \( y(x) \) everywhere. Since \( y(x) \) is now known so is \( y(x_1) = y_1 \) and \( y'(x_1) = y'_1 \). The two solutions will in general not be the same: \( \hat{y}(x_1) \neq y(x_1) \) and \( \hat{y}'(x_1) \neq y'(x_1) \), leading to a contradiction; the system is over determined. On the other hand, requiring \( \varepsilon = 0 \) at the boundaries is equivalent to requiring that \( y \) have a pre-determined value at the boundaries. This would then require that \( k_2 y e' \)
vanish at the boundaries, too, otherwise $\delta F \neq 0$. However, setting $\varepsilon'$ to zero at the boundaries is equivalent to requiring that $y'$ have a fixed value on either boundary. Again, this system is overdetermined because the four values $y_0, y_0', y_1$ and $y_1'$ are already defined, but the second order o.d.e. can only accommodate two independent constants. We note two exceptions: first, having $k_2 = 0$ at the boundaries effectively removes two of the equations in (4.9) from consideration. Second, having a fixed boundary value $y(x_0) = y(x_1) = 0$: Having a fixed value of $y$ at the boundary sets $\varepsilon = 0$, which removes $g_1|x_0 = g_1|x_1 = 0$ from the system. Because $y = 0$ the remaining equations $g_2|x_0 = g_2|x_1 = 0$ are automatically satisfied. Thus the only constants are $y_0$ and $y_1$ and the system can be solved. However, we assume that in a physical system $k_2 y \neq 0$ at the boundaries.

The boundary conditions (4.8a) are of the form $[g_s\varepsilon^{(s-1)}]_{x_k} = 0$, i.e., either the $g_s$ or $\varepsilon^{(s-1)}$ have to vanish at the boundary, and the latter case corresponds to rigid boundary conditions, where $y^{(s-1)}$ has a fixed value. Strictly speaking, in a physical system the boundary conditions are always of the type $g_s = 0$ , not $\varepsilon^{(s-1)} = 0$. One can never exactly fix boundary values in a physical system. Rather, one makes an assumption about a potential in a restricted region on space. For example, this potential may make it very hard for the nematic director to rotate away from a given direction. Thus the boundary values in Eq. (4.6) are always such that $\varepsilon$ and all its derivatives are free and therefore it is the corresponding coefficients that must vanish. These coefficients may be such that, e.g., $G_{,y}$ is much larger than $(k_1 + \frac{k_2}{2}) y'$ and the latter can therefore be ignored. If $G_{,y}$ is a function of $y$ only and $G_{,y}(y(x_0)) = 0$ has
a unique solution one recovers the boundary condition $y(x_0) =$const., equivalent to $\varepsilon(x_0) = 0$.

One may be tempted to take a virtual boundary $\partial \Omega_{\text{vir}}$, away from the actual physical boundary, for which $k_2 y = 0$. Even if we assume that the coefficients $k_1$ and $k_2$ were continuously differentiable throughout $\Omega_{\text{vir}}$, as is required to solve the boundary value problem (b.v.p.), the value of $y$ at this boundary is meaningless: it cannot be controlled. The boundary conditions are the external controlling forces on the system, e.g., the grooves in the polyimid layer holding the nematic director in place. Thus $y$ at $\partial \Omega_{\text{vir}}$ may be a result of the boundary values at $\partial \Omega$, but not a cause of these; it does not impose boundary conditions.

4.3 Variations on a gradient dependent functional: a solvability condition

The free energy in the example given in the previous section is an integral over a locally defined gradient-dependent free energy density. We have seen that the minimization problem of such a free energy density does not always lead to a well-posed boundary value problem (b.v.p). Therefore we must add well-posedness of the resulting b.v.p. to the conditions for a minimum of the free energy density: vanishing first variation and positive second variation.

4.3.1 Definitions

**Definition 1** A function identically vanishes if it is zero for all argument values on its domain, and it does not identically vanish if it is non-zero for at least one value of its argument on its domain.
\[ f : D \to R \]  \hspace{1cm} (4.10a)

\[ f \equiv 0 : \iff f(x) = 0 \forall x \in D \]  \hspace{1cm} (4.10b)

\[ f \neq 0 : \iff \exists x \in D : f(x) \neq 0 \]  \hspace{1cm} (4.10c)

**Definition 2 (Order of a function)** The order of a function \( f \) with respect to \( y \) is the largest non-negative integer \( n \) for which \( \partial f / \partial y^{(n)} \) does not identically vanish.

\[ \text{order}_y (f) \equiv \max \left\{ n \in \mathbb{N}_0 | \frac{\partial f}{\partial y^{(n)}} \neq 0 \right\} . \]  \hspace{1cm} (4.11)

We call a “function of order \( n \)” a function for which \( \text{order}_y (f) = n \). We call a “function of at most order \( n \)” a function for which \( \text{order}_y (f) \leq n \). We note: If \( f \) is of the form \( f(x, y, ..., y^{(n)}) = f(z_0, ..., z_{n+1}) \), i.e., \( z_0 \equiv x, z_1 \equiv y, z_2 \equiv y^{(1)}, ..., z_{n+1} \equiv y^{(n)} \) then

\[ \text{order}_y (f_{z_k}) \leq \text{order}_y (f) \]  \hspace{1cm} (4.12)

and from this for the order of any \( p \text{th} \) partial derivative

\[ \text{order}_y \left( f_{z_{k_1}, ..., z_{k_p}} \right) \leq \text{order}_y \left( f_{z_{k_2, ..., z_{k_{p-1}}} } \right) \leq ... \leq \text{order}_y (f) \]  \hspace{1cm} (4.13)

In other words, the order of a function cannot be increased by taking a partial derivative \( \partial f / \partial y^{(n)} \), or \( \partial f / \partial x \).

We now show: the \( k \text{th} \) derivative of a function of order \( n \) is a function of order \( n + k \). Consider a function of order \( n \)

\[ f(x, y, ..., y^{(n)}) : x \in D \subset R \to R \]  \hspace{1cm} (4.14)
then
\[
\left( \frac{d}{dx} \right) f = f_x + \sum_{l=0}^{n} f_{y^{(l)}} y^{(l+1)}
\] (4.15)
because \( f \) is a function of order \( n \), by definition \( f_{y^{(n)}} \neq 0 \), which is a function of at most order \( n \), therefore \( f_{y^{(n)}} y^{(n+1)} \) is a function of order \( n + 1 \):
\[
\left( f_{y^{(n)}} y^{(n+1)} \right)_{y^{(n+1)}} = f_{y^{(n)}} \neq 0,
\] (4.16)
or
\[
\text{order}_y \left( \left( \frac{d}{dx} \right) f \right) = \text{order}_y (f) + 1.
\] (4.17)
Repeating this \( k \) times yields
\[
\text{order}_y \left( \left( \frac{d}{dx} \right)^k f \right) = \text{order}_y (f) + k.
\] (4.18)

### 4.3.2 Variation: general solution

We consider a functional of the form
\[
F [y] = \int_{x_0}^{x_1} \mathcal{F} \left( x, y, y', ..., y^{(m)} \right) dx + \left[ \mathcal{G} \left( x, y, y', ..., y^{(m)} \right) \right]_{x_0}^{x_1},
\] (4.19)
where \( \mathcal{F} \) and \( \mathcal{G} \) are functions (not functionals) of order \( n \) and \( m \), respectively. Given a displacement in the field \( y (x) \rightarrow y (x) + \varepsilon (x) \) the displacement of the total free energy is given by
\[
\delta F = F [y + \varepsilon] - F [y] = \int_{x_0}^{x_1} \sum_{k=0}^{n} f_{y^{(k)}} \varepsilon^{(k)} dx + \delta G,
\] (4.20)
where \( f_{y^{(k)}} \equiv \frac{\partial}{\partial y^{(k)}} \mathcal{F} \), and \( \delta G \) is the displacement of the surface free energy. 

\[^3\]The domain of \( f_{y^{(k)}} \) may be different from the domain of \( \mathcal{F} \). We assume that all expressions are valid for the new domain.
the respective terms. A single partial integration yields
\[
\int_{x_0}^{x_1} \mathcal{F}_{y(k)} \varepsilon^{(k)} dx = \left[ \mathcal{F}_{y(k)} \varepsilon^{(k-1)} \right]_{x_0}^{x_1} - \int_{x_0}^{x_1} \left( \frac{d}{dx} \mathcal{F}_{y(k)} \right) \varepsilon^{(k-1)} dx,
\] (4.21)
and repeating this \( l \) times, \( l \in \{1, \ldots, k\} \) yields
\[
\int_{x_0}^{x_1} \mathcal{F}_{y(k)} \varepsilon^{(k)} dx = \sum_{i=1}^{l} \left[ \left( \frac{d}{dx} \right)^{i-1} \mathcal{F}_{y(k)} \varepsilon^{(k-i)} \right]_{x_0}^{x_1} + \int_{x_0}^{x_1} \left( \frac{d}{dx} \right)^l \mathcal{F}_{y(k)} \varepsilon^{(l)} dx.
\] (4.22)
Thus, setting \( l = k \) in Eq. (4.22) and inserting the result in Eq. (4.20) for each term \( k > 0 \) we arrive at
\[
\delta F = \delta F_{\text{bulk}} + \delta F_{\text{surface}} + \delta G
\] (4.23a)
\[
\delta F_{\text{bulk}} = \int_{x_0}^{x_1} \left( \sum_{k=0}^{n} \left( \frac{d}{dx} \right)^k \mathcal{F}_{y(k)} \right) \varepsilon(x) dx
\] (4.23b)
\[
\delta F_{\text{surface}} = \sum_{k=1}^{n} \left[ \sum_{i=1}^{k} \left( \frac{d}{dx} \right)^{i-1} \mathcal{F}_{y(k)} \varepsilon^{(k-i)} \right]_{x_0}^{x_1}.
\] (4.23c)
The surface terms can be reordered to collect the same orders of \( \varepsilon^{(k-i)} \):
\[
\delta F_{\text{surface}} = \sum_{s=1}^{n} \left[ g_s \left( x, y, \ldots, y^{(2n-s)} \right) \varepsilon^{(s-1)} \right]_{x_0}^{x_1},
\] (4.24)
with
\[
g_s = \sum_{k=s}^{n} \left( \frac{d}{dx} \right)^{k-s} \mathcal{F}_{y(k)}.
\] (4.25)
(\( \mathcal{F}_{y(k)} \) is a function of at most order \( n \), therefore \( \left( \frac{d}{dx} \right)^{k-s} \mathcal{F}_{y(k)} \) is a function of at most order \( n + k - s \). Since \( s \leq k \leq n \), the highest acquired order in Eq. (4.25) is \( 2n - s \), leading to \( g_s \) being a function of at most order \( 2n - s \).) The displacement of the surface potential is given by
\[
\delta G = \sum_{s=1}^{m+1} \left[ G_{y(s-1)} \varepsilon^{(s-1)} \right]_{x_0}^{x_1}.
\] (4.26)
If the surface potential is included in the free energy, the total surface contribution of the free energy displacement is given by

\[ \delta F_{\text{surface}} = \delta F_{\text{surface}}^* + \delta G \]  

\[ = \sum_{s=1}^{n} \left[ g_s^* \left( x, y, \ldots, y^{(2n-s)} \right) \varepsilon^{(s-1)} \right]_{x_0} + \sum_{s=1}^{m+1} \left[ \mathcal{G}_{y^{(s-1)}} \varepsilon^{(s-1)} \right]_{x_0}. \]  

(4.27a)

(4.27b)

We assume that \( m + 1 \geq n \). If \( m + 1 < n \), simply define \( \mathcal{G}_{y^{(s)}} = 0 \) for all \( s - 1 > m \).

The value of \( \delta F_{\text{surface}} \) is now

\[ \delta F_{\text{surface}} = \sum_{s=1}^{\max(n,m+1)} g_s \varepsilon^{(s-1)} \]  

(4.28a)

\[ g_s \equiv \begin{cases} 
  g_s^* + \mathcal{G}_{y^{(s-1)}} & s \leq n \\
  \mathcal{G}_{y^{(s-1)}} & s > n 
\end{cases} \]  

(4.28b)

A necessary condition for a minimum of \( F \) is that \( F \) is stationary, or \( \delta F = 0 \).

Because the displacement \( \varepsilon \) is arbitrary, the bulk-term must vanish independently from \( \varepsilon \) and independently from the surface terms. A neccessary condition for \( y(x) \) to minimize \( F \) is then that

\[ \frac{\delta F_{\text{bulk}}}{\delta y} = \sum_{k=0}^{n} \left( -\frac{d}{dx} \right)^k \mathcal{F}_{y^{(k)}} = 0, \]  

(4.29)

and if the derivative terms on the surface are independent of each other, then each term in the boundary conditions must vanish independently as well:

\[ \left[ g_s \left( x, y, \ldots, y^{(\max(2n-s,m))} \right) \varepsilon^{(s-1)} \right]_{x_0} = 0 \quad \text{for each } s \in \{1, \ldots, \max\{n, m+1\} \}; \]  

(4.30)

resulting in \( 2 \max(n, m+1) \) boundary conditions, which may be either of the form \( \varepsilon^{(s)} = 0 \), corresponding to fixing the derivative \( y^{(s)} \) at the boundary, or of the form \( g_s = 0 \).
4.3.3 Solvability condition

The boundary value problem is solvable if the order of the o.d.e, $O_{\text{ode}}$, in Eq. (4.29) matches the number of (linearly independent) boundary conditions, $N_{\text{bc}}$.

$$O_{\text{ode}} \equiv \text{order}_y \left( \frac{\delta F_{\text{bulk}}}{\delta y} \right) = N_{\text{bc}}. \quad (4.31)$$

The order of the o.d.e can be determined as follows. Each term in Eq. (4.29) is of the form

$$\left( \frac{d}{dx} \right)^k \mathcal{F}_{,y^{(k)}} = \mathcal{F}_{,y^{(k)},x} + \sum_{l=0}^{n} \mathcal{F}_{,y^{(k)},y^{(l)}} y^{(l+k)} \quad (4.32)$$

The order of this term is the maximum of all orders occurring in the sum

$$O_{k,-1} \equiv \text{order}_y \left( \mathcal{F}_{,y^{(k)},x} \right) \quad (4.33a)$$

$$O_{kl} \equiv \text{order}_y \left( \mathcal{F}_{,y^{(k)},y^{(l)}} y^{(l+k)} \right) \quad (4.33b)$$

$$O_{\text{ode}} = \max \{ O_{kl} | k \in \{0, \ldots, n\}, l \in \{-1, \ldots, k\} \} \quad (4.33c)$$

Because $\text{order}(\mathcal{F}_{,y^{(k_1)},\ldots,y^{(k_p)}}) \leq \text{order}(\mathcal{F}_{,y^{(k)}}) \leq \text{order}(\mathcal{F}) \leq n$, the maximum order that can be attained is $O_{nn} = 2n$, leading to a term $\mathcal{F}_{,y^{(n)},y^{(n)}} y^{(2n)}$. This maximum is attained only if $\mathcal{F}_{,y^{(n)},y^{(n)}} \neq 0$.

The evaluation of the number of boundary conditions is complicated by the fact that a boundary condition $g_s y^{(s-1)}$ may be either of the form $y^{(s-1)} = 0$, i.e., $y^{(s-1)} = \text{const.}$, or of the form $g_s = 0$. In a physical system, however, even hard boundary conditions are imposed by means of an external potential: such boundary conditions are always of the form $g_s = 0$, and an approximate form of $y^{(s-1)} = \text{const.}$ may be acquired if the respective term is much larger than all other terms in the corresponding boundary condition. Thus we ignore boundary conditions of the form
$\varepsilon^{(s-1)} = 0$. The number of boundary conditions is then the number of linearly independent non-vanishing $g_s$\textsuperscript{4}. In the simplest case all non-vanishing $g_s$ are linearly independent and the number of boundary conditions is $2\max(n, m + 1)$ minus the number $\mu_0$ of all trivially vanishing $g_s$\textsuperscript{5}

$$\mu_0 \equiv \text{card} \left\{ s \in \{1, \ldots, \max\{n, m + 1\}\} | \exists x \in \{x_0, x_1\} : \begin{array}{l} g_s = 0 \text{ for all choices of } y^{(k)}(x) \text{ for all } k \\ N_{bc} = 2\max(n, m + 1) - \mu_0 \end{array} \right\} \quad (4.34)$$

If none of the $g_s$ vanish trivially, the number boundary conditions is simply $2\times \max(n, m + 1)$. At this point we consider only the case that all $g_s$ are linearly independent, and the surface potential is not of the form that any $g_s$ trivially vanish. Since the largest possible order of eqn. 4.29 is $2n$, we find as the first solvability condition that $m < n$. Specifically, given that the $g_s, s \in \{1, \ldots, \max(m, n)\}$ are linearly independent and none do trivially vanish, the system is solvable if and only if

$$\mathcal{F}_{y^{(n)}, y^{(n)}} \neq 0 \text{ and } m < n. \quad (4.36)$$

**Proof.** The $g_s$ are linearly independent and do not trivially vanish and $m < n$, therefore $N_{bc} = 2n$. If $\mathcal{F}_{y^{(n)}, y^{(n)}} \equiv 0$ then $O_{ode} < 2n$, but $N_{bc} = 2n$, thus $\mathcal{F}_{y^{(n)}, y^{(n)}} \neq 0$ is required for solvability. On the other hand, if $\mathcal{F}_{y^{(n)}, y^{(n)}} \neq 0$ then $O_{ode} = 2n = N_{bc}$. \blacksquare

\textsuperscript{4}It may be possible to define this exactly even for $g_s$ that are non-linear in $y$ and its derivatives. This is beyond the scope of this work, however.

\textsuperscript{5}By “trivially vanishing” we mean vanishing for arbitrary choices of $y$ and its derivatives at the boundary.
4.3.4 Summary

A functional of the form

\[ F[y] = \int_{x_0}^{x_1} \mathcal{F}(x, y, y', y'', y''', \ldots, y^{(n)}) \, dx + \left[ \mathcal{G}(x, y, y', \ldots, y^{(m)}) \right]_{x_0}^{x_1}, \]  

(4.37)

with

\[ \text{order}_y (\mathcal{F}) = n \quad \text{and} \quad \text{order}_y (\mathcal{G}) = m \]  

(4.38a)

may have a minimum if

\[ \sum_{k=0}^{n} \left( -\frac{d}{dx} \right)^k \mathcal{F}_{y^{(k)}} = 0 \]  

(4.39)

and

\[ [g_s(x, y, \ldots, y^{(\max\{2n-s,m\})})]_{x_0}^{x_1} = 0 \quad \text{for each} \quad s \in \{1, \ldots, \max\{n, m+1\}\}, \]  

(4.40)

where

\[ g_s = \begin{cases} 
\mathcal{G}_{y^{(s-1)}} + \sum_{k=s}^{n} \left( -\frac{d}{dx} \right)^{k-s} \mathcal{F}_{y^{(k)}} & s \leq n \\
\mathcal{G}_{y^{(s-1)}} & s > n 
\end{cases} \]  

(4.41)

We assume that \( \varepsilon^{(s)} \) is arbitrary, including at the boundaries. The problem has a solution if and only if

\[ N_{bc} = O_{ode}, \]  

(4.42)

where the number of boundary conditions is given by

\[ N_{bc} = 2 \max(n, m+1) - \mu_0 - \mu_{dep} \]  

(4.43a)

\[ \mu_0 = \text{number of trivially vanishing } g_s \]  

(4.43b)

\[ \mu_{dep} = \text{number of linearly dependent (non-vanishing) } g_y \]  

(4.43c)
and the order $O_{ode}$ of the o.d.e. is given by

$$O_{kl} \equiv \begin{cases} \text{order}_y \left( \mathcal{F}_{y(k)x} \right) & l = -1 \\ \text{order}_y \left( \mathcal{F}_{y(k)x(y)^{(l+k)}} \right) & 0 \leq l \leq k \end{cases}$$

$$O_{ode} = \max \{ O_{kl} | k \in \{0, ..., n\}, l \in \{-1, 0, ..., k\} \}$$ \hspace{1cm} (4.44a)

If $\mu_0 = \mu_{dep} = 0$ then $N_{bc} = O_{ode}$ if and only if

$$\frac{\partial^2 \mathcal{F}}{\partial y^{(m)} \partial y^{(n)}} \neq 0 \text{ and } m < n.$$ \hspace{1cm} (4.45)

In Eq. (4.4) $m = 1$ and $n = 2$. However, $\mathcal{F}_{y(2),y(2)} \equiv 0$ and therefore it is possible that no solution exists. On the other hand, the surface potentials may be of a form such that the boundary functions $g_s$ are linear dependend, leading to a well-posed problem. For the free energy Eq. (4.4) one such surface potential is given by

$$g_b(y, y') = b \left( \frac{y^2}{2} + vy' + \frac{(y')^2}{2} \right) + \frac{k_2 y^2}{2} + \left( \frac{k_2}{2} + k_1 \right) \frac{(y')^2}{2}$$ \hspace{1cm} (4.46)

for arbitrary $b$. However, unless one can explicitly determine the surface potential, we cannot assume that it is of this form, or any other leading to linear dependent boundary conditions.

### 4.4 The origin of gradient terms

#### 4.4.1 Pair-interaction method

In the previous sections we have assumed that the terms in the free energy are derived heuristically from symmetry considerations alone. The underlying assumption is that in a physical theory all terms that are not symmetry-forbidden are mandatory. However, this does not give any insight into the origin of such terms, neither gives it
insight in their coefficient's values or their dependence on other system parameters. One may suspect that, because including the second derivative term in the free energy density makes the system ill-posed, it should be forbidden. This section will demonstrate that the second derivative term occurs naturally when developing the free energy for a inhomogenous system. We will do this for a three-dimensional system.

We assume particles at locations \( \mathbf{r}_i \) and \( \mathbf{r}_j \), respectively that interact via a pair-potential of the form

\[
E = -y(\mathbf{r}_i) K(|\mathbf{r}_i - \mathbf{r}_j|) y(\mathbf{r}_j) + E_{\text{surface}}. \tag{4.47}
\]

where \( K \) is a geometric kernel and \( y \) the pair-wise interacting quantity (e.g., charge, magnetic moment, etc.) The total energy for a system of \( n \) such particles is given by

\[
E = -\frac{1}{2} \sum_{i \neq j} y(\mathbf{r}_i) K(|\mathbf{r}_i - \mathbf{r}_j|) y(\mathbf{r}_j) + E_{\text{surface}}. \tag{4.48}
\]

The surface term may be of the form

\[
E_{\text{surface}} = \sum_{\mathbf{r}_i \in \partial \Omega} (y(\mathbf{r}_i) - \bar{y}(\mathbf{r}_i))^2, \tag{4.49}
\]

where \( \mathbf{r}_i \in \partial \Omega \) denotes that the sum is to be taken only for particles whose location is on the surface. We ignore these surface terms here. We assume here (and only here, in this example) that the temperature is sufficiently low so that we do not need to distinguish between the energy and the free energy. In a continuum limit we write the double sum as a double integral

\[
F = -\frac{1}{2} \int y(\mathbf{r}) \rho(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \tilde{K}(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') y(\mathbf{r}') d^3 \mathbf{r} d^3 \mathbf{r}'. \tag{4.50}
\]
The kernel $\tilde{K}$ is a purely geometric function of the vector $\mathbf{r} - \mathbf{r}'$. In a continuum approach we consider probabilities rather than exact particle locations and invoke the term $\rho(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$, where $\rho(\mathbf{r}) d^3r$ is the (expectation value of the) number of particles in the volume element $d^3r$, and $g(\mathbf{r}, \mathbf{r}')$ is the pair-distribution function. This term yields the probability to find a particle in the volume element $d^3r'$, given that one is present in the volume element $d^3r$. For interaction between molecules, the pair distribution will, in general, depend on their shape and their relative orientation.

A simple form of the pair distribution function is given by

$$
g = \begin{cases} 
c > 0 & |\mathbf{r} - \mathbf{r}'| > r_0 \\
0 & |\mathbf{r} - \mathbf{r}'| \leq r_0
\end{cases} \quad (4.51)$$

with some cut-off length $r_0$. If the pair-distribution function is not isotropic, the cut-off length will depend on the relative orientation of molecules and the direction of the connecting vector $\mathbf{r}' - \mathbf{r}$:

$$r_0 = r_0(\mathbf{n}_1, \mathbf{n}_2, (\mathbf{r}' - \mathbf{r})/|\mathbf{r}' - \mathbf{r}|), \quad (4.52)$$

with $\mathbf{n}_1$ and $\mathbf{n}_2$ the expectation value of the orientation of the molecules at $\mathbf{r}$ and $\mathbf{r}'$, respectively. In the following we assume a simplified pair-distribution function as given in Eq. (4.51) and also that $r_0$ is isotropic and the density is constant. Absorbing $\rho(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$ into the kernel yields

$$F = -\frac{1}{2} \int_{|\mathbf{r}' - \mathbf{r}| > r_0} y(\mathbf{r}) K(\mathbf{r} - \mathbf{r}') y(\mathbf{r}') d^3r d^3r'. \quad (4.53)$$
We express the integral over $d^3r'$ as a function $G(r)$,

$$F = -\frac{1}{2} \int y(r) G(r) \, d^3r \quad (4.54)$$

$$G(r) \equiv \int_{|r'-r|>r_0} K(r-r') y(r') \, d^3r'. \quad (4.55)$$

Next, we only consider $G(r)$, which we express in terms of the chord $u = r'-r$. The magnitude of the chord is $u \equiv |r'-r|$ and $u_k \equiv (r'-r) \cdot \hat{e}_k / |r'-r|$ its direction. We expand $y(r') = y(r + u)$ in $u = 0$ to second order and get

$$G(r) \simeq \int_{\Omega(r), u > r_0} \left(y_{||r} + y_{\alpha|r} u u_\alpha + \frac{1}{2} y_{\alpha\beta|r} u^2 u_\alpha u_\beta\right) K(u) \, d^3u \quad (4.56a)$$

$$= y_{||r} \int_{\Omega(r), u > r_0} K(u) \, d^3u + y_{\alpha|r} \int_{\Omega(r), u > r_0} K(u) \, uu_\alpha d^3u$$

$$+ \frac{1}{2} y_{\alpha\beta|r} \int_{\Omega(r), u > r_0} K(u) \, uu_\alpha u_\beta d^3u \quad (4.56b)$$

$$= y_{||r} I_0(r) + y_{\alpha|r} I_\alpha(r) + \frac{1}{2} y_{\alpha\beta|r} I_{\alpha\beta}(r). \quad (4.56c)$$

with $I_0$, $I_i$, and $I_{ij}$ defined as the respective factors in (4.56b). The integral is taken over a region $\Omega$. If the integrand is expressed in terms of $u$ alone, then the $r$-dependence of the integral is taken from the location of $\Omega$ in relation to $r$, which we express by writing $\Omega(r)$. (For a concrete choice of coordinates this is the dependence of the integration limits on $r$.) For any $r$ the integral also excludes the sphere $u \leq r_0$ from the region of integration.

We consider a surface whose radius curvature is much larger than $r_0$ and denote as $r^*$ the point on the surface that is closest to $r$. (We assume a shape of $\Omega$ for which degeneracy of $r^*$ occurs only at locations $r$ far away from the surface. In such cases the interaction with the surface is negligible and we pick any one of the possible values of $r^*$ for the evaluation of the integral.) To the lowest order approximation the
particle “sees” a planar surface at distance $\Delta = |r^* - r|$. We take a coordinate frame with the $\hat{e}_3$-axis along the negative surface normal at $r^*$ and spherical coordinates

$$\mathbf{u} = u_{\alpha} \hat{e}_{\alpha} = \cos \phi \sin \theta \hat{e}_1 + \sin \phi \sin \theta \hat{e}_2 + \cos \theta \hat{e}_3.$$  

This geometry is displayed in figure 4.2. The integrals $I_0$, $I_i$ and $I_{ij}$ with a kernel $K(u) = K_0 u^{-2p}$ for $p \geq 3$ will then be of the form

$$J/K_0 = \int_{r_0}^{\infty} u^{2+q_j-2p} du \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi f_J(\theta, \phi) \int_0^{\pi - \arccos(\min(1, \Delta/u))} \sin \theta d\theta \int_0^{2\pi} d\phi f_J(\theta, \phi)$$

$$\quad = \int_{r_0}^{\max(r_0, \Delta)} u^{2+q_j-2p} du \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi f_J(\theta, \phi) + \int_{\max(r_0, \Delta)}^{\infty} u^{2+q_j-2p} du \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi f_J(\theta, \phi),$$

(4.58a)  

(4.58b)

where $J$ is one of $I_0$, $I_i$, and $I_{ij}$. Both the function $f_j(\theta, \phi)$ and the exponent $q_J$ depend on the choice of $J$, e.g., $f_J = 1$ and $q_J = 0$ for $J = I_0$. The interval end is
set at \( \max(r_0, \Delta) \) to ensure that \( u \geq r_0 \), even if \( \Delta < r_0 \). The simplest cases, which can be readily evaluated, are a) when \( \Delta \gg r_0 \), i.e., \( r \) is deep in the bulk and b) when \( \Delta = 0 \), i.e., \( r \) is on the surface. For the first case, the second term in Eq. (4.58b) vanishes, because the integral over the orientation is of order unity and the integral over \( du \) becomes very small:

\[
J (\Delta \gg r_0) \approx K_0 \int_{r_0}^{\infty} u^{2+q_J-2p} du \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi f_J (\theta, \phi). \tag{4.59}
\]

For the second case, \( \arccos (\min(1, \Delta/u)) = \arccos (0) = \pi/2 \), and the first term in Eq. (4.58b) vanishes:

\[
J (\Delta = 0) = K_0 \int_{r_0}^{\infty} u^{2+q_J-2p} du \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi f_J (\theta, \phi). \tag{4.60}
\]

For both cases the integration over \( du \) is independent from the integration over \( d\phi d\theta \).

\[
J = K_0 J_u (q_J) J_{\theta,\phi} (f_J) \tag{4.61}
\]

For \( 2 + q_J - 2p \leq 2 \)

\[
J_u (q_J) = \int_{r_0}^{\infty} u^{2+q_J-2p} du = \frac{1}{2p - 3 - q_J} \gamma^{3+q_J-2p} \tag{4.62}
\]

By performing all integrals one can easily verify that, a) for \( \Delta \gg r_0 \)

\[
J_{\theta,\phi} (f_{i_0}) = \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi = 4\pi \tag{4.63a}
\]

\[
J_{\theta,\phi} (f_{i_i}) = \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi u_i = 0 \text{ for all } i \in \{1, 2, 3\} \tag{4.63b}
\]

\[
J_{\theta,\phi} (f_{i_j}) = \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi u_i u_j = \frac{4\pi}{3} \delta_{ij} \tag{4.63c}
\]
and b) for $\Delta = 0$

\[
J_{\theta,\phi} (f_{l_0}) = \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi = 2\pi \tag{4.64a}
\]

\[
J_{\theta,\phi} (f_{l_i}) = \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi u_i = \pi \delta_{3i} \tag{4.64b}
\]

\[
J_{\theta,\phi} (f_{l_{i3}}) = \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi u_i u_j = \frac{2\pi}{3} \delta_{ij} \tag{4.64c}
\]

Thus, the coupling integrals become

\[
\Delta \gg r_0 \quad \Delta = 0
\]

\[
I_0/\pi K_0 r_0^{3-2p} = \frac{4}{2p-3} - \frac{2}{2p-3}
\]

\[
I_i/\pi K_0 r_0^{4-2p} = 0 - \frac{1}{2p-4} \delta_{3i}
\]

\[
I_{ij}/\pi K_0 r_0^{5-2p} = \frac{4}{3} \frac{1}{2p-5} - \frac{2}{3} \frac{1}{2p-6} \delta_{ij} \tag{4.65}
\]

Inserting the expression (4.56c) for $G$ into (4.54), using the coupling integrals (4.65), we finally see that the free energy density deep within the bulk is of the form

\[
F_{\text{bulk}} = -a y_{\mid r} y_{\mid r} - c y_{\mid r} y_{\text{ao} \mid r}, \tag{4.66}
\]

while at the surface it is of similar form, except that the coefficients for the bulk terms are replaced by half their value and an additional term linear in the derivative along the surface normal direction:

\[
F_{\text{near-surface}} = -\frac{1}{2} a y_{\mid r} y_{\mid r} - b y_{\mid r} y_{z \mid r} - \frac{1}{2} c y_{\mid r} y_{\text{ao} \mid r}. \tag{4.67}
\]

(Note that this is not a surface free energy density - energy per area - but the free energy density of a small volume element very close to the surface.)
4.4.2 Enumeration method

In the previous section we demonstrated that deriving the free energy density from pair-interaction, we incur a second derivative in the field \( y(r) \). Instead of taking the direct approach researchers often resort to enumeration of the possible terms that can appear if the free energy density is considered a power series of all locally defined physical quantities, which are represented by tensors of some rank. This may enable one to find the structure of the free energy density without explicit knowledge of the microscopic detail, which may be unknown or too complex. We outline this procedure and show that such an enumeration method inevitably fails, because the solvability condition (4.36) cannot be met to any order in the derivatives.

We assume that the free energy density is a function of temperature \( T \), density \( \rho \) and scalar order parameter \( S \), as well as their gradients\(^6\):

\[
\mathcal{F} = \mathcal{F} (T; \rho, \rho', ..., S, S', ...)
\] (4.68)

(We take \( T \) to be constant throughout the system.) In the following we call the "degree of an expansion" the largest number of times that the gradient operator occurs in a single term. For example, terms in which the gradient operator occurs three times are \( S''S', S''' \) and \( S'S'S' \), respectively. The "order of a function" \( \mathcal{F} \) is given by definition 2, page 2 as the highest spatial derivative occurring in \( \mathcal{F} \). We expand the free energy density in a power series of its arguments. A second degree

\(^6\)We use the notation \( S', S'' \) to symbolize gradient terms, in order to facilitate the following discussion – using the full index notation does not add anything to the argument.
power series in $S$ yields

$$
\mathcal{F} = g_0 (T, \rho, \rho', \rho'', S) + f_1 (T, \rho, \rho', S) S' \\
+ f_{21} (T, \rho, S) S' S' + f_{22} (T, \rho, S) S''.
$$

(4.69)

Here $\mathcal{F}, S', S'' \equiv 0$, thus the condition (4.36) is violated, and the minimization may be ill-posed. We require a term $S'' S''$ as well, in order to have a non-vanishing partial derivative with respect to $S''$. We next expand $\mathcal{F}$ up to fourth degree in the derivatives. This yields the desired term

$$
f_{42} (T, \rho, S) S'' S''
$$

(4.70)

but unfortunately it also incurs a term

$$
f_{44} (T, \rho, S) S''' S.
$$

(4.71)

Thus we arrive at the same problem as before: the solvability condition (4.36) is violated. This process can be repeated ad infinitum. The minimization problem will be ill-posed for a gradient expansion in $S$ of any order, unless some boundary condition are linearly dependent or are fulfilled for any value of $S$.

We now argue an approach that may work around this problem: We require that the highest derivative terms in the expansion be forbidden. This leads to a condition for permitted lower order terms, as well. We assume an expansion of degree $m$, in which a term

$$
f_m (T, \rho, S) S^{(m)}
$$

(4.72)

occurs and which is to be forbidden. We know that condition (4.36) is violated unless the highest derivative term is a square or higher power, i.e. $(S^{(m)})^n$, where $n \geq 2$.
Thus the lowest degree of a power series that would permit a term linear in $S^{(m)}$ is $2m$. We therefore consider a power-series expansion of degree $2m$ yielding a term

$$f(T, \rho, S) S^{(m)} S^{(m)}$$

and a term $f(T, \rho, S) S^{(2m)}$, which is to be forbidden, too. Going from the degree $m$ expansion to the degree $2m$ expansion did, however, not change the coefficients of the lower order terms - we did after all only add more terms. But the added terms are all of higher degree than $m$. Thus the term linear in $S^{(m)}$ is to be forbidden in the higher-degree expansion as well. This argument is independent of the choice of $m$ and therefore all terms must end in a square of the highest derivative of that term, assuming that the factors are sorted ascending by derivatives. For example, a term of order 3 is given by

$$S^{a_0} (S')^{a_1} (S'')^{a_2} (S''')^{a_3} (S'^m)^2,$$

where the powers $a_k$ are arbitrary non-negative integers. Thus condition (4.36) implies that the free energy density written as a power series of degree $2m$ is of the form

$$\mathcal{F} = f_0 \left( T; \rho, \ldots, \rho^{(2m)}, S \right)$$

$$+ f_2 \left( T; \rho, \ldots, \rho^{(2m-2)}, S, S' \right) (S')^2$$

$$+ f_4 \left( T; \rho, \ldots, \rho^{(2m-4)}, S, S', S'' \right) (S'')^2$$

$$+ \ldots + f_{2k} \left( T; \rho, \ldots, \rho^{(2m-2k)}, S, \ldots, S^{(\min(2m-2k,k))} \right) (S^{(k)})^2$$

$$+ \ldots + f_{2m} \left( T; \rho, S \right) (S^{(m)})^2.$$  

(4.75)

We compare this with equations (4.66) and (4.67). If we ignore for the moment the
fact that we incur boundary conditions when performing partial integration, we can transform the term \(-yy_{\alpha\alpha}\) to a term \(+y_{\alpha}y_{\alpha}\), which is a permitted term in (4.75). The linear gradient term \(yy_{\alpha}\) in (4.67), however, cannot be transformed to yield a term that is legal in (4.75). This indicates that this approach, of requiring that all permitted terms in the expansion end on a quadratic or higher term of the highest derivative of the order parameter, omits too many terms.

4.5 Conclusion and discussion

Many problems in physics involve solving a minimization problem on one of the thermodynamic potentials, for example the Helmholtz free energy. Ideally, one would derive the potential explicitly from knowledge of the microscopic details of the system. Unfortunately, these details are often unknown, or they may be too complex. Researchers thus resort to enumeration of symmetry-allowed terms and keep only those that yield a certain magnitude of change in the potential under deformations away from equilibrium. An example for such a free energy is Oseen's free energy (4.1) in nematic liquid crystals, which did not include the symmetry allowed terms later introduced by Nehring and Saupe. After Oldano and Barbero had demonstrated that the version of the free energy that includes all symmetry allowed terms cannot be minimized, a number of researchers attempted to "repair" the situation. We have shown in this chapter that the cause of the problem lies with the derivation of the deformation free energy by using a gradient expansion. The ill-posedness of the resulting boundary-value problem may be lifted by a complete knowledge of the surface free energy, as Oldano and Barbero had pointed out in their original paper about
this problem – this may lead to boundary conditions of which sufficiently many are linearly dependent to yield a well-posed minimization problem. In fact, since physics dictates that a state exists that minimizes the thermodynamic potential, we must assume that either such a set of linearly dependent boundary conditions exists, or no terms occur whose highest gradient appears to less than second power. In the former case, this is contrary to the original intent to determine the structure of the thermodynamic potential without resorting to microscopic details, not to mention that surface physics may be significantly more involved than even microscopic details of the bulk (and often only poorly understood). The latter case, on the other hand, can always be transformed into the first one by partial integration.

The problem is far more general than the so-called “$K_{13}$-problem,” which is well known to liquid crystal researchers. It applies to any problem for which deformational free energy is represented by gradients.

We suggest that, instead of deriving the free energy just from symmetry considerations, we start with a microscopic model, perform the calculations to arrive at a generalized force expressed in fully non-local form, and then do the gradient expansion. Since the gradient expansion is done after the functional derivative, no partial integrations are required, thus not incurring additional surface terms. This approach is, of course, more complicated than just enumerating symmetry-allowed terms, but we do avoid the need to analyze the detailed surface physics. As a bonus we will find the dependence of the coefficients of the gradient terms on other parameters of the system (e.g., density, temperature and their gradients) and get an
insight as to which assumptions have led to the structure of the generalized force. (It will, for example be obvious that the degeneracy in the elastic theory for nematic tensor order parameter due to de Gennes may be lifted by considering an anisotropic pair-distribution function. While Marruci and Greco's theory [22] does in principle just that, it is pleasing to know that our approach shows this automatically.)
Chapter 5

Mean field theory

5.1 Construction of a mean field theory

One of the most important connections between physics at a molecular level and bulk matter in statistical mechanics is made by mean field theory, originally invented by Pierre Weiss to explain ferromagnetism [23]. In mean field theory, the molecular interactions are replaced by an effective field acting on a single molecule. This effective field is interpreted as the macroscopic observed average of some molecular quantity, or its order parameter. In the further treatment we will usually ignore quantum effects.

5.1.1 Partition function for pair-wise interaction

Consider a system of $N$ pairwise interacting particles with a total energy of the form

$$\mathcal{E} = -U \sum_{i \neq j}^{1} \frac{\sigma_i \sigma_j}{|\mathbf{r}_i - \mathbf{r}_j|^K},$$  \hspace{1cm} (5.1)

where the index labels the particle and $\mathbf{r}_i$ denotes the current position of the $i^{th}$ particle. Each sum runs from 1 to $N$. This pair potential can, for example, be the interaction of two spins at locations $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, in which case the $\sigma_i$ are vectors representing the magnetic moments. The parameter $K$ indicates the range

55
of the potential. We write Eq. (5.1) more general as:

$$\mathcal{E} = - \sum_{i \neq j} \sigma^{(i)} J^{(ij)} \sigma^{(j)}, \tag{5.2}$$

where $J^{(ij)}$ is some kernel, or coupling tensor, which depends on the vector $r_i - r_j$. If the $\sigma^{(i)}$ are $k-$th rank tensors, then the coupling tensor $J^{(ij)}$ must be a $2k$-th rank tensor. We use the notation of superscript in parentheses to point out that they are labels for interacting pairs, not tensor components. Even more concise we write, using the summation convention defined in the preface

$$\mathcal{E} = -\sigma^{(\alpha)} J^{(\alpha\beta)} \sigma^{(\beta)} \tag{5.3}$$

and understand that the diagonal elements of $J^{(ij)}$ vanish. This total energy can also be written as

$$\mathcal{E} = -\sigma^{(\alpha)} h^{(\alpha)} [\sigma] = \sum_k \mathcal{E}_k, \tag{5.4}$$

with the total field $h^{(i)} [\sigma]$ acting on $\sigma^{(i)}$:

$$h^{(i)} [\sigma] \equiv J^{(\alpha)} \sigma^{(\alpha)}, \tag{5.5}$$

and we use square brackets to denote functional dependence, i.e., dependence on all $\sigma_k$ in the discrete system, or $h [\sigma] \equiv h (\sigma_1, \sigma_2, ..., \sigma_N)$. The canonical partition sum is given by

$$Z_c = \frac{1}{N!} \sum_{\{\sigma_1\}} \sum_{\{\sigma_2\}} ... \sum_{\{\sigma_N\}} e^{-\beta \sigma^{(1)} h^{(1)} [\sigma]} e^{-\beta \sigma^{(2)} h^{(2)} [\sigma]} ... e^{-\beta \sigma^{(N)} h^{(N)} [\sigma]} \tag{5.6}$$

or,

$$= \frac{1}{N!} \sum_{\{\sigma_1\}} \sum_{\{\sigma_2\}} ... \sum_{\{\sigma_N\}} e^{-\beta \mathcal{E}_1 [\sigma]} e^{-\beta \mathcal{E}_2 [\sigma]} ... e^{-\beta \mathcal{E}_N [\sigma]}, \tag{5.7}$$
where \( \sum_{\{\sigma_k\}} \) indicates sum over all available states of \( \sigma^{(k)} \). The factor \( 1/N! \) must be omitted for distinguishable particles, e.g., if the \( \sigma^{(k)} \) are spins fixed on a lattice. (The dependence on the position of each particle is included in the definition of \( h^{(k)}[\sigma] \) and \( J^{(kl)} \), respectively.)

### 5.1.2 Mean field approximation

The mean field approximation is to replace the actual field \( h^{(i)}[\sigma] \) by an effective field, \( \{ \eta^{(i)} \}^N_{i=1} \). This field does not depend on the actual state \( \sigma^{(i)} \) of each of the particles, but only on their respective averages.

Writing the potential in terms of the effective field replaces \( E_k[\sigma] \) with \( \varepsilon_k[\eta] \), the single particle potential which depends on the state of the \( k^{th} \) molecule, \( \sigma^{(k)} \), and on the field \( \{ \eta \} \). The partition function for the whole system can then be written as a product of single particle partition functions for the individual molecules:

\[
Z_{mf} = \frac{1}{N!} \sum_{\{\sigma_1\}} e^{-\beta \varepsilon_1[\eta]} \sum_{\{\sigma_2\}} e^{-\beta \varepsilon_2[\eta]} \ldots \sum_{\{\sigma_N\}} e^{-\beta \varepsilon_N[\eta]} \tag{5.8a}
\]

\[
= \frac{1}{N!} \prod_k \left( \sum_{\{\sigma_k\}} e^{-\beta \varepsilon_k[\eta]} \right) = \frac{1}{N!} \prod_k Z_k, \tag{5.8b}
\]

with the single particle partition function \( Z_k \) defined as

\[
Z_k \equiv \sum_{\{\sigma_k\}} \exp(-\beta \varepsilon_k[\eta]). \tag{5.9}
\]

The mean field free energy is then

\[
\beta F_{mf} = -\ln Z_{mf} = \ln N! - \sum_k \ln Z_k. \tag{5.10}
\]

The problem of constructing a self-consistent mean field theory is constructing the effective single particle potential \( \varepsilon_k \) of a particle \( \sigma_k \) interacting with a field \( \{ \eta \} \). This
effective single particle potential must, of course, be constructed in such a way that
the underlying physics is not violated.

5.1.3 Averages

In the following we will need to distinguish different averages. The average of a
quantity $\xi$ is defined as the sum over all possible states $\xi_r$, weighted by their respective
probabilities,

$$\text{avg} (\xi) = \sum \xi_r P_r .$$

(5.11)

If the $\xi$ obeys the Boltzmann distribution, we write

$$\langle \xi \rangle = \sum \xi_r P_r^{\text{Boltzmann}}.$$  

(5.12)

For a system not in thermal equilibrium we may assume that we can measure the
average of $\xi$ but do not know the underlying distribution. We then denote the average
with an overbar:

$$\bar{\xi} = \sum \xi_r P_r^* .$$

(5.13)

We interpret any average such that it is meaningful locally: 1) We assume that the
out-of-equilibrium average for a single molecule can be measured at all. This implies
that the state of the molecule that we are interested in changes much more rapidly
than the out-of-equilibrium distribution $P^*$ and traces out a representative sample
such that the measured $\bar{\xi}$ is a good approximation. 2) We would like to define the
order parameter as an average over molecular orientation that is defined locally. In
order to do so we assume that a particle remains at some location for a finite time
during which it traces out a representative subset of all possible orientations, such
that the resulting average orientation is approximately the same as the averages in Eq. (5.13) and (5.12), where the sum is taken over all available states.

5.1.4 Construction of the single particle potential

The single particle potential in section 5.1.2 is a functional of the effective field \( \eta \). It is not sufficient, however, to simply write the pair-potential (5.4) by replacing the molecular state \( \sigma_k \) in (5.5) by its average \( \eta_k \); this works only for a homogenous system in equilibrium and by invoking a self-consistency condition that requires that the equilibrium average of \( \sigma_k \) equals the effective field \( \eta \). Our interest is in inhomogenous systems that are close to but not quite in equilibrium. This section lines out a number of conditions that must be met by the single particle potential. We then suggest a method of construction one that meets all these requirements.

The equilibrium state of the system is characterized by a field \( \eta \) for which the free energy is at a (global) minimum. We first consider a homogenous system and take the effective field to be the system average of \( \sigma \):

\[
\eta = S = \frac{1}{N} \sum_{k=1}^{N} \sigma_k. \tag{5.14}
\]

The free energy given an effective field \( \eta \) is the sum over all states compatible with \( \eta \):

\[
F(\eta) = -k_B T \ln Z_{\mid \eta}, \tag{5.15}
\]

where \( Z_{\mid \eta} \) expresses that the partition sum is taken with the constraint that \( \sum \sigma_k = N\eta \). Solving for \( Z_{\mid \eta} \) yields

\[
Z_{\mid \eta} = \exp (-\beta F(\eta)). \tag{5.16}
\]
The probability that the system is in a state characterized by the effective field $\eta$ is the number of states compatible with $\eta$ divided by all accessible states

$$P[\eta] = \frac{Z[\eta]}{Z}.$$  \hspace{1cm} (5.17)

For a thermodynamic system the equilibrium state is the most probable state and therefore the equilibrium is characterized by a maximum in $Z[\eta]$ or a minimum in $F[\eta]$, respectively. Next we consider an inhomogenous system. We want to define an effective field that varies from molecule to molecule. Instead of defining the field as a system average of $\sigma$, we define it as the average over the states that a single molecule attains during a short time interval $\tau$:

$$\eta_k(t) \equiv \frac{1}{\tau} \int_{t}^{t+\tau} \sigma_k(t') \, dt'.$$ \hspace{1cm} (5.18)

We divide this time average into $n$ small time intervals. Each molecule $\sigma_k$ is now assigned to $m$ time slots

$$\eta_k(t) = \frac{1}{m} \sum_{l=1}^{m} \sigma_k(t + l\tau) = \frac{1}{m} \sum_{l=1}^{m} \sigma_k^l.$$ \hspace{1cm} (5.19)

The original system of $N$ molecules characterized by a state $\{\sigma_k\}_{k=1}^{N}$ can be formally interpreted as a system of $Nm$ molecules in a state $\{\{\sigma_k^l\}_{k=1}^{N}\}_{l=1}^{m}$. The partition function $Z^*$ is the number of all accessible, distinct states $\{\sigma_k^l\}$, and the probability that the field has a value $\{\eta_k\}_{k=1}^{N}$ is given by

$$P[\eta] = \frac{Z^*[\eta]}{Z^*},$$ \hspace{1cm} (5.20)

where $Z^*[\eta]$ is the number of all states $\{\sigma_k^l\}$ that obey the constraint that

$$\frac{1}{n} \sum_{i=1}^{n} \sigma_k^l = \eta_k \text{ for all } k.$$ \hspace{1cm} (5.21)
As before, the equilibrium state, which is the most probable state, is characterized by a minimum in the free energy.

Palffy-Muhoray [24] points out two constraints for the single particle potential in a homogenous system: 1) The equilibrium average of the total energy must be the equilibrium average of the single particle energy times the number of particles, \( E = N \langle \varepsilon_s \rangle \) and 2) the equilibrium average of the derivative of the single particle potential with respect to the effective field must vanish, \( \langle \partial \varepsilon_s / \partial \eta \rangle = 0 \). We show now that for an inhomogenous system these requirements become

1. The equilibrium average of the total energy is the sum of the equilibrium average of all individual particles,

\[
\langle E \rangle = \sum_k \langle \varepsilon_k \rangle_k.
\] (5.22)

2. The generalized force\(^1\), which drives the effective field towards equilibrium, should vanish in equilibrium,

\[
\sum_j \langle \partial \varepsilon_j / \partial \eta^{(k)} \rangle_j = 0 \quad \text{for all } k,
\] (5.23)

where we define the canonical average in the \( j \)th single particle potential of a quantity \( X \) to be

\[
\langle X (\sigma^{(j)}) \rangle_j = \frac{\sum_{\{\sigma^{(j)}\}} X (\sigma^{(j)}) \exp (-\beta \varepsilon_j [\eta] (\sigma_j))}{\sum_{\{\sigma^{(j)}\}} \exp (-\beta \varepsilon_j [\eta] (\sigma_j))},
\] (5.24)

and \( \sum_{\{\sigma^{(j)}\}} \) denotes the trace over all accessible states of \( \sigma^{(j)} \).

\(^1\)Here we use the discrete version of the functional derivative.
The partition function of the whole system is the sum over all distinguishable states

\[ Z = \sum_r \exp(-\beta \mathcal{E}_r). \quad (5.25) \]

The equilibrium expectation value for the total energy is given by

\[ \langle \mathcal{E} \rangle = \frac{1}{Z} \sum_r \mathcal{E}_r \exp(-\beta \mathcal{E}_r) = -\frac{\partial}{\partial \beta} \ln Z, \quad (5.26) \]

thus for a mean field partition function

\[ \langle \mathcal{E} \rangle = \frac{\partial}{\partial \beta} \ln Z_{\text{mf}} = \sum_k \frac{1}{Z_k} \varepsilon_k \exp(-\beta \varepsilon_k) = \sum_k \langle \varepsilon_k \rangle_k, \quad (5.27) \]

which proves claim 1. We require that in equilibrium the system is stationary. The effective field \( \eta \) is a function of the system state. The system is stationary if the free energy is at an extremum with respect to the effective field.

\[ 0 = \frac{\partial}{\partial \eta^{(k)}} \ln Z = \sum_k \frac{\partial}{\partial \eta^{(k)}} \ln Z_k = \sum_j \left\langle \frac{\partial \varepsilon_j}{\partial \eta^{(k)}} \right\rangle_j \quad \text{for all } k, \quad (5.28) \]

which proves claim 2. In addition to the given constraints we also require that \( F \) is not only stationary but a minimum:

3. In equilibrium \( F \) is a minimum. If \( \bar{\eta} \) is the effective field for an equilibrium state, then for all permissible displacements \( \varepsilon \) from this field we require that

\[ F[\bar{\eta} + \varepsilon] \leq F[\bar{\eta}] \quad (5.29) \]

Obviously requirement (5.29) implies (5.23) as well. This requirement will be important when we attempt to naively extend to the inhomogenous problem the
construction of the single particle potential for a homogenous system suggested by [24].

5.1.5 Homogenous case

The common way to interpret the effective field \( \eta \) is to assume that \( \eta_k \) is the out-of-equilibrium average of \( \sigma^{(k)} \), i.e., \( \eta^{(k)} = \overline{\sigma}^{(k)} \), then Eq. (5.3) with (5.4) can be written in terms of \( \eta^{(k)} \) as

\[
\varepsilon_i^* = -\sigma^{(i)} J^{(i\alpha)} \overline{\sigma}^{(\alpha)} = -\sigma^{(i)} J^{(i\alpha)} S^{(\alpha)},
\]

(5.30)

where the star is a bookkeeping device; it keeps track of the stage in the mean field procedure that this single particle potential belongs to. In this first stage we have replaced the local field (5.4) by its average. For the case that \( \eta^{(k)} \) is interpreted this way we write exchangably \( \eta^{(k)} \), \( \overline{\sigma}^{(k)} \) and \( S^{(k)} \). In a homogenous system the field is the same for all single particle potentials, \( S^{(i)} = S e^{(i)} \), where \( e^{(i)} \) is the \( i \)th component of a tuple consisting only of ones:

\[
\varepsilon_i^* = -\sigma^{(i)} S J^{(i\alpha)} e^{(\alpha)} = -\sigma^{(i)} S J^{(i)},
\]

(5.31)

with

\[
J^{(i)} \equiv J^{(i\alpha)} e^{(\alpha)}.
\]

(5.32)

The requirement Eq. (5.23) yields

\[
0 = \sum_j \left( \frac{\partial \varepsilon^*_j}{\partial S^{(k)}} \right)_j = - \sum_j J^{(j)} \left( \langle \sigma^{(j)} \rangle_j \right),
\]

(5.33)

and in a homogenous field each of the terms in the sum are equal, so that

\[
J^{(i)} \left( \langle \sigma^{(i)} \rangle_i \right) = 0,
\]

(5.34)
therefore \( \langle \sigma^{(i)} \rangle_i = 0 \) and no phase transition can occur and Eq. 5.30 cannot be the correct form of the single particle potential. Palffy-Muhoray [24] shows that for the homogenous case a viable choice for the single particle potential, which conforms to the constraints (5.22) and (5.23), is given by taking the effective field \( \varepsilon^*_i \) of Eq. (5.30) and subtracting half its non-equilibrium average, which is the second (and for the homogenous case final) stage of the mean field procedure:

\[
\varepsilon_i = \varepsilon^*_i - \frac{1}{2} \varepsilon^*_i \quad \text{(5.35a)}
\]

\[
= -\sigma^{(i)} J^{(i\alpha)} \sigma^{(\alpha)} + \frac{1}{2} \sigma^{(i)} J^{(i\alpha)} \sigma^{(\alpha)} = -\sigma^{(i)} J^{(i\alpha)} S^{(\alpha)} + \frac{1}{2} S^{(i)} J^{(i\alpha)} S^{(\alpha)}. \quad \text{(5.35b)}
\]

This yields for the homogenous case

\[
\varepsilon_i = -\sigma^{(i)} J^{(i)} S + \frac{1}{2} S J^{(i)} S, \quad \text{(5.36)}
\]

for which one finds that

\[
\sum_j \left< \frac{\partial \varepsilon}{\partial S} \right>_j = -\sum_j \left( \langle \sigma^{(j)} \rangle_j - S \right) J^{(j)}, \quad \text{(5.37)}
\]

and again, since the field is homogenous, all terms in the sum have to vanish individually, yielding

\[
\langle \sigma^{(i)} \rangle_i - S = 0, \quad \text{(5.38)}
\]

which is the self-consistency and consistent with mean field theory of equilibrium homogenous systems. It turns out, however that the constructed single particle potential in (5.35b) fails to describe inhomogenous systems because it violates constraint (5.29).
5.1.6 Inhomogeneous case

Failure of the naive approach: the linear Ising chain

We now show that the effective field construction (5.30) fails to conform to (5.29). First, we illustrate this problem using a linear chain of Ising spins. Then we will perform linear stability analysis for a system with an energy of form (5.3), which shows that the indicated free-energy minimum state is unstable for short wavelengths perturbations (hence not a minimum).

We consider a linear chain of Ising spins with nearest neighbor interactions. The total energy for the system is given by

\[ E = -U \sum_{i=1}^{N} \sigma^{(i)} \frac{\sigma^{(i+1)} + \sigma^{(i-1)}}{2}. \] (5.39)

The coupling tensor \( J^{(ij)} \) in Eq. (5.3) is here given by

\[ J^{(ik)} = U \frac{\delta^{i+1,k} + \delta^{i-1,k}}{2}. \] (5.40)

As for the homogenous case we attempt to interpret the field as the out-of-equilibrium average of the spins (Eq. 5.30), then subtract half its average to obtain the effective single particle potential

\[ \varepsilon_i^* = -\sigma^{(i)} \langle \sigma^{(i)} \rangle \] (5.41a)

\[ \varepsilon_i = - \left( \sigma^{(i)} \langle J^{(i\alpha)} \rangle \langle \sigma^{(\alpha)} \rangle - \frac{1}{2} \langle J^{(i\alpha)} \rangle \langle J^{(i\alpha)} \rangle \right). \] (5.41b)

The expectation value for the total energy is given by

\[ \langle E \rangle = \sum_i \langle \varepsilon_i \rangle, \] (5.42)
which yields, with $\varepsilon_i$ and $J^{(ik)}$ defined above:

$$
\langle E \rangle = -U \sum_i \left( \frac{\langle \sigma^{(i)} \rangle_i}{2} - \frac{1}{2} S^{(i)} \right) \frac{S^{(i+1)} + S^{(i-1)}}{2}.
$$

(5.43)

The canonical average of $\sigma^{(i)}$ in its respective effective field is given by

$$
\langle \sigma^{(i)} \rangle_i = \tanh \left( \beta U \frac{S^{(i+1)} + S^{(i-1)}}{2} \right).
$$

(5.44)

Taking the low temperature limit this yields either +1 or −1, depending on the sign of the argument of the hyperbolic tangent ($\beta \equiv (k_B T)^{-1}$):

$$
\langle \sigma^{(i)} \rangle_i = \text{sign} \left( S^{(i+1)} + S^{(i-1)} \right) \text{ for } T \to 0.
$$

(5.45)

For low $T$ the expectation value for the total energy becomes the total energy for the given state and we can write

$$
E = \langle E \rangle = -U \sum_i \left( \frac{S^{(i+1)} + S^{(i-1)}}{2} - \frac{1}{2} S^{(i)} \frac{S^{(i+1)} + S^{(i-1)}}{2} \right).
$$

(5.46)

We now divide the field into spins at odd sites, $S_{\text{odd}}$, and spins at even sites, $S_{\text{even}}$. Consider two cases: 1) all spins are parallel, $S_{\text{odd}} S_{\text{even}} = 1$ and

$$
E = \langle E \rangle = -U \sum_i \left( 1 - \frac{1}{2} \right) = -\frac{N}{2} U;
$$

(5.47)

and: 2) all spins are anti-parallel, $S_{\text{odd}} S_{\text{even}} = -1$ and

$$
E = \langle E \rangle = -\sum_i \left( 1 + \frac{1}{2} \right) = -\frac{3}{2} N U
$$

(5.48)

and the anti-parallel configuration of all spins has a lower total energy, in contradiction to the original potential (5.39), which favors the parallel configuration of all spins. In order to discuss the problem consider Eq. (5.43): The first term in
the sum, together with Eq. (5.44) depends only on the odd (or even) sites, and only the second term couples odd and even sites, but with the wrong sign (positive energy for parallel alignment of neighbors). Eq. (5.44) states that the canonical average of the spin at site \( i \) equals the average of the field at the neighboring sites:
\[
\langle \sigma^{(i)} \rangle = \frac{\langle S^{(i+1)} + S^{(i-1)} \rangle}{2}.
\]
However, in accord with the interpretation of the field \( \tilde{\sigma}_i \) as the out-of-equilibrium average it should actually be the field at its own site:
\[
\langle \sigma^{(i)} \rangle = \langle S^{(i)} \rangle.
\]

**Failure of the naive approach: stability analysis**

We now show formally for scalar state variables \( \sigma^{(i)} \) and given an interaction energy (5.3) that the single particle potential, Eq. 5.35b, is always unstable for short wavelengths. We denote the single particle potential now with \( \mathcal{E}^{(k)} \), instead of \( \varepsilon_k \), to avoid confusion with the displacement field \( \varepsilon \), where \( \delta F[\eta + \varepsilon] \) is the change in free energy when the field changes from \( \eta \) to \( \eta + \varepsilon \). The free energy is given by
\[
\beta F_{mf} = -\ln Z_{mf} = -\sum_k \ln Z_k = -\sum_k \ln \text{Tr}_{\{\sigma^{(k)}\}} \exp \left( -\beta \mathcal{E}^{(k)} \right),
\]
and a displacement \( \varepsilon \) in the field \( \eta \) yields a displacement in the free energy of
\[
\delta \beta F_{mf} \equiv \beta F_{mf}[\eta + \varepsilon] - \beta F_{mf}[\eta]
\]
\[
= -\sum_k \ln \text{Tr}_{\{\sigma^{(k)}\}} \exp \left( -\beta \left( \mathcal{E}^{(k)} + \delta \mathcal{E}^{(k)} \right) \right) + \sum_k \ln \text{Tr}_{\{\sigma^{(k)}\}} \exp \left( -\beta \mathcal{E}^{(k)} \right)
\]
which, after a few steps of arithmetic yields
\[
\delta \beta F_{mf} \simeq \beta \sum_k \langle \delta \mathcal{E}^{(k)} \rangle_k + \frac{\beta^2}{2} \sum_k \text{Var}_k \left( \delta \mathcal{E}^{(k)} \right),
\]
where we define the (canonical) variance for a quantity \( X \left( \sigma^{(k)} \right) \) in the effective field \( \eta_k \) as

\[
\text{Var}_k (X) \equiv \langle X^2 \rangle_k - \langle X \rangle_k^2 , \tag{5.52}
\]

and the canonical average \( \langle X \rangle_k \) is defined in Eq. (5.24). The single particle potential \( \mathcal{E}^{(k)} \) of the \( k \)th particle is given by

\[
\mathcal{E}^{(k)} = - \left( \sigma^{(k)} - \frac{1}{2} S^{(k)} \right) J^{(k)} \varepsilon^{(\alpha)} . \tag{5.53}
\]

A displacement \( \{ \varepsilon^{(k)} \} \) of the effective field leads to a displacement in the single particle potential

\[
\delta \mathcal{E}^{(k)} = - \left( \sigma^{(k)} - \frac{1}{2} S^{(k)} \right) J^{(k)} \varepsilon^{(\alpha)} + \frac{1}{2} \varepsilon^{(k)} J^{(k)} \varepsilon^{(\alpha)} . \tag{5.54a}
\]

\[
= - \sigma^{(k)} J^{(k)} \varepsilon^{(\alpha)} + \frac{1}{2} S^{(k)} J^{(k)} \varepsilon^{(\alpha)} + \frac{1}{2} \varepsilon^{(k)} J^{(k)} \varepsilon^{(\alpha)} . \tag{5.54b}
\]

Consider the case that the \( \sigma^{(k)} \) are scalar quantities. Then the order of multiplication is irrelevant and we can write

\[
\text{Var}_k (\delta \mathcal{E}^{(k)}) = \langle \left( \sigma^{(k)} J^{(k)} \varepsilon^{(\alpha)} \right) \rangle_k - \langle \sigma^{(k)} \rangle_k \langle J^{(k)} \varepsilon^{(\alpha)} \rangle_k . \tag{5.55}
\]

With Eq. (5.44) we define a susceptibility \( \chi^{(k)}_\langle \rangle \) of the average \( \langle \sigma^{(k)} \rangle_k \) with respect to the field \( S^{(i)} \):

\[
\chi^{(k)}_\langle \rangle \equiv \frac{\partial \langle \sigma^{(k)} \rangle_k}{\partial S^{(i)}} = \beta \left( \langle \sigma^{(k)} \rangle_k \langle J^{(k)} \varepsilon^{(\alpha)} \rangle_k - \langle \sigma^{(k)} \rangle_k \langle \sigma^{(k)} \rangle_k \langle J^{(k)} \varepsilon^{(\alpha)} \rangle_k \right) . \tag{5.56}
\]

The variance of \( \delta \mathcal{E}^{(k)} \) (Eq. (5.55)) can be written as

\[
\text{Var}_k (\delta \mathcal{E}^{(k)}) = \beta^{-1} \frac{\partial \langle \sigma^{(k)} \rangle_k}{\partial S^{(\alpha)}} \varepsilon^{(\alpha)} J^{(k)} \varepsilon^{(\beta)} = \beta^{-1} \chi^{(k)}_\langle \rangle \varepsilon^{(\alpha)} J^{(k)} \varepsilon^{(\beta)} , \tag{5.57}
\]
and the displacement in the free energy is then given by

$$\delta \beta F_{mf} \simeq \left( S^{(a)} - \langle \sigma^{(a)} \rangle \right) \beta J^{(a\gamma)} \varepsilon^{(\gamma)} + \frac{\beta}{2} \varepsilon^{(a)} J^{(a\gamma)} \varepsilon^{(\gamma)} + \frac{\beta}{2} \varepsilon^{(a)} N^{(a\gamma)} J^{(a\gamma)} \varepsilon^{(\gamma)}. \tag{5.58}$$

For low temperatures, the susceptibility term is negligible: For example, consider the case that $\sigma^{(k)}$ is an Ising spin and $J^{(ij)}$ is for nearest neighbor interaction

$$\langle \sigma^{(k)} \sigma^{(k)} \rangle = \frac{\text{Tr} \left\{ \sigma^{(k)} \right\} (\sigma^{(k)})^2 \exp \left( \beta U \sigma^{(k)} \frac{S^{(k+1)} + S^{(k-1)}}{2} \right)}{\text{Tr} \left\{ \sigma^{(k)} \right\} \exp \left( \beta U \sigma^{(k)} \frac{S^{(k+1)} + S^{(k-1)}}{2} \right)} = 1, \tag{5.59}$$

and from Eq. (5.44) we get that

$$\beta \left( \langle \sigma^{(k)} \sigma^{(k)} \rangle - \langle \sigma^{(k)} \rangle \langle \sigma^{(k)} \rangle \right) = \beta^2 \left( 1 - \tanh^2 \left( \beta U \frac{S^{(k+1)} + S^{(k-1)}}{2} \right) \right), \tag{5.60}$$

which is much smaller than unity if $|\beta U (S^{(k+1)} + S^{(k-1)})| >> 1$:

$$1 - \tanh^2 x = \left( \frac{2}{\exp(x) + \exp(-x)} \right)^2 \simeq 4 \exp(-2 |x|) \quad \text{for} \quad |x| >> 1. \tag{5.61}$$

Similar calculations can be performed for any scalar state variable $\sigma$. Ignoring the susceptibility term, one gets for the displacement of the free energy

$$\delta \beta F_{mf} \simeq \left( S^{(a)} - \langle \sigma^{(a)} \rangle \right) \beta J^{(a\gamma)} \varepsilon^{(\gamma)} + \frac{\beta}{2} \varepsilon^{(a)} J^{(a\gamma)} \varepsilon^{(\gamma)}. \tag{5.62}$$

If $\varepsilon$ is a displacement from the equilibrium, then the linear terms in the displacement must vanish, $S^{(a)} - \langle \sigma^{(a)} \rangle = 0$, and the free-energy displacement becomes

$$\delta \beta F_{mf} = \frac{\beta}{2} \varepsilon^{(a)} J^{(a\gamma)} \varepsilon^{(\gamma)}. \tag{5.63}$$

The system is in a state that minimizes the free energy, if the linear terms in the displacement vanish and the quadratic terms are positive definite. This second condition is violated here: For nearest neighbor interaction the displacement in the free
energy is given by
\[ \delta \beta F_{mf} = \frac{\beta}{2} \sum_k \varepsilon^{(k)} \left( \frac{\varepsilon^{(k+1)} + \varepsilon^{(k-1)}}{2} \right), \] (5.64)

which is not positive definite: choosing the displacements \( \varepsilon \) of the effective field at odd and even sites to be of opposite sign yields a negative displacement of the free energy (and therefore the system is not in a minimum state of the free energy). For a coupling tensor of the form (5.1)

\[ j^{(ij)} = \frac{U}{|r_i - r_j|^K}, \] (5.65)

the free energy displacement from equilibrium is given by
\[ \delta \beta F_{mf} = \beta U \sum_{i \neq j} \frac{\varepsilon^{(i)} \varepsilon^{(j)}}{|r_i - r_j|^K} = \left( \frac{1}{\Delta V} \right)^2 \sum_{i} \varepsilon^{(i)} \Delta V \sum_{j} \frac{\varepsilon^{(j)}}{|r_i - r_j|^K} \Delta V, \] (5.66)

which, for \( \varepsilon \) varying slowly with respect to \( (\Delta V)^{1/3} \), can be written as an integral
\[ \delta F' \equiv \frac{(\Delta V)^2}{U} \delta F_{mf} \simeq \int \varepsilon (\mathbf{r}) \int_{|r-r'|>r_0} \frac{\varepsilon (r')}{|r-r'|^K} d^3 r' d^3 r. \] (5.67)

Substituting \( \mathbf{u} \equiv \mathbf{r}' - \mathbf{r} \) yields
\[ \delta F' = \int \varepsilon (\mathbf{r}) \int_{|\mathbf{u}|>r_0} \frac{\varepsilon (\mathbf{u} + \mathbf{r})}{|\mathbf{u}|^K} d^3 \mathbf{u} d^3 \mathbf{r}, \] (5.68)

which in spherical coordinates gives
\[ \delta F' = \int \varepsilon (\mathbf{r}) 2\pi \int_{-1}^{1} d(cos \theta) \int_{r_0}^{\infty} u^2 du \frac{\varepsilon (\mathbf{u} + \mathbf{r})}{u^K} d^3 \mathbf{r}. \] (5.69)
Next consider the effect of a single fourier mode, $\varepsilon (r) = \varepsilon_k \cos \theta$ . Choosing the coordinate systems such that $k \cdot n = kr \cos \theta$ and $k \cdot u = ku \cos \theta$ we get

$$\delta F' = 2\pi \varepsilon_k^2 \int \cos (k \cdot r) \left[ \int_{r_0}^{\infty} u^{2-K} du \int_{-1}^{1} \cos (k \cdot u + k \cdot r) d\cos \theta \right] d^3r$$

(5.70a)

$$= 2\pi \varepsilon_k^2 \int \left\{ \cos^2 (k \cdot r) \int_{r_0}^{\infty} u^{2-K} du \int_{-1}^{1} \cos (kux) dx \right. \right.$$

$$- \cos (k \cdot r) \int_{r_0}^{\infty} u^{2-K} du \int_{-1}^{1} \sin (kux) dx \left. \right\} d^3r$$

(5.70b)

$$= 4\pi \varepsilon_k^2 \int \left[ \cos^2 (k \cdot r) \int_{r_0}^{\infty} u^{2-K} du \frac{\sin (ku)}{ku} \right] d^3r$$

(5.70c)

$$= \frac{4\pi \varepsilon_k^2}{r_0^{K-3}} \int \cos^2 (k \cdot r) d^3r \left\{ (kr_0)^{K-3} \int_{kr_0}^{\infty} \frac{\sin (ku)}{(ku)^{K-1}} d (ku) \right\}$$

(5.70d)

$$= \frac{1}{2} V \varepsilon_k^2 \left( \frac{4\pi}{(K-3) r_0^{K-3}} \Phi_K (kr_0) \right),$$

(5.70e)

where we define a function $\Phi_K (x)$ as

$$\Phi_K (x) \equiv (K-3) x^{K-3} \int_x^{\infty} \frac{\sin \xi}{\xi^{K-1}} d\xi.$$  

(5.71)

For example, for Van-der-Waals interaction $K = 6$, and we find that $\Phi_6 (kr_0) > 0$ for $kr_0 \in [0.2.5467]$ and $\Phi_6 (kr_0)$ negative for some $kr_0 > 2.5467$. Therefore the system is not positive definite but unstable with respect to short wavelength perturbations.

For $K = 6$ the function $\Phi_K (x)$ can also be written as

$$\Phi_6 (x) = \frac{1}{8} x^3 \left( 6 \frac{\sin x}{x^4} + 2 \frac{\cos x}{x^3} - \frac{\sin x}{x^2} - \frac{\cos x}{x} + \frac{1}{2} \pi - \text{Si} (x) \right),$$

(5.72)

where $\text{Si} (x)$ is the sine integral

$$\text{Si} (x) \equiv \int_0^x \frac{\sin u}{u} du.$$  

(5.73)
5.1.7 Corrected construction

In the discussion about the Ising spin we found that the molecular field depended only on the neighboring sites, \( \langle \sigma^{(i)} \rangle = \left( S^{(i+1)} + S^{(i-1)} \right) / 2 \), which does not lead to the equilibrium state, where \( \langle \sigma_i \rangle = S_i \). We suggest a slightly different construction of the single-particle potential that distinguishes local and non-local terms, and that applies only the local part as a field acting on \( \sigma \).

We split the single-particle potential \( \mathcal{E}^{(i)} \) into a local and a non-local part:

\[
\mathcal{E}^{(i)} = - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) J^{(i) \alpha} S^{(\alpha)} - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) J^{(i) \alpha} \left( S^{(\alpha)} + S^{(i)} \mathcal{E}^{(\alpha)} - S^{(i)} \mathcal{E}^{(\alpha)} \right),
\]

(5.74)

where \( \mathcal{E}^{(k)} \) is the \( k \)th component of a vector consisting only of ones (i.e., \( A_{i \alpha} \mathcal{E}^{\alpha} = \sum_{k=1}^{\text{rank}(A)} A_{i k} \)). Thus

\[
\mathcal{E}^{(i)} = - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) S^{(i)} J^{(i) \alpha} \mathcal{E}^{(\alpha)} - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) J^{(i) \alpha} \left( S^{(\alpha)} - S^{(i)} \mathcal{E}^{(\alpha)} \right).
\]

(5.75)

The first term is purely local - it does only depend on \( \sigma^{(i)} \) and \( S^{(i)} \) and a location-dependent factor \( J^{(i) \alpha} \mathcal{E}^{(\alpha)} \). The second term is non-local: it couples the molecular direction to the difference between \( S \) at \( r_i \) and the neighboring sites \( S^{(j)} \), \( j \neq i \). The non-local field couples to \( \sigma^{(i)} \), but we require that it does not couple to \( \sigma^{(i)} \) directly but to its average, \( S^{(i)} \). Therefore we replace \( \sigma^{(i)} \) here with \( S^{(i)} \):

\[
\mathcal{E}^{(i)}_{\text{new}} = - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) S^{(i)} J^{(i) \alpha} \mathcal{E}^{(\alpha)} - \frac{1}{2} S^{(i)} J^{(i) \alpha} \left( S^{(\alpha)} - S^{(i)} \mathcal{E}^{(\alpha)} \right).
\]

(5.76)

We argued here heuristically for replacing \( \sigma^{(i)} \) in the non-local part. This construction does not follow from a general theory. It is justified because this single particle
potential leads to a well-posed minimization problem unlike a gradient expansion or the naïve construction.

**Stability analysis**

We still need to show that the so constructed single particle potential obeys the constraints (5.22), (5.23) and (5.29). A displacement \( \{ \varepsilon^k \}_k^{N} \) in the field \( \{ S^k \}_k^{N} \) yields a displacement in the single particle potential of the \( i \)th molecule:

\[
\delta \mathcal{E}^{(i)} = - \left( \sigma^{(i)} - \frac{1}{2} S^{(i)} \right) \varepsilon^{(i)} J^{(i\alpha)} \varepsilon^{(\alpha)} + \frac{1}{2} \varepsilon^{(i)} S^{(i)} J^{(i\alpha)} \varepsilon^{(\alpha)} \\
- \frac{1}{2} \varepsilon^{(i)} J^{(i\alpha)} (S^{(\alpha)} - S^{(i)} \varepsilon^{(\alpha)}) - \frac{1}{2} S^{(i)} J^{(i\alpha)} (\varepsilon^{(\alpha)} - \varepsilon^{(i)} \varepsilon^{(\alpha)}) \\
+ \frac{1}{2} \varepsilon^{(i)} J^{(i\alpha)} (\varepsilon^{(\alpha)} - \varepsilon^{(i)} \varepsilon^{(\alpha)}).
\]  

(5.77)

If the state variables are scalar, and the coupling term is symmetric, \( J^{(ij)} = J^{(ji)} \), we write this as

\[
\delta \mathcal{E}^{(i)} = - \left( \sigma^{(i)} - S^{(i)} \right) \varepsilon^{(i)} J^{(i\alpha)} \varepsilon^{(\alpha)} \\
- \left( \frac{S^{(\alpha)} \varepsilon^{(i)} + S^{(i)} \varepsilon^{(\alpha)}}{2} - S^{(i)} \varepsilon^{(i)} \varepsilon^{(\alpha)} \right) J^{(i\alpha)} \\
+ \left( \varepsilon^{(i)} \varepsilon^{(i)} \varepsilon^{(\alpha)} - \frac{1}{2} \varepsilon^{(i)} \varepsilon^{(\alpha)} \right) J^{(i\alpha)}.
\]

(5.78)

and the free energy displacement

\[
\delta \beta F_{mt} = \beta \sum_k \langle \delta \mathcal{E}^{(k)} \rangle_k + \frac{\beta^2}{2} \sum_k \left( \langle (\delta \mathcal{E}^{(k)})^2 \rangle_k - \langle \delta \mathcal{E}^{(k)} \rangle_k^2 \right).
\]

(5.79)
becomes

\[ \delta \beta F_{nf} = \]
\[ \beta \sum_i \left( S^{(i)} - \langle \sigma^{(i)} \rangle_i \right) J^{(i)} e^{(i)} - \beta \left( S^{(i)} J^{(i)} - \sum_i S^{(i)} J^{(i)} \right) e^{(i)} \]
\[ + \beta \sum_i \left( e^{(i)} e^{(i)} - \frac{1}{2} e^{(i)} e^{(i)} \right) J^{(i)} \]
\[ + \frac{\beta^2}{2} \sum_i \left( \langle \sigma^{(i)} \rangle_i - \langle \sigma^{(i)} \rangle_i \right) e^{(i)} J^{(i)} e^{(i)} J^{(i)} e^{(i)} e^{(i)}. \]  

(5.80a)

(5.80b)

Ignoring terms linear in \( \varepsilon \) yields

\[ \delta \beta F_{nf} = \beta \sum_i \left( e^{(i)} e^{(i)} - \frac{1}{2} e^{(i)} e^{(i)} \right) J^{(i)} + \frac{\beta^2}{2} \sum_i \beta^{-1} \chi^{(i)} e^{(i)} J^{(i)} e^{(i)} e^{(i)} e^{(i)}. \]

(5.81a)

We constructed the single particle potential such that \( \langle \sigma^{(i)} \rangle_i \) does not depend on the field of the neighbors \( S^{(j)}, j \neq i \), thus

\[ \chi^{(i)} = \chi^{(i)} \delta_{ij}, \]

(5.82)

and the free energy displacement simplifies to

\[ \delta \beta F_{nf} = \beta \sum_i \left( e^{(i)} e^{(i)} - \frac{1}{2} e^{(i)} e^{(i)} \right) J^{(i)} + \frac{\beta^2}{2} \sum_i \chi^{(i)} e^{(i)} J^{(i)} e^{(i)} e^{(i)} e^{(i)} \]

(5.83a)

\[ = \beta \sum_{i,j} \left( e^{(i)} e^{(i)} e^{(j)} - \frac{1}{2} e^{(i)} e^{(j)} \right) J^{(ij)} + \frac{\beta^2}{2} \sum_{i,j} \chi^{(i)} e^{(i)} J^{(ij)} e^{(i)} e^{(i)} e^{(i)} \]

(5.83b)

\[ = \beta \sum_{i,j} \left( e^{(i)} e^{(i)} \left( 1 + \frac{1}{2} \chi^{(i)} \right) - \frac{1}{2} e^{(i)} e^{(j)} \right) J^{(ij)}. \]

(5.83c)

We define

\[ \delta \beta F_0 \equiv \frac{1}{2} \beta U \sum_{i,j} \frac{e^{(i)} e^{(i)} \chi^{(i)}}{|r_i - r_j|^K} \]

(5.84a)

\[ \delta \beta F_1 \equiv \beta U \sum_{i,j} \left( \frac{e^{(i)} e^{(i)} - \frac{1}{2} e^{(i)} e^{(j)}}{|r_i - r_j|^K} \right), \]

(5.84b)
so that

$$\delta \beta F = \delta \beta F_0 + \delta \beta F_1. \quad (5.85)$$

We assume that $\chi^{(i)}_i$ is strictly positive\(^2\), thus always $\delta \beta F_0 > 0$ and show only that $\delta \beta F_1 > 0$: As before in (5.67) we write this as an integral

$$\delta F' = \frac{(\Delta V)^2}{U} \delta F_1 \simeq \int_{|r-r'|>r_0} \left( \frac{\varepsilon^2(r) - \frac{1}{2} \varepsilon(r) \varepsilon(r')}{|r-r'|^K} \right) d^3rd^3r'. \quad (5.86)$$

Considering a single fourier mode, $\varepsilon(r) = \varepsilon_k \cos(k \cdot r)$ and evaluating the double integrals as in the previous section yields

$$\delta F' = \varepsilon_k^2 \frac{V}{2} \frac{4\pi}{r_0^{K-3}} \frac{1}{K-3} \left( 1 - \frac{1}{2} \Phi_K(r_0k) \right), \quad (5.87)$$

with $\Phi_K$ defined in (5.71). And since $|\Phi_K(x)| \leq 1$ for all $x \geq 0$ it is clear that $\delta F'$ does increase for perturbations of all wavelengths.

\(^2\)If $< \sigma >$ is degree of molecular orientation it will surely increase if an external field $S$ is applied to it.
Chapter 6

Application to nematic mixtures

6.1 Van-der-Waals interaction

It is generally accepted that induced dipole-induced dipole interactions (or London or dispersion or Van-der-Waals forces) are the cause of the nematic phase. The original theory by Maier and Saupe [7][8][9] on the nematic-isotropic phase transition was derived for a scalar system. Maier and Saupe derived the effective mean field potential using a second order perturbation calculation on a dipole-dipole system [8]. We will present a semi-classical approach for determining the single particle potential, instead.

6.1.1 Semi-classical derivation

We start with the induced dipole-induced dipole interaction between a pair of molecules. The electric field at $r_1$ due to a dipole $\mu_2$ at $r_2$ is given by

$$E^{(2)}_1 (r_1) = \mu_2 (r_2) \cdot \frac{3\hat{r} - 1}{4\pi\varepsilon_0 r^3} = \mu_2 \cdot T$$  \hspace{1cm} (6.1)

(see, e.g., Griffiths [25]), where

$$T \equiv \frac{3\hat{r} - 1}{4\pi\varepsilon_0 r^3} \hspace{1cm} (6.2a)$$

$$r \equiv |r_{12}| \equiv |r_2 - r_1| \hspace{1cm} (6.2b)$$

$$\hat{r} \equiv \hat{r}_{12} = \frac{r_2 - r_1}{|r_2 - r_1|} \hspace{1cm} (6.2c)$$

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In index notation
\[ E^{(2)}_{1i}(r_1) = \mu^{(2)}_{\alpha}(r_2) T_{\alpha i}, \] (6.3a)
and the same holds for the field at \( r_2 \) due to \( \mu_2 \) at \( r_1 \):
\[ E^{(1)}_{2i}(r_2) = \mu^{(1)}_{\alpha}(r_1) T_{\alpha i}. \] (6.3b)

The coupling tensor \( T \) is symmetric with respect to its indices and with respect to the vector \( r_{12} \):
\[ T_{ij} = T_{ji} \] (6.4)
\[ T(r_{12}) = T(r_{21}). \] (6.5)

We write for ease of notation
\[ E^{(2)}_{1i}(r_1) = E^{(2)}_{1i}, \text{ and } E^{(1)}_{2i}(r_2) = E^{(1)}_{2i}. \] (6.6)

Thus \( E_1 \equiv E^{(2)}_{1\alpha}(r_1) \hat{e}_\alpha \) denotes the field at \( r_1 \) due to \( \mu_2 \). The dipole \( \mu_2 \) is composed of a fixed part \( s_2 \) due to quantum-mechanical fluctuations and an induced part \( m_2 \) due to the field of the dipole \( \mu_1 \) at \( r_1 \)
\[ \mu_2 = s_2 + m_2, \] (6.7a)
and conversely for \( \mu_1 \)
\[ \mu_1 = s_1 + m_1. \] (6.7b)

The induced dipole \( m_2 \) of molecule 2 is the dot-product of the polarizability tensor \( \alpha_2 \) of molecule 2 and the field \( E_2 \) due to \( \mu_1 \) at \( r_2 \)
\[ m_2 = \alpha_2 \cdot E_2. \] (6.8)
Therefore we have a recursive relation for the dipoles

\[ m_2 = \alpha_2 \cdot E_2 \]  \hspace{1cm} \text{(6.9a)}

\[ E_2 = (m_1 + s_1) \cdot T = T \cdot (m_1 + s_1) \]  \hspace{1cm} \text{(6.9b)}

\[ m_1 = \alpha_1 \cdot E_1 \]  \hspace{1cm} \text{(6.9c)}

\[ E_1 = T \cdot (m_2 + s_2) \]  \hspace{1cm} \text{(6.9d)}

The set of equations (6.9a) to (6.9d) can be solved for \( m_2 \), eliminating \( m_1, E_1 \) and \( E_2 \):

\[ m_2 = \alpha_2 \cdot (T \cdot s_1 + T \cdot m_1) \]  \hspace{1cm} \text{(6.10a)}

\[ = \alpha_2 \cdot T \cdot s_1 + \alpha_2 \cdot T \cdot (\alpha_1 \cdot (T \cdot s_2 + T \cdot m_2)) \]  \hspace{1cm} \text{(6.10b)}

\[ = \alpha_2 \cdot T \cdot s_1 + \alpha_2 \cdot T \cdot \alpha_1 \cdot T \cdot s_2 + \alpha_2 \cdot T \cdot \alpha_1 \cdot T \cdot m_2, \]  \hspace{1cm} \text{(6.10c)}

which is of the form

\[ m_2 = a + B^{(21)} \cdot m_2 \]  \hspace{1cm} \text{(6.11)}

with

\[ a \equiv \alpha_2 \cdot T \cdot s_1 + B \cdot s_2 \]  \hspace{1cm} \text{(6.12)}

and

\[ B^{(21)} \equiv \alpha_2 \cdot T \cdot \alpha_1 \cdot T. \]  \hspace{1cm} \text{(6.13)}

This can be solved for \( m_2 \)

\[ m_2 = (1 - B^{(21)})^{-1} \cdot a. \]  \hspace{1cm} \text{(6.14)}

Assuming that the eigenvalues \( \lambda_k \) of \( B \) are small, \( |\lambda_k| < < 1 \) we can expand to lowest order in \( B^{(21)} \)

\[ (1 - B^{(21)})^{-1} \approx 1 + B^{(21)}. \]  \hspace{1cm} \text{(6.15)}
This approximation can be justified as long as $|T_{\beta \gamma \alpha \gamma \beta}| = O \left( (r_{\text{mol}}/r_{12})^3 \right)$ is small\(^1\), i.e., the distance between molecules is sufficiently larger than the molecular radius. If the molecules come very close to one another, one cannot approximate them as point charges anymore and one needs, in principle, to include higher multipole moments to the field applied to the molecule at $\mathbf{r}_1$ in Eq. (6.1). We assume that, on average in a thermodynamic system, only the dipole term is relevant. Inserting (6.15) into (6.14) yields

$$m_2 = (1 - B^{(21)})^{-1} \cdot \mathbf{a} \simeq (1 + B^{(21)}) \cdot \mathbf{a} \quad (6.16a)$$

$$= (1 + B^{(21)}) \cdot (\alpha_2 \cdot \mathbf{T} \cdot \mathbf{s}_1 + B^{(21)} \cdot \mathbf{s}_2) \quad (6.16b)$$

$$\simeq \alpha_2 \cdot \mathbf{T} \cdot \mathbf{s}_1 + B^{(21)} \cdot \mathbf{s}_2 + B^{(21)} \cdot \alpha_2 \cdot \mathbf{T} \cdot \mathbf{s}_1, \quad (6.16c)$$

which to second order in $|\alpha \mathbf{T}|$ yields

$$m_2 = \alpha_2 \cdot \mathbf{T} \cdot \mathbf{s}_1 + (\alpha_2 \cdot \mathbf{T} \cdot \alpha_1 \cdot \mathbf{T}) \cdot \mathbf{s}_2 + O \left( |\alpha \mathbf{T}|^3 \right). \quad (6.17)$$

Therefore the dipole moments are given to second order in $|\alpha \mathbf{T}|$ by

$$\mu_2 = \mathbf{s}_2 + \alpha_2 \cdot \mathbf{T} \cdot \mathbf{s}_1 + (\alpha_2 \cdot \mathbf{T} \cdot \alpha_1 \cdot \mathbf{T}) \cdot \mathbf{s}_2 \quad (6.18a)$$

$$\mu_1 = \mathbf{s}_1 + \alpha_1 \cdot \mathbf{T} \cdot \mathbf{s}_2 + (\alpha_1 \cdot \mathbf{T} \cdot \alpha_2 \cdot \mathbf{T}) \cdot \mathbf{s}_1. \quad (6.18b)$$

The energy of dipole 1 in the field $E_1$ is given by

$$\mathcal{E}_1 = -s_1 E_1 - \frac{1}{2} m_1 E_1, \quad (6.19)$$

\(^1\alpha\) is a molecular polarizability and has a characteristic magnitude of $4\pi \varepsilon_0 r_{\text{mol}}^3$, where $r_{\text{mol}}$ is a characteristic length of the molecule.
where the second term is an induced-dipole term (hence the factor $\frac{1}{2}$).

$$
-\mathcal{E}_1 = \left( s_1 + \frac{1}{2} m_1 \right) \cdot T \cdot \left( m_2 + s_2 \right) \tag{6.20a}
$$

\begin{align*}
&= \left( s_1 + \frac{1}{2} (\alpha_1 T s_2 + (\alpha_1 \cdot T \cdot \alpha_2 \cdot T) s_1) \right) \\
&\quad \cdot T \cdot (\alpha_2 T s_1 + (\alpha_2 \cdot T \cdot \alpha_1 \cdot T) s_2 + s_2) \tag{6.20b}
\end{align*}

which to $O \left( |T\alpha|^2 \right)$ yields

$$
-\mathcal{E}_1 = s_1^{(1)} T_{\alpha\beta} \alpha_{\beta\gamma}^{(2)} T_{\gamma\lambda} s_1^{(1)} + s_1^{(1)} T_{\alpha\beta} \delta_{\beta}^{(2)} + \frac{1}{2} \alpha_{\alpha\beta}^{(1)} T_{\beta\gamma} s_1^{(2)} T_{\alpha\mu} s_\mu^{(2)} \tag{6.21a}
$$

or,

$$
-\mathcal{E}_1 = s_1 T \alpha_2 T s_1 + s_1 T s_2 + \frac{1}{2} (\alpha_1 T s_2) (T s_2) \tag{6.22}
$$

The energy can be averaged over a short time such that we can use the average of the quantum mechanical fluctuations instead of their instantaneous values. We assume that the quantum-mechanical oscillators for molecules at different locations are uncorrelated, $\langle s_{1i} s_{2j} \rangle = 0$, then

$$
-\mathcal{E}_1 = \langle s_{1\alpha} s_{1\beta} \rangle T_{\alpha\gamma} \alpha_{\lambda\beta}^{(2)} T_{\lambda\alpha} + \langle s_{1\alpha} s_{2\beta} \rangle T_{\alpha\beta} + \frac{1}{2} \langle s_{2\alpha} s_{2\beta} \rangle \alpha_{\gamma\lambda}^{(1)} T_{\lambda\beta} T_{\gamma\alpha} \tag{6.23}
$$

We need to relate the permanent dipoles $s$ to the polarizability.

$$
\begin{align*}
s_i &= \alpha_{i\beta} E_\beta \tag{6.24} \\
\gamma^{-1} s_\gamma &= \alpha_{\gamma\beta} E_\beta \alpha_{\gamma\gamma}^{-1} = E_i \tag{6.25}
\end{align*}
$$

but also

$$
\beta E_\beta = \mathcal{E} = \hbar \nu \tag{6.26}
$$
therefore
\[ s_\gamma \alpha_\gamma^{-1} s_\beta = \hbar \nu \]  
(6.27)

in the eigenframe of \( \alpha \)
\[ \langle s_\alpha^2 \rangle \delta_{\alpha \beta} \lambda^{-1}_\beta = \hbar \nu \]  
(6.28)

where \( \lambda_k \) is the \( k \)th eigenvalue of \( \alpha_{ij} \). For isotropic polarizability
\[ \langle s^2 \rangle = \hbar \nu \lambda = \hbar \nu \alpha, \]  
(6.29)

and we can show that
\[ \langle s_{1\alpha} s_{1\beta} \rangle = a_1 \alpha_\alpha^{(1)} \]  
(6.30)
\[ \langle s_{2\alpha} s_{2\beta} \rangle = a_2 \alpha_\alpha^{(2)} \]  
(6.31)
then
\[ \mathcal{E}_1 = a_1 \alpha_\alpha^{(1)} T_{\alpha \gamma} T_{\lambda \beta} \alpha_\gamma^{(2)} + \frac{1}{2} a_2 \alpha_\alpha^{(2)} \alpha_\gamma^{(1)} T_{\lambda \beta} T_{\gamma \alpha} \]  
(6.32)

and relabelling yields
\[ \mathcal{E}_1 = \left( a_1 + \frac{1}{2} a_2 \right) \alpha_\alpha^{(1)} T_{\alpha \gamma} T_{\lambda \beta} \alpha_\gamma^{(2)}. \]  
(6.33)

This energy was derived for molecule 1 in a fixed external field. In reality, half of the energy will be assigned to molecule 2. The total energy is now
\[ \mathcal{E} = \frac{1}{2} (\mathcal{E}_1 + \mathcal{E}_2) : \]
\[ \mathcal{E} = \frac{3}{2} \left( a_1 + a_2 \right) \alpha_\alpha^{(1)} T_{\alpha \gamma} T_{\lambda \beta} \alpha_\gamma^{(2)}. \]  
(6.34)

In London’s theory [26][27][28], however, the oscillator strength of the system is not the arithmetic but the harmonic mean of the individual oscillator strengths. Our result is different because we assumed (incorrectly) that the oscillator strengths for
molecules 1 and 2 are uncorrelated\textsuperscript{2}. In reality we would need to consider the frequency of the system of the coupled electrons. Thus we replace the term \( (a_1 + a_2) / 2 \) in Eq. (6.34) by the respective harmonic mean, yielding

\[
\mathcal{E} = \frac{3}{2} \left( \frac{a_1 a_2}{a_1 + a_2} \right) \alpha_{\alpha \beta}^{(1)} T_{\alpha \gamma} T_{\lambda \beta} \alpha_{\gamma \lambda}^{(2)}.
\]  

(6.35)

We note that \( T \) has dimension \( [\varepsilon_0 m^3]^{-1} \) and \( \alpha \) has dimension \( [\varepsilon_0 m^3] \), therefore \( \alpha T \) is dimensionless. Eq. (6.35) yields the pair energy that we will use as the basis for our theory.

6.1.2 Single-particle potential

Before we construct the single particle potential we first rewrite equation (6.35) and define some notation. We consider a mixture of \( n \) different kinds of molecules, \( A_1, ..., A_n \). We write the pair interaction between two molecules of type \( X \) and \( Y \) as

\[
W_{XY} = \frac{3}{2} \left( \frac{a_1 a_2}{a_1 + a_2} \right) \frac{1}{(4\pi \varepsilon_0)^2 \rho^6} \alpha_{\alpha \beta}^{(X)} (3r_\alpha r_\gamma - \delta_{\alpha \gamma})(3r_\gamma r_\beta - \delta_{\lambda \beta}) \alpha_{\gamma \lambda}^{(Y)},
\]

(6.36a)

where \( X \in \{ A_1, ..., A_n \} \) and \( Y \in \{ A_1, ..., A_n \} \). We assume uniaxial molecular polarizability and write the polarizability tensor as

\[
\alpha_{ij} = \alpha_1 \delta_{ij} + (\alpha_\parallel - \alpha_\perp) \left( \frac{2\sigma_{ij} + \delta_{ij}}{3} \right) \quad (6.37a)
\]

\[
= \delta_{ij} \left( \frac{2\alpha_1 + \alpha_\parallel}{3} \right) + \frac{2}{3} \sigma_{ij} (\alpha_\parallel - \alpha_\perp) \quad (6.37b)
\]

\[
= \overline{\alpha} (\delta_{ij} + \alpha_0 \sigma_{ij}) \quad (6.37c)
\]

\textsuperscript{2}For interaction between molecules of the same kind (6.34) and (6.35) are identical, however.
where $\bar{\alpha}$ is the average polarizability, $a_a$ the relative polarizability-anisotropy and $\sigma_{ij}$ the molecular orientation:

$$\bar{\alpha} \equiv \frac{2\alpha_\perp + \alpha_\parallel}{3} \quad (6.38a)$$
$$a_a \equiv \frac{2\alpha_\parallel - \alpha_\perp}{3\bar{\alpha}} \quad (6.38b)$$
$$\sigma \equiv \frac{3}{2} \hat{I} \frac{1}{2} 1 \quad (6.38c)$$

where $\hat{I}$ is the molecular long axis. The assumption of uniaxial molecular polarizability is valid if we assume that the molecule rotates very fast about the short axis such that any properties of the molecules perpendicular to its long axis can be replaced by their respective averages. This should not be confused with macroscopic uniaxiality.

We simplify Eq. (6.36a) to

$$W_{XY} \equiv -\frac{A_{XY}}{r^6} \left( \delta_{\alpha\beta} + a_a^{(X)} \sigma_{a\beta}^{(X)} \right) J_{\alpha\beta\gamma\lambda} \left( \delta_{\gamma\lambda} + a_a^{(Y)} \sigma_{a\gamma}^{(Y)} \right), \quad (6.39)$$

with

$$A_{XY} \equiv \frac{3}{2} \left( \frac{a_1 a_2}{a_1 + a_2} \right) \frac{\bar{\alpha} X \bar{\alpha} Y}{(4\pi\varepsilon_0)^2} \quad (6.40a)$$
$$J_{ijkl} = (3r_ir_k - \delta_{ik})(3r_jr_l - \delta_{ij}) \quad (6.40b)$$

and $\bar{\alpha} X \bar{\alpha} Y / 4\pi\varepsilon_0$ is a characteristic molecular volume, while $a_{X,Y}$ is an energy that may be estimated by the first ionization energy of the molecule. We can further simplify by noting the following identities:

$$\delta_{\alpha\beta}\delta_{\gamma\lambda} J_{\alpha\beta\gamma\lambda} = 9 - 3 - 3 + 3 = 6 \quad (6.41a)$$
$$\delta_{\alpha\beta} J_{\alpha\beta\gamma\lambda} = 9r_\gamma r_\lambda - 3r_\gamma r_\lambda - 3r_\gamma r_\lambda + \delta_{\gamma\lambda} = 3r_\gamma r_\lambda - \delta_{\gamma\lambda} \quad (6.41b)$$
$$\delta_{\gamma\lambda} J_{\alpha\beta\gamma\lambda} = 3r_\alpha r_\beta - \delta_{\alpha\beta} \quad (6.41c)$$
arriving at

$$-\frac{r^6}{A_{XY}} W_{XY} (r_1, r_2)$$

$$= \quad 6 + 3 \left( \sigma^X_{a\beta} (r_1) + \sigma^Y_{a\beta} (r_2) \right) r_\alpha r_\beta + \alpha^X_{a\alpha} \sigma^X_{a\beta} (r_1) \sigma^Y_{\gamma\lambda} (r_2) J_{\alpha\beta\gamma\lambda} (\tilde{r}_{12}) .$$

(6.42)

We now construct the single particle potential. We do this by first constructing an effective pair-potential, employing the procedure for constructing a single particle potential. The single particle potential will then be the sum over all effective pair-potentials. (It is irrelevant if we perform first the mean-field procedure and then the spatial averaging or vice-versa. We use this order for book-keeping purposes.) The first step is to replace the orientation $\sigma^Y (r_2)$ by its (out-of-equilibrium) average,

$$-\frac{r^6}{A_{XY}} w^{**}_{XY} (r_1, r_2)$$

$$\equiv \quad 6 + 3 \left( \sigma^X_{a\beta} (r_1) + \sigma^Y_{a\beta} (r_2) \right) r_\alpha r_\beta + \alpha^X_{a\alpha} \sigma^X_{a\beta} (r_1) \sigma^Y_{\gamma\lambda} (r_2) J_{\alpha\beta\gamma\lambda} (\tilde{r}_{12}) ,$$

(6.43)

where $w^{**}_{XY}$ is the "first-step" effective pair-potential for particle X interacting with a particle of kind Y. The stars are used to keep track of the stage of the mean-field procedure. The second step is to subtract half the out-of-equilibrium average:

$$w^*_{XY} \equiv w^{**}_{XY} (r_1, r_2) - \frac{1}{2} w^{**}_{XY} (r_1, r_2) ,$$

(6.44)

thus

$$-\frac{r^6}{A_{XY}} w^*_{XY} \equiv \quad 3 + 3 \left( \sigma^X_{a\beta} (r_1) - \frac{1}{2} Q^X_{a\beta} (r_1) \right) + \frac{1}{2} \alpha^Y_{a\alpha} Q^Y_{a\beta} (r_2) r_\alpha r_\beta$$

$$+ \alpha^X_{a\alpha} \sigma^X_{a\beta} (r_1) - \frac{1}{2} Q^X_{a\beta} (r_1) \right) Q^Y_{\gamma\lambda} (r_2) J_{\alpha\beta\gamma\lambda} (\tilde{r}_{12}) .$$

(6.45a)
Third, we separate the interaction into local and non-local term

\[
- \frac{r^6}{A_{XY}} w^*_{XY} = 3 + 3 \left( \alpha^X_\alpha \sigma^X_{\alpha \beta} (r_1) + \frac{1}{2} (\alpha^Y_\alpha Q^Y_{\alpha \beta} (r_2) - \alpha^X_\alpha Q^X_{\alpha \beta} (r_1)) \right) r_\alpha r_\beta \\
+ \alpha^X_\alpha \alpha^Y_\alpha \left( \sigma^X_{\alpha \beta} (r_1) - \frac{1}{2} Q^X_{\alpha \beta} (r_1) \right) \left( Q^Y_{\gamma \lambda} (r_2) - Q^Y_{\gamma \lambda} (r_1) \right) J_{\alpha \beta \gamma \lambda} (r_{12}) \\
+ \alpha^X_\alpha \alpha^Y_\alpha \left( \sigma^X_{\alpha \beta} (r_1) - \frac{1}{2} Q^X_{\alpha \beta} (r_1) \right) Q^Y_{\gamma \lambda} (r_1) J_{\alpha \beta \gamma \lambda} (r_{12}) .
\]  

(6.45b)

Fourth, we replace the molecular orientation in the non-local part \((Q_{ij} (r_2) - Q_{ij} (r_1))\) by its out-of-equilibrium average

\[
- \frac{r^6}{A_{XY}} w_{XY} = 3 + 3 \left( \alpha^X_\alpha \sigma^X_{\alpha \beta} (r_1) + \frac{1}{2} (\alpha^Y_\alpha Q^Y_{\alpha \beta} (r_2) - \alpha^X_\alpha Q^X_{\alpha \beta} (r_1)) \right) r_\alpha r_\beta \\
+ \frac{1}{2} \alpha^X_\alpha \alpha^Y_\alpha Q^X_{\alpha \beta} (r_1) \left( Q^Y_{\gamma \lambda} (r_2) - Q^Y_{\gamma \lambda} (r_1) \right) J_{\alpha \beta \gamma \lambda} (r_{12}) \\
+ \alpha^X_\alpha \alpha^Y_\alpha \left( \sigma^X_{\alpha \beta} (r_1) - \frac{1}{2} Q^X_{\alpha \beta} (r_1) \right) Q^Y_{\gamma \lambda} (r_1) J_{\alpha \beta \gamma \lambda} (r_{12}) .
\]

(6.46a)

This is the final effective pair potential. Instead we sometimes also write:

\[
- \frac{r^6}{A_{XY}} w_{XY} = 3 + 3 \left( \alpha^X_\alpha \sigma^X_{\alpha \beta} (r_1) + \frac{1}{2} (\alpha^Y_\alpha Q^Y_{\alpha \beta} (r_2) - \alpha^X_\alpha Q^X_{\alpha \beta} (r_1)) \right) r_\alpha r_\beta \\
+ \frac{1}{2} \alpha^X_\alpha \alpha^Y_\alpha Q^X_{\alpha \beta} (r_1) Q^Y_{\gamma \lambda} (r_2) J_{\alpha \beta \gamma \lambda} (r_{12}) \\
+ \alpha^X_\alpha \alpha^Y_\alpha \left( \sigma^X_{\alpha \beta} (r_1) - Q^X_{\alpha \beta} (r_1) \right) Q^Y_{\gamma \lambda} (r_1) J_{\alpha \beta \gamma \lambda} (r_{12}) .
\]

(6.47a)

The single particle potential for a particle of kind \(X\) located at \(r_1\) is the sum over the pair-interaction with all surrounding molecules

\[
E^{\text{single particle}}_X (r_1) = \sum_k \int g_{XA_k} (r_1, r_2) \rho_{A_k} (r_2) w_{XA_k} (r_1, r_2) d^3 r_2 .
\]

(6.48)

where \(g_{XA_k}\) is the pair-distribution function and \(g_{XA_k} (r_1, r_2) \rho_{A_k} (r_2)\) is the probability to find a molecule of kind \(A_k\) in the volume element \(d^3 r_2\), given that a molecule
of kind $X$ is present at $r_1$. The single particle potential is a functional of all densities and all nematic order parameters. It is also a functional of the respective pair-distribution functions, which we take as parameters.

$$E^\text{single particle}_X (r_1) = E^\text{xp.}_X [\rho_{A_1}, \ldots, \rho_{A_n}, Q^{A_1}, \ldots, Q^{A_n}, g_{X A_1}, \ldots, g_{X A_n}] (r_1).$$  \hspace{1cm} (6.49)

We define quantities $e_{XA_k}$ and $U_{XA_k}$

$$e_{XA_k} \equiv -\frac{r^6}{A_{XY}} w_{XA_k} \hspace{1cm} (6.50)$$

$$U_{XA_k} \equiv A_{XA_k} \frac{g_{XA_k} (r_1, r_2)}{r^6}, \hspace{1cm} (6.51)$$

where the right hand side of (6.50) is defined in (6.47a); this is the part of the interaction due to relative orientation of the molecules. We finally write for the effective single particle potential

$$E^\text{single-particle}_X (r_1) = \int U_{XA_k} (r_1, r_2) \rho_{A_k} (r_2) e_{XA_k} (r_1, r_2) d^3r_2. \hspace{1cm} (6.52)$$

6.2 Mixtures of liquid crystals

6.2.1 Structure of the free energy

The free energy, $F$, is defined as

$$F \equiv -k_B T \ln Z, \hspace{1cm} (6.53)$$

where $k_B$ is Boltzmann’s constant, $T$ the absolute temperature, and $Z$ the canonical partition function. In mean field theory, the partition function is a product of single
particle partition functions. For a single material of indistinguishable molecules this is

\[ Z = \frac{1}{N!} Z_1^N. \]  

(6.54)

For a mixture of \( M \) different materials the partition function is a product out of partition functions for each material

\[ Z = \prod_{k=1}^{M} \frac{1}{N_k!} Z_{1k}^{N_k}, \]  

(6.55)

where \( Z_{1k} = Z_1(A_k) \) is the single-particle partition function for material \( A_k \). Each single particle-partition function is the trace over the Boltzmann distribution:

\[ Z_1(A_k) = C \int \exp \left( -\beta E_k \right) d^d q_k d^d p_k, \]  

(6.56)

where \( q \) and \( p \) are the canonical coordinates and their conjugate momenta, respectively. E.g., for rigid molecules with cylindrical symmetry \( d = 5 \), where \( q \) corresponds to three spatial coordinates and the two independent coordinates of a three dimensional unit vector. The classical trace contains a factor of quantum mechanical origin \( C \), corresponding to the inverse volume of a unit cell in phase space. Since \( C \) only adds a constant to the free energy we omit it in general. We assume that the single particle potential \( E_k \) is a sum of a part depending only on coordinates, \( q \), and a part depending only on conjugate momenta \( p \), and each may couple to a set of external fields \( H_{\text{ext}} \). The effective mean field can also be considered an external field, but its definition depends on the species \( k \). Thus the single particle potential for the \( k^{th} \)
particle is now:

\[ E_k (p, q, H_{ext}, H_{mf}) = E^q_k (q, H_{ext} (q), H_{mf}^k [Y] (q)) + E^p_k (p, H_{ext} (q), H_{mf}^k [Y] (q)). \]  

(6.57)

And \( H_{mf}^k \) is a functional of the nematic order parameters, densities and mutual pair-distribution functions for all materials, for which we write shorthand

\[ Y (r) = \{ \rho_k \}_{k=1}^n \cup \{ Q^k_{ij} \}_{k=1}^n \cup \{ g_{kl} \}_{k,l=1}^n. \]  

(6.58)

To save some writing, we write both fields as a single field \( H_k = H_{ext} + H_{mf} \):

\[ E_k (p, q, H_k) = E^q_k (q, H_k) + E^p_k (p, H_k). \]  

(6.59)

The free energy of a mixture is the sum of the free energies for each material:

\[ \beta F = \sum_{k=1}^M \beta F_k = -\sum_{k=1}^M \ln Z_k = \sum_{k=1}^M (N_k \ln N_k - N_k \ln Z_{1k}), \]  

(6.60)

and the single material free energy is given by

\[ \beta F_k = N_k \ln N_k - N_k \ln \left[ \int \exp \left( -\beta E^q_k (q, H_k) - \beta (E^p_k (p), H_k) \right) d^D q d^D p \right]. \]  

(6.61)

We separate the canonical coordinates into spatial coordinates of the centers of masses of the molecules, \( r \) and other degrees of freedom, \( \tilde{q} \) (e.g., the three Euler-angles to describe the orientation of a rigid molecule):

\[ q = (r | \tilde{q}). \]  

(6.62)

The dimension of the spatial coordinates is denoted as \( D \) and typically \( D = 3 \). We assume that \( E^q_k \) will only depend on location \( r \) through the dependence on \( H_k (r) \).

\[ \beta F_k = N_k \ln N_k - N_k \ln \int \exp \left( -\beta E^q_k (\tilde{q}, H_k (r)) - \beta (E^p_k (p), H_k (r)) \right) d^D r d^{D-D} \tilde{q} d^D p. \]  

(6.63)
If we divide the total volume into small subvolumes such that $H_k$ is approximately constant throughout such volume, we can integrate out the spatial coordinates and write for the free energy of the subvolume

$$\frac{\Delta \beta F^i}{\Delta V_i} = \sum_k \rho_k(i) \ln N_k(i) - \rho_k(i) \ln \Delta V(i) \int \exp(-\beta E_k(\tilde{\mathbf{q}}, \mathbf{p}, H_k(i))) d^{d-D} \tilde{\mathbf{q}} d^d \mathbf{p}$$

(6.64a)

$$= \sum_k \rho_k(i) \ln \rho_k(i) - \rho_k(i) \ln \int \exp(-\beta E_k(\tilde{\mathbf{q}}, \mathbf{p}, H_k(i))) d^{d-D} \tilde{\mathbf{q}} d^d \mathbf{p},$$

(6.64b)

where $\rho_k(i) \equiv N_k(i)/\Delta V(i)$. Writing formally $\mathcal{F}_i \equiv \Delta F^i/\Delta V_i$ and taking the continuum limit yields

$$F = \sum_i \mathcal{F}_i \Delta V_i \to \int \mathcal{F}(\mathbf{r}) d^D \mathbf{r}.$$  

(6.65)

Then the free energy density is given by

$$\beta \mathcal{F}(\mathbf{r}) = \sum_k \rho_k(\mathbf{r}) \ln (V^* \rho_k(\mathbf{r})) - \rho_k(\mathbf{r}) \ln \int \exp(-\beta E_k(\tilde{\mathbf{q}}, \mathbf{p}, H_k(\mathbf{r}))) d^{d-D} \tilde{\mathbf{q}} d^d \mathbf{p},$$

(6.66)

where, in order to make the argument of the logarithm dimensionless, we added an arbitrary term linear in $\rho$ to the free energy that will not enter the dynamic equations:

$$\sum_k \rho_k(\mathbf{r}) \ln V^*.$$ The total free energy is given by

$$\beta F = \int \beta \mathcal{F}(\mathbf{r}) d^D \mathbf{r}$$

(6.67a)

$$= \sum_k \int \rho_k(\mathbf{r}) \ln (V^* \rho_k(\mathbf{r})) d^D \mathbf{r} - \sum_k \rho_k(\mathbf{r}) \ln \int \exp(-\beta E_k(\tilde{\mathbf{q}}, \mathbf{p}, H_k[Y](\mathbf{r}))) d^d \mathbf{q} d^d \mathbf{p}.$$  

(6.67b)
6.2.2 Structure of the functional derivatives

The total free energy is given by Eq. (6.67b). A displacement in either nematic order parameter or density of one material will give rise to a displacement in all single particle potentials, \( \{ E_k \}_{k=1}^n \), and the displacement of the free energy \( \delta F \) becomes

\[
\delta \beta F = \sum_k (\beta F_k [E_k + \delta E_k] - \beta F [E_k])
\]

(6.68a)

\[
= - \sum_k \int \rho^k (r) \ln \int \exp (-\beta E_k - \beta \delta E_k) d\Gamma + \sum_k \int \rho_k (r) \ln \int \exp (-\beta E_k) d\Gamma
\]

(6.68b)

\[
\simeq - \sum_k \int \rho^k (r) \ln \left( 1 - \beta \langle \delta E_k \rangle_k + \frac{\beta^2}{2} \langle \delta E_k^2 \rangle_k + O (\delta E_k^3) \right) d^D r.
\]

(6.68c)

(For displacements in either \( \rho^k \), or \( Q_{ij}^k \), the displacement \( \delta \beta F \) will have a term of this form. An additional term is added below, which only occurs if the displacement is in \( \rho^k \).) We have defined the canonical average in the single particle potential \( E_k \) of a quantity \( \xi \) to be

\[
\langle \xi \rangle_k = \frac{\int \xi \exp (-\beta E_k) d^{d-D} q d^d p}{\int \exp (-\beta E_k) d^{d-D} q d^d p}.
\]

(6.69)

We note here that, unless \( E_k \) is not a function of \( \xi \), the generalized displacement operator and the average operator do not commute, since \( \langle \xi \rangle \) is then not linear in \( \xi \):

\[
\delta \langle \xi \rangle_k \neq \langle \delta \xi \rangle_k.
\]

(6.70)

Thus to second order in the displacements \( \delta E_k \)

\[
\delta \beta F = \sum_k \int \rho^k (r) \left( \langle \beta \delta E_k \rangle_k - \frac{\beta^2}{2} \left( \langle \delta E_k^2 \rangle_k - \langle \delta E_k \rangle_k^2 \right) \right) d^D r + O (\delta E_k^3),
\]

(6.71)
which we separate (6.71) in a first-order and a second-order term:

\[
\delta \beta F^{(1)} = \sum_k \int \rho^k (\mathbf{r}) \langle \beta \delta E_k \rangle_k \ d^D \mathbf{r} \tag{6.72a}
\]

\[
\delta \beta F^{(2)} = -\frac{\beta}{2} \sum_k \int \rho^k (\mathbf{r}) \left( \langle \delta E_k^{2} \rangle_k - \langle \delta E_k \rangle_k^2 \right) \ d^D \mathbf{r}. \tag{6.72b}
\]

We can make explicit that the \(E_k\) depend only on the coordinates of molecules of species \(k\):

\[
E_k = E_k (\mathbf{q}_k, \mathbf{p}_k). \tag{6.73}
\]

Then it is clear that the average of a quantity \(\xi\) depending on \((\mathbf{q}_l, \mathbf{p}_l)\) will only enter the canonical average \(\langle \xi \rangle_k\) in field \(E_k\) if \(l = k\):

\[
\langle \xi (\mathbf{q}_l, \mathbf{p}_l) \rangle_k = \xi (\mathbf{q}_l, \mathbf{p}_l) \text{ if } l \neq k. \tag{6.74}
\]

If the displacement is due to a displacement in the density \(\rho_k\), i.e., \(\delta E_k [\rho_k] = E_k [\rho_k + \delta \rho_k] - E [\rho_k]\) then the displacement of the total free energy, Eq. (6.71), will be augmented by the term

\[
(\delta \beta F)^*_{\rho_k} = \sum_k \int \left( \delta \rho^k (\mathbf{r}) \left( 1 + \ln \left( V^* \rho^k (\mathbf{r}) \right) - \ln Z_{1k} \right) + \frac{1}{2} \frac{\left( \delta \rho^k (\mathbf{r}) \right)^2}{\rho^k (\mathbf{r})} \right) \ d^D \mathbf{r}, \tag{6.75}
\]

with a single particle partition function

\[
Z_{1k} [Y] (\mathbf{r}) \equiv \int \exp \left( -\beta E_k (\bar{\mathbf{q}}, \mathbf{p}, H_k [Y] (\mathbf{r})) \right) \ d^{d-D} \mathbf{q} d^D \mathbf{p}. \tag{6.76}
\]

The single particle potential for the interaction of any single molecule is the sum of the interaction with the effective field due to all materials, including its own

\[
E_k = \sum_{l=1}^{n} E_{kl}, \tag{6.77}
\]
and each effective pair-potential is of the form (Eq. (6.52))

\[ E_{kl} = \int e_{kl}(\mathbf{r}_1, \mathbf{r}_2) U_{kl}(\mathbf{r}_1, \mathbf{r}_2) \rho^j(\mathbf{r}_2) \, d^D\mathbf{r}_2, \tag{6.78} \]

where the respective indices indicate the number of the material in \( \{A_1, \ldots, A_n\} \). Apart from \( e_{kl} \), the geometric kernel \( U_{kl} \) will in general also depend on the nematic order parameters \( Q^k_{ij} \) and \( Q^l_{ij} \), albeit in an unknown fashion\(^3\) (due to the dependence of the pair-distribution function \( g_{kl} \) on both order parameters). If the displacement \( \delta E_{kl} \) is due to a displacement in nematic order parameter, it is given by

\[ (\delta E_{kl})_{Q^m} = \int \left\{ (\delta e_{kl})_{Q^m}(\mathbf{r}_1, \mathbf{r}_2) U_{kl}(\mathbf{r}_1, \mathbf{r}_2) + e_{kl}(\mathbf{r}_1, \mathbf{r}_2) (\delta U_{kl})_{Q^m}(\mathbf{r}_1, \mathbf{r}_2) \\
+ (\delta e_{kl} \delta U_{kl})_{Q^m} \right\} \rho^l(\mathbf{r}_2) \, d^D\mathbf{r}_2, \tag{6.79} \]

while the displacement of \( E_{kl}[\rho^m] \) due to a displacement in density \( \rho^m \) is given by

\[ (\delta E_{kl})_{\rho^m} = \int e_{kl} \left\{ U_{kl}(\delta \rho^l)_{\rho^m}(\mathbf{r}_2) + (\delta U_{kl})_{\rho^m} \rho^l(\mathbf{r}_2) \right\} \, d^D\mathbf{r}_2, \tag{6.80} \]

where the index \( (\delta X)_{Q^m} \) and \( (\delta X)_{\rho^m} \) denotes the order parameter that the displacement is with respect to. Thus the displacement of the free energy to first order with respect to a displacement in a nematic order parameter is given by

\[ (\delta \beta F^{(1)})_{Q^m} = \sum_k \int \rho_k(\mathbf{r}_1) \left\langle \beta (\delta E_{k})_{Q^m} \right\rangle_k d^D\mathbf{r}_1 \tag{6.81a} \]

\[ = \beta \sum_{k,j} \int \rho^k(\mathbf{r}_1) \left\langle (\delta E_{kl})_{Q^m}(\mathbf{r}_1, \mathbf{r}_2) U_{kl}(\mathbf{r}_1, \mathbf{r}_2) \rho^j(\mathbf{r}_2) \right\rangle_k \, d^D\mathbf{r}_2 d^D\mathbf{r}_1 \tag{6.81b} \]

\[ = \beta \sum_{k,j} \int \rho^k(\mathbf{r}_1) \left\langle (\delta e_{kl})_{Q^m}(\mathbf{r}_1, \mathbf{r}_2) (\delta U_{kl})_{Q^m}(\mathbf{r}_1, \mathbf{r}_2) \rho^j(\mathbf{r}_2) \right\rangle_k \, d^D\mathbf{r}_2 d^D\mathbf{r}_1 \tag{6.81c} \]

\(^3\)At least it is beyond the scope of this work to identify this dependency.
while the displacement in the free energy due to a displacement in a concentration field is

\[
(\delta \beta F^{(1)})_{\rho^m} = \beta \sum_{k,l} \int \rho^k (\mathbf{r}_1) \left( \langle e_{kl} U_{kl} \rangle_{k} (\delta \rho^m)_{\rho^m} (\mathbf{r}_2) + \langle e_{kl} (\delta U_{kl})_{\rho^m} \rangle_{k} \rho^l (\mathbf{r}_2) \right) d^D r_2 d^D r_1 \\
+ \sum_k \int (\delta \rho^k)_{\rho^m} (\mathbf{r}_1) \left( 1 + \ln V^* \rho^k (\mathbf{r}_1) - \ln Z_{1k} (\mathbf{r}_1) \right) d^D r_1,
\]

(6.82a)

where the last line is the augmentation term given in Eq. (6.75). We now express the displacements in functional derivatives by using the identity for a displacement of a functional $\xi$ due to a displacement of $Q^m_{ij}$:

\[
(\delta \xi)_{Q^m} = P_{ijkl} \int \frac{\delta \xi}{\delta Q^k_{\alpha \beta} (\mathbf{r})} \delta Q_{\gamma \lambda}^l (\mathbf{r}) d^D r,
\]

(6.83)

with $P_{ijkl}$ the traceless, symmetric projector. And the identity for a displacement of $\xi$ due to a displacement in density $\rho^m$:

\[
(\delta \xi)_{\rho^m} = \int \frac{\delta \xi}{\delta \rho^m (\mathbf{r})} \delta \rho^m (\mathbf{r}).
\]

(6.84)

The displacement of the free energy with respect to $Q^m_{ij}$ is thus:

\[
(\delta \beta F^{(1)})_{Q^m_{ij}} = P_{ijkl} \beta \sum_{k,l} \int \rho^k (\mathbf{r}_1) \rho^l (\mathbf{r}_2) \times \\
\left\langle \frac{\delta e_{kl} (\mathbf{r}_1, \mathbf{r}_2)}{\delta Q^m_{\alpha \beta} (\mathbf{r})} U_{kl} (\mathbf{r}_1, \mathbf{r}_2) + e_{kl} (\mathbf{r}_1, \mathbf{r}_2) \frac{\delta U_{kl} (\mathbf{r}_1, \mathbf{r}_2)}{\delta Q^m_{\alpha \beta} (\mathbf{r})} \right\rangle_k d^D r_2 d^D r_1 \delta Q_{\gamma \lambda}^m (\mathbf{r}) d^D r,
\]

(6.85)

and the functional derivative with respect to $Q^m_{ij}$:

\[
\frac{\delta \beta F}{\delta Q^m_{ij} (\mathbf{r})} = P_{ijkl} \beta \sum_{k,l} \int \rho^k (\mathbf{r}_1) \rho^l (\mathbf{r}_2) \times \\
\left\langle \frac{\delta e_{kl} (\mathbf{r}_1, \mathbf{r}_2)}{\delta Q^m_{\alpha \beta} (\mathbf{r})} U_{kl} (\mathbf{r}_1, \mathbf{r}_2) + e_{kl} (\mathbf{r}_1, \mathbf{r}_2) \frac{\delta U_{kl} (\mathbf{r}_1, \mathbf{r}_2)}{\delta Q^m_{\alpha \beta} (\mathbf{r})} \right\rangle_k d^D r_2 d^D r_1.
\]

(6.86)
Similarly, the functional derivative with respect to $\rho^m$ is given by:

\[
\frac{\delta \beta F}{\delta \rho^m (r)} = \beta \sum_{k,l} \int \rho^k (r_1) \left( \left\langle e_{kl} (r_1, r_2) U_{kl} (r_1, r_2) \right\rangle_k \frac{\delta \rho^l (r_2)}{\delta \rho^m (r)} \right) \, d^D r_2 d^D r_1 \\
+ \beta \sum_{k,l} \int \rho^k (r_1) \left( \left\langle e_{kl} (r_1, r_2) \frac{\delta U_{kl} (r_1, r_2)}{\delta \rho^m (r)} \right\rangle_k \rho^l (r_2) \right) \, d^D r_2 d^D r_1 \\
+ \sum_k \int \frac{\delta \rho^k (r_1)}{\delta \rho^m (r)} \left( 1 + \ln \left( V^* \rho_k (r_1) \right) - \ln Z_{1k} (r_1) \right) \, d^D r_1,
\]

or

\[
\frac{\delta \beta F}{\delta \rho^m (r)} = \beta \sum_k \int \rho^k (r_1) \left\langle e_{km} (r_1, r) U_{km} (r_1, r) \right\rangle_k \, d^D r_1 \\
+ \beta \sum_{k,l} \int \rho^k (r_1) \left\langle e_{kl} (r_1, r_2) \frac{\delta U_{kl} (r_1, r_2)}{\delta \rho^m (r)} \right\rangle_k \rho^l (r_2) \, d^D r_2 d^D r_1 \\
+ \ln \rho_m (r) - \ln Z_{1m} (r),
\]

where we ignored constant terms in the chemical potential as they do not enter the dynamic equations.

### 6.2.3 Summary of results and definitions

Equations (6.86) and (6.88) are the most general form of the generalized forces and we summarize them here together with all definitions. For material $m$, the generalized force on the nematic order parameter is given by

\[
\frac{\delta \beta F}{\delta Q_{ij}^m (r)} = P_{\alpha \gamma \lambda} \beta \sum_{k,l} \int \rho^k (r_1) \rho^l (r_2) \times \\
\left\langle \frac{\delta e_{kl} (r_1, r_2)}{\delta Q_{\alpha \beta}^m (r)} U_{kl} (r_1, r_2) + e_{kl} (r_1, r_2) \frac{\delta U_{kl} (r_1, r_2)}{\delta Q_{\alpha \beta}^m (r)} \right\rangle_k \, d^D r_2 d^D r_1.
\]
and its the chemical potential by

\[
\frac{\delta \beta F}{\delta \rho^m (r)} = \beta \sum_k \int \rho^k (r_1) \langle e_{km} (r_1, r) U_{km} (r_1, r) \rangle_k d^D r_1 \\
+ \beta \sum_{k,l} \int \rho^k (r_1) \langle e_{kl} (r_1, r_2) \frac{\delta U_{kl} (r_1, r_2)}{\delta \rho^m (r)} \rangle_k \rho^l (r_2) d^D r_2 d^D r_1 \\
+ \ln \rho_m (r) - \ln Z_{1m} (r). 
\]  

(6.90)

The part \( U_{kl} \) of the interaction kernel is defined by

\[
U_{kl} (r_1, r_2) \equiv \frac{3}{2} \frac{\nu_k \nu_l}{\nu_k + \nu_l (4\pi \varepsilon_0 r^3)^2} g_{kl} (r_1, r_2),
\]  

(6.91)

and the part \( e_{kl} \), respectively by

\[
e_{kl} (r_1, r_2) = - \left\{ 3 + 3 \left( \alpha_a^k \sigma_{a\beta}^k (r_1) + \frac{1}{2} \left( \alpha_a^l Q_{a\beta}^l (r_2) - \alpha_a^k Q_{a\beta}^k (r_1) \right) \right) r_\alpha r_\beta \\
+ \alpha_a^k \alpha_a^l \left\{ \sigma_{a\beta}^k (r_1) - Q_{a\beta}^k (r_1) \right\} Q_{\gamma\lambda}^l (r_1) J_{a\beta\gamma\lambda} (\hat{r}_{12}) \\
+ \frac{1}{2} \alpha_a^k \alpha_a^l Q_{a\beta}^k (r_1) Q_{\gamma\lambda}^l (r_2) J_{a\beta\gamma\lambda} (\hat{r}_{12}) \right\}. 
\]  

(6.92)

The logarithmic term of the single particle partition function, ignoring a constant term due to the momentum integral, and the canonical average \( \langle \xi \rangle_k \), respectively are given by

\[
\ln Z_{1m} [Y] (r_1) \equiv \ln \int \exp (-\beta E_k (r_1)) d^2 \sigma^m 
\]  

(6.93)

\[
\langle \xi \rangle_k (r_1) \equiv \frac{\int \xi \exp (-\beta E_k (r_1)) d^2 \sigma^m}{\int \exp (-\beta E_k (r_1)) d^2 \sigma^m}, 
\]  

(6.94)

where the integral \( d^2 \sigma^m \) is over all orientation of the molecule of type \( m \) located at \( r \), and the single particle potential \( E_k \) is given by

\[
E_k (r_1) = \sum_{k=1}^n \int e_{mk} (r_1, r_2) U_{mk} (r_1, r_2) \rho^k (r_2) d^D r_2. 
\]  

(6.95)
The tensor $P_{ijkl} \equiv (\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk})/2 - \delta_{ij}\delta_{kl}/3$ is the traceless, symmetric projector, $\beta \equiv k_B T$ is inverse “temperature,” and the polarizabilities are defined as

$$\alpha^k = (2\alpha'^k + \alpha'^k) / 3 \quad \text{and} \quad \alpha'^k = \frac{2\alpha'^k - \alpha'^k}{3},$$

(6.96)

where $\alpha'^k$ is the largest eigenvalue of the molecular polarizability, and $\alpha'^k$ the two (degenerate) smaller eigenvalues. The distance $r$ and the vector components $r_i$ are defined by

$$r_{12} \equiv r_2 - r_1 \quad \text{and} \quad r_i = r_{ki} \cdot \hat{e}_i / |r_{kl}| \quad \text{and} \quad r \equiv |r_{12}|.$$

(6.97)

The fourth rank tensor $J_{ijkl}$ is defined

$$J_{ijkl} (\hat{r}_{12}) = (3r_ir_k - \delta_{ik})(3r_jr_j - \delta_{ij}).$$

(6.98)

The terms $h\nu_k$ are the the characteristicic energies $a_k$ of the ground state oscillations of molecules of material $k$, defined in chapter 6.1.

6.2.4 Isotropic pair-distribution function

Equations (6.86) and (6.88) indicate a dependence of the kernel $U_{kl}$ (indirectly due to the pair-distribution function) on density and nematic order parameter. The pair-distribution function will depend on the nematic order parameter, because steric interactions are necessary to completely describe the deformed state of nematics (e.g., Marruci-Greco theory [22]), and these interactions enter the here presented theory via the pair-distribution function. In fact, the degeneracy of the elastic constants in the second order tensor theory of elastic deformations given by de Gennes [29] is lifted by incorporating steric anisotropy [22]. However, incorporation of this dependency is
beyond the scope of this work. Similarly, $g_{kl}$ should also depend on density, although this dependency may be weak. We assume that the pair-distribution function can be written as an isotropic part and an anisotropic part

$$g_{kl} = g_{kl}^{iso} + g_{kl}^{aniso} \quad (6.99)$$

And respectively

$$U_{kl} = U_{kl}^{iso} + U_{kl}^{aniso} \quad (6.100)$$

For the remaining part we will ignore $U_{kl}^{aniso}$ and only deal with $U_{kl}^{iso}$. The isotropic part $U_{kl}^{iso}$ should surely not depend on molecular orientation, $\sigma_k$. We also assume that $\delta U_{kl}/\delta Q_{ij} = 0$, although in principle the isotropic part of the pair-distribution function could still depend on the scalar invariants of $Q_{ij}$. Ignoring the anisotropic part of the pair-distribution function and assuming that its isotropic part does neither depend on $Q$ nor $\rho$ we write now for the functional derivatives

$$\frac{\delta \beta F}{\delta Q_{ij}^{m}} (\mathbf{r}) = P_{\alpha \beta \gamma \lambda} \sum_{k,l} \int \rho_k (\mathbf{r}_1) \rho_l (\mathbf{r}_2) \left\langle \frac{\delta e_{kl} (\mathbf{r}_1, \mathbf{r}_2)}{\delta Q_{ij}^{m}} (\mathbf{r}) \right\rangle_k U_{kl}^{iso} (\mathbf{r}_1, \mathbf{r}_2) d^D \mathbf{r}_2 d^D \mathbf{r}_1 \quad (6.101)$$

and

$$\frac{\delta \beta F}{\delta \rho^m (\mathbf{r})} = \beta \sum_k \int \rho_k (\mathbf{r}_1) \left\langle e_{km} (\mathbf{r}_1, \mathbf{r}) \right\rangle_k U_{km}^{iso} (\mathbf{r}_1, \mathbf{r}) d^D \mathbf{r}_1 + \ln \rho_m (\mathbf{r}) - \ln Z_{1m} (\mathbf{r}) . \quad (6.102)$$

We note that the functional derivatives with respect to the densities are not independent. They are coupled via the condition that the divergence of the total current vanishes [30].
6.2.5 \( \delta F/\delta Q_{ij} \)

We now consider the case of a mixture of (anisotropically) polarizable molecules with no internal degrees of freedom. The mean-field pair interaction was given by Eq. (6.52), with \( e_{XY} \equiv e_{kl} \) defined as

\[
e_{kl}(r_1, r_2) = -\{ 3 + 3 \left( \alpha_a^k \sigma_{\alpha \beta}^k (r_1) + \frac{1}{2} \left( \alpha_a^l Q_{\alpha \beta}^l (r_2) - \alpha_a^k Q_{\alpha \beta}^k (r_1) \right) \right) r_\alpha r_\beta \\
+ \alpha_a^k \alpha_a^l \left\{ \sigma_{\alpha \beta}^k (r_1) - Q_{\alpha \beta}^k (r_1) \right\} Q_{\gamma \lambda}^l (r_1) J_{\alpha \beta \gamma \lambda} \\
+ \frac{1}{2} \alpha_a^k \alpha_a^l Q_{\alpha \beta}^k (r_1) Q_{\gamma \lambda}^l (r_2) J_{\alpha \beta \gamma \lambda} \}.
\]

The functional derivatives of \( e_{kl} \) with respect to the order parameter \( Q_{ij}^m \) of material \( A_m \) are given by

\[
\frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^m(r)} = -\{ \frac{3}{2} \left( \alpha_a^l \delta_{in} \delta_{jo} \delta_{j\beta} \delta (r - r_2) - \alpha_a^k \delta_{km} \delta_{io} \delta_{j\beta} \delta (r - r_1) \right) r_\alpha r_\beta \\
+ \alpha_a^k \alpha_a^l \sigma_{\alpha \beta}^k (r_1) \delta_{i\gamma} \delta_{j\lambda} \delta_{in} \delta (r - r_1) K_{\alpha \beta \gamma \lambda} \\
- \alpha_a^k \alpha_a^l \left( \delta_{io} \delta_{j\beta} \delta_{km} \delta (r - r_1) Q_{\gamma \lambda}^l (r_1) + Q_{\alpha \beta}^k (r_1) \delta_{i\gamma} \delta_{j\lambda} \delta_{in} \delta (r - r_1) \right) K_{\alpha \beta \gamma \lambda} \\
+ \frac{1}{2} \alpha_a^k \alpha_a^l \left( \delta_{io} \delta_{j\beta} \delta_{km} \delta (r - r_1) Q_{\gamma \lambda}^l (r_2) + Q_{\alpha \beta}^k (r_1) \delta_{i\gamma} \delta_{j\lambda} \delta_{in} \delta (r - r_2) \right) K_{\alpha \beta \gamma \lambda} \}.
\]

where \( K_{ijkl} \equiv P_{ij \alpha \beta} J_{\alpha \beta \kl} \) and \( P_{ijkl} \) is the symmetric, traceless projector. Applying the contraction with the Kronecker-deltas and using the identity \( K_{ijkl} = K_{klij} \) and
collecting terms \( K_{\alpha\beta ij} \) yields

\[
\frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^{\alpha\beta}(r)} = -\frac{3}{2} \left( \alpha'_{\alpha} \delta_{lk} \delta (r - r_2) - \alpha_{\alpha} \delta_{km} \delta (r - r_1) \right) r_i r_j \\
- K_{\alpha\beta ij} \alpha'_{\alpha} \alpha'_{\alpha} \left\{ \sigma_{\alpha\beta}^k (r_1) \delta_{lm} \delta (r - r_1) \right\} \\
- (Q_{\alpha\beta}^l (r_1) \delta_{km} + Q_{\alpha\beta}^k (r_1) \delta_{lm}) \delta (r - r_1) \\
+ \frac{1}{2} \delta (r - r_1) \delta_{km} Q_{\alpha\beta}^l (r_2) + \frac{1}{2} Q_{\alpha\beta}^k (r_1) \delta_{lm} \delta (r - r_2) \right\} .
\] (6.105)

We now insert Eq. (6.105) into (6.101). The following procedure makes use of the identities

\[
U_{ki}(r_1, r_2) = U_{ik}(r_2, r_1) \quad (6.106)
\]

\[
K_{ijkl} = K_{klij}. \quad (6.107)
\]

We consider four parts of this functional derivative separately:

\[
\left( \frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^{\alpha\beta}(r)} \right)_1 = -\frac{3}{2} \left( \alpha'_{\alpha} \delta_{lk} \delta (r - r_2) - \alpha_{\alpha} \delta_{km} \delta (r - r_1) \right) r_i r_j 
\] (6.108)

\[
\left( \frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^{\alpha\beta}(r)} \right)_2 = K_{\alpha\beta ij} \alpha'_{\alpha} \alpha'_{\alpha} \left( Q_{\alpha\beta}^l (r_1) \delta_{km} + Q_{\alpha\beta}^k (r_1) \delta_{lm} \right) \delta (r - r_1) 
\] (6.109)

\[
\left( \frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^{\alpha\beta}(r)} \right)_3 = -K_{\alpha\beta ij} \alpha'_{\alpha} \alpha'_{\alpha} \sigma_{\alpha\beta}^k (r_1) \delta_{lm} \delta (r - r_1) 
\] (6.110)

\[
\left( \frac{\delta e_{kl}(r_1, r_2)}{\delta Q_{ij}^{\alpha\beta}(r)} \right)_4 = \frac{1}{2} K_{\alpha\beta ij} \alpha'_{\alpha} \alpha'_{\alpha} \left( \delta (r - r_1) \delta_{km} Q_{\alpha\beta}^l (r_2) + Q_{\alpha\beta}^k (r_1) \delta_{lm} \delta (r - r_2) \right) 
\] (6.111)
and perform the substitution on the subterms one through four, starting with the first:

\[
\left( \frac{\delta \beta F}{\delta Q_{ij}^m} \right)_1 = -\frac{3}{2} \beta \sum_{k,l} \int \rho^k(r_1) P_{ij\gamma\lambda} \alpha_\alpha^l \delta_{lm} \delta (r - r_2) U_{kl}^{iso} (r_1, r_2) \rho^l(r_2) r_\gamma r_\lambda d^D r_2 d^D r_1 \\
+ \frac{3}{2} \beta \sum_{k,l} \int \rho^k(r_1) P_{ij\gamma\lambda} \alpha_\alpha^l (\delta_{km} \delta (r - r_1)) U_{kl}^{iso} (r_1, r_2) \rho^l(r_2) r_\gamma r_\lambda d^D r_2 d^D r_1.
\]

(6.112)

Performing summation removes \( \delta_{lm} \) and \( \delta_{km} \) and rearranging yields

\[
\left( \frac{\delta \beta F}{\delta Q_{ij}^m} \right)_1 = \\
-\frac{3}{2} \beta \alpha_\alpha^m P_{ij\gamma\lambda} \sum_k \int \rho^k(r_1) \delta (r - r_2) U_{km}^{iso} (r_1, r_2) \rho^m(r_2) r_\gamma r_\lambda d^D r_2 d^D r_1 \\
+ \frac{3}{2} \beta \alpha_\alpha^m P_{ij\gamma\lambda} \sum_l \int \rho^l(r_2) \delta (r - r_1) U_{lm}^{iso} (r_2, r_1) \rho^m(r_1) r_\gamma r_\lambda d^D r_2 d^D r_1,
\]

(6.113)

and integrating over the delta functions yields

\[
\left( \frac{\delta \beta F}{\delta Q_{ij}^m} \right)_1 = -\frac{3}{2} \beta \alpha_\alpha^m P_{ij\gamma\lambda} \sum_k \int \rho^k(r_1) U_{km}^{iso} (r_1, r) \rho^m(r) r_\gamma r_\lambda d^D r_1 \\
+ \frac{3}{2} \beta \alpha_\alpha^m P_{ij\gamma\lambda} \sum_l \int \rho^l(r_2) U_{lm}^{iso} (r_2, r) \rho^m(r) r_\gamma r_\lambda d^D r_2,
\]

(6.114)

and both sums are the same and this term vanishes identically. Next the second term:

\[
\left( \frac{\delta \beta F}{\delta Q_{ij}^m} \right)_2 = \beta \sum_{k,l} \int d^D r_2 d^D r_1 \times \\
\rho^k(r_1) K_{ij\alpha\beta} \alpha_\alpha^k \alpha_\alpha^l \left( Q_{\alpha\delta}^l (r_1) \delta_{km} + Q_{\alpha\beta}^k (r_1) \delta_{lm} \right) \delta (r - r_1) U_{kl}^{iso} (r_1, r_2) \rho^l(r_2).
\]

(6.115)
Summing up removes $\delta_{km}$ and $\delta_{lm}$ and integrating removes the delta functions (re-labeling summation index from $l$ to $k$ and integration label from $r_2$ to $r_1$):

$$
\left( \frac{\delta \beta F}{\delta q_{ij}} \right)_2 = \beta \alpha_a^m \sum_k \rho^m(r) \alpha_a^k Q_{\alpha \beta}^k(r) \int d^D r_1 K_{ij \alpha \beta} U_{km}^{iso}(r, r_1) \rho^k(r_1) + \beta \alpha_a^m \sum_k \alpha_a^k \rho^k(r) Q_{\alpha \beta}^k(r) \int d^D r_1 K_{ij \alpha \beta} U_{km}^{iso}(r, r_1) \rho^m(r_1). \tag{6.116}
$$

Next the third term:

$$
\left( \frac{\delta \beta F}{\delta q_{ij}} \right)_3 = -\beta \sum_{k,l} \int \rho^k(r_1) K_{ij \alpha \beta} \alpha_a^k \alpha_a^l \times \langle \sigma_{\alpha \beta}^k \rangle_k(r_1) \delta_{im} \delta(r - r_1) U_{kl}^{iso}(r_1, r_2) \rho^l(r_2) \int d^D r_2 d^D r_1,
$$

(6.117)

remove $\delta_{lm}$ by summation and remove $\delta(r - r_1)$ by integration and relabel integral to get

$$
\left( \frac{\delta \beta F}{\delta q_{ij}} \right)_3 = -\beta \alpha_a^m \sum_k \alpha_a^k \rho^k(r) \langle \sigma_{\alpha \beta}^k \rangle_k(r) \int K_{ij \alpha \beta} U_{km}^{iso}(r, r_2) \rho^m(r_1) d^D r_1. \tag{6.118}
$$

Next the fourth term:

$$
\left( \frac{\delta \beta F}{\delta q_{ij}} \right)_4 = -\frac{1}{2} \beta \sum_{k,l} \int \rho^k(r_1) K_{ij \alpha \beta} \alpha_a^k \alpha_a^l \delta_{km} Q_{\alpha \beta}^l(r_2) U_{kl}^{iso}(r_1, r_2) \rho^l(r_2) d^D r_2 d^D r_1
$$

$$
-\frac{1}{2} \beta \sum_{k,l} \int \rho^k(r_1) K_{ij \alpha \beta} \alpha_a^k \alpha_a^l Q_{\alpha \beta}^k(r_1) \delta_{lm} \delta(r - r_2) U_{kl}^{iso}(r_1, r_2) \rho^l(r_2) d^D r_2 d^D r_1.
$$

(6.119)
Remove $\delta_{km}$ by summation remove $\delta_1 (r - r_1)$ and $\delta (r - r_2)$ by integration and relabel

\[
\frac{\delta \beta F}{\delta Q_{ij}} = -\frac{1}{2} \beta \sum_k \int \rho (r) K_{\alpha \beta ij} \alpha_\alpha Q_{\alpha \beta}^k (r_1) U_{km}^\text{iso} (r, r_1) \rho^k (r_1) dD r_1
\]

\[
-\frac{1}{2} \beta \sum_k \int \rho^k (r_1) K_{\alpha \beta ij} \alpha_\alpha Q_{\alpha \beta}^k (r_1) U_{km}^\text{iso} (r_1, r) \rho^m (r) dD r_1. \tag{6.120}
\]

Both sums are equal, thus

\[
\frac{\delta \beta F}{\delta Q_{ij}} = -\beta \alpha_\alpha \rho^m (r) \sum_k \alpha_\alpha^k \int K_{\alpha \beta ij} Q_{\alpha \beta}^k (r_1) U_{km}^\text{iso} (r, r_1) \rho^k (r_1) dD r_1. \tag{6.121}
\]

The functional derivative with respect to $Q_{ij}^m$ is finally given by

\[
\frac{\delta \beta F}{\delta Q_{ij}} = \frac{\delta \beta F}{\delta Q_{ij}} + \frac{\delta \beta F}{\delta Q_{ij}^m} + \frac{\delta \beta F}{\delta Q_{ij}^m} = -\beta \alpha_\alpha \rho^m (r) \sum_k \alpha_\alpha^k \int K_{\alpha \beta ij} U_{mk}^\text{iso} (r, r_1) \rho^k (r_1) (Q_{\alpha \beta}^k (r_1) - Q_{\alpha \beta}^k (r)) dD r_1
\]

\[
+ \beta \alpha_\alpha \sum_k \alpha_\alpha^k \rho^k (r) \left( Q_{\alpha \beta}^k (r) - \langle \sigma_{\alpha \beta}^k \rangle_k (r) \right) \int K_{\alpha \beta ij} U_{km}^\text{iso} (r, r_1) \rho^m (r_1) dD r_1, \tag{6.122}
\]

where $K_{ijkl} \equiv P_{ij \alpha \beta} J_{\alpha \beta kl}$. For the remaining definitions, in particular of of $U_{km}$ and $\langle \sigma_{ij}^k \rangle_k$, see page 94 to 96, as well as the definition of $U_{km}^\text{iso}$ in Eq. (6.100) on page 6.100.

6.2.6 $\delta F/\delta \rho$

We assume that $\delta U_{kl}^\text{iso} / \delta \rho_m = 0$, thus Eq. (6.88) becomes

\[
\frac{\delta \beta F}{\delta \rho_m (r)} = \ln \rho_m (r) - \ln Z_{1m} (r) + \beta \sum_{k=1}^n \int \rho_k (r_1) \langle \varepsilon_{km} \rangle_k (r_1, r) U_{km}^\text{iso} (r_1, r) dD r_1. \tag{6.123}
\]
The term in Eq. (6.102) due to the single-particle partition function for material $m$ can be written as

$$-\ln Z_{1m}(\mathbf{r}) = -\ln \int d^d \mathbf{p} - \ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^m(\mathbf{r}) \right) d^2 \sigma + \sum_{k=1}^{n} \left( \frac{\delta F}{\delta \rho^m(\mathbf{r})} \right)_{0k}, \quad (6.124)$$

where in the exponential we have separated terms that depend on $\sigma$ from terms that do not and therefore can be taken in front of the integral over $d^2 \sigma$. The terms that do not depend on $\sigma$ are forming the last term in Eq. (6.124), while the terms that do are written using an effective field $H_{ij}^m$, which is defined as

$$H_{ij}^m(\mathbf{r}) = -\beta \alpha_a^m \int \sum_k U_{mk}(\mathbf{r}, \mathbf{r}_1) \rho_k(\mathbf{r}_1) \left( 3 \mathbf{r}_i \mathbf{r}_j + \alpha_a^k \gamma_{\gamma\lambda} K_{ij\gamma} \right) d^2 \mathbf{r}_1. \quad (6.125)$$

We can write the last term in Eq. (6.124) explicitly in terms of the order parameters using the definitions for $Z_{1m}$, Eq. (6.76) and $\beta E_{mk}$, Eq. (6.52) and $\epsilon_{mk}$, Eqs. (6.47a) and (6.50). For $k \in \{1..n\}$ this yields

$$\left( \frac{\delta F}{\delta \rho^m(\mathbf{r})} \right)_{0k} \equiv -\beta \int U_{mk}(\mathbf{r}, \mathbf{r}_1) \rho_k(\mathbf{r}_1) d^2 \mathbf{r}_1 \times$$

$$\frac{3}{2} \left( \alpha_a^k \gamma_{\alpha\beta} \epsilon_{\alpha\beta \gamma\lambda} - \alpha_a^m \gamma_{\alpha\beta} \epsilon_{\alpha\beta \gamma\lambda} \right) r_{\alpha} r_{\beta} + \frac{1}{2} \alpha_a^m \gamma_{\alpha\beta} \epsilon_{\alpha\beta \gamma\lambda} \left( Q_{\gamma\lambda}^k - Q_{\gamma\lambda}^m \right) K_{\alpha\beta \gamma\lambda}$$

$$+ 3 - \frac{1}{2} \alpha_a^m \gamma_{\alpha\beta} \epsilon_{\alpha\beta \gamma\lambda} \left( Q_{\gamma\lambda}^k - Q_{\gamma\lambda}^m \right) K_{\alpha\beta \gamma\lambda}. \quad (6.126)$$

We also formally define a term for $k = 0$:

$$\left( \frac{\delta F}{\delta \rho^m(\mathbf{r})} \right)_{00} \equiv \ln \rho_m(\mathbf{r}) - \ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^m(\mathbf{r}) \right) d^2 \sigma. \quad (6.127)$$

With these definitions we can now write the functional derivative with respect to $\rho^m$, Eq. (6.123), as

$$\frac{\delta F}{\delta \rho_m(\mathbf{r})} = \left( \frac{\delta F}{\delta \rho_m(\mathbf{r})} \right)_{00} + \sum_{j=0}^{6} \sum_{k=1}^{n} \left( \frac{\delta F}{\delta \rho_m(\mathbf{r})} \right)_{jk}. \quad (6.128)$$
with the definitions for \( k \in \{1, ..., n\} \):

\[
\frac{\delta \beta E}{\delta \rho_m (r)}\bigg|_{00} = \ln \rho_r^m - \ln \int \exp \left( \sigma_{\alpha \beta} H^{\alpha \beta}_m (r) \right) d^2 \sigma
\]

\[
\frac{\delta F}{\delta \rho_m (r)}\bigg|_{0k} = -\beta \int U_{mk} (r, r_1) \rho_r^k d^D r_1 \left\{ 3 - \frac{1}{2} \alpha^m_a \alpha^m_a Q^{m}_{\alpha \beta \gamma \lambda} R^{k}_{\alpha \beta \gamma \lambda} K_{\alpha \beta \gamma \lambda} \right\}
\]

\[
+ \frac{3}{2} \alpha^m_a \alpha^m_a Q^{m}_{\alpha \beta \gamma \lambda} R^{k}_{\alpha \beta \gamma \lambda} K_{\alpha \beta \gamma \lambda}
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{1k} = -3\beta \int \rho_k (r_1) U_{km}^{\text{iso}} (r_1, r) d^D r_1
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{2k} = -3\beta \alpha^k \int \rho_k (r_1) \langle \sigma^k \rangle (r_1) U_{km}^{\text{iso}} (r_1, r) r_{\alpha \beta \gamma \lambda} d^D r_1
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{3k} = \frac{3}{2} \beta \alpha^m_a Q^{m}_{\alpha \beta \gamma \lambda} (r) \int \rho_k (r_1) U_{km}^{\text{iso}} (r_1, r) r_{\alpha \beta \gamma \lambda} d^D r_1
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{4k} = \frac{3}{2} \beta \alpha^k \int \rho_k (r_1) Q^{k}_{\alpha \beta \gamma \lambda} (r_1) U_{km}^{\text{iso}} (r_1, r) r_{\alpha \beta \gamma \lambda} d^D r_1
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{5k} = \alpha^m_a \alpha^m_a \beta \int \rho_k (r_1) \langle \sigma^k \rangle (r_1) U_{km}^{\text{iso}} (r_1, r) K_{\alpha \beta \gamma \lambda} d^D r_1
\]

\[
\frac{\delta \beta F}{\delta \rho_m (r)}\bigg|_{6k} = -\frac{1}{2} \alpha^m_a \alpha^m_a \beta Q^{m}_{\gamma \lambda} (r) \int \rho_k (r_1) Q^{k}_{\alpha \beta \gamma \lambda} (r_1) U_{km}^{\text{iso}} (r_1, r) K_{\alpha \beta \gamma \lambda} d^D r_1.
\]

(6.129a) (6.129b) (6.129c) (6.129d) (6.129e) (6.129f) (6.129g) (6.129h)

We note that the terms (6.129a) and (6.129c) and the first term in (6.129b) are present even in an isotropic system, while the remaining terms only occur for non-vanishing nematic order parameter of material \( k \).

### 6.3 Gradient expansion

After having performed the functional differentiation we can now evaluate the fields locally. The Taylor expansions for \( \rho \) and \( Q_{ij} \) to second order with respect to \( r \) is
given in our notation by

\[ \rho_{\mid r_1} \cong \rho_{\mid r} + \rho_{\alpha \mid r} r^\alpha + \frac{1}{2} \rho_{\alpha \beta \mid r} r^\alpha r^\beta \]  
\[ (6.130) \]

\[ Q_{ij \mid r_1} \cong Q_{ij \mid r} + Q_{ij, \alpha \mid r} r^\alpha + \frac{1}{2} Q_{ij, \alpha \beta \mid r} r^\alpha r^\beta , \]  
\[ (6.131) \]

where we recall that we have defined \( r \equiv |r - r_1| \) and \( r_k = (r_1 - r) \cdot \hat{e}_k / |r_1 - r| \),

thus \( r_1 - r = r r_\alpha \hat{e}_\alpha \). We define the following “local coupling tensors” for use in this section:

\[ w_{ij}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, d^D r_1 , \]  
\[ (6.132a) \]

\[ w_{ij}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, r r_i d^D r_1 , \]  
\[ (6.132b) \]

\[ (w_{ij}^{qr})_0 \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, r_i r_j d^D r_1 , \]  
\[ (6.132c) \]

\[ w_{ij}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, r^2 r_i r_j d^D r_1 , \]  
\[ (6.132d) \]

\[ w_{ij}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, r r_i r_j r_k d^D r_1 , \]  
\[ (6.132e) \]

\[ (w_{ijkl}^{qr})_0 \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, K_{ijkl} d^D r_1 , \]  
\[ (6.132f) \]

\[ w_{ijkl}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r_1, r) \, r^2 r_i r_j r_k r_l d^D r_1 , \]  
\[ (6.132g) \]

\[ w_{ijklm}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r, r_1) \, r K_{ijklm} d^D r_1 \]  
\[ (6.132h) \]

and \( w_{ijklmn}^{qr} \mid r \equiv \int \beta U_{q_1}^{iso} (r, r_1) \, r^2 K_{ijklm} r_n d^D r_1 \).  
\[ (6.132i) \]
Expansion of $\delta F/\delta Q_{ij}^m$

The functional derivative of $\beta F$ with respect to $Q_{ij}^m$ given in Eq. (6.122) is then approximately

$$\frac{\delta \beta F}{\delta Q_{ij}^m(r)} \approx -\beta \alpha_m^m \rho_{\mu \nu}^m \sum_k \alpha_k^k \int K_{\alpha \beta ij} U_{mk}^{iso}(r, r_1) \times$$

$$\left( \rho_{\mu \gamma}^k + \rho_{\mu \nu}^k r^\mu r_\gamma + \frac{1}{2} \rho_{\mu \nu}^k r^\mu r^\nu r_\lambda \right) \left( Q_{\alpha \beta, \gamma \lambda}^k r^\mu r_\gamma + \frac{1}{2} Q_{\alpha \beta, \gamma \lambda}^k r^\mu r^\nu r_\lambda \right) d^D r_1$$

$$+ \beta \alpha_m^m \sum_k \alpha_k^k \rho_{\mu \nu}^k \Delta \alpha_{\beta ij}^k \int K_{\alpha \beta ij} U_{km}^{iso}(r, r_1) \left( \rho_{\mu \nu}^m + \rho_{\mu \nu}^m r^\mu r_\gamma + \frac{1}{2} \rho_{\mu \nu}^m r^\mu r^\nu r_\lambda \right) d^D r_1,$$

(6.133)

where we define

$$\Delta \alpha_{ij}^k \equiv Q_{ij}^k(r) - \langle \sigma_{ij}^k \rangle_k(r).$$

(6.134)

We write this to second order in the gradients (using $K_{ijkl} = K_{klji}$):

$$\frac{\delta \beta F}{\delta Q_{ij}^m(r)} \approx -\beta \alpha_m^m \rho_{\mu \nu}^m \sum_k \alpha_k^k \rho_{\mu \nu}^k \int K_{\alpha \beta ij} U_{mk}^{iso}(r, r_1) \times$$

$$\left( \rho_{\mu \gamma}^k + \rho_{\mu \nu}^k r^\mu r_\gamma + \frac{1}{2} \rho_{\mu \nu}^k r^\mu r^\nu r_\lambda \right) \left( Q_{\alpha \beta, \gamma \lambda}^k r^\mu r_\gamma + \frac{1}{2} Q_{\alpha \beta, \gamma \lambda}^k r^\mu r^\nu r_\lambda \right) d^D r_1$$

$$- \beta \alpha_m^m \rho_{\mu \nu}^m \sum_k \alpha_k^k \rho_{\mu \nu}^k \int U_{mk}^{iso}(r, r_1) K_{\alpha \beta ij} r^\mu r_\gamma d^D r_1$$

$$+ \beta \alpha_m^m \sum_k \alpha_k^k \rho_{\mu \nu}^k \Delta \alpha_{\beta ij}^k \int K_{\alpha \beta ij} U_{km}^{iso}(r, r_1) \left( \rho_{\mu \nu}^m + \rho_{\mu \nu}^m r^\mu r_\gamma + \frac{1}{2} \rho_{\mu \nu}^m r^\mu r^\nu r_\lambda \right) d^D r_1,$$

(6.135)
Then we re-write this using the local coupling tensors given in Eq. (6.187a-i), collecting terms with the same tensor:

$$\frac{\delta \beta F}{\delta Q_{ij}^m} = \alpha_a^m \rho_{ir}^m \sum_k \alpha_a^k \rho_{ir}^k \Delta_{\alpha \beta |r}^k \left( w_{ij \alpha \beta |r}^k \right)^0$$

$$+ \alpha_a^m \sum_k \alpha_a^k \rho_{ir}^k \left( \rho_{\gamma |r}^m \Delta_{\alpha \beta |r}^k - \rho_{ir}^m Q_{\alpha \beta , \gamma |r}^k \right) w_{ij \alpha \beta \gamma |r}^k$$

$$- \frac{1}{2} \alpha_a^m \rho_{ir}^m \sum_k \alpha_a^k \left( \left( Q_{\alpha \beta \gamma |r}^k \right)^*_\rho \right) \left( Q_{\alpha \beta \gamma |r}^k \right) w_{ij \alpha \beta \gamma |r}^m$$

$$+ \frac{1}{2} \alpha_a^m \rho_{ir}^m \sum_k \alpha_a^k \rho_{ir}^k \Delta_{\alpha \beta |r}^k \left( w_{ij \alpha \beta \gamma |r}^m \right).$$

(6.136)

Expansion of $\delta F/\delta \rho^m$

The functional derivative with respect to $\rho_m$ is treated in analogous fashion: we first expand the terms to second order in the gradient and then collect all terms of the same local coupling tensor. The first term in the functional derivative was given by

$$\left( \frac{\delta F}{\delta \rho_m (r)} \right)_{00} = \ln \rho_{ir}^m - \ln \int \exp \left( \sigma_{\alpha \beta} H_{\beta \alpha}^m (r) \right) d^2 \sigma. \quad (6.137)$$

We break up the term Eq. (6.129b) again:

$$\left( \frac{\delta F}{\delta \rho_m (r)} \right)_{0k} \equiv \sum_{j=1}^5 \left( \frac{\delta F}{\delta \rho_m (r)} \right)^{(j)}_{0k}, \quad (6.138)$$
with

\[
\left( \frac{\delta F}{\delta \rho^m (r)} \right)_{0k} \supset -3\beta \int U_{mk\langle k r, r_1 \rangle} \left( \rho^k_{lr} + \rho^k_{\mu lr} r r_{\mu} + \frac{1}{2} \rho^k_{\mu \nu | r} r^2 r_{\mu} r_{\nu} \right) d^D r_1, \quad (6.139a)
\]

\[
\left( \frac{\delta F}{\delta \rho^m (r)} \right)_{0k} \supset \frac{1}{2} \beta \alpha^m_a \alpha^k Q^m_{\alpha \beta | r} Q^k \gamma^\lambda | r \int U_{nk\langle k r, r_1 \rangle} d^D r_1 \times \left( \rho^k_{lr} + \rho^k_{\mu lr} r r_{\mu} + \frac{1}{2} \rho^k_{\mu \nu | r} r^2 r_{\mu} r_{\nu} \right) K_{\alpha \beta \gamma \lambda}, \quad (6.139b)
\]

\[
\left( \frac{\delta F}{\delta \rho^m (r)} \right)_{0k} \supset -\frac{3}{2} \beta \alpha^k_a \int U_{mk\langle k r, r_1 \rangle} r^\alpha r_{\beta} d^D r_1 \times \left( \rho^k Q^k_{\alpha \beta | r} + \rho^k Q^k_{\alpha \beta \gamma | r} r r_{\gamma} + \frac{1}{2} \rho^k Q^k_{\alpha \beta \gamma | r} r^2 r_{\gamma} r_{\lambda} \right), \quad (6.139c)
\]

\[
\left( \frac{\delta F}{\delta \rho^m (r)} \right)_{0k} \supset \frac{3}{2} \beta \alpha^m_a Q^m_{\alpha \beta | r} \int U_{mk\langle k r, r_1 \rangle} r^\alpha r_{\beta} d^D r_1 \times \left( \rho^k_{lr} + \rho^k_{\mu lr} r r_{\mu} + \frac{1}{2} \rho^k_{\mu \nu | r} r^2 r_{\mu} r_{\nu} \right), \quad (6.139d)
\]

\[
\left( \frac{\delta F}{\delta \rho^m (r)} \right)_{0k} \supset -\beta \frac{1}{2} \alpha^m_a Q^m_{\alpha \beta | r} \int U_{mk\langle k r, r_1 \rangle} K_{\alpha \beta \gamma \lambda} d^D r_1 \times \left( \rho^k_{lr} + \rho^k_{\mu lr} r r_{\mu} + \frac{1}{2} \rho^k_{\mu \nu | r} r^2 r_{\mu} r_{\nu} \right) \left( Q^k_{\gamma \lambda | r} r r_{\gamma} + \frac{1}{2} Q^k_{\gamma \lambda \eta | r} r^2 r_{\gamma} r_{\lambda} \right). \quad (6.139e)
\]
Each of these terms yields to second order in the gradients:

\[
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k}^{(1)} \approx -3 \left( \rho_{\alpha}^k \omega_{\alpha \gamma}^m + \rho_{\alpha}^k \omega_{\alpha \beta}^m \right) + \frac{1}{2} \rho_{\alpha}^k \omega_{\alpha \beta}^m , \\
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k}^{(2)} \approx \frac{1}{2} \alpha_{\alpha}^k \alpha_{\alpha} \alpha_{\alpha}^m Q_{\alpha}^m Q_{\alpha}^m \left( \rho_{\alpha}^k \omega_{\alpha \gamma}^m \right)_{0r} + \rho_{\alpha}^k \omega_{\alpha \beta}^m + \frac{1}{2} \rho_{\alpha}^k \omega_{\alpha \beta}^m \omega_{\alpha \beta}^m , \\
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k}^{(3)} \approx -3 \frac{3}{2} \alpha_{\alpha}^k \left( \rho_{\alpha}^k Q_{\alpha}^m \omega_{\alpha \beta}^m \right)_{0r} + \left( \rho_{\alpha}^k Q_{\alpha} \omega_{\alpha \beta}^m \right)_{0r} \omega_{\alpha \beta}^m + \frac{1}{2} \left( \rho_{\alpha}^k Q_{\alpha} \omega_{\alpha \beta}^m \right)_{0r} \omega_{\alpha \beta}^m , \\
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k}^{(4)} \approx -3 \frac{3}{2} \alpha_{\alpha}^m Q_{\alpha}^m \left( \rho_{\alpha}^k \omega_{\alpha \beta}^m \right)_{0r} + \rho_{\alpha}^k \omega_{\alpha \beta}^m + \frac{1}{2} \rho_{\alpha}^k \omega_{\alpha \beta}^m \omega_{\alpha \beta}^m , \\
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k}^{(5)} \approx -3 \frac{3}{2} \alpha_{\alpha}^m Q_{\alpha}^m \left( \rho_{\alpha}^k \omega_{\alpha \beta}^m \right)_{0r} + \rho_{\alpha}^k \omega_{\alpha \beta}^m + \frac{1}{2} \rho_{\alpha}^k \omega_{\alpha \beta}^m \omega_{\alpha \beta}^m ,
\]

and

\[
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k} \approx -3 \beta \int \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k Q_{\gamma \lambda}^m \omega_{\alpha \beta}^m \right) U_{\gamma \lambda}^m (\mathbf{r}_1, \mathbf{r}) \, d^2 \mathbf{r}_1.
\]

The remaining terms, Eqs. (6.129c) through (6.129h), are given by

\[
\left( \frac{\delta F}{\delta \rho^m (\mathbf{r})} \right)_{0k} \approx -3 \beta \int \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k Q_{\gamma \lambda}^m \omega_{\alpha \beta}^m \right) U_{\gamma \lambda}^m (\mathbf{r}_1, \mathbf{r}) \, d^2 \mathbf{r}_1.
\]

\[
= -3 \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} \omega_{\alpha \beta}^m \right),
\]

\[
\left( \frac{\delta \beta F}{\delta \rho^m (\mathbf{r})} \right)_{1k} \approx -3 \beta \int \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k Q_{\gamma \lambda}^m \omega_{\alpha \beta}^m \right) U_{\gamma \lambda}^m (\mathbf{r}_1, \mathbf{r}) \, d^2 \mathbf{r}_1.
\]

\[
= -3 \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} \omega_{\alpha \beta}^m \right),
\]

\[
\left( \frac{\delta \beta F}{\delta \rho^m (\mathbf{r})} \right)_{1k} \approx -3 \beta \int \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k Q_{\gamma \lambda}^m \omega_{\alpha \beta}^m \right) U_{\gamma \lambda}^m (\mathbf{r}_1, \mathbf{r}) \, d^2 \mathbf{r}_1.
\]

\[
= -3 \left( \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \rho_{\alpha}^k r_{\alpha} r_{\alpha} + \frac{1}{2} \rho_{\alpha}^k r_{\alpha} r_{\alpha} \omega_{\alpha \beta}^m \right),
\]
\[
\left( \frac{\delta \beta F}{\delta \rho_m(r)} \right)_{2k} \simeq -3\beta \alpha_a^k \int U_{km}^{iso}(r_1, r) r_a r_{\beta} \times \\
\left\{ \rho_{ir}^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} + \left( \rho^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} \right)^{\gamma |r} r_{r_{\gamma}} + \frac{1}{2} \left( \rho^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} \right)^{\gamma |r} r^2 r_{r_{\gamma}} r_{\lambda} \right\} d^D r_1 
\]

(6.147)

\[
= -3\alpha_a^k \rho^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} (w_{\alpha \beta}^{km})^0 |r| - 3\alpha_a^k \left( \rho^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} \right)_{\gamma |r} w_{\alpha \beta}^{km} |r| - 3 \alpha_a^k \frac{1}{2} \left( \rho^k \langle \sigma_{\alpha \beta}^k \rangle_{\gamma |r} \right)_{\gamma |r} w_{\alpha \beta}^{km} |r|, 
\]

(6.148)

\[
\left( \frac{\delta \beta F}{\delta \rho_m(r)} \right)_{3k} = \\
-\frac{3}{2} \beta \alpha_a^m Q_{\alpha \beta}^m(r) \int \left( \rho_{ir}^k + \rho^k_{ir} r_{r_{\gamma}} + \frac{1}{2} \rho^k_{ir} r_{r_{\gamma}} r_{r_{\lambda}} \right) U_{km}^{iso}(r_1, r) r_a r_{\beta} d^D r_1 
\]

(6.149)

\[
= -\frac{3}{2} \alpha_a^m Q_{\alpha \beta}^m(r) \left( \rho_{ir}^k (w_{\alpha \beta}^{km})^0 |r| + \rho^k_{ir} w_{\alpha \beta}^{km} |r| + \frac{1}{2} \rho^k_{ir} w_{\alpha \beta}^{km} |r| \right), 
\]

(6.150)

\[
\left( \frac{\delta \beta F}{\delta \rho_m(r)} \right)_{4k} = \frac{3}{2} \beta \alpha_a^k \int U_{km}^{iso}(r_1, r) r_a r_{\beta} \times \\
\left\{ \rho_{ir}^k Q_{\alpha \beta}^k \gamma |r| + \left( \rho^k Q_{\alpha \beta}^k \right)_{\gamma |r} r_{r_{\gamma}} + \frac{1}{2} \left( \rho^k Q_{\alpha \beta}^k \right)_{\gamma |r} r^2 r_{r_{\gamma}} r_{\lambda} \right\} d^D r_1 
\]

(6.151)

\[
= \frac{3}{2} \alpha_a^k \left( \rho_{ir}^k Q_{\alpha \beta}^k \gamma |r| (w_{\alpha \beta}^{km})^0 |r| + \left( \rho^k Q_{\alpha \beta}^k \right)_{\gamma |r} w_{\alpha \beta}^{km} |r| + \frac{1}{2} \left( \rho^k Q_{\alpha \beta}^k \right)_{\gamma |r} w_{\alpha \beta}^{km} |r| \right), 
\]

(6.152)
\[
\left( \frac{\delta \beta F}{\delta \rho_m (r)} \right)_{5k} = \alpha_a^k \alpha_a^m \beta \int U_{km}^{iso} (r_1, r) K_{\alpha \beta \gamma \lambda} \times \\
\left\{ \rho_{\mu r}^k \Delta_{\alpha \beta \gamma \lambda}^k Q_{\mu r}^m + (\rho^k \Delta_{\alpha \beta \gamma \lambda}^k Q_{\mu r}^m)_{\mu \nu r} r^2 r^2 r^2 \right\} d^D r_1
\]

(6.153)

\[
= \alpha_a^k \alpha_a^m \rho_{\mu r}^k \Delta_{\alpha \beta \gamma \lambda}^k Q_{\mu r}^m \left( w_{\alpha \beta \gamma \lambda}^m \right)_{\mu r}^0 + \alpha_a^k \alpha_a^m \left( \rho^k \Delta_{\alpha \beta \gamma \lambda}^k Q_{\mu r}^m \right)_{\mu \nu r} w_{\alpha \beta \gamma \lambda \mu \nu r}^k + \alpha_a^k \alpha_a^m \frac{1}{2} \left( \rho^k \Delta_{\alpha \beta \gamma \lambda}^k Q_{\mu r}^m \right)_{\mu \nu r} w_{\alpha \beta \gamma \lambda \mu \nu r}^k \] (6.154)

and

\[
\left( \frac{\delta \beta F}{\delta \rho_m (r)} \right)_{6k} = -\frac{1}{2} \alpha_a^k \alpha_a^m Q_{\lambda \mu r}^m (r) \int U_{km}^{iso} (r_1, r) K_{\alpha \beta \gamma \lambda} \times \\
\left\{ \rho_{\mu r}^k Q_{\alpha \beta \gamma \lambda}^k + (\rho^k Q_{\alpha \beta \gamma \lambda})_{\mu \nu r} r^2 r^2 r^2 \right\} d^D r_1
\]

(6.155)

\[
= -\frac{1}{2} \alpha_a^k \alpha_a^m Q_{\lambda \mu r}^m \times \\
\left( \rho_{\mu r}^k Q_{\alpha \beta \gamma \lambda}^k \left( w_{\alpha \beta \gamma \lambda}^m \right)_{\mu r}^0 + (\rho^k Q_{\alpha \beta \gamma \lambda})_{\mu \nu r} w_{\alpha \beta \gamma \lambda \mu \nu r}^k + \frac{1}{2} (\rho^k Q_{\alpha \beta \gamma \lambda})_{\mu \nu r} w_{\alpha \beta \gamma \lambda \mu \nu r}^k \right) \] (6.156)

Next, we write the functional derivative with respect to \( \rho^m \) by collecting terms with the same coupling tensor. We do this by writing

\[
\frac{\delta F}{\delta \rho^m (r)} = \left( \frac{\delta F}{\delta \rho^m (r)} \right)_{00} + \sum_{i=1}^9 \sum_{j=1}^2 \sum_{k=1}^n B_{ij}^{mk} (r),
\]

(6.157)

where we define 18 terms \( B_{ij} \). The index \( i \) corresponds to one of the nine local coupling tensors \( w \), and the index \( j \) indicates coupling \( mk \) and \( km \), respectively. Collecting the corresponding terms we denote for reference which of the terms in Eq. (6.128) generated the respective term by labeling each term (superscript) with \((1k), (2k), \) etc.

\[
B_{11}^{mk} \equiv \left( -3 \rho_{\mu r}^{k(0k,1)} \right)_{\mu r}^{mk} \] (6.158)
\[ B_{12}^{mk} \equiv (-3 \rho_{\alpha|\gamma}^{(1k)})^{(1)} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{km} \end{pmatrix} \]  \hspace{1cm} (6.159)

\[ B_{21}^{mk} \equiv (-3 \rho_{\alpha|\gamma}^{(0k,1)})^{(0k,1)} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.160)

\[ B_{21}^{mk} \equiv (-3 \rho_{\alpha|\gamma}^{(1k)})^{(1k)} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{km} \end{pmatrix} \]  \hspace{1cm} (6.161)

\[ B_{31}^{mk} \equiv \left\{ (3 \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(0k,3)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \alpha\beta | \gamma \\ \alpha\beta | \alpha\beta | \gamma \end{pmatrix}^{(0k,4)} \right\} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.162)

\[ B_{32}^{mk} \equiv \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(3k)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(4k)} \right\} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.163)

\[ B_{41}^{mk} \equiv (-3 \rho_{\alpha|\gamma}^{(0k,1)})^{(0k,1)} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.164)

\[ B_{51}^{mk} \equiv (-3 \rho_{\alpha|\gamma}^{(1k)})^{(1k)} \begin{pmatrix} 0 \\ w_{\alpha|\gamma}^{km} \end{pmatrix} \]  \hspace{1cm} (6.165)

\[ B_{51}^{mk} \equiv \left\{ (3 \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(0k,3)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(0k,4)} \right\} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.166)

\[ B_{52}^{mk} \equiv \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(2k)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(4k)} \right\} \begin{pmatrix} 0 \\ w_{\alpha|\gamma}^{km} \end{pmatrix} \]  \hspace{1cm} (6.167)

\[ B_{61}^{mk} \equiv \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(3k)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(4k)} \right\} \begin{pmatrix} 0 \\ w_{\alpha\beta|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.168)

\[ B_{62}^{mk} \equiv \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(5k)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(6k)} \right\} \begin{pmatrix} 0 \\ w_{\alpha|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.169)

\[ B_{71}^{mk} \equiv \left\{ (3 \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(0k,3)} \right\} + \left\{ \begin{pmatrix} \alpha\beta | \gamma \\ \alpha\beta | \gamma \end{pmatrix}^{(0k,4)} \right\} \begin{pmatrix} 0 \\ w_{\alpha|\gamma}^{mk} \end{pmatrix} \]  \hspace{1cm} (6.170)
\[ B_{72}^{mk} \equiv \left\{ -\frac{3}{2} \alpha_a^k \left( \rho^k \langle \sigma_{\alpha\beta}^k \rangle_{\gamma\lambda|\mu} \right) \right\}^{(2k)} + \left\{ \left( \frac{3}{4} \alpha^m_a \rho^k \sigma_{\alpha\beta}^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{3k} + \left( \frac{3}{4} \alpha^m_a \rho^k \sigma_{\alpha\beta}^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{4k} \right\}^{(4k)} \{ w_{\alpha\beta\gamma\lambda|\mu}^{km} \}^{(6.172)} \]

\[ B_{81}^{mk} \equiv \left\{ \left( \frac{1}{2} \alpha^m_a \alpha_a^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{(0k,2)} + \left( \frac{1}{2} \alpha^m_a \alpha_a^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{(0k,5)} \right\}^{(6.173)} \]

\[ B_{82}^{mk} \equiv \left\{ \left( \alpha_a^k \alpha_a^m \rho^k \Delta_{\alpha\beta} Q_{\gamma\lambda|\mu} \right)^{(5k)} + \left( \frac{1}{2} \alpha^m_a \alpha_a^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{(6k)} \right\}^{(6.174)} \]

\[ B_{91}^{mk} \equiv \left\{ \left( \frac{1}{4} \alpha^m_a \alpha_a^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{(0k,2)} \right\}^{(6.175)} \]

\[ B_{92}^{mk} \equiv \left\{ \left( \alpha_a^k \alpha_a^m \frac{1}{2} \rho^k \Delta_{\alpha\beta} Q_{\gamma\lambda|\mu} \right)^{(5k)} + \left( \frac{1}{4} \alpha^m_a \alpha_a^k Q_{\alpha\beta|\gamma\lambda|\mu} \right)^{(6k)} \right\}^{(6.176)} \]

Expansion of the local field, \( H_{ij}^m (r) \)

We write the local field as a sum over local fields due to the different materials

\[ H_{ij}^m (r) \equiv \sum_k H_{ij|\mu}^{mk} \]  

(6.177)

where

\[ H_{ij|\mu}^{mk} \equiv \beta \alpha_a^m \int U_{mk} (r, r_1) \rho^k (r_1) \left( 3r_i r_j + \alpha_a^k Q_{\gamma\lambda|\mu} \right) K_{ij|\gamma\lambda} d^D r_1. \]  

(6.178)
and expanding the argument to second order in the gradients yields

\[
H_{ijr}^{mk} \simeq \beta \alpha_a^m \int U_{mk}(r, r_1) \times \left( \rho_{ajr}^k + \rho_{ajr}^k r_{ajr} + \frac{1}{2} \rho_{ajr}^k r_{ajr}^2 r_{ajr} \right) (3 r_{ijr} + \alpha_a^k Q_{ij}^k r_{ijr} K_{ij}^k) d^3r_1,
\]

(6.179)

which, expressed in the local coupling tensors Eq. (6.187a-i) yields

\[
H_{ijr}^{mk} \simeq 3 \alpha_a^m \rho_{ajr}^k \left( w_{ijr}^{mk} \right)_r^0 + \alpha_a^m \rho_{ajr}^k \alpha_a^k Q_{ijr}^k \left( w_{ijr}^{mk} \right)_r^0 + 3 \alpha_a^m \rho_{ajr}^k w_{ijr}^{mk} + \frac{3}{2} \alpha_a^m \rho_{ajr}^k w_{ijr}^{mk} - \alpha_a^m \rho_{ajr}^k \alpha_a^k Q_{ijr}^k w_{ijr}^{mk} + \frac{1}{2} \alpha_a^m \rho_{ajr}^k \alpha_a^k Q_{ijr}^k w_{ijr}^{mk}.
\]

(6.180)

### 6.3.1 Isotropic pair-distribution function

Next we make a few simplifying assumptions. The dimensionality will now be specialized to \( D = 3 \). We are only interested in functional derivatives evaluated sufficiently deep in the bulk, then the integral can be taken over all space, and the isotropic part of the pair-distribution function should only depend on the magnitude \( r \) of the chord \( r_1 - r \). Because of the latter, the integrals over orientation \( d^2\hat{r} \) and distance \( r \) can then be performed independently. For example

\[
w_{ijr}^{kl} = \left( \int \beta U_{kl}(r) r^4 dr \right) \int r_{ijr} d^2\hat{r}.
\]

(6.181)

We define an “effective cut-off” \( \lambda_{L}^{XY} \), where \( X \) and \( Y \) are from the set of materials and \( L \) is an integer, \( L < 3 \)

\[
(\lambda_{L}^{XY})^{L-3} \equiv (3 - L) \int_0^\infty g_{XY}(r) r^{L-4} dr
\]

(6.182)
This definition is chosen such that if \( g_{XY} \) is a constant for \( r > r_0 \) and zero otherwise then \( \lambda^X_Y = r_0 \) for all \( L < 3 \). Equation (6.51), page 86 is now:

\[
U_{kl} \equiv A_{kl} \frac{g_{kl}(r)}{r^6}
\]  

(6.183)

and therefore

\[
w^{kl}_{ijr} = \beta A_{kl} \int g_{kl}(r) r^{-2} dr \int r_i r_j d^2 \hat{r} = \beta A_{kl} (\lambda^k_l)^{-1} I_{ij}.
\]

(6.184)

We also define the \( n \)-th rank isotropic tensor \( I_{ij...} \):

\[
I_{i_1...i_n} = \int r_{i_1} ... r_{i_n} d^2 \hat{r}.
\]

(6.185)

The local coupling tensor are now given by

\[
w^{qr} = \frac{1}{3} \beta A_{qr} (\lambda^p_0)^{-3} I_0
\]

(6.186a)

\[
(w^{qr})^{0}_{ij} = \frac{1}{3} \beta A_{qr} (\lambda^p_0)^{-3} I_{ij}
\]

(6.186b)

\[
w^{qr}_{ij} = \beta A_{qr} (\lambda^p_2)^{-1} I_{ij}
\]

(6.186c)

\[
(w^{qr})^{0}_{ijkl} = \frac{1}{3} \beta A_{qr} (\lambda^p_0)^{-3} \Omega_{ijkl}
\]

(6.186d)

\[
w^{qr}_{ijkl} = \beta A_{qr} (\lambda^p_2)^{-1} I_{ijkl}
\]

(6.186e)

\[
w^{qr}_{ijklmn} = \beta A_{qr} (\lambda^p_2)^{-1} \Omega_{ijklmn}
\]

(6.186f)

and all terms with an odd number of indices vanish. The "kernel integrals" \( \Omega \) are defined by

\[
\Omega_{ijkl} \equiv \int K_{ijkl} d^2 \hat{r}
\]

(6.187a)

\[
\Omega_{ijklmn} \equiv \int K_{ijkl} r_m r_n d^2 \hat{r}.
\]

(6.187b)
The values for the isotropic and kernel integrals are derived in the appendix. We only summarize here their relevant contractions with tensors:

\[
\frac{T_{I_0}}{4\pi/15} = 15T \quad (6.188)
\]

\[
\frac{T_{\alpha\beta I_{\alpha\beta}}}{4\pi/15} = 5T_{\alpha\alpha} \quad (6.189)
\]

\[
\frac{T_{\alpha\beta I_{ij\alpha\beta}}}{4\pi/15} = (\delta_{ij} T_{\alpha\alpha} + T_{ij} + T_{ji}) \quad (6.190)
\]

\[
\frac{T_{\alpha\beta\gamma\lambda I_{\alpha\beta\gamma\lambda}}}{4\pi/15} = (T_{\alpha\beta\beta} + T_{\alpha\beta\alpha} + T_{\alpha\beta\gamma\lambda}) \quad (6.191)
\]

\[
\frac{T_{\alpha\beta\gamma\lambda \Omega_{ij\alpha\beta\gamma\lambda}}}{4\pi/15} = 3 \left( \frac{T_{ij} + T_{ji}}{2} - \delta_{ij} T_{\alpha\alpha} \right) \quad (6.192)
\]

\[
\frac{T_{\alpha\beta\gamma\lambda \Omega_{ij\alpha\beta\gamma\lambda}}}{4\pi/15} = 3 \left( \frac{T_{\alpha\beta\alpha} + T_{\alpha\beta\beta}}{2} - T_{\alpha\beta\beta} \right) \quad (6.193)
\]

\[
\frac{T_{\alpha\beta\gamma\lambda \Omega_{ij\alpha\beta\gamma\lambda}}}{4\pi/15} =
\begin{align*}
\frac{11}{7} \left\{ \frac{T_{ij\alpha\alpha} + T_{ji\alpha\alpha}}{2} - \frac{1}{3} \delta_{ij} T_{\alpha\alpha\beta\beta} \right\} - \frac{6}{7} \delta_{ij} T_{\alpha\alpha\beta\beta} \\
- \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{ia\alpha\beta} + T_{ja\alpha\beta}}{2} - \frac{1}{3} \delta_{ij} T_{\alpha\beta\alpha\beta} \right\} - \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{ia\beta\alpha} + T_{ja\beta\alpha}}{2} - \frac{1}{3} \delta_{ij} T_{\alpha\beta\alpha\beta} \right\} \\
- \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{ia\beta\gamma} + T_{ja\beta\gamma}}{2} - \frac{1}{3} \delta_{ij} T_{\alpha\beta\gamma\lambda} \right\} - \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{ia\beta\gamma} + T_{ja\beta\gamma}}{2} - \frac{1}{3} \delta_{ij} T_{\alpha\beta\gamma\lambda} \right\}
\end{align*} \quad (6.194)
\]

\[
\frac{T_{\alpha\beta\gamma\lambda\mu\nu \Omega_{\alpha\beta\gamma\lambda\mu\nu}}}{4\pi/15} =
\begin{align*}
\frac{11}{7} \left\{ \frac{T_{\alpha\beta\alpha\gamma\gamma\alpha} + T_{\alpha\beta\beta\gamma\gamma}}{2} - \frac{1}{3} T_{\alpha\alpha\beta\gamma\gamma} \right\} - \frac{6}{7} T_{\alpha\alpha\beta\gamma\gamma} \\
- \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{\alpha\beta\alpha\gamma\gamma} + T_{\alpha\beta\beta\gamma\alpha}}{2} - \frac{1}{3} T_{\alpha\alpha\beta\gamma\gamma} \right\} - \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{\alpha\beta\alpha\gamma\gamma} + T_{\alpha\beta\beta\gamma\alpha}}{2} - \frac{1}{3} T_{\alpha\alpha\beta\gamma\gamma} \right\} \\
- \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{\alpha\beta\gamma\alpha\beta} + T_{\alpha\beta\gamma\beta\alpha}}{2} - \frac{1}{3} T_{\alpha\alpha\beta\gamma\gamma} \right\} - \frac{12}{7} \frac{1}{4} \left\{ \frac{T_{\alpha\beta\gamma\alpha\beta} + T_{\alpha\beta\gamma\beta\alpha}}{2} - \frac{1}{3} T_{\alpha\alpha\beta\gamma\gamma} \right\}
\end{align*} \quad (6.195)
\]
Expansion of $\delta F/\delta Q_{ij}^m$

The functional derivative of the free energy with respect to the nematic order parameter expressed in local gradient expansion is given by Eq. (6.136). Writing the coupling integrals explicitly, using the assumptions for Eqs. (6.186a-f) yields

$$
\frac{15}{4\pi} \frac{\delta F}{\delta Q_{ij}^m} = \frac{1}{3} \alpha_a^m \rho_r^{m} \sum_k \alpha^k_a \alpha^k_{\beta} \Delta^k_{ij}\beta A_{km} (\lambda_{0}^{km})^{-3} \frac{\Omega_{ij\alpha\beta}}{4\pi/15} - \frac{1}{2} \alpha_a^m \rho_r^{m} \sum_k \alpha^k_a \left((Q_{ij}\rho^k_{\alpha})_{\gamma\lambda} - Q_{ij}\rho^k_{\alpha}\rho_{\gamma\lambda}\right) \beta A_{mk} (\lambda_{2}^{mk})^{-1} \frac{\Omega_{ij\alpha\beta\gamma\lambda}}{4\pi/15} + \frac{1}{2} \alpha_a^m \rho_r^{m} \sum_k \alpha^k_a \alpha^k_{\beta} \Delta^k_{ij}\beta A_{km} (\lambda_{2}^{km})^{-1} \frac{\Omega_{ij\alpha\beta\gamma\lambda}}{4\pi/15},
$$

(6.196)

and applying the contractions given in Eqs. (6.188) through (6.195) yields

$$
\frac{15}{4\pi} \frac{\delta F}{\delta Q_{ij}^m} = \alpha_a^m \rho_r^{m} \sum_k \alpha^k_a \alpha^k_{\beta} \Delta^k_{ij}\beta A_{km} (\lambda_{0}^{km})^{-3} - \alpha_a^m \rho_r^{m} \frac{11}{14} \sum_k \beta A_{mk} (\lambda_{2}^{mk})^{-1} \alpha^k_a \left((Q_{ij}\rho^k_{\alpha})_{\alpha\alpha}\rho_{\alpha\alpha}\right) + \alpha_a^m \rho_r^{m} \frac{12}{14} \sum_k \beta A_{mk} (\lambda_{2}^{mk})^{-1} \alpha^k_a \left([Q_{ij}\rho^k_{\alpha}]_{\alpha} - [Q_{ij}\rho^k_{\alpha}][Q_{ij}\rho^k_{\alpha}]\right) + \frac{11}{14} \alpha_a^m \sum_k \beta A_{km} (\lambda_{2}^{km})^{-1} \alpha^k_a \alpha^k_{\beta} \Delta^k_{ij}\rho_{\alpha\alpha}\rho_{\alpha\alpha} - \frac{12}{14} \alpha_a^m \sum_k \beta A_{km} (\lambda_{2}^{km})^{-1} \alpha^k_a \alpha^k_{\beta} \left[\Delta^k_{ij}\rho_{\alpha\alpha}\rho_{\alpha\alpha}\right],
$$

(6.197)

where $[T_{ij}]^\#$ is the symmetric, traceless projection of a tensor $T_{ij}$.

Expansion of $\delta F/\delta \rho^m$

Writing the coupling tensors in Eqs. (6.158) through (6.176) explicitly for the assumption of Eq. (6.186) yields

$$
B_{21}^m = B_{22}^m = B_{51}^m = B_{52}^m = B_{81}^m = B_{82}^m = 0.
$$

(6.198)
\[ B_{11}^{mk} = -\rho_{lr}^k \beta A_{mk} \left( \lambda_0^{mk} \right)^{-3} I_0, \]  
(6.199)

\[ B_{12}^{mk} = -\rho_{lr}^k \beta A_{km} \left( \lambda_0^{km} \right)^{-3} I_0, \]  
(6.200)

\[ B_{31}^{mk} = \frac{1}{2} \rho_{lr}^k \left\{ \alpha_a^m Q_{\alpha \beta | r}^m - \alpha_a^k Q_{\alpha \beta | r}^k \right\} \beta A_{mk} \left( \lambda_0^{mk} \right)^{-3} I_{\alpha \beta}, \]  
(6.201)

\[ B_{31}^{mk} = \frac{1}{2} \rho_{lr}^k \left\{ \alpha_a^k Q_{\alpha \beta | r}^k - \alpha_a^m Q_{\alpha \beta | r}^m - 2\alpha_a^k \left( \sigma_{\alpha \beta}^k \right)_{lr} \right\} \beta A_{km} \left( \lambda_0^{km} \right)^{-3} I_{\alpha \beta}, \]  
(6.202)

\[ B_{41}^{mk} = -\frac{3}{2} \rho_{\alpha \beta | r}^k \beta A_{mk} \left( \lambda_0^{mk} \right)^{-1} I_{\alpha \beta}, \]  
(6.203)

\[ B_{42}^{mk} = -\frac{3}{2} \rho_{\alpha \beta | r}^k \beta A_{km} \left( \lambda_0^{km} \right)^{-1} I_{\alpha \beta}, \]  
(6.204)

\[ B_{61}^{mk} = \frac{1}{6} \alpha_a^m \alpha_a^k Q_{\alpha \beta | r}^m Q_{\lambda | r}^k \Delta_{\alpha \beta | r}^k \left( \sigma_{\alpha \beta}^k \right)_{lr} \beta A_{mk} \left( \lambda_0^{mk} \right)^{-3} \Omega_{\alpha \beta \gamma \lambda}, \]  
(6.205)

\[ B_{62}^{mk} = \frac{1}{3} \alpha_a^k \alpha_a^m Q_{\gamma \lambda | r}^m Q_{\alpha | r}^k \left\{ \Delta_{\alpha \beta | r}^k \left( \sigma_{\alpha \beta}^k \right)_{lr} - \frac{1}{2} Q_{\alpha \beta | r}^k \right\} \beta A_{km} \left( \lambda_0^{km} \right)^{-3} \Omega_{\alpha \beta \gamma \lambda}, \]  
(6.206)

\[ B_{71}^{mk} = \frac{3}{4} \left\{ \alpha_a^m Q_{\alpha \beta | r}^m Q_{\gamma \lambda | r}^k - \alpha_a^k \left( \rho \sigma_{\alpha \beta}^k \right)_{\gamma \lambda | r} \right\} \beta A_{mk} \left( \lambda_0^{mk} \right)^{-1} I_{\alpha \beta \gamma \lambda}, \]  
(6.207)

\[ B_{72}^{mk} = \frac{3}{2} \left\{ \alpha_a^k \left( \rho \sigma_{\alpha \beta}^k \right)_{\gamma \lambda | r} - \alpha_a^m Q_{\alpha \beta | r}^k \right\} \beta A_{km} \left( \lambda_0^{km} \right)^{-1} I_{\alpha \beta \gamma \lambda}, \]  
(6.208)

\[ B_{91}^{mk} = -\alpha_a^m \alpha_a^k Q_{\alpha \beta | r}^m \left\{ \frac{1}{4} Q_{\gamma \lambda | r}^k \rho_{\mu \nu | r}^k + \frac{1}{4} \rho_{\mu \nu | r}^k Q_{\gamma \lambda, \mu \nu | r} + \frac{1}{2} \rho_{\mu \nu | r}^k Q_{\gamma \lambda, \nu \mu | r} \right\} \times \beta A_{mk} \left( \lambda_0^{mk} \right)^{-1} \Omega_{\alpha \beta \gamma \lambda, \mu \nu}, \]  
(6.209)

\[ = -\frac{1}{4} \alpha_a^m \alpha_a^k Q_{\alpha \beta | r}^m \left\{ \left( \rho \sigma_{\alpha \beta}^k \right)_{\mu \nu | r} \right\} \beta A_{mk} \left( \lambda_0^{mk} \right)^{-1} \Omega_{\alpha \beta \gamma \lambda, \mu \nu}, \]  
(6.210)

and

\[ B_{92}^{mk} = -\frac{1}{2} \alpha_a^k \alpha_a^m \left\{ \frac{1}{2} Q_{\gamma \lambda | r}^k \left( \rho \sigma_{\alpha \beta}^k \right)_{\mu \nu | r} - \left( \rho \Delta_{\alpha \beta}^k Q_{\gamma \lambda | r}^m \right)_{\mu \nu | r} \right\} \beta A_{km} \left( \lambda_0^{km} \right)^{-1} \Omega_{\alpha \beta \gamma \lambda, \mu \nu}. \]  
(6.211)
Performing the contractions with the isotropic integrals and the kernel integrals yields

\[
\frac{B_{11}^{mk} + B_{12}^{mk}}{4\pi/15} = -15\rho^k_{i\nu} \left( \beta A_{mk} \left( \lambda_0^{mk} \right)^{-3} + \beta A_{km} \left( \lambda_0^{km} \right)^{-3} \right), 
\]

(6.212)

\[ B_{31} = B_{32} = 0, \]

(6.213)

\[
\frac{B_{41}^{mk} + B_{42}^{mk}}{4\pi/15} = -\frac{15}{2} \rho^k_{\alpha\lambda i\nu} \left( \beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} + \beta A_{km} \left( \lambda_2^{km} \right)^{-1} \right),
\]

(6.214)

\[
\frac{B_{51}^{mk} + B_{52}^{mk}}{4\pi/15} = \alpha^m_\alpha \alpha^k_\beta \rho^k_{\alpha\beta i\nu} Q^m_{\alpha\beta i\nu} \times
\left( \Delta^k_{\alpha\beta i\nu} - \frac{1}{2} Q^k_{\alpha\beta i\nu} \right) \beta A_{km} \left( \lambda_0^{km} \right)^{-3} + \frac{1}{2} Q^k_{\beta\alpha i\nu} \beta A_{mk} \left( \lambda_0^{mk} \right)^{-3},
\]

(6.215)

\[
\frac{B_{61}^{mk}}{4\pi/15} = \frac{3}{2} \left\{ \alpha^m_\alpha \alpha^k_\beta \rho^k_{\alpha\beta i\nu} - \alpha^k_\alpha \left( \rho^k_{\alpha\beta} \right)^{(k)} \beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} \right\},
\]

(6.216)

\[
\frac{B_{71}^{mk}}{4\pi/15} = -3 \left\{ \alpha^k_\alpha \left( \rho^k_{i\nu} \left( \sigma^k_{\alpha\beta} \right)^{(k)} \right) \beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} \right\},
\]

(6.217)

\[
B_{91}^{mk} = -\alpha^m_\alpha \alpha^k_\beta \alpha^m_\gamma \alpha^k_\nu \left\{ \frac{1}{4} Q^k_{\gamma\lambda i\nu} \rho^k_{\mu\nu i\nu} + \frac{1}{4} \rho^k_{i\nu} Q^k_{\gamma\lambda,\mu\nu} + \frac{1}{2} \rho^k_{i\nu} Q^k_{\gamma,\mu\nu i\nu} \right\} \times
\beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} \Omega_{\alpha\beta\gamma\lambda i\nu},
\]

(6.218)

\[
= -\frac{1}{4} \alpha^m_\alpha \alpha^k_\beta \alpha^m_\gamma \alpha^k_\nu \left\{ \left( \rho^k_{\gamma\lambda} \right)_{\mu\nu i\nu} \right\} \beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} \Omega_{\alpha\beta\gamma\lambda i\nu},
\]

(6.219)

and

\[
\frac{B_{91}^{mk}}{4\pi/15} = -\frac{1}{4} \alpha^m_\alpha \alpha^k_\beta \alpha^m_\gamma \alpha^k_\nu \beta A_{mk} \left( \lambda_2^{mk} \right)^{-1} \times
\left\{ \begin{array}{l}
\frac{11}{7} \left\{ \left( \rho^k_{\gamma\lambda} \right)_{\beta\alpha i\nu} \right\} \\
- \frac{12}{7} \left\{ \left( \rho^k_{\gamma\lambda} \right)_{\beta\gamma i\nu} \right\} - \frac{12}{7} \left\{ \left( \rho^k_{\gamma\lambda} \right)_{\gamma\alpha i\nu} \right\} \\
- \frac{12}{7} \left\{ \left( \rho^k_{\gamma\lambda} \right)_{\gamma\beta i\nu} \right\}
\end{array} \right. \}
\]

(6.220)
where \([A_{ij}]^S\) is the symmetric projection of \(A_{ij}\). Since \(Q_{ij}\) is symmetric and the derivatives are symmetric, Eqs. (6.219) and (6.220) yield:

\[
\frac{B_{y_1}^{mk}}{4\pi/15} = -\frac{1}{2} \alpha^m_k \alpha^k_a Q_{\alpha\beta}^m \beta A_{mk} \left( \lambda^a_m \right)^{-1} \times 
\left\{ \frac{11}{14} \left\{ (\rho^k Q_{\beta\gamma}^k)_{\gamma\beta r} \right\} - \frac{12}{14} \left\{ (\rho^k Q_{\alpha\gamma}^k)_{\gamma\beta r} \right\} \right\},
\]

(6.221)

and

\[
\frac{B_{y_2}^{mk}}{4\pi/15} = -\alpha^k_a \alpha^m_a \beta A_{km} \left( \lambda^a_m \right)^{-1} \times 
\left\{ \frac{11}{14} \left\{ \frac{1}{2} (\rho^k Q_{\alpha\beta}^k)_{\gamma\beta r} Q_{\gamma m}^a \beta_{\alpha r} - (\rho^k Q_{\alpha\beta}^k)_{\gamma\beta r} \right\} - \frac{12}{14} \left\{ \frac{1}{2} (\rho^k Q_{\alpha\beta}^k)_{\gamma\beta r} - (\rho^k Q_{\alpha\beta}^k)_{\gamma\beta r} \right\} \right\}.
\]

(6.222)

Using \(A_{km} \lambda^k_L = A_{mk} \lambda^k_L\), we write Eqs. (6.198) through (6.211) as

\[
B_{km}^{\prime} \equiv B_{t1}^{mk} + B_{t2}^{mk},
\]

(6.223)

where now

\[
\frac{B_1^{mk}}{4\pi/15} = -30 \alpha^k_a \beta A_{km} \left( \lambda^a_0 \right)^{-3},
\]

(6.224)

\[
B_2^{mk} = 0,
\]

(6.225)

\[
B_3^{mk} = B_{31} = B_{32} = 0,
\]

(6.226)

\[
\frac{B_4^{mk}}{4\pi/15} = -15 \alpha^k_a \beta A_{km} \left( \lambda^a_2 \right)^{-1},
\]

(6.227)

\[
B_5^{mk} = 0,
\]

(6.228)

\[
B_6^{mk} = \alpha^m_a \alpha^k_a \rho^k \Delta_{\alpha\beta}^k \beta A_{km} \left( \lambda^a_0 \right)^{-3},
\]

(6.229)

\[
B_7^{mk} = -3 \alpha^k_a \Delta^k_{\alpha\beta} \rho^k \beta A_{km} \left( \lambda^a_2 \right)^{-1}
\]

(6.230)
\[ B_{\gamma l}^{mk} = 0. \]  

\[ \frac{B_{\gamma l}^{mk}}{4\pi/15} = \frac{1}{2} \alpha_m \alpha_k \alpha_{\lambda \beta} \alpha_{\lambda \beta \gamma \beta \lambda \mu} \beta A_{mk} (\lambda_2)^{-1} \times \]
\[ \left\{ \frac{11}{14} \left( \rho^k Q_\beta^m \gamma_{\gamma \beta r} Q_\delta^m \eta_{\gamma \beta r} - \rho^k \Delta_\alpha^k Q_\beta^m \gamma_{\gamma \beta r} \right) \right\}, \]

\[ \left( \frac{12}{14} \left( \rho^k Q_\beta^m \gamma_{\beta \gamma r} Q_\delta^m \eta_{\gamma \beta r} \right) - \rho^k \Delta_\alpha^k Q_\beta^m \gamma_{\beta \gamma r} \right) \}, \]

\[ \frac{B_{\gamma l}^{mk}}{4\pi/15} = -\alpha_k^m \alpha_m \beta A_{km} (\lambda_2)^{-1} \times \]
\[ \left\{ \frac{11}{14} \left( \frac{1}{2} \rho^k Q^k_{\alpha \beta} \gamma_{\gamma \beta r} Q^m_{\alpha \beta} \eta_{\gamma \beta r} - \left( \rho^k \Delta_\alpha^k Q^m_{\alpha \beta} \gamma_{\gamma \beta r} \right) \right) \right\} \]

\[ -\frac{12}{14} \left( \frac{1}{2} Q^m_{\gamma \beta r} \rho^k Q^k_{\beta \alpha} \gamma_{\beta \gamma r} - \left( \rho^k \Delta_\alpha^k Q^m_{\beta \alpha} \gamma_{\beta \gamma r} \right) \right) \}, \]

\[ B_{\gamma l}^{mk} = \alpha_m^k \alpha_k^m \beta A_{km} (\lambda_2)^{-1} \times \]
\[ \left\{ \frac{11}{14} \left( \frac{12}{14} \rho^k Q^k_{\alpha \beta} \gamma_{\gamma \beta r} \left( \rho^k \Delta_\alpha^k Q^m_{\alpha \beta} \gamma_{\gamma \beta r} \right) \right) \right\} \]

\[ +\frac{11}{14} \left( \rho^k \Delta_k^{\alpha \lambda} \gamma_{\alpha \beta \gamma \beta r} \right) \gamma_{\gamma \beta r} \right\} \left\{ \frac{12}{14} \left( \rho^k \Delta_k^{\alpha \lambda} Q^m_{\alpha \beta} \gamma_{\gamma \beta r} \right) \right\}. \]

And equation (6.157) becomes now

\[ \frac{\delta F}{\delta \rho^m (r)} = \left( \frac{\delta F}{\delta \rho^m (r)} \right)_{00} + \sum_{i=1}^{9} \sum_{k=1}^{n} B_{ij}^{mk} (r). \]

**Expansion of the local field, \( H_{ij}^{mk} \)**

We write \( \sigma_{\alpha \beta}^m H_{ij}^{mk} \), with \( H_{ij}^{mk} \) defined in Eq. (6.180):

\[ \sigma_{\alpha \beta}^m H_{ij}^{mk} \sim \]

\[ 3 \alpha_a \rho^k_{\alpha \beta} \sigma_{\alpha \beta}^m (w_{\alpha \beta})_{\gamma \beta}^0 + \alpha_a \alpha_k \alpha_{\gamma \lambda \beta}^k \sigma_{\alpha \beta}^m (w_{\alpha \beta \gamma \lambda \mu})_{\gamma \beta}^0 \]

\[ + \alpha_a \rho^k_{\alpha \beta} \sigma_{\alpha \beta}^m (w_{\alpha \beta \gamma \lambda \mu})_{\gamma \beta}^0 + \frac{3}{2} \alpha_a \rho^k_{\gamma \lambda \beta} \sigma_{\alpha \beta}^m (w_{\alpha \beta \gamma \lambda \mu})_{\gamma \beta}^0 \]

\[ + \alpha_a \rho^k_{\alpha \beta} \sigma_{\alpha \beta}^m (w_{\alpha \beta \gamma \lambda \mu})_{\gamma \beta}^0 + \frac{1}{2} \sigma_{\alpha \beta}^m \rho^k_{\alpha \beta} \sigma_{\alpha \beta}^m (w_{\alpha \beta \gamma \lambda \mu})_{\gamma \beta}^0. \]
For the assumptions made in Eqs. (6.186a) to (6.186f) this yields

$$\sigma_{\alpha\beta}^m H_{\alpha\beta|r}^{mk} \approx$$

$$\frac{1}{3} \alpha_a^m \rho_{\alpha a}^k \alpha_a^k Q^k_{\gamma\lambda|r} \sigma_{\alpha\beta}^m \beta A_{mk} \left( \lambda_{0}^{mk} \right)^{-3} \Omega_{\alpha\beta\gamma\lambda}$$

$$+ \frac{3}{2} \alpha_a^m \rho_{\gamma\lambda|r}^k \sigma_{\alpha\beta}^m \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1} I_{\alpha\beta\gamma\lambda}$$

$$+ \frac{1}{2} \alpha_a^m \rho_{\mu\nu|r}^k \alpha_a^k Q^k_{\gamma\lambda|r} \sigma_{\alpha\beta}^m \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1} \Omega_{\alpha\beta\gamma\lambda\mu\nu|r}. \quad (6.239)$$

And the corresponding contractions with the isotropic and kernel tensors yields

$$\frac{15}{4\pi} \sigma_{\alpha\beta}^m H_{\alpha\beta|r}^{mk} \approx$$

$$\alpha_a^m \rho_{\alpha a}^k \alpha_a^k Q^k_{\beta\alpha|r} \beta A_{mk} \left( \lambda_{0}^{mk} \right)^{-3}$$

$$+ \sigma_{\alpha\beta}^m \rho_{\alpha a}^k \alpha_a^k \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1}$$

$$+ \frac{1}{2} \sigma_{\beta\alpha}^m \alpha_a^k \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1} \times .$$

$$\left\{ - \frac{11}{7} \rho_{\gamma\lambda|r}^k Q^k_{\beta\alpha|r} \sigma_{\alpha\beta}^m \right. $$

$$+ \frac{12}{7} \frac{1}{4} \rho_{\gamma\beta|r}^k Q^k_{\alpha\gamma|r} \sigma_{\alpha\beta}^m + \frac{12}{7} \frac{1}{4} \rho_{\beta\gamma|r}^k Q^k_{\alpha\gamma|r} \sigma_{\alpha\beta}^m $$

$$+ \frac{12}{7} \frac{1}{4} \rho_{\gamma\beta|r}^k Q^k_{\gamma\alpha|r} \sigma_{\alpha\beta}^m + \frac{12}{7} \frac{1}{4} \rho_{\beta\gamma|r}^k Q^k_{\gamma\alpha|r} \sigma_{\alpha\beta}^m \right\}, \quad (6.240)$$

or

$$\frac{15}{4\pi} H_{ij}^{mk} = \alpha_a^m \rho_{\alpha a}^k \alpha_a^k Q^k_{ij|r} \beta A_{mk} \left( \lambda_{0}^{mk} \right)^{-3} + 3 \alpha_a^m \rho_{ij|r}^k \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1}$$

$$+ \frac{1}{2} \alpha_a^m \alpha_a^k \beta A_{mk} \left( \lambda_{2}^{mk} \right)^{-1} \left( \frac{11}{7} \rho_{\gamma\lambda|r}^k Q^k_{ij|r} - \frac{12}{7} \left[ Q^k_{\gamma\lambda|r} \rho_{ij|r}^k \right]^\# \right). \quad (6.241)$$

### 6.3.2 Binary mixture, incompressible system

For the incompressible case it is easier to represent the functional derivatives in terms of the volume fraction rather than the density. Volume fraction and density
are related by these equations:

\[ \phi^X = \frac{N^X v^X}{V} = v^X \rho^X \]  \hspace{1cm} (6.242)

where \( v^X \) is the average volume occupied per molecule of species \( X \) in the mixture. In an incompressible system mass-conservation is mapped to volume conservation and the volume fractions are related by

\[ V^{\text{tot}} = V^{\text{free}} + \sum_{k=1}^{n} N^k v^k \]  \hspace{1cm} (6.243)

or

\[ \phi^{\text{free}} + \sum_{k=1}^{n} \phi^k = 1 \]  \hspace{1cm} (6.244)

where \( V^{\text{free}} \) and \( \phi^{\text{free}} \) is the total volume and volume fraction, respectively that is not occupied by any molecules. In the following we scale the functional derivate by a reference volume \( v_{\text{ref}} \) and a reference temperature \( T_{\text{ref}} \) (or its inverse \( k_B \beta_{\text{ref}} \), respectively).
Expansion of \( \delta F/\delta Q^m \)

Equation (6.197) yields for an incompressible, binary system:

\[
\begin{align*}
&v_{\text{ref}} \delta \beta_{ijr}^F \frac{\delta F}{\delta Q^m_{ijr}} (\mathbf{r}) = \
&\quad \alpha_a^m \phi^m_{ijr} \alpha_a^m \phi^m_{ijr} \Delta^{A}_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Am}}{v_{Am}} \right) \frac{v_{\text{ref}}}{(\lambda_0^m)^3} \
&\quad + \alpha_a^m \phi^m_{ijr} \alpha_a^m \phi^m_{ijr} \Delta^{B}_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Bm}}{v_{Bm}} \right) \frac{v_{\text{ref}}}{(\lambda_0^m)^3} \
&\quad - \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Am}}{v_{Am}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \left( \left( Q_{ijr}^A \phi^A \right)_{\alpha a} - Q_{ijr}^A \phi^A_{\alpha a} \right) \
&\quad - \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Bm}}{v_{Bm}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \left( \left( Q_{ijr}^B \phi^B \right)_{\alpha a} - Q_{ijr}^B \phi^B_{\alpha a} \right) \
&\quad + \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Am}}{v_{Am}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \left( \left( Q_{ijr}^A \phi^A \right)_{\alpha a} - \left( Q_{ijr}^A \phi^A_{\alpha a} \right) \right) \
&\quad + \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Bm}}{v_{Bm}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \left( \left( Q_{ijr}^B \phi^B \right)_{\alpha a} - \left( Q_{ijr}^B \phi^B_{\alpha a} \right) \right) \
&\quad + \frac{11}{14} \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Am}}{v_{Am}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \phi^m_{ijr} \Delta^{A}_{ijr} + \frac{12}{14} \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Bm}}{v_{Bm}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \phi^m_{ijr} \Delta^{B}_{ijr} \
&\quad - \frac{12}{14} \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Am}}{v_{Am}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \phi^m_{ijr} \Delta^{A}_{ijr} \
&\quad - \frac{12}{14} \alpha_a^m \phi^m_{ijr} \left( \frac{4 \pi \beta_{ijr} A_{Bm}}{v_{Bm}} \right) \frac{v_{\text{ref}}}{\lambda_0^m} \alpha_a^m \phi^m_{ijr} \Delta^{B}_{ijr},
\end{align*}
\]

for \( m \in \{A, B\} \).

Expansion of \( \delta F/\delta \rho \)

The functional derivative with respect to volume fraction is given by

\[
\frac{\delta F}{\delta \rho^X (\mathbf{r})} = v^A \frac{\delta F}{\delta \phi^X (\mathbf{r})}.
\]

For a binary, incompressible mixture the total volume fraction is constant, \( \phi_{ijr}^A + \phi_{ijr}^B + \phi^{\text{free}} = 1 \), where \( \phi^{\text{free}} \) is the volume fraction not occupied by any molecules, and only one functional derivative is linearly independent. Since \( \phi^{\text{free}} \) is not associated with any pair-potential it will not enter the dynamic equations and we set it to zero.
The free energy for a binary system

\[ F[\phi^A, \phi^B] \] (6.247)

becomes in a constrained system a free energy of the form

\[ F[\phi^A, \phi^B(\phi^A)] = \frac{\delta F}{\delta \phi^A} \phi^A_{\text{fixed}} - \frac{\delta F}{\delta \phi^B} \phi^B_{\text{fixed}} \] (6.248)

thus

\[ \frac{\delta F}{\delta \phi^A} = \left( \frac{\delta F}{\delta \phi^A} \right)_{00} + \sum_{i=1}^{9} \left( \frac{\delta F}{\delta \phi^A} \right)^{(i)} \] (6.249)

where "\( \phi^A \) fixed" and "\( \phi^B \) fixed" denotes that the first and second argument, respectively in the free energy Eq. (6.248) is held constant when taking the functional derivative. Equation (6.235), for a binary mixture can then be rewritten as

\[ \frac{\delta \beta F}{\delta \phi^A}(\mathbf{r}) = \left( \frac{\delta \beta F}{\delta \phi^A}(\mathbf{r}) \right)_{00} + \sum_{i=1}^{9} \left( \frac{\delta \beta F}{\delta \phi^A}(\mathbf{r}) \right)^{(i)} \] (6.250)

with

\[ \left( \frac{\delta \beta F}{\delta \phi^A} \right)^{(i)} \equiv \frac{1}{v_i^A} \left( B_i^{AA} + B_i^{AB} \right) - \frac{1}{v_i^B} \left( B_i^{BA} + B_i^{BB} \right) \] (6.251)

and

\[ \frac{\delta \beta F}{\delta \phi^A} = \left( \frac{\delta \beta F}{\delta \phi^A} \right)_{00} - \left( \frac{\delta \beta F}{\delta \phi^B} \right)_{00} \] (6.252)

And using Eq. (6.224) through (6.234) yields for each individual term

\[ \left( \frac{\delta F}{\delta \phi^A}(\mathbf{r}) \right)^{(2)} = \left( \frac{\delta F}{\delta \phi^A}(\mathbf{r}) \right)^{(3)} = \left( \frac{\delta F}{\delta \phi^A}(\mathbf{r}) \right)^{(5)} = \left( \frac{\delta F}{\delta \phi^A}(\mathbf{r}) \right)^{(8)} = 0, \] (6.253)

\[ v_{ref} \left( \frac{\delta \beta_{\text{ref}} F}{\delta \phi^A}(\mathbf{r}) \right)_{00} = \frac{v_{ref} \beta_{\text{ref}}}{v_i^A} \left( \ln \frac{\phi^A}{v_i^A} - \ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^A(\mathbf{r}) \right) d^2 \sigma \right) \]

\[ - \frac{v_{ref} \beta_{\text{ref}}}{v_i^B} \left( \ln \frac{\phi^B}{v_i^B} - \ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^B(\mathbf{r}) \right) d^2 \sigma \right), \] (6.254)
or, ignoring constant terms

\[
v_{\text{ref}} \left( \delta \beta_{\text{ref}} F \left( \frac{\delta \phi^A(r)}{\phi^A} \right) \right) = v_{\text{ref}} \frac{T}{v^A} \frac{T_{\text{ref}}}{v^B} \ln \phi^A - v_{\text{ref}} \frac{T}{v^B} A_{\text{ref}} \phi^A \ln (1 - \phi^A)
\]

\[-v_{\text{ref}} \frac{T}{v^A} T_{\text{ref}} \ln \int \exp \left( \sigma_{\alpha \beta} H_{\alpha \beta}^A (r) \right) d^2 \sigma + v_{\text{ref}} \frac{T}{v^B} T_{\text{ref}} \ln \int \exp \left( \sigma_{\alpha \beta} H_{\alpha \beta}^B (r) \right) d^2 \sigma,
\]

\[v_{\text{ref}} \left( \frac{\delta \beta_{\text{ref}} F}{\phi^A(r)} \right) = \]

\[= \quad 8 \pi \left( 2 \frac{\beta_{\text{ref}} A_{AB}}{v^A B^B} \frac{v_{\text{ref}}}{(\lambda^A_0)^3} - \frac{\beta_{\text{ref}} A_{BB}}{v^B B^B} \frac{v_{\text{ref}}}{(\lambda^B_0)^3} - \frac{\beta_{\text{ref}} A_{AA}}{v^A A^A} \frac{v_{\text{ref}}}{(\lambda^A_0)^3} \right) \phi^A_{\text{ref}}, \]

\[(6.255)\]

\[v_{\text{ref}} \left( \frac{\delta \beta_{\text{ref}} F}{\phi^A(r)} \right) = \]

\[= \quad 4 \pi \phi^A_{\alpha \beta} \delta_{\text{ref}} \left( 2 \frac{\beta_{\text{ref}} A_{AB}}{v^A B^B} \frac{v_{\text{ref}}}{(\lambda^A_0)^3} - \frac{\beta_{\text{ref}} A_{BB}}{v^B B^B} \frac{v_{\text{ref}}}{(\lambda^B_0)^3} - \frac{\beta_{\text{ref}} A_{AA}}{v^A A^A} \frac{v_{\text{ref}}}{(\lambda^A_0)^3} \right), \]

\[(6.257)\]

\[v_{\text{ref}} \left( \frac{\delta \beta_{\text{ref}} F}{\phi^A(r)} \right) = \]

\[\alpha_a^A \alpha_a^B \phi^A_{\alpha \beta} \phi^B_{\alpha \beta} = \frac{4 \pi}{15} \frac{\beta_{\text{ref}} A_{AA}}{v^A A^A} \frac{v_{\text{ref}}}{(\lambda^A_0)^3} - \frac{\beta_{\text{ref}} A_{BB}}{v^B B^B} \frac{v_{\text{ref}}}{(\lambda^B_0)^3} + \frac{\phi^A_{\alpha \beta} \Delta_{\alpha \beta}^A}{\phi^A_{\alpha \beta} \Delta_{\alpha \beta}^B} \frac{\phi^B_{\alpha \beta} \Delta_{\alpha \beta}^A}{\phi^B_{\alpha \beta} \Delta_{\alpha \beta}^B} \frac{4 \pi}{15} \frac{\beta_{\text{ref}} A_{AB}}{v^A v^B} \frac{v_{\text{ref}}}{(\lambda^{AB}_0)^3}, \]

\[(6.258)\]

\[v_{\text{ref}} \left( \frac{\delta \beta_{\text{ref}} F}{\phi^A(r)} \right) = \]

\[\quad \frac{\phi^B_{\alpha \beta} \left( \phi^B_{\alpha \beta} \phi^B_{\alpha \beta} \right)}{5} \frac{\beta_{\text{ref}} A_{BB}}{v^B v^B} \frac{v_{\text{ref}}}{(\lambda^B_0)^3} - \frac{\beta_{\text{ref}} A_{BA}}{v^A v^B} \frac{v_{\text{ref}}}{(\lambda^{BA}_0)^3} + \frac{\phi^A_{\alpha \beta} \left( \phi^A_{\alpha \beta} \phi^A_{\alpha \beta} \right)}{5} \frac{\beta_{\text{ref}} A_{AA}}{v^A v^A} \frac{v_{\text{ref}}}{(\lambda^{AA}_0)^3}, \]

\[(6.259)\]
and

\[
\begin{align*}
&\frac{v_{\text{ref}}}{\frac{\delta F}{\delta \phi^A(\mathbf{r})}} = \\
&\alpha_a^A \alpha_a^A \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^A v^A}} \right) \lambda_2^A \lambda_2^A \{ Q_{\alpha\beta\gamma} \left( \frac{12 \frac{\delta^A Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{11 \frac{\delta^A Q_{\alpha\gamma}}{\gamma\delta\gamma}}{\gamma\delta\gamma} \right) \\
&+ \frac{11 \frac{\delta^A A_{\alpha\beta} Q_{\alpha\gamma}}{A_{\alpha\beta} Q_{\alpha\gamma}} - \frac{12 \frac{\delta^A A_{\alpha\beta} Q_{\alpha\gamma}}{A_{\alpha\beta} Q_{\alpha\gamma}}}{\gamma\delta\gamma} \right) \\
&+\alpha_a^A \alpha_a^B \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^B v^A}} \right) \lambda_2^B \lambda_2^B \{ Q_{\alpha\beta\gamma} \left( \frac{12 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{11 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma}}{\gamma\delta\gamma} \right) \\
&+ \frac{11 \frac{\delta^B A_{\alpha\beta} Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{12 \frac{\delta^B A_{\alpha\beta} Q_{\alpha\gamma}}{A_{\alpha\beta} Q_{\alpha\gamma}}}{\gamma\delta\gamma} \right) \\
&-\alpha_a^B \alpha_a^A \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^A v^B}} \right) \lambda_2^A \lambda_2^B \{ Q_{\alpha\beta\gamma} \left( \frac{12 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{11 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma}}{\gamma\delta\gamma} \right) \\
&+ \frac{11 \frac{\delta^B A_{\alpha\beta} Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{12 \frac{\delta^B B_{\alpha\beta} Q_{\alpha\gamma}}{A_{\alpha\beta} Q_{\alpha\gamma}}}{\gamma\delta\gamma} \right) \\
&-\alpha_a^B \alpha_a^B \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^B v^B}} \right) \lambda_2^B \lambda_2^B \{ Q_{\alpha\beta\gamma} \left( \frac{12 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{11 \frac{\delta^B Q_{\alpha\gamma}}{\gamma\delta\gamma}}{\gamma\delta\gamma} \right) \\
&+ \frac{11 \frac{\delta^B B_{\alpha\beta} Q_{\alpha\gamma}}{\gamma\delta\gamma} - \frac{12 \frac{\delta^B B_{\alpha\beta} Q_{\alpha\gamma}}{B_{\alpha\beta} Q_{\alpha\gamma}}}{\gamma\delta\gamma} \right) \} .
\end{align*}
\]

(6.260)

Expansion of the local field, \( H_{ij}^{mk} \)

The effective field \( H_{ij}^{mk} \) in terms of volume fractions is given by

\[
\begin{align*}
H_{ij}^{mk} &= \frac{\beta}{\beta_{\text{ref}}} \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^m v^k}} \right) (\lambda_m^{mk})^{-3} \alpha_m^a \alpha_m^b v^m v^k\phi_{ijr}^k Q_{ijr}^k \\
&+ \frac{3}{2} \frac{\beta}{\beta_{\text{ref}}} \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^m v^k}} \right) (\lambda_m^{mk})^{-1} \alpha_m^a v^m v^k \phi_{ijr}^k \\
+ \frac{1}{2} \frac{\beta}{\beta_{\text{ref}}} \left( \frac{4 \pi}{15 \frac{\beta_{\text{ref}}}{v^m v^k}} \right) (\lambda_m^{mk})^{-1} \alpha_m^a \alpha_m^b v^m \left( \frac{11}{7} \phi_{ijr}^k Q_{ijr}^k \right) - \frac{12}{7} [Q_{ijr}^k \phi_{ijr}^k]'.
\end{align*}
\]

(6.261)

6.3.3 Results

The functional derivatives \( \delta F/\delta Q_{ij}^m \) and \( \delta F/\delta \rho^m \), respectively for an incompressible, binary mixture and ignoring the isotropic part of the pair-distribution function are
given by equation (6.245) and (6.250), respectively, with Eqs. (6.253) and (6.255) through (6.260). We now simplify these results. First we define some terms. We define a characteristic energy $u_{XY}$ of the interaction between a pair of molecules

$$u_{XY} \equiv \frac{4\pi}{15} \frac{A_{XY}}{v^X v^Y}. \quad (6.262)$$

In order to keep the expressions compact, we also define a dimensionless energy $a_{XY}$, by absorbing the reference energy $\beta_{\text{ref}}$ into $u_{XY}$

$$a_{XY} \equiv \frac{4\pi}{15} \frac{\beta_{\text{ref}} A_{XY}}{v^X v^Y}. \quad (6.263)$$

The constant $A_{XY}$ is defined in (6.40a), which we give here for reference:

$$A_{XY} = \frac{3}{2} (h\nu)_{XY} \frac{\bar{\alpha}^X \bar{\alpha}^Y}{(4\pi\varepsilon_0)^2}, \quad (6.264)$$

with $(h\nu)_{XY}$ the oscillator energy for a pair $X - Y$, $\bar{\alpha}$ the average polarizability $(\alpha_\parallel + 2\alpha_\perp)/3$, and $\bar{\alpha}/4\pi\varepsilon_0$ has the dimension of a molecular volume. We define scaled molecular volumes

$$s_X \equiv \frac{v_{\text{ref}}}{v^X} \quad (6.265)$$

and

$$s_{XY} \equiv \frac{v_{\text{ref}}}{(\lambda_{XY}^0)^\frac{3}{3}} \quad (6.266)$$

Second, we can further simplify by relating some of the terms to transition temperatures in the homogenous system. We show in the appendix, section A.4, that for a reduced chemical potential of the form

$$\beta\mu = -a \frac{T_c}{T} \phi + u \ln \phi - s \ln (1 - \phi), \quad (6.267)$$
where $T_c$ is the phase-separation critical temperature of the isotropic, homogenous system, the factor $a$ relates to $u$ and $s$ by

$$a = (\sqrt{u} + \sqrt{s})^2. \quad (6.268)$$

The chemical potential in Eq. (6.267) is that of a homogenous and isotropic system. For such a system all terms involving gradients and nematic order parameters in the chemical potential Eq. (6.250) are zero or constant, yielding

$$v_{\text{ref}} \left( \frac{\delta \beta F}{\delta \phi^A_{\text{ref}}(r)} \right) = -a_1 \frac{T_{\text{ref}}}{T} \phi^A_{\text{ref}} + s_A \ln \phi^A_{\text{ref}} - s_B \ln (1 - \phi^A_{\text{ref}}), \quad (6.269)$$

with

$$a_1 \equiv 30 \beta_{\text{ref}} \left( \frac{u_{BB}}{\lambda_0^{BB}} \frac{v_{\text{ref}}}{\lambda_0^{AB}} \right)^3 + u_{AA} \frac{v_{\text{ref}}}{\lambda_0^{AA}} - 2u_{AB} \frac{v_{\text{ref}}}{\lambda_0^{AB}} \right), \quad (6.270)$$

and a comparison of (6.269) with equations (6.267) and (6.268) yields

$$a_1 T_{\text{ref}} = (\sqrt{s_A} + \sqrt{s_B})^2 T_c. \quad (6.271)$$

Inserting (6.270) into (6.271) and using the definition of $s_A$ and $s_B$ yields an expression relating various molecular parameters to the critical phase-separation temperature

$$30 \frac{v^A v^B}{\sqrt{(v^A)^2 + (v^B)^2}} \left( \frac{u_{BB}}{(\lambda_0^{BB})^3} + u_{AA} \frac{1}{(\lambda_0^{AA})^3} - 2u_{AB} \frac{1}{(\lambda_0^{AB})^3} \right) = k_B T_c. \quad (6.272)$$

The factor containing molecular volumes can be written as a volume $(\Lambda^*_{AB})^3$, defined as

$$(\Lambda^*_{AB})^3 \equiv \frac{v^A v^B}{\sqrt{(v^A)^2 + (v^B)^2}}. \quad (6.273)$$
Similarly, the nematic pseudo-critical temperature $T_{AA}^*$ can be related to the molecular parameters. The functional derivative $\beta_{\text{ref}} v_{\text{ref}} \delta F / \delta Q_{ij}$, Eq. (6.245), for a homogenous system with only the order parameter $Q^A$ of material $A$ nonzero is of the form

$$\frac{\delta F}{\delta Q_{ij}} = \lambda(\phi) \left( Q_{ij} - \langle \sigma_{ij} \rangle_{H_{ij}} \right),$$

(6.274)

where $\lambda(\phi)$ is some arbitrary function of $\phi$, and the effective field (6.261) simplifies to

$$H_{ij} = b \phi Q_{ij}(r).$$

(6.275)

We show in the appendix, section A.5, that for such a case

$$b = \frac{10 T_{AA}^*}{3 T},$$

(6.276)

with $T_{AA}^*$ the pseudo-critical temperature of the nematic phase of the pure and homogenous system of material $A$. For such a system, omitting the gradients in Eq. (6.261) yields

$$H_{ij}^{mk} = \frac{T_{\text{ref}}}{T} \alpha^m_a \alpha^k_a a_{mk} \frac{v^m}{(\lambda_0^{mk})^3 \Phi^k_{ij} Q_{ij}^{k}},$$

(6.277)

and the local field on a molecule of material $A$ is given by

$$H_{ij}^A = H_{ij}^{AA} + H_{ij}^{AB} = H_{ij}^{AA} = \frac{T_{\text{ref}}}{T} \alpha^A_a \alpha^A_a a_{AA} \frac{v^A}{(\lambda_0^{AA})^3 Q_{ij}^{A}},$$

(6.278)

thus

$$\frac{10 T_{AA}^*}{3 T_{\text{ref}}} = \alpha^A_a \alpha^A_a a_{AA} \frac{v^A}{(\lambda_0^{AA})^3},$$

(6.279)

and vice versa for a pure, homogenous system of material $B$, where $T_{BB}^*$ is the pseudo-critical temperature of a pure homogenous system of material $B$. From this we find
that the nematic-isotropic transition temperature is related to molecular material parameters by

\[ k_B T_{AA}^* = \frac{4\pi}{75} (h\nu)_{AA} \frac{\Delta \alpha^A}{(4\pi\varepsilon_0)^2 v^A (\lambda_0^{AA})^3}, \]

where \( \Delta \alpha^A \equiv (\alpha^A_\parallel - \alpha^A_\perp) \) is the anisotropy of the molecular polarizability. We also define formally a temperature \( T_{AB}^* \) such that

\[ \frac{10}{3} \frac{T_{AB}^*}{T_{\text{ref}}} = \alpha_a^A \alpha_a^B a_{AB}. \]  

(6.280)

We furthermore define the following lengths:

\[ s_\sigma \Lambda_\sigma^2 \equiv 3\beta_{\text{ref}} \left( u_{AA} \frac{v_{\text{ref}}}{\lambda_2^{AA}} - u_{AB} \frac{v_{\text{ref}}}{\lambda_2^{AB}} \right) \]

(6.281)

\[ s_\tau \Lambda_\tau^2 \equiv 3\beta_{\text{ref}} \left( u_{BB} \frac{v_{\text{ref}}}{\lambda_2^{BB}} - u_{AB} \frac{v_{\text{ref}}}{\lambda_2^{AB}} \right), \]

(6.282)

where \( s_\sigma \) and \( s_\tau \) is the sign of the right-hand side of (6.282) and (6.281). (We prefer that a squared length is a positive quantity.) Imagine that the generalized forces are derived from a gradient expanded free-energy density. Then the coefficient of the square gradient in volume fraction \( \phi_\alpha \phi_\alpha \) must be positive, or respectively that of \( \phi_\alpha \) in the chemical potential negative. Using the definitions for \( s_\sigma \Lambda_\sigma^2 \) and \( s_\tau \Lambda_\tau^2 \), the term containing this square gradient, Eq. (6.257) can be written as

\[ v_{\text{ref}} \left( \frac{\delta \beta_{\text{ref}}}{\delta \phi^A (r)} \right)^{(4)} = -5 \left( s_\sigma \Lambda_\sigma^2 + s_\tau \Lambda_\tau^2 \right) \phi_\alpha(r), \]  

(6.283)

which shows that \( s_\sigma \Lambda_\sigma^2 + s_\tau \Lambda_\tau^2 \) must be positive. However, it is not implied that each individual term \( s_\sigma \Lambda_\sigma^2 \) and \( s_\tau \Lambda_\tau^2 \) is positive. These lengths occur in (6.259) and (6.257). These lengths still depend on the reference volume and energy, and so we
define additionally lengths, which are material constants:

\[
\overline{\Lambda}_\sigma^2 \equiv \frac{\Lambda_\sigma^2}{a_1} \tag{6.284}
\]

\[
\overline{\Lambda}_\tau^2 \equiv \frac{\Lambda_\tau^2}{a_1}, \tag{6.285}
\]

which explicitly for \(\overline{\Lambda}_\sigma^2\) is given by

\[
\overline{\Lambda}_\sigma^2 = \frac{|u_{AA}/\lambda_2^{AA} - u_{AB}/\lambda_2^{AB}|}{10 \left( u_{BB}/\left(\lambda_0^{BB}\right)^3 + u_{AA}/\left(\lambda_0^{AA}\right)^3 - 2u_{AB}/\left(\lambda_0^{AB}\right)^3 \right)^{\frac{3}{2}}}, \tag{6.286}
\]

and using (6.272), which relates the denominator to the phase-separation critical temperature, yields

\[
\overline{\Lambda}_\sigma^2 = \frac{3 (\Lambda^*_{AB})^3}{k_B T_c} \left| u_{AA} \frac{1}{\lambda_2^{AA}} - u_{AB} \frac{1}{\lambda_2^{AB}} \right|. \tag{6.287}
\]

Exchanging \(A\) and \(B\) yields the analogous result for \(\overline{\Lambda}_\tau^2\). The rescaled squared lengths \(\Lambda_\sigma^2\) and \(\Lambda_\tau^2\) are thus

\[
\Lambda_\sigma^2 = \overline{\Lambda}_\sigma^2 \left( s_A + s_B \right)^2 \frac{T_c}{T_{ref}} \tag{6.288}
\]

\[
\Lambda_\tau^2 = \overline{\Lambda}_\tau^2 \left( s_A + s_B \right)^2 \frac{T_c}{T_{ref}}. \tag{6.289}
\]

Another place where these lengths appear is in the effective field \(H_{ij}^{mk}\). The effective field on a molecule of material \(A\) is \(H_{ij}^A = H_{ij}^{AA} + H_{ij}^{AB}\). We are only interested in the term containing \(\phi_{ij}\) but not \(Q_{ij}\) in (6.261), thus ignoring all other terms

\[
H_{ij}^A = H_{ij}^A (\phi_{ij} \text{ only}) + \text{ terms containing } Q_{ij} \tag{6.290}
\]

with

\[
H_{ij}^A (\phi_{ij} \text{ only}) = 3 \frac{\beta}{\beta_{ref}} \left( \frac{4\pi}{15} \frac{\beta_{ref} A_{AA}}{v^A} \right) \left( \Lambda_2^{AA} \right)^{-1} \alpha^A v^A \phi_{ij}^A + 3 \frac{\beta}{\beta_{ref}} \left( \frac{4\pi}{15} \frac{\beta_{ref} A_{AB}}{v^A v^B} \right) \left( \Lambda_2^{AB} \right)^{-1} \alpha^A v^A \phi_{ij}^B. \tag{6.291}
\]
For an incompressible, binary mixture $\phi^A_{ij} = -\phi^B_{ij}$, thus

$$H^A_{ij} (\phi_{ij} \text{ only}) = 3\beta \left( u_{AA} \left( \lambda^{AA}_2 \right)^{-1} - u_{AB} \left( \lambda^{AB}_2 \right)^{-1} \right) \alpha^A_a v^A \phi^A_{ij|r}$$  \hspace{1cm} (6.292)

and expressing this in terms of $\Lambda^A_2$ yields

$$H^A_{ij} (\phi_{ij} \text{ only}) = \frac{\beta}{\beta_{\text{ref}} v_{\text{ref}}} \Lambda^2_\sigma \alpha^A_a v^A \phi^A_{ij|r}$$  \hspace{1cm} (6.293)

or alternatively in terms $\Lambda^2_\sigma$, $v_A$ and $v_B$

$$H^A_{ij} (\phi_{ij} \text{ only}) = \frac{T_c}{T} \Lambda^2_\sigma \left( 1 + \sqrt{\frac{v^A}{v^B}} \right)^2 \alpha^A_a \phi^A_{ij|r}.$$  \hspace{1cm} (6.294)

Finally we define another length $\Lambda^2_{XY}$

$$\Lambda^2_{XY} \equiv (\Lambda^X_0)^3 / \lambda^X_2$$

and a rescaled free energy

$$F' \equiv v_{\text{ref}} \beta_{\text{ref}} F,$$  \hspace{1cm} (6.295)

such that the functional derivatives $\delta F'/\delta \phi^m_{ij}$ and $\delta F'/\delta Q^m_{ij|r}$ are of unit dimension. With these definitions we now write $\delta F'/\delta \phi^A$, $\delta F'/\delta Q^A_{ij}$ and $H^A_{ij}$, respectively. The results are tabulated below in table 6.1, 6.2, 6.3 and 6.4, respectively. The values with respect to $B$ follow by exchanging $A$ and $B$.

### 6.3.4 Special cases

It is useful to consider some special cases. We consider only mixtures of one nematic and one isotropic component, therefore all terms containing $Q^m_{ij}$ can be ignored.

First, consider the case of a homogenous system, where we simply set all gradient
\[
\delta F'/\delta Q^A_{ijr}(r) \equiv \sum c_k f_k(r)
\]

<table>
<thead>
<tr>
<th>k</th>
<th>(c_k)</th>
<th>(f_k(r))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\phi^A_{ijr} \phi^A_{ijr} \Lambda^A_{ijr})</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(-\frac{11}{14} \phi^A_{ijr} \left( \left( Q^A_{ijr} \phi^A_{ijr} \right)<em>{\alpha\alpha} \phi^A</em>{ijr} - Q^A_{ijr} \phi^A_{ijr} \right))</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\frac{12}{14} \phi^A_{ijr} \left( Q^A_{ijr} \phi^A_{ijr} \right)<em>{\alpha\alpha} - \left[ Q^A</em>{ijr} \phi^A_{ijr} \right]_{\alpha\alpha})</td>
</tr>
<tr>
<td>4</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\frac{11}{14} \phi^A_{ijr} \phi^A_{ijr} \phi^A_{ijr} \Lambda^A_{ijr})</td>
</tr>
<tr>
<td>5</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(-\frac{12}{14} \phi^A_{ijr} \Lambda^A_{ijr})</td>
</tr>
<tr>
<td>6</td>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\phi^A_{ijr} \phi^A_{ijr} \Lambda^A_{ijr})</td>
</tr>
<tr>
<td>7</td>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB} \Lambda^2_{AB})</td>
<td>(-\frac{12}{14} \phi^A_{ijr} \left[ Q^B_{ijr} \phi^B_{ijr} \right]<em>{\alpha\alpha} - Q^B</em>{ijr} \phi^B_{ijr} \right))</td>
</tr>
<tr>
<td>8</td>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB} \Lambda^2_{AB})</td>
<td>(\frac{12}{14} \phi^A_{ijr} \left( Q^B_{ijr} \phi^B_{ijr} \right)<em>{\alpha\alpha} - \left[ Q^B</em>{ijr} \phi^B_{ijr} \right]_{\alpha\alpha})</td>
</tr>
<tr>
<td>9</td>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB} \Lambda^2_{AB})</td>
<td>(\frac{12}{14} \phi^A_{ijr} \phi^A_{ijr} \phi^A_{ijr} \Lambda^A_{ijr})</td>
</tr>
<tr>
<td>10</td>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB} \Lambda^2_{AB})</td>
<td>(-\frac{12}{14} \phi^A_{ijr} \Lambda^B_{ijr})</td>
</tr>
</tbody>
</table>

Table 6.1: Generalized force \(\delta F'/\delta Q_{ijr}^A\) in an incompressible, binary mixture

\[
H^A_{ijr}(r) = \sum c_k f_k(r)
\]

<table>
<thead>
<tr>
<th>c_k</th>
<th>f_k(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\phi^A_{ijr} Q^A_{ijr})</td>
</tr>
<tr>
<td>(\frac{10 T_{AA}^A}{3 T_{ref}^A} S_A \Lambda^2_{AA})</td>
<td>(\left( 1 + \sqrt{\frac{\Lambda^A_{ijr}}{v_A}} \right)^2 c_A)</td>
</tr>
<tr>
<td>(\frac{11}{14} \phi^A_{ijr} Q^A_{ijr} - \frac{12}{14} \phi^A_{ijr} \phi^A_{ijr} \right)_{\alpha\alpha})</td>
<td></td>
</tr>
<tr>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB})</td>
<td>(\phi^B_{ijr} Q^B_{ijr})</td>
</tr>
<tr>
<td>(\frac{10 T_{AB}^A}{3 T_{ref}^A} S_{AB} S_{AA}^{-1} \Lambda_{AB})</td>
<td>(\phi^B_{ijr} Q^B_{ijr})</td>
</tr>
</tbody>
</table>

Table 6.2: Effective field \(H^A_{ijr}\) in a binary, incompressible mixture
\[ \frac{\delta F'}{\delta \phi^A_{ir}} = \sum_k c_k f_k (r) \]

<table>
<thead>
<tr>
<th>k</th>
<th>( c_k )</th>
<th>( f_k (r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( T/T_{ref} )</td>
<td>( s^A \ln \phi^A - s^B \ln (1 - \phi^A_{ir}) )</td>
</tr>
<tr>
<td>2</td>
<td>( \sqrt{s_A + \sqrt{s_B}}^2 T_c/T_{ref} )</td>
<td>( -\phi^A_{ir} )</td>
</tr>
<tr>
<td>3</td>
<td>( 5 \left( s_{\sigma} \bar{\Lambda}^2_{\sigma} + s_{\tau} \bar{\Lambda}^2_{\tau} \right) \times \left( \sqrt{s_A + \sqrt{s_B}}^2 T_c/T_{ref} \right) )</td>
<td>( -\phi^A_{\alpha\beta</td>
</tr>
<tr>
<td>4</td>
<td>( T/T_{ref} )</td>
<td>( -s^A \ln \int \exp \left( \sigma_{\alpha\beta} H^A_{\beta\alpha} (r) \right) d^2 \sigma )</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{10}{3} s_A T^*<em>{AA}/T</em>{ref} )</td>
<td>( \phi^A_{ir} Q_{\alpha\beta</td>
</tr>
<tr>
<td>6</td>
<td>( -\alpha^A_{\sigma} s_{\sigma} \bar{\Lambda}^2_{\sigma} \left( \sqrt{s_A + \sqrt{s_B}}^2 \right)^2 T_{ref} )</td>
<td>( \left( \phi^A_{ir} \langle \sigma_{\alpha\beta}^A \rangle \right)_{\beta\alpha</td>
</tr>
<tr>
<td>7</td>
<td>( \frac{10}{3} s_A \Lambda^2_{AA} T^*<em>{AA}/T</em>{ref} )</td>
<td>( Q^A_{\alpha\beta</td>
</tr>
<tr>
<td>8</td>
<td>( \frac{10}{3} s_A \Lambda^2_{AA} T^*<em>{AA}/T</em>{ref} )</td>
<td>( \frac{11}{14} \left( \phi^A \Delta^A_{\alpha\beta} Q^A_{\beta\alpha} \right)_{\gamma\beta</td>
</tr>
<tr>
<td>9</td>
<td>( T/T_{ref} )</td>
<td>( s^B \ln \int \exp \left( \sigma_{\alpha\beta} H^B_{\beta\alpha} (r) \right) d^2 \sigma )</td>
</tr>
<tr>
<td>10</td>
<td>( \frac{10}{3} s_B T^*<em>{BB}/T</em>{ref} )</td>
<td>( \phi^B_{ir} Q^B_{\alpha\beta</td>
</tr>
<tr>
<td>11</td>
<td>( \alpha^B_{\alpha} s_{\tau} \bar{\Lambda}^2_{\tau} \left( \sqrt{s_A + \sqrt{s_B}}^2 \right)^2 T_{ref} )</td>
<td>( \left( \phi^B_{ir} \langle \sigma_{\alpha\beta}^B \rangle \right)_{\beta\alpha</td>
</tr>
<tr>
<td>12</td>
<td>( \frac{10}{3} s_B \Lambda^2_{BB} T^*<em>{BB}/T</em>{ref} )</td>
<td>( Q^B_{\alpha\beta</td>
</tr>
<tr>
<td>13</td>
<td>( \frac{10}{3} s_B \Lambda^2_{BB} T^*<em>{BB}/T</em>{ref} )</td>
<td>( \frac{11}{14} \left( \phi^B \Delta^B_{\alpha\beta} Q^B_{\beta\alpha} \right)_{\gamma\beta</td>
</tr>
<tr>
<td>14</td>
<td>( \frac{10}{3} s_B T^*<em>{AB}/T</em>{ref} )</td>
<td>( \phi^B_{ir} Q^A_{\alpha\beta</td>
</tr>
<tr>
<td>15</td>
<td>( \frac{10}{3} s_B \Lambda^2_{AB} T^*<em>{AB}/T</em>{ref} )</td>
<td>( Q^A_{\alpha\beta</td>
</tr>
<tr>
<td>16</td>
<td>( \frac{10}{3} s_B \Lambda^2_{AB} T^*<em>{AB}/T</em>{ref} )</td>
<td>( \frac{11}{14} \left( \phi^B \Delta^A_{\alpha\beta} Q^B_{\beta\alpha} \right)_{\gamma\beta</td>
</tr>
<tr>
<td>17</td>
<td>( \frac{10}{3} s_B \Lambda^2_{AB} T^*<em>{AB}/T</em>{ref} )</td>
<td>( Q^B_{\alpha\beta</td>
</tr>
<tr>
<td>18</td>
<td>( -\frac{10}{3} \frac{11}{14} \left( \phi^A \Delta^A_{\alpha\beta} Q^B_{\beta\alpha} \right)_{\gamma\beta</td>
<td>r} - \frac{12}{14} \left( \phi^A \Delta^B_{\beta\alpha} Q^A_{\alpha\gamma} \right)_{\gamma\beta</td>
</tr>
</tbody>
</table>

Table 6.3: Generalized force on \( \phi^A_{ir} \) in an incompressible, binary mixture.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{ij}/\alpha_\perp )</td>
<td>larger/smaller eigenvalue of the molecular polarizability</td>
</tr>
<tr>
<td>( \bar{\alpha}^X )</td>
<td>average molecular polarizability ( \left( 2\alpha_\perp^X + \alpha_\parallel^X \right) / 3 )</td>
</tr>
<tr>
<td>( \alpha_a^X )</td>
<td>relative polarizability anisotropy of material ( X ), ( \left( \alpha_\parallel^X - \alpha_\perp^X \right) / \bar{\alpha}^X )</td>
</tr>
<tr>
<td>( (h\nu)_{XY} )</td>
<td>quantum-mech. oscillator-strength of pair ( X - Y ) (London theory)</td>
</tr>
<tr>
<td>( A_{XY} )</td>
<td>interaction parameter for the pair ( X - Y ), ( \frac{3}{2} (h\nu)_{XY} \bar{\alpha}^X \bar{\alpha}^Y / (4\pi\varepsilon_0)^2 )</td>
</tr>
<tr>
<td>( u_{XY} )</td>
<td>a characteristic energy of the pair ( X - Y ), ( \frac{4\pi}{15} A_{XY} / v^X v^Y )</td>
</tr>
<tr>
<td>( \langle \sigma_{ij}^X \rangle^{(X)} )</td>
<td>the canonical average of ( \sigma_{ij}^X ) in the field ( H_{ij}^X )</td>
</tr>
<tr>
<td>( \Delta_{ij}^X )</td>
<td>( Q_{ij}^X - \langle \sigma_{ij}^X \rangle^{(X)} )</td>
</tr>
<tr>
<td>( v_{\text{ref}} )</td>
<td>reference volume</td>
</tr>
<tr>
<td>( v^X )</td>
<td>molecular volume of material ( X )</td>
</tr>
<tr>
<td>( (\lambda_{L}^{XY})^{L-3} )</td>
<td>a moment of the pair-distribution fn., ( (3 - L) \int_0^\infty g_{XY}(r) r^{L-4} dr )</td>
</tr>
<tr>
<td>( s_X )</td>
<td>( v_{\text{ref}}/v^X )</td>
</tr>
<tr>
<td>( s_{XY} )</td>
<td>( v_{\text{ref}} / (\lambda_0^{XY})^3 )</td>
</tr>
<tr>
<td>( \Lambda_{XY}^2 )</td>
<td>( \left( \lambda_0^{XY} \right)^3 / \lambda_2^{XY} )</td>
</tr>
<tr>
<td>( \Lambda_{AB}^* )</td>
<td>( v^A v^B / \sqrt{(v^A)^2 + (v^B)^2} )</td>
</tr>
<tr>
<td>( \overline{\Lambda}_\sigma^2 )</td>
<td>( 3 (\Lambda^*_{AB}/k_B T_c)</td>
</tr>
<tr>
<td>( s_\sigma; s_\tau )</td>
<td>( \text{sign} (u_{AA}/\lambda_2^{AA} - u_{AB}/\lambda_2^{AB}) ; \text{sign} (u_{BB}/\lambda_2^{AA} - u_{AB}/\lambda_2^{AB}) )</td>
</tr>
<tr>
<td>( T_{\text{ref}} )</td>
<td>reference temperature</td>
</tr>
<tr>
<td>( T_{XX}^* )</td>
<td>nematic pseudo-critical temperature of pure ( X )-system</td>
</tr>
<tr>
<td>( T_{AB}^* )</td>
<td>a characteristic temperature</td>
</tr>
<tr>
<td>( T_c )</td>
<td>crit. temperature for a phase-separating system w/o nematic order</td>
</tr>
</tbody>
</table>

Table 6.4: Definition of terms used in \( \delta F'/\delta Q_{ij}^A, \delta F'/\delta \rho^A \) and effective field \( H_{ij}^A \).
\[ 0 < u_{BB}/\lambda_{2}^{BB} + u_{AA}/\lambda_{2}^{AA} - 2u_{AB}/\lambda_{2}^{AB} \]
\[ k_{B}T_{XX}^{*} = \frac{4\pi}{75} (h\nu)^{2} \Delta \alpha^{X} / (4\pi\varepsilon_{0})^{2} \nu^{X} \left( \lambda_{0}^{XX} \right)^{3} \]
\[ k_{B}T_{AB}^{*} = \frac{3\alpha_{a}^{A}\alpha_{a}^{B}}{10} u_{AB} \]
\[ k_{B}T_{c} = \frac{30\nu^{A}u_{B}}{\sqrt{(\nu^{A})^{2} + (\nu^{B})^{2}}} \left( u_{BB}/\left( \lambda_{0}^{BB} \right)^{3} + u_{AA}/\left( \lambda_{0}^{AA} \right)^{3} - 2u_{AB}/\left( \lambda_{0}^{AB} \right)^{3} \right) \]

Table 6.5: Additional relationships between terms used in generalized forces.

terms to zero in the generalized forces, Tables 6.1, 6.2 and 6.3. (Notation is defined in Table 6.4). This yields for the force on the nematic order parameter

\[ \left( \frac{\delta F'}{\delta Q_{ij}^{A}} \right)_{r} = \frac{10}{3} \frac{T_{AA}^{*}}{T_{ref}} s_{A} \left( \phi_{r}^{A} \right)^{2} \left( Q_{ij}^{A}_{r} - \langle \sigma_{ij} \rangle_{H^{A}(r)} \right) \]

and for the chemical potential

\[ \left( \frac{\delta F'}{\delta \phi^{A}} \right)_{r} = \frac{T}{T_{ref}} \left( s_{A} \ln \phi_{r}^{A} - s_{B} \ln \left( 1 - \phi_{r}^{A} \right) \right) - \frac{T_{c}}{T_{ref}} \left( \sqrt{s_{A}} + \sqrt{s_{B}} \right)^{2} \phi^{A} \]

\[ - \frac{T}{T_{ref}} \frac{s_{B}}{s_{A}} \ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^{A}(r) \right) d^{2}\sigma + \frac{10}{3} \frac{T}{T_{ref}} s_{A} \phi_{r}^{A} \left( Q_{\beta\alpha}^{A}|_{r} - \langle \sigma_{\beta\alpha} \rangle_{H^{A}(r)} \right) \]

where the canonical average \( \langle . \rangle \) is given by

\[ \langle \sigma_{ij} \rangle_{H^{A}(r)} = \frac{\int \sigma_{ij} \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^{A}(r) \right) d^{2}\sigma}{\int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^{A}(r) \right) d^{2}\sigma} \]

and the local field \( H_{ij}^{A}(r) \) is

\[ H_{ij}^{A}(r) = \frac{10}{3} \frac{T_{AA}^{*}}{T} \phi_{r}^{A} Q_{ij}^{A} \]
It can easily be verified that these generalized forces correspond to a free energy of the form

$$F' = \int (\mathcal{F}'_{\text{iso}} + \mathcal{F}'_{\text{nematic}}) \, d^3 r,$$  

(6.300)

with

$$\mathcal{F}'_{\text{iso}}(r) \equiv \frac{T}{T_{\text{ref}}} \left( s_A \phi^A_{|r|} \ln \phi^A_{|r|} + s_B \left( 1 - \phi^A_{|r|} \right) \ln \left( 1 - \phi^A_{|r|} \right) \right) + \frac{1}{2} \left( \sqrt{s_A} + \sqrt{s_B} \right)^2 \frac{T_c}{T_{\text{ref}}} \phi^A_{|r|} \left( 1 - \phi^A_{|r|} \right)$$  

(6.301)

the isotropic part of the free energy density, ignoring any constant terms and terms linear in $\phi^A$, which do only add a constant to the chemical potential and therefore do not enter the dynamic equations, and

$$\mathcal{F}'_{\text{nematic}}(r) \equiv -\frac{T}{T_{\text{ref}}} \phi^A_{|r|} \ln \int \exp \left( \frac{10 T^*}{3} \frac{T}{T} \phi^A_{|r|} \left( \sigma_{\alpha \beta} Q^A_{|\beta \alpha|} - \frac{1}{2} Q^A_{|\alpha \beta|} Q^A_{|\beta \alpha|} \right) \right) \, d^2 \sigma$$  

(6.302)

the nematic part of the free energy density. The isotropic part, $\mathcal{F}'_{\text{iso}}$, has the same structure as the Flory-Huggins free energy [31][32], which is used to describe phase separation in polymers, for example Refs. [33][34][35].

Second, consider the case for which the nematic order parameter vanishes. The chemical potential is then given by

$$\left( \frac{\delta F'}{\delta \phi^A} \right)_{|r|} = \frac{T}{T_{\text{ref}}} \left( s_A \ln \phi^A_{|r|} - s_B \ln \left( 1 - \phi^A_{|r|} \right) \right) - \frac{T_c}{T_{\text{ref}}} \left( \sqrt{s_A} + \sqrt{s_B} \right)^2 \phi^A - \kappa \phi^A_{|r|}$$  

(6.303)
with
\[
\kappa = 5 \left( s_\sigma \Lambda_\sigma^2 + s_\tau \Lambda_\tau^2 \right) (\sqrt{s_A} + \sqrt{s_B})^2 \frac{T_c}{T_{\text{ref}}}.
\]

(6.304)

This chemical potential corresponds to a free energy density, ignoring any surface contributions (which may lead to an ill-posed minimization problem for the free energy),
\[
F' = F'_{\text{iso}} + \frac{\kappa}{2} \phi^A_{\alpha \mid r} \phi^A_{\alpha \mid r},
\]

(6.305)

where $F'_{\text{iso}}$ is given in Eq. (6.301). This corresponds to Cahn-Hilliard theory [36][37], with a special choice for the homogenous part of the free energy density.

Third, consider the case for which the volume fraction is constant, the generalized force on the nematic order parameter then yields
\[
\frac{\delta F'_{\text{nematic-gradient}}}{\delta Q_{ij}} = \frac{10}{3} \frac{T^*}{T} s_A \Lambda^2_{AA} \phi^A_{\mid r} \left( \frac{11}{14} Q^A_{ij, \alpha \alpha \mid r} + \frac{12}{14} \left[ Q^A_{\alpha \alpha, \alpha j \mid r} \right]^\# \right),
\]

(6.306)

which, when surface contributions are ignored, corresponds to the free energy density
\[
F' = F'_{\text{nematic}} + \frac{10}{3} \frac{T^*}{T} s_A \Lambda^2_{AA} \phi^A_{\mid r} \left( \frac{11}{7} Q_{\alpha \beta, \gamma \mid r} Q_{\alpha \beta, \gamma \mid r} - \frac{12}{7} Q_{\alpha \beta, \beta \mid r} Q^A_{\alpha \gamma, \gamma \mid r} \right),
\]

(6.307)

where $F'_{\text{nematic}}$ is given in Eq. (6.302). The gradient terms in (6.307) have the same structure as the de Gennes elastic terms [29] for a nematic tensor order parameter
\[
F_{\text{de-Gennes}} = \frac{L_1}{2} Q_{\alpha \beta, \gamma \mid r} Q_{\alpha \beta, \gamma \mid r} + \frac{L_2}{2} Q_{\alpha \beta, \beta \mid r} Q_{\alpha \gamma, \gamma \mid r},
\]

(6.308)

with $L_2 = -(12/11) L_1$. (Note that the stability analysis by de Gennes [29] requires that for a positive definite free energy $L_1 > 0$ and $L_1 + 2L_2/3 > 0$, but not necessarily $L_2 > 0$.)
6.4 Summary

We started with a pair of molecules interacting solely via London dispersion forces and derived the potential for such a pair in a semi-classical approach. This potential is given in Eq. (6.35). This assumes that the interaction is purely between induced dipoles. In general one need include higher multipole moments as well, since in a liquid the dominant interaction is between near molecules. We assume that, even in a liquid, the dipole-dipole interaction dominates. A further assumption is that the molecular polarizability is uniaxial (Eq. (6.37a)). Applying the procedure outlined in section 5.1, we constructed the mean-field single-particle potential $E_X^{\text{single-particle}}(r)$ of a particle of material $X \in \{A_k\}_{k=1}^n$, which is given by Eq. (6.52). This construction includes steric interactions via the pair-distribution function. The single-particle potential is a functional of the nematic order parameters and densities for all materials. It is also a functional of the mutual pair-distribution functions, which themselves will be functionals of the respective order parameters and densities.

We next derived a mean-field free energy for a mixture of several materials. This free energy is given in Eq. (6.67b). The functional derivatives of the free energy with respect to the nematic order-parameter and density, respectively are given by Eq. (6.86) and (6.88), respectively, without a specified single particle potential. Ignoring the anisotropic part of the pair-distribution function and assuming that the isotropic part does not depend on molecular orientation, nematic order-parameter or density, these simplify to Eqs. (6.101) and (6.102), respectively. Specifying the single particle potential as Eq. (6.52) that we had previously derived for Van-der-Waals
interaction finally yields eqns. (6.122) and (6.128) for the functional derivatives. At this point, the generalized forces on nematic order parameters and densities, Eq. (6.122) and (6.128), respectively, are still fully non-local.

Subsequently we expanded the functional derivatives locally in gradients, leading to the second order gradient approximation given in Eqn. (6.136) for $\delta F/\delta Q_{ij}^m$, Eq. (6.157) for $\delta F/\delta \rho^m$ and Eq. (6.180) for the local field $H_{ij}^m$, respectively. Restricting the functional derivatives to locations sufficiently far from surfaces yields equations (6.235), (6.197) and (6.241), respectively, where the coupling tensors can be expressed as linear combinations of isotropic tensors, and any odd-order terms of gradients vanish. For an incompressible, binary system the generalized forces yield equations (6.245) for $Q_{ij}^A$, (6.250) (with (6.255) through (6.260)) for $\rho^A$, and (6.261) for the local field $H_{ij}^A$. The results are tabulated in Tables 6.1, 6.3 and 6.2, with the constants in the tables defined in Table 6.4.

The presented results are under the following assumptions. We apply mean field theory. We only consider London dispersion forces, i.e., the molecules have no internal degrees of freedom (therefore this theory does not describe polymers). Higher order multipole moments are omitted. The molecular polarizability tensor is uniaxial. Steric interaction are included via the pair-distribution function, which will lift the degeneracy found in a second order elastic theory using nematic tensor order parameters (c.f., de Gennes theory [29] and Marrucci-Greco theory [22]). We ignore the anisotropic part of the pair-distribution function. The isotropic part may depend on scalar invariants of the nematic order parameters and on densities. We disregard
any such dependency. If, in addition to these assumptions and after gradient expansion, we consider the limiting case of vanishing order parameter, we recover the same chemical potential as for the Cahn-Hilliard-Flory-Huggins free energy without any surface terms. For the limiting case of constant concentration field we recover the same Euler-Lagrange equations as for a free energy with de Gennes' elastic terms for a nematic tensor order parameter, ignoring any surface terms in the free energy.
Chapter 7

Dynamic equations and dissipation

In this chapter we justify the form of the dynamic equations we use. Assuming purely dissipative dynamics we relate the dissipative forces to the functional derivatives on the fields of the system. Purely dissipative dynamics of a binary system with one conserved and one non-conserved order parameter, including the addition of Langevin noise, is Model C in the classification scheme of Hohenberg and Halperin [38]. Model C refers to a scalar non-conserved order parameter, while we use a tensor. Also, Model C can be applied only to dynamics of the conserved order parameter, when its mobility is not concentration dependent; the Langevin equation for a concentration dependent mobility is undefined. (For the same reason do we not consider Langevin noise in the conserved order parameter dynamics.)

7.1 Forces and fluxes

7.1.1 The general system of equations

The set of generalized fluxes is a linear function of the set of generalized forces. The generalized forces for material $l$ (here we use the index $l$, rather than the material $A_i$) are the gradient of the chemical potential and the functional derivative with respect to the nematic order parameter, respectively. Thus the set of all generalized forces
for all materials is given by

\[
\text{forces} = \left\{ \mu_{ik}^l = \frac{\partial}{\partial x_k} \frac{\delta F}{\delta \rho^i}, \frac{\delta F}{\delta Q^l_{ij}} \right\}_{i=1}^M.
\]  

(7.1)

The corresponding generalized fluxes are the volume current and the time derivative of the nematic order parameter, respectively:

\[
\text{fluxes} = \left\{ j^i = \rho^i \mathbf{v}^i, Q^l_{ij} \right\}_{i=1}^M,
\]

(7.2)

where \( \mathbf{v}^i \) is the average velocity of a molecule of material \( l \). We will call \( j^i \) the "particle current" of material \( l \). The most general linear relation between all the forces and fluxes is given by

\[
\begin{align*}
\frac{\partial}{\partial t} Q^k_{ij} &= \sum_l M^{Q^k Q^l}_{ij \alpha \beta} \frac{\delta F}{\delta Q^l_{ij}} + \sum_l M^{\mu_k \mu_i}_{ij \alpha} \mu^l_{,\alpha}, \\
\end{align*}
\]

(7.3a)

\[
\begin{align*}
\dot{j}^k_i &= \sum_{\alpha} M^{\rho^k Q^l}_{ij \alpha \beta} \frac{\delta F}{\delta Q^l_{ij \beta}} + \sum_l M^{\mu_k \mu_i}_{ij \alpha} \mu^l_{,\alpha},
\end{align*}
\]

(7.3b)

where the \( M^{Q^k Q^l}_{ij \alpha \beta} \), etc. are phenomenological transport coefficients coupling the forces and fluxes. Each coefficient coupling a force of rank \( q \) to a flux of rank \( r \) has rank \( r + q \). The dynamic equations are subject to several constraints.

### 7.1.2 Constraints

**Mass conservation**

Mass is conserved for each material as long as no chemical reactions take place:

\[
\partial_\mathbf{t} \rho^i + \nabla \cdot j^i = 0 \text{ for all materials } l.
\]

(7.4)

**Incompressibility**

We assume incompressibility. Given a volume element \( \Delta V \) fixed in the lab frame, the total number \( dN_l \) of particles of species \( l \) entering in time \( dt \) is given by the flux
of the particle current $j^i$ through the boundary $\partial \Delta V$ of the volume element:

$$dN_i = \int_{\partial \Delta V} J_A \cdot dS dt$$

and the total change in volume occupied by molecules of species $l$ by

$$dV_l = v_l dN_i = \int_{\partial \Delta V} v_l j^i \cdot dS dt.$$  \hspace{1cm} (7.6)

Incompressibility implies (assuming that every volume element of the whole system is incompressible by itself) that the free volume is constant, or equivalently, the volume occupied by all molecules (the “volume occupancy”) is constant:

$$0 = \sum_{i=1}^{\Delta M} dV_i = \sum_{i=1}^{\Delta M} v_i \int_{\partial \Delta V} j^i \cdot dS dt.$$ \hspace{1cm} (7.7)

This can be expressed in terms of a volume integral using the divergence theorem:

$$\int_V \left\{ \nabla \cdot \sum_i v_i j^i \right\} dV.$$ \hspace{1cm} (7.8)

The integrand must vanish because the extent of the volume element is arbitrary. Thus enforcing the incompressibility constraint is equivalent to requiring that the divergence of the total “volume-occupancy current”\(^1\) vanishes:

$$\nabla \cdot \sum_i v^i j^i = 0.$$ \hspace{1cm} (7.9)

This constraint has been pointed out by E and Palffy-Muhoray [30][39]. A less general, but commonly used, constraint that the total volume-occupancy current vanishes, was introduced by de Gennes [40]:

$$\sum_i v^i j^i = 0.$$ \hspace{1cm} (7.10)

\(^1\)Standard terminology is “volume current.” The term “volume-occupancy current” describes the physical process better, however.
This obviously implies (7.9). Specifically, for problems that only vary along one
direction (7.9) and (7.10) are equivalent[30]. Enforcing (7.9) involves solving for the
global pressure field over the system[30][39]. We will instead assume the simpler
constraint (7.10), which can be enforced locally. De Gennes original intent was to
describe the onset of phase separation. Otto and E[39], however, have demonstrated
that (7.10) leads to a different intermediate time scaling behavior of domain growth
than the constraint (7.9).

**Entropy production**

The entropy production must be non-negative. This may be enforced by applying
Onsager's reciprocal relations[41], which relate the transport coefficients in (7.3a)
and (7.3b). However, we will below assume the simpler case that the system is
diagonal, with positive eigenvalues.

**7.1.3 Dynamics from dissipation**

We assume that the response is purely viscous: all energy gained by moving the order
parameter fields into a lower free-energy state is dissipated, any inertial effects are
neglected. We consider the case of a non-conserved scalar field $Y (r,t)$, for illustration
purposes, a non-conserved vector field $\{Z_k (r,t)\}_{k=1}^{n}$, which will be mapped to the
nematic tensor order parameter field, as well as one conserved scalar field $\rho$, which
will correspond to the liquid crystal density:

$$
\int D (r,t) d^D r = -\frac{d}{dt} F [Y, \{Z_k\}, \rho] (t),
$$

(7.11)
where the dissipation function $\mathcal{D}$ is the dissipated energy per volume per time, which, for non-conserved fields, is given by the drag force times the generalized velocity, and for the conserved field is proportional to the particle current times velocity:

$$
\mathcal{D} = f_{\text{drag}}^Y (r,t) \dot{Y} (r,t) + f_{\text{drag}}^{Z_\alpha} (r,t) \dot{Z}_\alpha (r,t) + \gamma^j \dot{j} \cdot \mathbf{v}.
$$

(7.12)

The dissipation function must be positive definite. This is ensured if is is given by

$$
\mathcal{D} = \gamma^Y \dot{\varepsilon}_Y^2 + \sum_k \gamma^{Z_k} \dot{\varepsilon}_z^2 + \gamma^j \dot{j} \cdot \mathbf{v},
$$

(7.13)

where $\dot{j} \equiv \rho \mathbf{v}$. More generally, if we write the generalized velocities as a vector

$$
\eta \equiv (\dot{\varepsilon}_Y, \dot{\varepsilon}_{Z_1}, \ldots, \dot{\varepsilon}_{Z_n}, \dot{x}, \dot{y}, \dot{z})
$$

(7.14)

then the dissipation function may be given by

$$
\mathcal{D} = \eta^T \cdot \gamma \cdot \eta,
$$

(7.15)

and $\mathcal{D}$ is positive definite, if $\gamma$ is positive definite. We will, however, assume that $\gamma$ is diagonal, and all diagonal elements are positive. Expanding the fields $Y(t)$, $Z_k(t)$ and $\rho(t)$ about $Y(t_0)$, $Z_k(t_0)$ and $\rho(t_0)$ at some fixed time $t_0$ yields

$$
\frac{d}{dt} F = \lim_{t \to t_0} \frac{F[Y(t_0) + \varepsilon_Y(t), \{Z_k(t_0) + \varepsilon_{Z_k}(t)\}_{k=1}^n, \rho(t_0) + \varepsilon_\rho(t)] - F[Y, \{Z_k\}_{k=1}^n, \rho_{t_0}]}{t - t_0}
$$

(7.16)

$$
= \int\left\{ \frac{\delta F}{\delta Y} \right|_{r,t_0} \dot{\varepsilon}_Y (r,t_0) + \left( \frac{\delta F}{\delta Z_\alpha} \right) \right|_{r,t_0} \dot{\varepsilon}_{Z_\alpha} (r,t_0) + \left( \frac{\delta F}{\delta \rho} \right) \right|_{r,t_0} \dot{\rho} \right\} d^DR.
$$

(7.17)

We treat the conserved field separately. Fixing all other fields, the dissipation function is given by

$$
\mathcal{D} = \gamma^j \dot{j} \cdot \mathbf{v}
$$

(7.18)
and

\[ \frac{d}{dt} F = \int \frac{\delta F}{\delta \rho} \dot{\rho} d^D r. \]  

(7.19)

The displacement of \( \rho \) is subject to the constraint that mass is conserved for any volume element,

\[ \dot{\rho} = -\nabla \cdot \mathbf{j}. \]  

(7.20)

Replacing \( \dot{\rho} = \dot{\rho} \) by the divergence of the volume current yields

\[ \int \gamma^j \mathbf{j} \cdot \mathbf{v} d^D r = \int \frac{\delta F}{\delta \rho} \nabla_{\alpha} j_{\alpha} d^D r. \]  

(7.21)

We integrate the second term by parts. We write a total divergence

\[ \int_{\Omega} \nabla_{\alpha} \left( \frac{\delta F}{\delta \rho} j_{\alpha} \right) d^D r = \int_{\Omega} \left( \nabla_{\alpha} \frac{\delta F}{\delta \rho} \right) j_{\alpha} d^D r + \int_{\Omega} \frac{\delta F}{\delta \rho} \nabla_{\alpha} j_{\alpha} d^D r. \]  

(7.22)

Applying the divergence theorem yields (for \( D = 1 \) and \( D = 3 \))

\[ \int_{\partial \Omega} \left( \frac{\delta F}{\delta \rho} j_{\alpha} \right) dS_{\alpha} = \int_{\Omega} \left( \nabla_{\alpha} \frac{\delta F}{\delta \rho} \right) j_{\alpha} d^D r + \int_{\Omega} \frac{\delta F}{\delta \rho} \nabla_{\alpha} j_{\alpha} d^D r. \]  

(7.23)

For a closed system there is no flow through the boundary and we get

\[ \int \left( \nabla_{\alpha} \frac{\delta F}{\delta \rho} \right) j_{\alpha} d^D r = - \int \frac{\delta F}{\delta \rho} \nabla_{\alpha} j_{\alpha} d^D r, \]  

(7.24)

thus (7.21) can now be written as

\[ \int \gamma^j j_{\alpha} u_{\alpha} d^D r = - \int \left( \nabla_{\alpha} \frac{\delta F}{\delta \rho} \right) j_{\alpha} d^D r. \]  

(7.25)

Equation (7.11) is now

\[ \int \left( \gamma^Y \ddot{\epsilon}_Y^2 + \sum_k \gamma^{Z(k)} \ddot{\epsilon}_{Z(k)} + \gamma^j \dot{j}_{\alpha} u_{\alpha} \right)_{r,t_0} d^D r \]

\[ = - \int \left( \left( \frac{\delta F}{\delta Y} \right) \dot{\epsilon}_Y |_{r,t_0} + \left( \frac{\delta F}{\delta Z} \right) \dot{\epsilon}_{Z(a)} |_{r,t_0} + \nabla_{\alpha} \left( \frac{\delta F}{\delta \rho} \right) j_{\alpha} \right)_{r,t_0} d^D r. \]  

(7.26)

\(^2\)In \( D = 2 \) we would need to use the curl-theorem. Eq. (7.22) does not have the right structure for applying Stokes' theorem for a two-dimensional manifold.
Rewriting this slightly yields

\[
0 = \int \left\{ \gamma^Y \dot{\gamma}_Y + \left( \frac{\delta F}{\delta Y} \right) \right\}_{r,t_0} \dot{\gamma}_Y d^D r + \sum_k \int \left\{ \gamma^Z_k \dot{\gamma}^{Z(k)}_k + \left( \frac{\delta F}{\delta Z^{(k)}} \right) \right\}_{r,t_0} \dot{\gamma}^{Z(k)}_k d^D r + \int \left\{ \gamma^j \nu_\alpha + \nabla_\alpha \left( \frac{\delta F}{\delta \rho} \right) \right\}_{r,t_0} j_\alpha d^D r. \tag{7.27}
\]

Assuming that each integrand vanishes independently, we arrive at the dynamic equations governing the evolution of \(Y, Z_k\) and \(\rho\):

\[
\gamma^Y \dot{Y} = -\frac{\delta F}{\delta Y}, \tag{7.28}
\]

\[
\gamma^Z_k \dot{Z}_k = -\frac{\delta F}{\delta Z_k}, \tag{7.29}
\]

\[
\gamma^j \nu_\alpha \dot{\nu}_\alpha = -j_\alpha \nabla_\alpha \mu, \tag{7.30}
\]

where we denote the chemical potential \(\delta F/\delta \rho\) with \(\mu\). The gradient in the chemical potential can be separated in a part parallel to \(\nu\) and one perpendicular.

\[
\nabla \mu = (\nabla \mu)_|| + (\nabla \mu)_\perp \tag{7.31}
\]

\[
(\nabla_k \mu)_|| \equiv \mu_\alpha v_\alpha v_k \tag{7.32}
\]

\[
(\nabla_k \mu)_\perp \equiv \mu_\alpha (\delta_{\alpha k} - v_\alpha v_k). \tag{7.33}
\]

Since \(j_\alpha = \rho \nu_\alpha\), this yields

\[
\gamma^j \nu_\alpha v_\alpha = -v_\alpha \mu_\alpha, \tag{7.34}
\]

or

\[
\gamma^j \nu = - (\nabla \mu)_|. \tag{7.35}
\]
Equation (7.35) implies that $\nabla \mu$ may have a component not parallel to $\mathbf{v}$. Thus $\mathbf{v}$ should be written as

$$\mathbf{v} = -\gamma_{ij}^{-1} \mathbf{M} \cdot \nabla \mu,$$

for some second rank tensor $\mathbf{M}$. Specifically, in a system with local anisotropy, the direction of $\mathbf{v}$ may not coincide with $\nabla \mu$, because of increased mobility along the nematic director, which does not need to be parallel to $\nabla \mu$.

### 7.1.4 Nematic mixtures

We ignore the dynamics on the scalar non-conserved order parameter $Y$. We write the nematic order parameter $Q_{ij}^A$ in the orthonormal tensor representation introduced in section 8.3, $Q_{ij} = q^{(a)} Q_{ij}^{(a)}$, with $Q_{ij}^{(k)}$ the $k$th basis tensor, see (8.36), page 166, and set $Z_k$ to the five-component vector $q^{(k)}$. The dynamic equations for material $A$ are now given by

$$\gamma_{q^{(k)} A} \frac{\partial}{\partial t} Q_{ij}^{(k)} = -\frac{\delta F}{\delta q_{ij}^{(k)}}$$

$$\frac{\partial}{\partial t} \rho_A = -\nabla \cdot \mathbf{j} = -\nabla \cdot \rho_A \mathbf{v} = \nabla \cdot \left( \rho_A \gamma_{ij}^{-1} M^{ij} A \cdot \nabla \mu_A \right).$$

The mapping between $Q_{ij}^A$ and $q^{(k)}_A$ is given by

$$Q_{ij}^A = q^{(a)}_A Q_{ij}^{(a)}$$

$$q_{ij}^{(k)} = Q_{\alpha \beta}^{A} q_{\alpha \beta}^{(k)}.$$

and the mapping between the functional derivatives, respectively by

$$\frac{\delta F}{\delta Q_{ij}^A} = \frac{\delta F}{\delta q_{ij}^{(a)} A} \frac{\partial q_{ij}^{(a)} A}{\partial Q_{ij}^A} = Q_{ij}^{(a)} A \frac{\delta F}{\delta q_{ij}^{(a)} A}$$

$$\frac{\delta F}{\delta q_{ij}^{(k)} A} = \frac{\delta F}{\delta Q_{\alpha \beta}^{A}} \frac{\partial Q_{\alpha \beta}^{A}}{\partial q_{ij}^{(k)} A} = Q_{\alpha \beta}^{(k)} A \frac{\delta F}{\delta Q_{\alpha \beta}^{A}}.$$
Using these to map the orthonormal tensor representation back into the nematic tensor representation yields

\[
\dot{Q}_{ij}^A = \dot{q}_A^{\alpha(i)} Q_{ij}^{(\alpha)} = - \sum_k \gamma_{q_A}^{-1} \frac{\delta F}{\delta q_A^{(k)}} Q_{ik}^{(k)} = - \sum_k \gamma_{q_A}^{-1} q_{ij}^{(k)} Q_{ij}^{(k)} \frac{\delta F}{\delta Q_A^{\alpha\beta}} \tag{7.41}
\]

\[
= - M_{ij\alpha\beta}^{QQ} \frac{\delta F}{\delta Q_A^{\alpha\beta}}, \tag{7.42}
\]

with

\[
M_{ijkl}^{Q^AQ^A} = \sum_r \gamma_{q_A}^{-1} Q_{ij}^{(r)} Q_{kl}^{(r)} \tag{7.43}
\]

We will, for simplicity, assume that \(\gamma_{q_A}^{(k)}\) is the same for all \(k\). We define \(f^{(k)}\) as the \(k^{th}\) coefficient of \(\delta F / \delta Q_{ij}^{(k)}\) in the orthonormal tensor basis:

\[
Q_{ij}^{(\alpha)} f^{(\alpha)} = \frac{\delta F}{\delta Q_{ij}}. \tag{7.44}
\]

Factoring \(\gamma_{q_A}\) out of the sum in (7.41) and the identity

\[
Q_{ij}^{(\alpha)} Q_{ij}^{(\lambda)} \frac{\delta F}{\delta Q_A^{\alpha\beta}} = Q_{ij}^{(\alpha)} Q_{ij}^{(\lambda)} f^{(\alpha)} Q_{ij}^{(\lambda)} = Q_{ij}^{(\alpha)} f^{(\alpha)} \delta_{\alpha\lambda} = Q_{ij}^{(\alpha)} f^{(\alpha)} = \frac{\delta F}{\delta Q_{ij}}.
\]

Therefore (7.41) becomes:

\[
\gamma_{q_A} \dot{Q}_{ij}^A = - \frac{\delta F}{\delta Q_{ij}^A}. \tag{7.45}
\]

It is clear, however, that the assumption that all \(\gamma_{q_A}^{(k)}\) have the same value, cannot be true in general: consider a nematic liquid crystal and a local frame, where the \(z\)-axis is along the director. Under these circumstances, a rotation of the director about the \(z\)-axis, represented by mode \(Q_{ij}^{(3)}\), dissipates less energy than a rotation about the \(x\)-axis, represented by \(Q_{ij}^{(5)}\), therefore \(\gamma_{q_A}^{(3)}\) is surely larger than \(\gamma_{q_A}^{(5)}\). This also demonstrates that the viscosities \(\gamma_{q_A}^{(k)}\) must depend on location unless the system is homogenous.
7.2 Viscosities

Consider the dissipation function (7.13):

\[ D = \sum_{l=1}^{M} \left( \sum_{r=1}^{5} \gamma_{q_{l}^{(r)}} \left( \dot{q}_{l}^{(r)} \right)^{2} + \gamma^{jA_{l}} \mathbf{i}_{A_{l}} \cdot \mathbf{v}_{A_{l}} \right) . \]  

(7.46)

The dissipation function for the nematic tensor order parameter relates the decrease in free energy to the rate of change of the order parameter. The dissipated energy for a molecule should be proportional to the number of collisions that this molecule experiences. This number should be proportional to the volume occupied by all molecules in a volume element \( \Delta V \), and to the volume that itself occupies. The likelihood that such collisions occur on a molecule of species \( A \) is furthermore given by the number of \( A \) molecules in \( \Delta V \), thus, within \( \Delta V \)

\[ \gamma_{q_{l}^{(r)}} = \gamma_{l}^{j} \left( H_{ij}^{A} \right) v^{A} \rho^{A} \left( 1 - \phi_{\text{free}} \right) \]  

(7.47)

As argued above, the coefficient \( \gamma_{l}^{j} \) should be a function of the local field, call it \( H_{ij} \). This field depends on the nematic order parameter, the gradient of the concentration field and possibly external fields. Next we consider the dissipation due to the concentration field \( \left( \mathbf{i}_{A_{l}} = \rho_{A_{l}} \mathbf{v}_{A_{l}} \right) \)

\[ D = \sum_{l=1}^{M} \left( \gamma^{jA_{l}} \rho_{A_{l}} \left( \dot{x}_{k}^{A_{l}} \right)^{2} \right) . \]  

(7.48)

This has the same structure as the dissipation of the non-conserved field, except that the density \( \rho^{A} \) is already factored out of the viscosity. The same argument as for the non-conserved field applies and we write thus

\[ \gamma^{jA} = \gamma_{j, bA} \left( H_{ij}^{A} \right) v^{A} \left( 1 - \phi_{\text{free}} \right) . \]  

(7.49)
Here \( b_A \) is a function of the local field. Instead we absorb the dependency on \( Q_{ij} \) into the mobility matrix \( M^{jA}_{jA} \).

\[
\mathbf{v}_A = -\frac{1}{\nu^A (1 - \phi_{\text{free}})} \mathbf{D}_A \left( H_{ij}^A \right) \cdot \nabla \mu^A, \tag{7.50}
\]

where

\[
\mathbf{D}_A (H_{ij}) \equiv \frac{\mathbf{M}^{jA}_{jA}}{\gamma'_{jA} b_A (H_{ij})}. \tag{7.51}
\]

We still need to enforce incompressibility:

\[
v_A \mathbf{j}^A + v_B \mathbf{j}^B = 0 \tag{7.52}
\]

with the current \( \mathbf{j}_A = \rho_A \mathbf{v}_A \) given by

\[
\mathbf{j}^A = -\frac{\rho^A}{v_A (1 - \phi_{\text{free}})} \mathbf{D}_A \cdot \nabla \frac{\delta F}{\delta \rho^A}, \tag{7.53}
\]

and vice versa for \( \mathbf{j}^B \). With \( \delta F/\delta \rho^B = -\left( v_B / v^A \right) \delta F/\delta \rho^A \), we arrive at

\[
\left( v^A \rho^A \mathbf{D}_A - v_B \rho^B \mathbf{D}_B \right) \cdot \nabla \frac{\delta F}{\delta \rho^A} = 0. \tag{7.54}
\]

This can be solved in various ways. One set of solutions is given by

\[
\mathbf{D}_A = \frac{1}{\nu^A \rho^A} \mathbf{D}_0^{AB} \tag{7.55}
\]

\[
\mathbf{D}_B = \frac{1}{\nu^B \rho^B} \mathbf{D}_0^{BA}. \tag{7.56}
\]

where \( \mathbf{D}_0^{AB} = \mathbf{D}_0^{BA} \) is a function of densities and nematic order parameters. This leads to a dynamic equation for the volume fraction \( \phi^A \)

\[
\partial_t \phi^A = -\frac{1}{1 - \phi_{\text{free}}} \nabla \cdot \mathbf{D}_0^{AB} \nabla \frac{\delta F}{\delta \phi^A}. \tag{7.57}
\]
A second solution set of (7.54) is given by

\[ D_A = v_B \phi^B \tilde{D}_0^{AB} = \phi^B \tilde{D}_0^{AB} \]  
(7.58)

\[ D_B = u_A \phi^A \tilde{D}_0^{BA} = \phi^A \tilde{D}_0^{BA}, \]  
(7.59)

leading to

\[ \partial_t \phi^A = \frac{1}{1 - \phi_{\text{tree}}} \nabla \cdot \phi^A \phi^B \tilde{D}_0^{AB} \cdot \nabla \frac{\delta F}{\delta \phi^A}. \]  
(7.60)

This case is covered by (7.57) as well. Common choices are

\[ D_0^{AB} = D_0 1, \]  
(7.61)

where 1 is the identity, and

\[ D_0^{AB} = \frac{v_A \phi^A v_B \phi^B}{u_A \phi^A + v_A \phi^B} 1. \]  
(7.62)

The last case is e.g., used by Liu and Fredrickson [42], who determine the Onsager coefficients for mixtures of rod-like (liquid crystal) and coil-like (flexible polymer) molecules, while (7.61) is often used in computer simulations and in stability analysis, for example in Ref. [34]. Also, for a concentration-dependent mobility, the the addition of noise cannot be accomplished by a Langevin equation, which locally adds white noise. Either forms are only valid under the incorrect assumption that the total volume-occupancy current vanishes by itself. Nevertheless, in order to keep the system sufficiently simple and to be able to compare it to other researchers work, we will take (7.62) (incorrectly) as the equation of motion for our system.

7.3 Summary

With the assumptions that 1) the dissipation matrix \( \gamma \) is diagonal, 2) and the viscosities are the same for five components \( q^{(k)} \) in the normal tensor representation,
\( Q_{ij} = q^{(a)} Q_{ij}^{(a)} \) and the viscosities are independent of the local field, we arrive at the dynamic equations for a binary, incompressible mixture:

\[
\frac{\partial}{\partial t} Q_{ij}^{A_k} = -\frac{v_{A_k}}{\gamma_{A_k} \phi_{A_k}} \frac{\delta F}{\delta Q_{ij}^{A_k}} \\
\frac{\partial}{\partial t} \phi^A = \nabla \cdot \left( \frac{v^A \phi^A v^B \phi^B}{v^A \phi^A + v^B \phi^B} \nabla \frac{\delta F}{\delta \phi^A} \right) = -\frac{\partial}{\partial t} \phi_B,
\]

(7.63a) (7.63b)

with \( A_1 \equiv A \) and \( A_2 \equiv B \).
Chapter 8

Noise

8.1 Motivation

Systems described by statistical mechanics are subject to thermal fluctuations. It should be preferable to add such fluctuation to any variational algorithm, since a physical system is closer represented by a simulation incorporating the “correct” thermal noise than otherwise. In many cases, fluctuations are even required in order to take the physical system out of metastable states. However, the inclusion of noise into a numerical simulation has some drawbacks. First of all, if the evaluation of a single time step is computationally relatively cheap for the noise-free equations, the evaluation of noise may dominate the computation time. Second, the addition of noise may lead to less “clean” results, e.g., the interfaces in spinodal decomposition may be less sharp, the director configuration for nematic liquid crystals less defined. Third, the system does not exhibit a final state, because the noise will move it out of any current state. Instead it will continue to evolve forever, possibly moving between metastable states. Even should this be desired, the available computation time may be insufficient to observe a transition, because the relative height of the potential barrier between metastable states increases exponentially with system size: the probability distribution for the order parameter is given by $P[S] \propto \exp(-\beta F)$ c.f. Eq. (5.16), page 59, and $F$ is an extensive quantity. (Apparently there should
be an intermediate system size for which the states are sufficiently well defined but the noise is strong enough to move between metastable states over the course of a run of a simulation.) Finally, finding the correct noise may be far from trivial, even impossible. For example, the fluctuation-dissipation theorem relating the noise amplitude in the classical Langevin equation to the Boltzmann factor in the single particle potential breaks down for a spatially varying mobility.

The coupled dynamics of the nematic order parameter and the concentration field, however, requires the addition of noise for the following reasons. For a fixed concentration field, and ignoring gradients, the effect of the local concentration on the equilibrium nematic order parameter is to rescale the effective temperature. Therefore, the nematic order parameter will "feel" a high effective temperature in regions of low liquid crystal concentrations and a low effective temperature in regions of high concentration. Since the concentration field is continuous, the effective temperature will attain any value between these extremes throughout the domain of the simulation. In the case of pure liquid crystals the effective temperature is constant throughout the domain and one may choose it below the pseudo-critical temperature. This is a freedom that we do not have here. Next, the configuration of the director field may be metastable. Such is the case, e.g., for liquid crystal enclosed in a spherical cavity, where a radial hedgehog configuration may be separated by a strong barrier from the actual equilibrium configuration, a biaxial ring defect[43]. Finally, the appearance of the nematic phase within the system changes the phase diagram. We consider the phase diagram in Fig. 9.6, page 9.6 and assume that an
initially homogenous system is quenched into the spinodal region. The now unstable system subsequently phase separates into regions of high and low liquid crystal concentrations, respectively. If the effective temperature in the liquid crystal rich regions is low enough for a nematic phase to appear, the liquid crystal poor region is within the binodal region of the phase diagram and is therefore locally metastable. The system can now evolve by two mechanisms: locally by nucleation (requiring noise), leading to small droplets within larger regions, and globally by diffusion, leading to further coarsening of the large regions. Therefore a complete description of the phase separation process requires the addition of noise.

8.2 Langevin equation

The Langevin equation for a scalar non-conserved dynamic system is given by the dynamic equation augmented by a random force term\cite{44}:

$$\gamma \frac{\partial S}{\partial t} = -\frac{\delta F}{\delta S} + \eta,$$  \hspace{1cm} (8.1)

and the noise term has zero mean and is uncorrelated in space and time:

$$\langle \eta(\mathbf{r},t) \rangle = 0$$  \hspace{1cm} (8.2)

$$\langle \eta(\mathbf{r},t)\eta(\mathbf{r}',t') \rangle = q\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \hspace{1cm} (8.3)$$

Since the noise term’s power spectrum is flat, the noise is also called ”white noise”. This is necessarily a simplification as physical noise cannot be truly uncorrelated on a molecular time and length scale. We must therefore assume that our discretized equations use a timestep much larger than the molecular correlation time. The amplitude of the noise, $q$, can be determined from the equipartition theorem.
8.2.1 Fluctuation amplitude

We consider a system in thermal equilibrium, \( S(\mathbf{r}) = \overline{S}(\mathbf{r}) \), where the overbar denotes the equilibrium value. We define the displacement from equilibrium as \( \varepsilon(\mathbf{r}) \equiv S(\mathbf{r}) - \overline{S}(\mathbf{r}) \). The displacement of the total free energy is denoted \( \delta F \).

We assume that the functional \( \delta F \) can be written as an expansion in “powers” of \( \varepsilon \), analogous to a Taylor expansion for functions:

\[
\delta F = \delta F_1 [\varepsilon] + \delta F_2 [\varepsilon^2] + \delta F_3 [\varepsilon^3] + \ldots . \tag{8.4}
\]

The linear term necessarily vanishes, since \( \delta F \equiv F[\varepsilon] - F[0] \) is the displacement of the free energy from equilibrium. The average square displacement \( \langle \varepsilon^2 \rangle \) of the order parameter in a system in thermal equilibrium with its surrounding is given by

\[
\langle \varepsilon^2 \rangle = \frac{\int \varepsilon^2 \exp(-\beta F[\varepsilon]) \mathcal{D}\varepsilon}{\int \exp(-\beta F[\varepsilon]) \mathcal{D}\varepsilon} = \frac{\int \varepsilon^2 \exp(-\beta (F[0] + \delta F[\varepsilon])) \mathcal{D}\varepsilon}{\int \exp(-\beta (F[0] + \delta F[\varepsilon])) \mathcal{D}\varepsilon} = \frac{\int \varepsilon^2 \exp(-\beta \delta F[\varepsilon]) \mathcal{D}\varepsilon}{\int \varepsilon \exp(-\beta \delta F[\varepsilon]) \mathcal{D}\varepsilon} , \tag{8.5}
\]

where \( \mathcal{D}\varepsilon \) is a functional integral, i.e., the trace over all possible states of \( \varepsilon(\mathbf{r}) \) within the subsystem, subject to any constraints. A strictly formal approach for evaluating this functional would require to solve the Fokker-Planck equation (see e.g.,[45]).

However, we note that we already require the noise to be white noise, i.e., the noise strength to be the same for all wavevectors. Therefore we can pick out one convenient wavevector: we choose homogenous, or zero-wavevector displacements. Then \( \delta F \) is reduced to a function of \( \varepsilon \) and can be expanded in a Taylor series

\[
\delta F[\varepsilon] = \delta F_2 (\varepsilon^2) + O(\varepsilon^3) = \int \left( \left. \frac{\partial^2 F}{\partial \varepsilon^2} \right|_{\varepsilon=0} \varepsilon(t) + \frac{1}{2!} \left. \frac{\partial^2 F}{\partial \varepsilon^2} \right|_{\varepsilon=0} \varepsilon^2(t) \right) d^3\mathbf{r} + O(\varepsilon^3) , \tag{8.6}
\]
with $F = \mathcal{F}/V$ the free energy density, which may depend on $r$—e.g., $\mathcal{F}(\rho(r), S(r))$. The coefficient of the linear term vanishes and to the lowest non-vanishing order

$$\delta F[\varepsilon] = \frac{1}{2} V \bar{K} \varepsilon^2. \quad (8.7)$$

The average coupling parameter $\bar{K}$ is given by

$$\bar{K} = \frac{1}{V} \int \left( \frac{\partial^2 \mathcal{F}}{\partial \varepsilon^2} \right)_{r, \varepsilon = 0} d^3r, \quad (8.8)$$

and the average squared displacement of the order parameter is now

$$\langle \varepsilon^2 \rangle = \frac{\int_{-\infty}^{\infty} \varepsilon^2 \exp \left( -\frac{1}{2} \beta V \bar{K} \varepsilon^2 \right) d\varepsilon}{\int_{-\infty}^{\infty} \exp \left( -\frac{1}{2} \beta V \bar{K} \varepsilon^2 \right) d\varepsilon} = \frac{1}{\beta VK}. \quad (8.9)$$

Next, Eq. (8.1) for homogenous fluctuations can be written as

$$\ddot{\varepsilon}(t) + a \varepsilon(t) = \Gamma(t) \quad (8.10)$$

with

$$a = \frac{\bar{K}}{\gamma} \quad \text{and} \quad \Gamma(t) = \frac{\eta(t)}{\gamma}. \quad (8.11)$$

(The following paragraph follows Ref. [46].) The ODE Eq. (8.10) has a general solution

$$\varepsilon(t) = \varepsilon_0 e^{-at} + \int_0^t e^{-a(t-\tau)} \Gamma(\tau) d\tau. \quad (8.12)$$
We want to evaluate the average square displacement \( \langle \varepsilon^2 \rangle (t) \) of Eq. (8.12):

\[
\langle \varepsilon^2 \rangle (t) = \left( \varepsilon_0 e^{-at} + \int_0^t e^{-a(t-\tau)} \Gamma (\tau) d\tau \right) \left( \varepsilon_0 e^{-at} + \int_0^t e^{-a(t-\tau')} \Gamma (\tau') d\tau' \right)
\]

\[= \varepsilon_0^2 e^{-2at} + 2\varepsilon_0 e^{-at} \int_0^t e^{-a(t-\tau)} \langle \Gamma (\tau) \rangle d\tau + \int_0^t \int_0^t e^{-a(t-\tau)} e^{-a(t-\tau')} \langle \Gamma (\tau) \Gamma (\tau') \rangle d\tau d\tau'
\]

\[= \varepsilon_0^2 e^{-2at} + \frac{q}{\gamma^2} \int_0^t \int_0^t e^{-a(2t-\tau-\tau')} \delta (\tau - \tau') d\tau d\tau' \quad (8.13b)
\]

\[= \varepsilon_0^2 e^{-2at} + \frac{q}{\gamma^2} \int_0^t e^{-2a(t-\tau)} d\tau \quad (8.13c)
\]

\[= \varepsilon_0^2 e^{-2at} + \frac{q}{2a\gamma^2} (1 - e^{-2at}) \quad (8.13d)
\]

For long times \( t >> (2a)^{-1} \) we can ignore the exponentials and get that

\[\langle \varepsilon^2 \rangle = \frac{q}{2a\gamma^2} = \frac{q}{2K\gamma} \quad (8.14)
\]

and comparing this with \( \langle \varepsilon^2 \rangle \) from Eq. (8.9) gives for the fluctuation amplitude

\[q = \frac{2\gamma}{\beta V} \quad (8.15)
\]

which is independent of the coupling parameter \( K \).

### 8.2.2 Finite step fluctuations

Eq. (8.1) integrated over a finite time step yields

\[S (t + \tau, r) = S (t, r) - \frac{\tau}{\gamma} \left( \frac{\delta F}{\delta S} \right)_{t, r} + \frac{1}{\gamma} \int_t^{t+\tau} \eta (t', r) dt'. \quad (8.16)
\]
We define a random variable $\Delta S^*$, the displacement from the noise-free equation:

$$
\Delta S^*(t, \mathbf{r}) = \frac{1}{\gamma} \int_t^{t+\tau} \eta(t', \mathbf{r}) \, dt',
$$

which has a mean square amplitude of

$$
\langle (\Delta S^*)^2 \rangle = \frac{1}{\gamma^2} \int_t^{t+\tau} \langle \eta(t') \eta(t) \rangle \, dt dt' = \frac{q}{\gamma^2} \int \delta(t-t') \, dt dt' = \frac{2\tau}{\gamma^2} = \frac{2\tau}{\gamma \beta V}.
$$

The normal distribution is defined as

$$
P(x) = \frac{\exp\left(-\frac{1}{2} \left( \frac{x-\bar{x}}{\sigma} \right)^2 \right)}{\int \exp\left(-\frac{1}{2} \left( \frac{x-\bar{x}}{\sigma} \right)^2 \right) \, dx}
$$

and has a variance of $\langle (x - \bar{x})^2 \rangle = \int (x - \bar{x})^2 P(x) \, dx = \sigma^2$. We define $G_{N(\bar{x}, \sigma^2)}$ as a realization (an event) of a normal distributed random variable with average $\bar{x}$ and variance $\sigma^2$. Events at different lattice cells and at different discrete times are independent:

$$
\langle G_{N(\bar{x}, \sigma^2)} \rangle = \bar{x}
$$

$$
\langle G_{N(\bar{x}, \sigma^2)}(\mathbf{r}_k, t_l) G_{N(\bar{x}, \sigma^2)}(\mathbf{r}_m, t_n) \rangle = (\sigma^2 + \bar{x}^2) \delta_{km} \delta_{ln}.
$$

In order to generate a realization of a random displacement $\Delta S^*$ we use a random number generator which returns normal distributed numbers with zero mean and a variance $\sigma^2 = 2\tau/\gamma \beta V$. A realization $G_{N(\bar{x}, \sigma^2)}$ for a random variable with mean $\bar{x}$ and variance $\sigma^2$ can be generated from a realization $G_{N(0,1)}$ for a standard normal distributed variable by scaling and shifting the returned value: $G_{N(\bar{x}, \sigma^2)} = \bar{x} + \sigma G_{N(0,1)}$, as can be seen from Eqs. (8.21a) and (8.21b). Thus a realization of $\Delta S^*$ is given by

$$
\Delta S^* = G_{N(0, \sigma^2)} = \sigma G_{N(0,1)} = \sqrt{\frac{2\tau}{\gamma \beta V}} G_{N(0,1)} = \sqrt{\frac{2k_B T \tau}{\gamma V}} G_{N(0,1)},
$$
and a realization of a Langevin time step is, defining $\tau_k \equiv t_{k+1} - t_k$:

$$
S(t_{k+1}, r_l) = S(t_k, r_l) - \frac{\tau_k}{\gamma} \left( \frac{\delta F}{\delta S} \right)_{t_k, r_l} + \sqrt{\frac{2k_B T \tau_k}{\gamma V}} G_{N(0,1)}(t_k, r_l).
$$

(8.23)

We define

$$
\Gamma_k \equiv \frac{k_B T^* \tau_k}{\gamma V} N \quad \text{and} \quad F' \equiv \frac{F}{\rho_{\text{tot}} k_B T^*}
$$

(8.24)

with some arbitrary reference energy $k_B T^*$ and $\rho_{\text{tot}}$ the total number density, thus

$$
S(t_{k+1}, r_l) = S(t_k, r_l) - \Gamma_k \frac{\rho_{\text{tot}}}{\rho} \left( \frac{\delta F'}{\delta S} \right)_{t_k, r_l} + \sqrt{\frac{2\Gamma_k}{N T^*}} G_{N(0,1)}(t_k, r_l).
$$

(8.25)

For the special case of a homogeneous system consisting of $N$ non-interacting subsystems with reduced free energies $F'_1$ this can be written as

$$
S^{k+1} = S^k - \Gamma_k \rho_{\text{tot}} \left( \frac{1}{V} \left( \frac{\partial (N F'_1)}{\partial S} \right) \right)_k + \sqrt{\frac{2\Gamma_k}{N T^*}} G^k_{N(0,1)} \quad \text{(8.26)}
$$

$$
S^{k+1} = S^k - \Gamma_k \left( \frac{\partial (\beta^* F_1)}{\partial S} \right)_k + \sqrt{\frac{2\Gamma'_k}{N T^*}} G^k_{N(0,1)}, \quad \text{(8.27)}
$$

where $\beta^* \equiv k_B T^*$.

### 8.2.3 Example

Consider the Maier-Saupe single particle free energy for a scalar order parameter in a single-component system:

$$
\beta^* F_1 = -\theta \ln \int_0^1 \exp \left( \frac{5}{\theta} \left( P_2(x) S - \frac{1}{2} S^2 \right) \right) dx
$$

(8.28)

where $\theta = T/T^*$, $T^*$ is the pseudo-critical temperature for the nematic phase and $P_2(x) = \frac{3}{2} x^2 - \frac{1}{2}$ the second Legendre polynomial. The $N$-particle probability
distribution for the order parameter is

\[ P(S) = \frac{\exp(-\beta NF_1)}{\int_{-\infty}^{\infty} \exp(-\beta NF_1(S)) \, dS}, \tag{8.29} \]

and we assume that the domain of \( S \) is not restricted to \([-0.5...1]\). The dynamic equation becomes

\[ \gamma \dot{S} = -\frac{\delta F}{\delta S} + \eta \tag{8.30} \]

and in discretized form

\[ S^{k+1} = S^k - \Gamma_k \left( \frac{\partial (\beta^* F_1)}{\partial S} \right)_k + \sqrt{\frac{2\Gamma'_k}{N} \theta G^k_{N(0,1)}} \tag{8.31} \]

\[ = S^k - 5\Gamma'_k \left( S^k - \langle P_2 \rangle_{S^k} \right) + \sqrt{\frac{2\Gamma'_k}{N} \theta G^k_{N(0,1)}} \tag{8.32} \]

with

\[ \langle P_2 \rangle_{S^k} = \frac{\int_0^1 P_2(x) \exp \left( \frac{15}{2} \frac{S^k}{\theta} x^2 \right) \, dx}{\int_0^1 \exp \left( \frac{15}{2} \frac{S^k}{\theta} x^2 \right) \, dx} \tag{8.33} \]

Fig. 8.1 shows the relative frequency distribution of the order parameter \( S \) as function of \( S \) for a numerical integration of Eq. (8.31) and compares it to the Boltzmann distribution. We see that, although the derivation of the noise strength was taken at equilibrium, applying it to non-equilibrium states as well leads to the correct distribution. This is as it should be, since (white) noise does not depend on the state of the system.

### 8.3 Tensor Noise

Again we start from the Langevin equation

\[ \gamma \frac{\partial Q_{ij}}{\partial t} = -\frac{\delta F}{\delta Q_{ij}} + \eta_{ij}, \tag{8.34} \]
Figure 8.1: Random walk in the Maier-Saupe single particle potential for a scalar order parameter for different system sizes at the nematic-isotropic transition temperature.

where the noise $\eta_{ij}$ must be a tensor of the same symmetry as $Q_{ij}$. We note that any symmetric traceless tensor $T_{ij}$ can be written as [47]

$$T_{ij} = a^{(a)} Q^{(a)}_{ij}, \quad (8.35)$$

where $\{Q^{(k)}\}_{k=1}^{5}$ is a basis of five tensors:

$$Q^{(1)} = \frac{1}{\sqrt{6}} \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad Q^{(2)} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$
\[ Q^{(3)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad Q^{(4)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad Q^{(5)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \]

(8.36)

This basis is orthonormal in the sense that \( Q^{(i)}_{\alpha \beta} Q^{(j)}_{\alpha \beta} = \delta_{ij} \). From this orthonormality it follows that

\[ T_{\alpha \beta} T_{\alpha \beta} = a^{(a)} Q^{(a)} \]

(8.37a)

and

\[ a^{(k)} = T_{\alpha \beta} Q^{(k)}_{\alpha \beta} \]

(8.37b)

Because of eqns. 8.35 and 8.37b we have a one-to-one mapping for symmetric traceless tensors between the matrix representation \( T_{ij} \) and orthonormal basis representation, \( \{ a^{(k)} \}^5_{k=1} \). We write now in this basis the order parameter as \( Q_{ij} = q^{(a)} Q^{(a)}_{ij} \) and the noise as \( \eta_{ij} = \eta^{(a)} Q^{(a)}_{ij} \). The Langevin equation can be written:

\[ \gamma \frac{\partial q^{(a)}_{ij}}{\partial t} = -\frac{\delta F}{\delta q^{(a)}_{ij}} \frac{\partial q^{(a)}_{ij}}{\partial Q^{(a)}_{ij}} + \eta^{(a)} Q^{(a)}_{ij}, \]

(8.38)

and from the orthogonality condition, 8.37b, and the definition of \( q^{(k)} \) it follows that

\[ \gamma \frac{\partial q^{(a)}_{ij}}{\partial t} Q^{(a)}_{ij} = -\frac{\delta F}{\delta q^{(a)}_{ij}} Q^{(a)}_{ij} + \eta^{(a)} Q^{(a)}_{ij}. \]

(8.39)

Multiplying by \( Q^{(k)}_{ij} \) and summing over the pairs of indices yields

\[ \gamma \frac{\partial q^{(k)}}{\partial t} = -\frac{\delta F}{\delta q^{(k)}} + \eta^{(k)}, \]

(8.40)

which is the Langevin equation in terms of the coefficients \( q^{(k)} \). As in the previous section we write the free energy displacement as

\[ \delta F = \delta F_1 [\varepsilon] + \delta F_2 [\varepsilon^2] + \delta F_3 [\varepsilon^3] + \ldots \]

(8.41)
and choose homogenous fluctuations the functional $\delta F$ which therefore becomes a function of $\varepsilon$:

$$
\delta F = \int \left( \frac{\partial F}{\partial \varepsilon_{\alpha\beta}} \right)_{|\varepsilon=0} \varepsilon_{\alpha\beta}(t) + \frac{1}{2} \left( \frac{\partial^2 F}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\lambda}} \right)_{|\varepsilon=0} \varepsilon_{\alpha\beta}(t) \varepsilon_{\gamma\lambda}(t) \right) d^3r + O(\varepsilon^3).
$$

(8.42)

The displacement $\varepsilon$ is with respect to equilibrium, therefore the linear term vanishes and to second order

$$
\delta F = \frac{1}{2} V K_{\alpha\beta\gamma\lambda} \varepsilon_{\alpha\beta} \varepsilon_{\gamma\lambda},
$$

(8.43)

and the average coupling parameter is now a tensor:

$$
\bar{K}_{ijkl} \equiv \frac{1}{V} \int \left( \frac{\partial^2 F}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\lambda}} \right)_{|\varepsilon=0} d^3r.
$$

(8.44)

The squared displacement of a normal mode is given by

$$
\left\langle \left( \varepsilon^{(k)} \right)^2 \right\rangle = \frac{\int \left( \varepsilon^{(k)} \right)^2 \exp\left( -\beta F_2 [\varepsilon^2] \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}}{\int \exp\left( -\beta F_2 [\varepsilon^2] \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}}
$$

$$
= \frac{\int \left( \varepsilon^{(k)} \right)^2 \exp\left( -\frac{\beta V}{2} \varepsilon_{\alpha\beta} \bar{K}_{\alpha\beta\gamma\lambda} \varepsilon_{\gamma\lambda} \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}}{\int \exp\left( -\frac{\beta V}{2} \varepsilon_{\alpha\beta} \bar{K}_{\alpha\beta\gamma\lambda} \varepsilon_{\gamma\lambda} \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}}.
$$

(8.45)

We expand $\varepsilon_{ij}$ in the tensor basis; the mapping between $\varepsilon^{(k)}$ and $\varepsilon_{ij}$ is given by

$$
\varepsilon_{ij} = \varepsilon^{(\alpha)} Q_{ij}^{(\alpha)}
$$

(8.46a)

$$
\varepsilon^{(k)} = \varepsilon_{\alpha\beta} Q_{\alpha\beta}^{(k)}.
$$

(8.46b)

Then

$$
\frac{\partial F}{\partial \varepsilon_{ij}} = \frac{\partial F}{\partial \varepsilon^{(\alpha)}} \frac{\partial \varepsilon^{(\alpha)}}{\partial \varepsilon_{ij}} = \frac{\partial F}{\partial \varepsilon^{(\alpha)}} Q_{ij}^{(\alpha)} = f^{(\alpha)} Q_{ij}^{(\alpha)}
$$

(8.47)

$$
\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{\partial}{\partial \varepsilon_{ij}} \left( \frac{\partial F}{\partial \varepsilon^{(\alpha)}} Q_{ij}^{(\alpha)} \right) = \frac{\partial f^{(\alpha)}}{\partial \varepsilon^{(\beta)}} \frac{\partial \varepsilon^{(\beta)}}{\partial \varepsilon_{ij}} Q_{ij}^{(\alpha)} = \frac{\partial f^{(\alpha)}}{\partial \varepsilon^{(\beta)}} Q_{ij}^{(\alpha)} Q_{ij}^{(\beta)} Q_{kl}^{(\alpha)}
$$

(8.48)

$$
= f^{(\alpha)\beta} Q_{ij}^{(\alpha)} Q_{kl}^{(\beta)} Q_{ij}^{(\alpha)}
$$

(8.49)
where we define

\[ f^{(k)} = \frac{\partial F}{\partial \varepsilon^{(k)}} \quad (8.50a) \]

and

\[ f^{(kl)} = \frac{\partial^2 F}{\partial \varepsilon^{(k)} \partial \varepsilon^{(l)}}. \quad (8.50b) \]

Conversely, from

\[ \frac{\partial F}{\partial \varepsilon^{(a)}} Q^{(a)}_{\gamma \lambda} Q^{(k)}_{\gamma \lambda} = \frac{\partial F}{\partial \varepsilon_{\gamma \lambda}} Q^{(k)}_{\gamma \lambda} \quad (8.51a) \]

and

\[ \frac{\partial^2 F}{\partial \varepsilon^{(a)} \partial \varepsilon^{(b)}} Q^{(a)}_{\gamma \lambda} Q^{(n)}_{\mu \nu} Q^{(k)}_{\gamma \lambda} Q^{(l)}_{\mu \nu} = \frac{\partial^2 F}{\partial \varepsilon_{\gamma \lambda} \partial \varepsilon_{\mu \nu}} Q^{(k)}_{\gamma \lambda} Q^{(l)}_{\mu \nu} \quad (8.51b) \]

follows that

\[ \frac{\partial F}{\partial \varepsilon^{(k)}} = \frac{\partial F}{\partial \varepsilon_{\gamma \lambda}} Q^{(k)}_{\gamma \lambda} \quad (8.52a) \]

and

\[ \frac{\partial^2 F}{\partial \varepsilon^{(k)} \partial \varepsilon^{(l)}} = \frac{\partial^2 F}{\partial \varepsilon_{\gamma \lambda} \partial \varepsilon_{\mu \nu}} Q^{(k)}_{\gamma \lambda} Q^{(l)}_{\mu \nu}. \quad (8.52b) \]

The displacement of the free energy is now

\[
\delta F = \frac{1}{2} V K_{\alpha \beta \gamma \lambda} e_{\alpha \beta} \varepsilon_{\gamma \lambda} = \frac{1}{2} V \left( \int f^{(\mu \nu)} d^3r \right) Q^{(n)}_{\alpha \beta} Q^{(\nu)}_{\gamma \lambda} e_{\alpha \beta} \varepsilon_{\gamma \lambda}
\]

\[
= \frac{1}{2} V \left( \int f^{(\mu \nu)} d^3r \right) Q^{(n)}_{\alpha \beta} Q^{(\nu)}_{\gamma \lambda} Q^{(\nu)}_{\alpha \beta} \varepsilon_{\gamma \lambda} \varepsilon_{(n)}
\]

\[
= \frac{1}{2} V \left( \int f^{(\mu \nu)} d^3r \right) \delta^{\mu \nu} \varepsilon_{(n)} \varepsilon_{(\zeta)} = \frac{1}{2} V \left( \int f^{(\mu \nu)} d^3r \right) \varepsilon^{(n)} \varepsilon^{(\zeta)}
\]

\[
= \frac{1}{2} V K^{(\mu \nu)} \varepsilon^{(\mu)} \varepsilon^{(\nu)}
\]

(8.53)

with the average coupling matrix in the orthogonal tensor frame defined as

\[
\overline{K}^{(ij)} = \frac{1}{V} \int \left( \frac{\partial^2 F}{\partial \varepsilon^{(i)} \partial \varepsilon^{(j)}} \right)_{|\varepsilon \rightarrow 0} d^3r.
\]

(8.54)

At this point we note that \( \overline{K}^{(ij)} \) may not be diagonal if the equilibrium value for the nematic order parameter \( \overline{Q}_{ij} \neq 0 \). We take as an example a homogenous system for
which we have shown that the generalized force is given by

$$\frac{\partial F}{\partial \varepsilon_{ij}} = \frac{\partial F}{\partial Q_{ij}} = \frac{10}{3t} \phi^2 (Q_{ij} - \langle \sigma_{ij} \rangle).$$  \hspace{1cm} (8.55)$$

Therefore the second derivative with respect to the displacement is given by

$$\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{10}{3t} \phi^2 \frac{\partial (Q_{kl} - \langle \sigma_{kl} \rangle)}{\partial \varepsilon_{ij}} = \delta_{ik} \delta_{jl} - \chi_{ijkl}$$  \hspace{1cm} (8.56)$$

where

$$\chi_{ijkl} \equiv \frac{\partial \langle \sigma_{kl} \rangle}{\partial \varepsilon_{ij}}$$  \hspace{1cm} (8.57)$$

thus

$$\overline{K}^{(ij)} = \frac{1}{V} \alpha_{\beta \gamma \lambda} Q^{(i)}_{\alpha \beta} Q^{(j)}_{\gamma \lambda} \int \left( \frac{\partial^2 F}{\partial \varepsilon_{\alpha \beta} \partial \varepsilon_{\gamma \lambda}} \right)_{|r, s = 0} d^3 r = \frac{1}{V} \alpha_{\beta \gamma \lambda} Q^{(i)}_{\alpha \beta} Q^{(j)}_{\gamma \lambda} \int \left( \delta_{\alpha \gamma} \delta_{\beta \lambda} - \chi_{\alpha \beta \gamma \lambda} Q^{(j)}_{\gamma \lambda} \right) d^3 r$$

$$= \frac{1}{V} \int \left( \delta_{ij} - Q^{(i)}_{\alpha \beta} \chi_{\alpha \beta \gamma \lambda} Q^{(j)}_{\gamma \lambda} \right) d^3 r,$$  \hspace{1cm} (8.58)$$

and it can be shown that $Q^{(i)}_{\alpha \beta} \chi_{\alpha \beta \gamma \lambda} Q^{(j)}_{\gamma \lambda}$ may not be diagonal. We are looking for the average of the squared displacement. More general

$$\langle \varepsilon^{(k)} \varepsilon^{(l)} \rangle = \frac{\int \varepsilon^{(k)} \varepsilon^{(l)} \exp \left( -\frac{1}{2} \beta V \overline{K}^{(\mu \nu)} \varepsilon^{(\mu)} \varepsilon^{(\nu)} \right) d\varepsilon^{(1)} ... d\varepsilon^{(5)}}{\int \exp \left( -\frac{1}{2} \beta V \overline{K}^{(\mu \nu)} \varepsilon^{(\mu)} \varepsilon^{(\nu)} \right) d\varepsilon^{(1)} ... d\varepsilon^{(5)}}$$  \hspace{1cm} (8.59)$$

which, in vector/matrix notation is

$$\left( \hat{\varepsilon}^{(k)} \cdot \varepsilon \right) \left( \varepsilon^T \cdot \hat{\varepsilon}^{(l)} \right) = \hat{\varepsilon}^{(k)} \cdot \frac{\int \varepsilon \varepsilon^T \exp \left( -\frac{1}{2} \beta V \varepsilon^T \overline{K} \cdot \varepsilon \right) d\varepsilon^{(1)} ... d\varepsilon^{(5)}}{\int \exp \left( -\frac{1}{2} \beta V \varepsilon^T \cdot \overline{K} \cdot \varepsilon \right) d\varepsilon^{(1)} ... d\varepsilon^{(5)}} \cdot \hat{\varepsilon}^{(l)}$$

$$= \hat{\varepsilon}^{(k)} \cdot \langle \varepsilon \varepsilon^T \rangle \cdot \hat{\varepsilon}^{(l)}$$  \hspace{1cm} (8.60)$$

and $\langle \varepsilon \varepsilon^T \rangle$ is the correlation matrix for $\varepsilon$ ($\langle \varepsilon \rangle \langle \varepsilon^T \rangle = 0$). The coupling term $\overline{K}^{(ij)}$ is a 5 by 5 non-singular symmetric matrix and can therefore be diagonalized by a unitary transformation, $U$. (The coupling matrix $K^{(ij)}$ must be non-singular because
otherwise the system would not be in equilibrium.) We write the correlation matrix in the diagonal frame of $\bar{K}$ as

$$
\langle \varepsilon \varepsilon^T \rangle = \int \varepsilon \varepsilon^T \exp \left( -\frac{\beta V}{2} \varepsilon^T \cdot \bar{U}^T \cdot \bar{U} \cdot \bar{K} \cdot \bar{U}^T \cdot \bar{U} \cdot \varepsilon \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}
$$

(denominator analogous)

$$
= \int \varepsilon \varepsilon^T \exp \left( -\frac{\beta V}{2} \bar{w}^T \cdot \Lambda \cdot \bar{w} \right) d\varepsilon^{(1)}...d\varepsilon^{(5)}
$$

(denominator analogous),  

(8.61)

where $\bar{U}$ is a unitary matrix, chosen to be orthogonal, $\bar{w} \equiv \bar{U} \cdot \varepsilon$ and $\bar{U}^T \cdot \Lambda \cdot \bar{U} = \text{diag}(\lambda_1, ..., \lambda_5)$. The Jacobian is unity and therefore

$$
\langle \bar{w} \bar{w}^T \rangle = \int \bar{w} \bar{w}^T \exp \left( -\frac{\beta V}{2} \sum_{k=1}^5 w_k^2 \lambda_k \right) dw^{(1)}...dw^{(5)}
$$

(denominator analogous).

(8.62)

The correlation matrix is now

$$
\langle \varepsilon \varepsilon^T \rangle = \left\langle \left( \bar{U}^T \cdot \bar{w} \right) \left( \bar{w}^T \cdot \bar{U} \right) \right\rangle = \bar{U}^T \cdot \langle \bar{w} \bar{w}^T \rangle \cdot \bar{U}
$$

(8.63)

$$
\langle \varepsilon^{(k)} \varepsilon^{(l)} \rangle = \bar{U}^T_{k\alpha} \langle w^\alpha w^\beta \rangle U_{\beta l}.
$$

(8.64)

The off-diagonal terms in $\langle w^i w^j \rangle$ are zero (as obvious from eqn. 8.62), hence

$$
\langle \varepsilon^{(k)} \varepsilon^{(l)} \rangle = \sum_{i=1}^5 \bar{U}^T_{ki} \langle (w^{(i)})^2 \rangle U_{il}
$$

(8.65)

with $\langle (w^{(i)})^2 \rangle = 1/\beta V \lambda_i$, therefore

$$
\langle \varepsilon^{(k)} \varepsilon^{(l)} \rangle = \frac{1}{\beta V} \sum_{i=1}^5 \frac{1}{\lambda_i} \bar{U}^T_{ki} U_{il}.
$$

(8.66)

The coupling matrix $\bar{K}$ is non-singular and therefore $\lambda_k \neq 0$. The correlation matrix is obviously in general not diagonal unless either the coupling matrix $\bar{K}^{(ij)}$ is diagonal (then $U_{ij} = \delta_{ij}$), or all eigenvalues are the same (because $U_{k\alpha}^T U_{\alpha l} = \delta_{kl}$). The square of the displacement is the trace of the correlation matrix

$$
\langle \varepsilon_{\alpha \beta} \varepsilon_{\alpha \beta} \rangle = \langle \varepsilon^{(\alpha)} \varepsilon^{(\alpha)} \rangle = \frac{1}{\beta V} \sum_{i=1}^5 \frac{1}{\lambda_i}.
$$

(8.67)
The modes $w^{(k)}$ are uncorrelated and therefore we can realize a Langevin noise for each mode separately, analogous to the isotropic case. As before we find that the noise amplitude for each mode is $\eta^{(i)} = 2\gamma/\beta V$, which is independent of $\lambda_i$. We do not, however, know in general the mapping back to the original representation, $\epsilon_{ij}$ or $\epsilon^{(k)}$, unless we know the transformation matrix $U$. Therefore, at this point we make the assumption that $U$ is the identity and further analysis of the problem is required. In the normal mode representation

$$
\gamma \frac{\partial w^{(k)}}{\partial t} = -\frac{\delta F}{\delta w^{(k)}} + w^{(k)},
$$

(8.68)

and since $w^{(k)}$ are uncorrelated, the approach put forth in the last section of determining the Langevin force in an isotropic system can be applied. As before we assume that for a finite time step $\Delta w^{(k)}$ is the difference in change with respect to the noise free equation, and $\Delta w$ is a random variable, uncorrelated in time and space with mean square amplitude

$$
\langle (\Delta w^{(k)})^2 \rangle = \frac{2\tau}{\gamma \beta V}.
$$

(8.69)
Chapter 9

Phase diagrams: general considerations

In order to check the validity of the results of numerical simulations, we need to know what we expect their outcome to be. This chapter develops the phase diagrams for the steady state solutions of the dynamic equations given by Eqs. (7.63a) and (7.63b), page 155, with the generalized forces given in Tables 6.1 and 6.3, with Table 6.2 and 6.4. Other researchers have presented similar phase diagrams for nematic/isotropic mixtures, e.g., Kyu and Chiu [4] and Lapeña and co-workers [5]. A phase diagram for nematic/nematic mixtures was presented by Palfy-Muhoray and de Bruyn [48].

In a phase diagram we always ignore effects due to the presence of interfaces, i.e., we assume the system is a) in equilibrium and b) large enough that the gradient terms in the free energy are negligible. For an isotropic phase-separated system, this means that it has evolved long enough that the free energy located within the interfaces is small compared to the total free energy. It means that the deformation of the director is sufficiently weak in any nematic phase such that we can assume it to be constant for a sufficiently small subsystem. With these assumptions, the phase diagrams we are going to develop are for the free energy given in equation (6.300), with (6.301) and (6.302). In this section we simplify further by taking $s_A = s_B = 1$ and $T_{\text{ref}} = T$ (next section) and $T_{\text{ref}} = T_c$, respectively.
9.1 Nematic order parameter diagram

The reduced free energy density, \( F' = \beta_{\text{ref}} v_{\text{ref}} F \), of a homogenous subsystem with a nematic order parameter \( Q_{ij} \) and a volume fraction of liquid crystal \( \phi \) is given by Eq. (6.302), which for \( T_{\text{ref}} = T \) yields

\[
F' = -\phi \ln \int \exp \left( \frac{10}{3} \frac{T^*}{T} \phi \left( \sigma_{\alpha\beta} - \frac{1}{2} Q_{\alpha\beta} \right) Q_{\alpha\beta} \right) d^2 \sigma .
\]  

(9.1)

At this point we assume vanishing biaxiality \( P \). (It may be possible to prove vanishing biaxiality in equilibrium for a homogenous system lacking molecular biaxiality.) Since the subsystem is spatially uniform, we have a constant director. Using Eq. (A.4) we write Eq. (9.1) as

\[
F' = \frac{5}{2} \frac{T^*}{T} \phi^2 S^2 - \phi \ln \int \exp \left( 5 \frac{T^*}{T} \phi S P_2 \left( \hat{n} \cdot \hat{N} \right) \right) d^2 \hat{n} ,
\]  

(9.2)

where \( \hat{N} \) represents the director, \( \hat{n} \) is the direction of the molecular long axis, and \( P_2 (x) = \frac{3}{2} x^2 - \frac{1}{2} \) is the second Legendre polynomial. Using spherical coordinates with \( \cos \theta = \hat{n} \cdot \hat{N} \), the integral over the unit sphere, \( \int d^2 \hat{n} \), becomes \( \int \sin^2 \theta d\phi d\theta \); integrating out the azimuth \( d\phi \) and defining \( \cos \theta = x \) yields:

\[
F' = \frac{5}{2} \frac{T^*}{T} \phi^2 S^2 - \phi \ln \int_0^1 \exp \left( \left( 5 \frac{T^*}{T} \phi S \right) P_2 (x) \right) dx - (\phi - 1) \ln 4\pi ,
\]  

(9.3)

where we have added a constant \( \ln 4\pi \) to the reduced free energy density; this ensures that \( F' = 0 \) for \( S = 0 \) in a purely liquid crystalline system. A necessary condition for equilibrium is that the first derivative of the free energy with respect to the order parameter vanishes:

\[
\frac{\partial F'}{\partial S} = 5 \frac{T^*}{T} \phi^2 (S - \langle P_2 (x) \rangle_S) = 0 ,
\]  

(9.4)
Figure 9.1: Left: The value of \( \langle P_2(x) \rangle_S \) vs. \( S \) for some (effective) temperatures. Right: \( \langle P_2(x) \rangle_S - S \) vs. \( S \)

where pointed brackets denote the Boltzmann average:

\[
\langle P_2(x) \rangle_S = \frac{\int_0^1 P_2(x) \exp \left( \left( 5 \frac{T^*}{T} \phi S \right) P_2(x) \right) dx}{\int_0^1 \exp \left( \left( 5 \frac{T^*}{T} \phi S \right) P_2(x) \right) dx}.
\] (9.5)

In the remaining part of this section we interpret temperature as an “effective temperature,” i.e., we tacitly replace \( T \) by \( T/\phi \). The Boltzmann average of \( \langle P_2 \rangle_S \) is a function of the order parameter \( S \). Figure 9.1 shows this function for various fixed temperatures. The intersections of the graphs of \( \langle P_2(x) \rangle_S \) with the diagonal (the graph of \( S \)) correspond to solutions to Eq. (9.4). Since all curves go through the origin, the isotropic order parameter, \( S = 0 \), is always a solution. For temperatures \( T > T^\dagger \), the graphs intersect only at the origin, while for \( T < T^\dagger \), the graphs intersect at two additional points – with two exceptions: at \( T = T^\dagger \), the graph of \( \langle P_2(x) \rangle_S \) touches the graph of \( S \) at exactly one additional point (at \( S = 0.323596... \)), and at \( T = T^* \), the graph of \( \langle P_2(x) \rangle_S \) straddles the graph of \( S \) at the origin. (This is
barely visible in the plot \( \langle P_2(x) \rangle_s \) vs. \( S \) on the left side of Fig. (9.1). The right side of the same figure shows the difference \( \langle P_2 \rangle_s - S \) instead, permitting the reader to see this more clearly.) A sufficient condition for a local minimum of the free energy is that the second derivative is positive, in addition to the requirement that the first derivative vanishes. However, this is not a sufficient condition for a global minimum: this requires a direct comparison of the values of the free energy for the solutions of Eq. (9.4). Figure 9.2 shows the reduced free energy for some temperatures. The nematic-isotropic transition temperature \( T_{NI} \) is defined as the temperature where the free energy has two global minima. The phase diagram for \( S \) can now be created by varying the reduced temperature, \( \phi I/T^* \), finding all possible roots of Eq. (9.4), and comparing the free energies. Figure 9.3 shows the phase diagram \( S(\phi I/T^*) \): the solid lines correspond to the solutions of \( S = \langle P_2 \rangle_s \) and the labels s, m and u indicate whether the free energy for this \( S \) corresponds to a stable, metastable or
unstable state, respectively.

9.2 Phase diagram

9.2.1 Double tangent construction

We start with an initially homogenous system with a volume fraction of liquid crystal $\phi_0$, which then separates into two homogenous subsystems with a volume fraction of liquid crystal $\phi_-$ and $\phi_+$, respectively. These subsystems will be separated by an interface. We assume that in the final state the system had sufficient time to evolve such that the volume assigned to interface regions is much smaller than the total volume, in the sense that the integral of the free energy density over the interface regions is negligible compared to the total free energy. The total number of particles $N$ is fixed, as is the total number of liquid crystal molecules $N_{\text{lc}}$. We ask the question: what is the total number of particles in each of the subsystems? We use $S_1$ and $S_2$ to denote the system with a volume fraction of liquid crystal $\phi_+$ and $\phi_-$, respectively. The number of liquid crystal molecules in $S_1$ and $S_2$ is $N_-$ and $N_+$, respectively, while the total number of molecules in either system is $N_1$ and $N_2$, respectively. Then $\phi_-=N_-/N_1$ and $\phi_+=N_+/N_2$. The total number of liquid crystal molecules is

$$N_{\text{lc}} = N_+ + N_- = \phi_- N_1 + \phi_+ N_2. \quad (9.6)$$

The volume fraction of liquid crystal in the original system is

$$\phi_0 = \frac{N_+ + N_-}{N}. \quad (9.7)$$
Figure 9.3: The phase diagram $S(T)$ for the nematic order parameter. The reduced temperature is $t = \phi T / T^*$. The labels are for stable (s), metastable (m) and unstable (u) states.
Therefore

\[ \phi_0 N = \phi_- N_1 + \phi_+ N_2, \]

and because \( N_2 = N - N_1 \), this is the same as

\[ \phi_0 N = \phi_- N_1 + \phi_+ (N - N_1), \]

and solving for \( N_1 \) results in

\[ N_1 = \frac{\phi_+ - \phi_0}{\phi_+ - \phi_-} N. \]

The same procedure can be applied for \( N_2 \) (exchanging \( N_1 \) with \( N_2 \) and \( \phi_+ \) with \( \phi_- \)):

\[ N_2 = \frac{\phi_0 - \phi_-}{\phi_+ - \phi_-} N. \]

Eqs. (9.10) and (9.11) are called the "lever rule." The total free energy per particle is given by

\[ \overline{F} = \frac{N_1 \mathcal{F}_1 + N_2 \mathcal{F}_2}{N} = \frac{\phi_+ - \phi_0}{\phi_+ - \phi_-} \mathcal{F}_1 + \frac{\phi_0 - \phi_-}{\phi_+ - \phi_-} \mathcal{F}_2. \]

It is easy to see that the points \( p_- \equiv (\mathcal{F}_1, \phi_-), p_0 \equiv (\overline{F}, \phi_0) \), and \( p_+ \equiv (\mathcal{F}_1, \phi_+) \) lie on a straight line: taking the derivative \( \partial \overline{F} / \partial \phi_0 \) yields

\[ \frac{\partial \overline{F}}{\partial \phi_0} = \frac{\mathcal{F}_2 - \mathcal{F}_1}{\phi_+ - \phi_-}, \]

which is independent of \( \phi_0 \). The endpoints of \( \overline{F}(\phi_0) \) are given by \( \overline{F}(\phi_0 = \phi_-) = \mathcal{F}_1 \) and \( \overline{F}(\phi_0 = \phi_+) = \mathcal{F}_2 \), proving the claim. This motivates the double tangent construction approach to minimizing the total free energy. Fig. 9.4 illustrates this approach. The thick solid line is the graph of the free energy density, \( \text{graph}(\mathcal{F}) \). The grey squares correspond to the points \( p_0 \), the total free energy per particle vs. the
Figure 9.4: The double tangent construction minimizes the total free energy. The minimized total free energy is the projection of the initial concentration onto the convex hull.

average concentration of liquid crystal. The white circles correspond to the points $p_-$ and $p_+$, free energy density vs. the liquid crystal concentration in the two homogenous subsystems $S$ and $S_2$. Initially, the system is homogenous and the point $p_0$ corresponds to the topmost square. We assume that it then separates into two homogenous subsystems. (In reality it may separate into a multitude of subsystems, but here we are only interested in the final state which will not be affected by this assumption.) $\mathcal{F}$ attains a minimum when the point $p_0$ lies on the convex hull of $\text{graph}(\mathcal{F})$, $\text{c-h}(\text{graph}(\mathcal{F}))$. We call this point $p_0^* \equiv (\mathcal{F}^*, \phi_0)$. An equilibrium configuration is a pair $(p_-^*, p_+^*)$ which obeys all of the following constraints: a) $\phi_-^* \leq \phi_0$ and $\phi_+^* \geq \phi_0$ (equality if and only if $\phi_-^* = \phi_+^*$), b) $p_-^* \in \text{graph}(\mathcal{F})$ and $p_+^* \in \text{graph}(\mathcal{F})$,
c) \( p^*_-, p^*_0, \) and \( p^*_+ \) are co-linear. We assume that \( p^*_- \) and \( p^*_+ \) are not degenerate, i.e., there is only one such pair of points. (The center graph in Fig. 9.5 shows an exception to this assumption.\(^{1}\)) We call the “convexification set” of the graph of \( \mathcal{F} \) the set of points on the convex hull of \( \text{graph}(\mathcal{F}) \) which are not also on \( \text{graph}(\mathcal{F}) \). This will generally be a set of disjoint open line segments, which we call “open tangent lines.” We use “tangent line” to denote the longest line segment that contains an open tangent line and whose endpoints are contained in \( \text{graph}(\mathcal{F}) \). More than one tangent line may exist. Because of conditions b) and c), the points \( p^*_- \) and \( p^*_+ \) are the only points on \( \text{graph}(\mathcal{F}) \) which are also in one of the tangent lines of \( \text{graph}(\mathcal{F}) \). Thus we arrive at the algorithm to determine the possible equilibrium concentrations:

1. Construct \( \text{graph}(\mathcal{F}) \) and convex hull, \( \text{c-h}(\text{graph}(\mathcal{F})) \).

2. Find all points on the convexification set, \( T = \{ p | p \in \text{c-h}(\text{graph}(\mathcal{F})) \text{ and } p \notin \text{graph}(\mathcal{F}) \} \).

3. Partition the convexification set into \( n \) disjoint line segments (the open tangent lines). These can be represented by their endpoints, \( \{ q^k_0, q^k_1 \} \), \( k = 1...n \) alone.

4. For each open tangent line \( \{ q^k_0, q^k_1 \} \), find the farthest point on \( \text{graph}(\mathcal{F}) \) to the left of \( q^k_0 \) and to the right of \( q^k_1 \) which is co-linear with \( q^k_0 q^k_1 \). These points are \( q^k_0 \) and \( q^k_1 \), and the endpoint of the tangent lines are \( \{ q^k_0, q^k_1 \} \).

\(^{1}\)If \( \text{graph}(\mathcal{F}) \) has straight line segments whose intersection with the tangent line is not empty, then the equilibrium concentration points degenerate into a range of concentrations. This never happens in the systems we are considering.
5. (If graph(\(\mathcal{F}\)) contains straight line segments: determine \(\overline{r_0^k}\), the last point right of \(\overline{q_0^k}\) which is on graph(\(\mathcal{F}\)). This determines the continuous range of equilibrium values \(q_0^* \in [q_0^k...r_0^k]\). Apply the analogous procedure for \(\overline{q_1^k}\) to get \(q_1^* \in [r_1^k...q_1^k]\).)

Numerically this can be accomplished as follows: one creates a polygon approximation to graph(\(\mathcal{F}\)) as an array of points \((\mathcal{F}(\phi_k), \phi_k)\). The convex hull can be created using a standard convexification algorithm for polygons [49]. Straightforward operations for discrete sets can be be used to perform the remaining steps. We note that the double tangent construction can be extended to higher dimensions (e.g., Ref. [50]): For ternary systems, the domain for \(\phi\) is a triangle (the “Gibbs triangle”), the tangent lines become tangent planes, and the equilibrium points become tangent lines (so-called “tie-lines”); for \(n\)-ary systems, the tangent lines become \(n - 1\) dimensional hyperplanes, the tie-lines become \(n - 2\) dimensional hyperplanes, and the domain for the concentrations will be a \(n - 1\)-dimensional simplex. The behavior of the physical system can now be characterized depending on the initial concentration:

1. The initial concentration does not fall within the end points of a tangent line.
   
   In this case, the total free energy is already at its minimum and no phase separation will take place.

2. The initial concentration falls within the end points of a tangent line. Then, the system will evolve such that the concentrations of \(S_1\) and \(S_2\) are given by the end points of the tangent line.
(a) The graph of the free energy density is convex down (negative curvature) at the initial concentration. Any small deviation from the initial concentration will then decrease the total free energy and the system will spontaneously phase separate. This is called the "spinodal" region.

(b) The graph of the free energy density is convex up (positive curvature) at the initial concentration. In this case, a small fluctuation in concentration will increase the total free energy; only large fluctuations may decrease it. This is called the "binodal" region.

(c) These regions are only properly defined for the initial concentration. (An initially unstable system may later become metastable, and vice versa, c.f. Fig. 9.4.)

The transition line between positive and negative curvature is called the "spinodal." The endpoints of the tangent lines are called "binodals."

\[ \text{9.2.2 Free energy density} \]

To create the phase diagram, we must first create the graph of the free energy density. For a homogenous subsystem, the mixing free energy density of two molecules with only translational degrees of freedom is given by

\[ \frac{\mathcal{F}_{\text{iso}}(\phi)}{kT_c} = \frac{T}{T_c} \left( \phi \ln \phi + (1 - \phi) \ln (1 - \phi) \right) + 2\phi (1 - \phi), \quad (9.14) \]

where \( T_c \) is the critical temperature for phase separation. If a nematic order parameter is present, the mixing free energy is augmented by an anisotropic part:

\[ \frac{\mathcal{F}_{\text{aniso}}(\phi)}{kT_c} = -\frac{T}{T_c} \phi \ln \int \exp \left( \frac{10}{3} \frac{T^*}{T} \phi \left( \sigma_{\alpha\beta} Q_{\beta\alpha} - \frac{1}{2} Q_{\alpha\beta} Q_{\beta\alpha} \right) \right) d^2 \sigma, \quad (9.15) \]
and as in section 9.1, we write this in terms of the scalar order parameter as

\[
\frac{\mathcal{F}_{\text{aniso}}(\phi)}{kT_c} = -\frac{T}{T_c} \phi \ln \int_0^1 \exp \left( \frac{5T^*}{T} \phi \left( SP_2(x) - \frac{1}{2} S^2 \right) \right) dx + \frac{T}{T_c} (1 - \phi) \ln 4\pi. \tag{9.16}
\]

We are only interested in the equilibrium state and therefore restrict values of the nematic order parameter to equilibrium. Its equilibrium values are denoted by \( S_{\text{eq}}(\phi) \) and the free energy becomes a function of \( \phi \) alone:

\[
\frac{\mathcal{F}(\phi)}{kT^*} = \frac{T}{T^*} \left( \phi \ln \phi + (1 - \phi) \ln (1 - \phi) \right) + 2 \frac{T_c}{T^*} \phi (1 - \phi) + \frac{5}{2} \phi^2 S_{\text{eq}}(\phi) \left( S_{\text{eq}}(\phi) + 1 \right) - \frac{T}{T^*} \phi \ln \int_0^1 \exp \left( \frac{15 T^*}{2T} \phi S_{\text{eq}}(\phi) x^2 \right) dx + \frac{T}{T^*} (1 - \phi) \ln 4\pi. \tag{9.17}
\]

The graph of this free energy density is the basis for the double tangent construction described above. It has two parameters, \( T/T^* \) and \( T_c/T^* \). The boundary values for \( \mathcal{F}_{\text{iso}} \) and \( \mathcal{F}_{\text{aniso}} \), respectively, are given by

\[
\lim_{\phi \to 0} \frac{\mathcal{F}_{\text{iso}}(\phi)}{kT_c} = \lim_{\phi \to 1} \frac{\mathcal{F}_{\text{iso}}(\phi)}{kT_c} = \lim_{\phi \to 0} \frac{\mathcal{F}_{\text{aniso}}(\phi)}{kT_c} = 0 \tag{9.18a}
\]

and

\[
\lim_{\phi \to 1} \frac{\mathcal{F}_{\text{aniso}}(\phi)}{kT_c} = -\frac{T}{T_c} \ln \int_0^1 \exp \left( \frac{5T^*}{T} \left( S_{\text{eq}} P_2(x) - \frac{1}{2} S_{\text{eq}}^2 \right) \right) dx. \tag{9.18b}
\]

The binonals are determined by the inflection points of the free energy density:

\[
\frac{d^2 \mathcal{F}_{\text{iso}}}{d\phi^2} = \frac{\frac{T}{T_c}}{(1 - \phi) \phi} - 4 \tag{9.19a}
\]

\[
\frac{d^2 \mathcal{F}_{\text{aniso}}}{d\phi^2} = -10 \frac{T^*}{T} \frac{T}{T_c} S \left( \langle P_2 \rangle - \frac{1}{2} S \right) - 5S \frac{T^*}{T_c} \phi \frac{d \langle P_2 \rangle}{d\phi} - \frac{45}{4} S \phi \frac{T^*}{T} \left( \langle x^4 \rangle - \langle x^2 \rangle^2 \right) \tag{9.19b}
\]

\[
= -5 \frac{T^*}{T_c} S \left( 3 \langle x^2 \rangle - 1 - S \right) + \frac{45}{4} S \phi \frac{T^*}{T} \left( \langle x^4 \rangle - \langle x^2 \rangle^2 \right) \tag{9.19c}
\]
For a purely isotropic system, the inflection point \( d^2 F_{iso} / d\phi^2 = 0 \) yields

\[
\phi_{\text{infl}} = \frac{1}{2} \left( 1 \pm \sqrt{(1 - T/T_c)} \right). \tag{9.20}
\]

A root finder can be used to determine the inflection point for a liquid crystalline system. To that end, we note the following boundary values for the first and second derivatives of \( F \):

\[
\lim_{\phi \to 0} \left( \frac{d}{d\phi} F (\phi) \right) = -\infty \quad , \quad \lim_{\phi \to 1} \left( \frac{d}{d\phi} F (\phi) \right) = +\infty \tag{9.21a}
\]

\[
\lim_{\phi \to 0} \left( \frac{d^2}{d\phi^2} F (\phi) \right) = +\infty \quad , \quad \lim_{\phi \to 0} \left( \frac{d^2}{d\phi^2} F (\phi) \right) = +\infty \tag{9.21b}
\]

9.2.3 Interpretation

We consider a representative phase diagram with a ratio of phase separation critical to nematic critical temperature \( T_c / T^* = 1.0 \). Fig. 9.5 shows the graphs of the free energy density and its convex hull for three different temperatures. The left-most graph is for \( T/T_c = 0.96 \), which is above the triple point temperature, \( T_i \): the convexification contains two tangent lines and thus four binodals. The center graph is for \( T/T_c = \)

![Graphs showing free energy density for different temperatures](image)

Figure 9.5: Free energy density for \( T^*/T_c=1.0 \) and varying \( T/T_c \).
Figure 9.6: A representative phase diagram of an isotropic/liquid crystal mixture

0.9458, which is at the triple point temperature. The left-most picture is for $T < T_i$: the convexification consists of a single tangent line and the phase diagram has only two binodals. Fig. 9.6 shows the corresponding phase diagram. The binodals are the thick solid lines. Above $T_i$, the two leftmost binodals are the same as for an isotropic system. The dotted continuation line of the binodal below $T_i$ indicates the phase diagram for an isotropic system. Below $T_i$, the binodals are further outward compared to the isotropic system. The reason for this is apparent in the leftmost
graph in Fig. 9.5: because of the presence of the nematic branch of the free energy density, the tangent line tilts right and down at lower temperatures and the tangent point at the isotropic branch moves upward. Fig. 9.8 illustrates the relation of the lines in Fig. 9.6 to specific points on the free energy density graph. The free energy graph is for a temperature $T = 0.95T_c$ that is slightly above $T_c$. The convexification has two tangent lines at this temperature. The graph is divided into nine regions. Concentrations between two adjacent regions belong to the following curves in the phase diagram from left to right: the first binodal, the first spinodal, the second spinodal, the second binodal, the third binodal, the nematic-isotropic transition line, the nematic spinodal and the fourth binodal. The binodals separate alternating regions in which phase separation will or will not take place. No phase separation occurs if the initial concentration is in regions (1), (5) and (9). Phase separation by nucleation occurs for $\phi_0$ in regions (2), (4), (6) and (8), while spinodal decomposition occurs in regions (3) and (7). Concentrations to the right of the nematic-isotropic transition line lead in equilibrium to a nematic phase, while concentrations left of it lead in equilibrium to an isotropic phase. An additional line is the nematic critical curve, which has no corresponding region in Fig. 9.8: the isotropic phase is unstable for concentrations right of it. (Conversely, if the system has a concentration left of it the isotropic phase may be metastable – the addition of noise is then required in the dynamic equations to overcome the potential barrier.) The nematic critical curve is the rightmost dotted line in Fig. 9.8. It is always a straight line below the nematic-isotropic transition line.
Figure 9.7: Phase diagrams for different ratios $T_c/T^*$

Above the triple point temperature, the system, if phase separating, will separate into either two isotropic phases ($\phi_0$ between the first and second binodal), or into one isotropic and one nematic phase ($\phi_0$ between the third and fourth binodal). Below $T_t$ it can only separate into one nematic and one isotropic phase. Fig. 9.7 illustrates that some ratios of $T_c/T^*$ do not exhibit a triple point: in such cases a phase separating system always separates into one isotropic and one nematic phase.
Figure 9.8: Illustration of the relations of the curves in the phase diagram to points in the free energy density graph.
Chapter 10

Numerics

10.1 Finite difference

The numerical integration of the dynamic equations (7.63a) and (7.63b), page 155 are performed on a cubic grid using the forward-time-centered-space method. The field is divided into a cubic lattice with $n_x, n_y$ and $n_z$ nodes with spacing $h$ along each axis respectively. The exact values of the field are known and stored only for points $\mathbf{r}_{ijk} = h (i\hat{e}_1 + j\hat{e}_2 + k\hat{e}_3)$ with $i \in \{1, \ldots, n_x\}$, $j \in \{1, \ldots, n_y\}$ and $k \in \{1, \ldots, n_z\}$, and $\{\hat{e}_1, \hat{e}_2, \hat{e}_3\}$ is an orthonormal basis. In the following $f(t, \mathbf{r})$ may stand for any field variable, i.e., the concentration field $\phi$ and components of $Q_{ij}$, respectively. We also omit any noise terms. The value at a node $\mathbf{r}$ at a later time $t + \tau$ is estimated from the linear rate of change of $f$, evaluated at $\mathbf{r}$ at the current time $t$

$$f_{t+\tau, \mathbf{r}} = f_{t, \mathbf{r}} + \left( \frac{\partial f}{\partial t} \right)_{t, \mathbf{r}} \tau + O(\tau) ,$$  

(10.1)

where $\partial f/\partial t$ is given by the dynamic equations. The spatial derivatives occurring there are estimated by finite difference to $O(h^2)$, for example, the Laplacian (in a polynomial basis) is given by

$$f_{\alpha\alpha, \mathbf{r}} + O(h^2) = \frac{1}{h^2} \sum_{k=1}^{3} (f(\mathbf{r} + h\hat{e}_k) + f(\mathbf{r} - h\hat{e}_k) - 2f(\mathbf{r})) ,$$  

(10.2)

which is a well-known result (e.g., Ref. [51]). These finite difference operators can easily be derived by setting up a linear system of Taylor-expansions of $f$ around $\mathbf{r}$. For
example, we consider the one-dimensional case and define \( f \equiv f(x) \), \( f_p \equiv f(x+h) \) and \( f_{pp} \equiv f(x+2h) \), respectively and \( f_m \) and \( f_{mm} \) analogous. The Taylor expansions for \( f(x \pm h) \) and \( f(x \pm 2h) \) can be written as a system of four equations

\[
\begin{pmatrix}
-f + f_p + R_p \\
-f + f_m + R_m \\
-f + f_{pp} + R_{pp} \\
-f + f_{mm} + R_{mm}
\end{pmatrix}
= \begin{pmatrix}
 h & \frac{1}{2}h^2 & \frac{1}{3!}h^3 & \frac{1}{4!}h^4 \\
-h & \frac{1}{2}h^2 & -\frac{1}{3!}h^3 & \frac{1}{4!}h^4 \\
 2h & 2h^2 & \frac{4}{3}h^3 & \frac{2}{3}h^4 \\
-2h & 2h^2 & -\frac{4}{3}h^3 & \frac{2}{3}h^4
\end{pmatrix}
\begin{pmatrix}
 f' \\
f'' \\
f''' \\
f^{(IV)}
\end{pmatrix},
\] (10.3)

with \( R_p \), etc. the respective remainder terms. (The three-dimensional case is a bit more involved but works along the same principle.) The evaluation of the dynamic equations requires up to fourth order spatial derivatives, which may also couple to the nematic order parameter tensor. While it is possible to derive all terms explicitly in this manner, this would give rise to a large number of subroutines and therefore be quite error prone. We will show that it is permissible to use only second order finite difference operations instead.

10.1.1 Concatenation of finite difference operators for a polynomial basis

Let \( f \in C^\infty \) and \( \delta_k^{(k')} f \) denote a finite difference operator that can be written in the following form\(^1\):

\[
\delta_k^{(k')} f = f^{(k)}_{|x} h^k + h^{k+k'} \sum_{\gamma=0}^{\infty} \gamma_{\gamma',k-k'} f^{(\gamma)}_{|x} h^{n-(k+k')},
\] (10.4)

\(^1\)It may be possible to show the same for \( f \notin C^\infty \), but the remainder term could not be written as a power series in \( h \) with constant coefficients.
where \( f^{(n)} \) denotes \( d^n f / dx^n \). This is the form resulting from a linear systems of Taylor expansions as shown above, e.g.,

\[
\delta_2^{(2)} f \equiv f_p + f_m - 2f = f'' h^2 + h^{2+2} \sum_{n=4}^{\infty} \gamma_n f^{(n)}_{xx} h^{n-4}
\]

(10.5)

with \( \gamma_n = \frac{2}{n!} \) for \( n \) even and \( \gamma_n = 0 \) otherwise. The finite difference operator \( h^{-k} \delta_k^{(k')} \) applied to \( f \) estimates \( f^{(k)} \) to \( O\left(h^{k'}\right) \):

\[
h^{-k} \delta_k^{(k')} f = f^{(k)} + O\left(h^{k'}\right).
\]

(10.6)

We claim that the concatenation of two finited difference operators yields the accuracy of the operator with the lesser accuracy:

\[
h^{-l} \delta_l^{(l')} h^{-k} \delta_k^{(k')} f = f^{(l+k)} + O\left(h^{\min(l',k')}\right).
\]

(10.7)

The finite difference \( \delta_k^{(k')} f \) is itself a function of \( x \) and we define

\[
g \equiv \delta_k^{(k')} f.
\]

(10.8)

Then we can apply an operator \( \delta_l^{(l')} \) to \( g \) and get

\[
\delta_l^{(l')} g = g^{(l)} h^l + h^{l+l'} \sum_{n=l+l'}^{\infty} \tilde{\gamma}_n g^{(n)} h^{n-(l+l')},
\]

(10.9)

where the \( \tilde{\gamma}_n \) will be different from the \( \gamma_n \) unless we consider the same operator applied twice. Substituting \( \delta_k^{(k')} f \) from Eq. (10.4) back into \( g \), Eq. (10.9), and using the shorthand

\[
a(x, h) \equiv \sum_{n=k+k'} \gamma_n f^{(n)}_{xx} h^{n-(k+k')}
\]

(10.10)
yields
\[
\delta_l^{(l')} \delta_k^{(k')} f = \left( f^{(k)} h^k + h^{k+k'} a(x; h) \right)^{(l)} h^l \\
+ h^{l+l'} \sum_{n=l+l'} \gamma_n h^{n-(l+l')} \left( f^{(k)} h^k + h^{k+k'} a(x; h) \right)^{(n)} \\
= f^{(k+l)} h^{k+l} + a^{(l)} (x, h) h^{k+l+k'} + h^{k+l+l'} b(x, h)
\] (10.11a)

with \( b \equiv \sum_{n=l+l'}^{\infty} \left( \gamma_n h^{n-(l+l')} f^{(k+n)} + h^{k+n} a^{(n)} (x; h) \right) \). Both \( a \) and \( b \) are power series in \( h \) with coefficients independent of \( h \). Therefore, \( h^p a^{(l)} = O(h^p) \) and \( h^q b = O(h^q) \), respectively and \( h^p a^{(l)} + h^q b = O(h^{\min(p,q)}) \). Dividing by \( h^{k+l} \) yields
\[
h^{-(k+l)} \delta_l^{(l')} \delta_k^{(k')} f = f^{(k+l)} + h^{k'} a^{(l)} + h^{l'} b \\
= f^{(k+l)} + O(h^{\min(k'+l')})
\] (10.12a)

which is what we set out to show (qed). We conclude that the accuracy for the concatenation of finite difference operators is the accuracy of the least accurate operator.

This can be extended to \( N \) dimensions. The Taylor expansion for a function \( f : \mathbb{R}^N \rightarrow \mathbb{R} \) is given by
\[
f(r + h) - f(r) = f_{\alpha|r} h_\alpha + \frac{1}{2} h^2 f_{\alpha\beta|r} h_\alpha h_\beta + \ldots, \] (10.13)

where \( h_\alpha \) is the \( \alpha \)'th component of the direction of \( h \), \( h_\alpha \equiv h \cdot \hat{e}_\alpha / |h| \). One can set up a linear system of equations for different displacements, \( h_i \) as in Eq.(10.3). We define a finite difference operator \( h^{-k} \delta_{\xi_1, \ldots, \xi_k} \) that applied to \( f \) approximates \( f_{\xi_1, \ldots, \xi_k} = \frac{\partial^k f}{\partial x_{\xi_1} \ldots \partial x_{\xi_k}} \) by a Taylor polynomial to \( O(h^{k'}) \) analogous to Eq.(10.4):
\[
\delta_{\xi_1, \ldots, \xi_k}^{(k')} f = f_{\xi_1, \ldots, \xi_k} h^k + h^{k'} \sum_{n=k+k'}^{\infty} \phi^{(n)} h^{n-(k+k')},
\] (10.14)
where $\phi^{(n)}$ is a linear combination of $n^{th}$-order partial derivatives of $f$:

$$
\phi^{(n)} = \gamma_{\alpha_1 \ldots \alpha_n} f_{\alpha_1 \ldots \alpha_n},
$$

(10.15)

and $\gamma_{\alpha_1 \ldots \alpha_n}$ is a $n^{th}$ rank tensor with constant coefficients (these coefficients depend on the coordinate system as they depend on the directions of the $h_i$). Eq. (10.14) has the same structure as Eq. (10.4), and we can apply the same procedure as before.

### 10.2 Evaluation of $\langle \sigma_{ij} \rangle$ and $\ln \int \exp (\sigma_{\alpha \beta} H_{\beta \alpha}) \, d^2 \sigma$

The dynamic equations (7.63a) and (7.63b), where the definition of the functional derivatives is given in Tables 6.1 and 6.3, with Table 6.2 and 6.4, require the evaluation of two functions of a tensor field, $H_{ij}$:

$$
I^{(1)} (H_{ij}) \equiv \ln \int \exp \left( \sigma_{\alpha \beta} H_{\beta \alpha} \right) \, d^2 \sigma,
$$

(10.16)

and

$$
I^{(2)} (H_{ij}) \equiv \langle \sigma_{ij} \rangle_H = \frac{\int \sigma_{ij} \exp \left( \sigma_{\alpha \beta} H_{\beta \alpha} \right) \, d^2 \sigma}{\int \exp \left( \sigma_{\alpha \beta} H_{\beta \alpha} \right) \, d^2 \sigma},
$$

(10.17)

where $\sigma_{ij}$ is the molecular orientation and $\langle \sigma_{ij} \rangle_H$ its thermal equilibrium average in the reduced effective external field $H_{ij}$. We only permit uniaxial molecular orientation, i.e., we assume any molecular biaxiality averaged out. Then we have

$$
\sigma_{ij} = \frac{3}{2} n_i n_j - \frac{1}{2} \delta_{ij},
$$

(10.18)

with $n_i = \hat{n} \cdot \hat{e}_i$ the $i^{th}$ component of the molecular long axis and $d^2 \sigma_{ij}$ is the integral over all possible orientations of $\hat{n}$. We need to evaluate five components for the traceless and symmetric tensor $I^{(2)}_{ij}$ and one for the scalar $I^{(1)}$. Each component needs to be evaluated at each discrete lattice site and each time step because the
argument $\overline{H}_{ij}$ is a functional of the nematic order parameter $Q_{ij}$ and the volume fraction of liquid crystal $\phi$ and therefore changes in time and varies in space. It would be possible but not very efficient to integrate numerically over $d^2\sigma$ for each component at each discrete point in time and space. Instead, we would like to tabulate the field $H_{ij}$ for a set of values and use this table for interpolation. It appears that one would need a rather large table of $5 \times 6$ components for each interpolation node in this table: the first five for each component of the argument $H_{ij}$ and the second 6 for all components of the result $I^{(1)}$ and $I^{(2)}$. Fortunately, it turns out that $I^{(2)}_{ij}$ is co-diagonal with $\overline{H}_{ij}$ and evaluation within the diagonal frame reduces the number of parameters for each node in the interpolation table to two.

The effective field $\overline{H}$ may be written in terms of a dyadic expansion in its eigenframe. We consider only the traceless, symmetric part of $\overline{H}$, as only this enters the interaction: $H_{\alpha\beta}\sigma_{\alpha\beta} = H'_{\alpha\beta}\sigma_{\alpha\beta}$, where $H'_{ij}$ is the traceless, symmetric part of $H_{ij}$, see section ???. Then $\overline{H}$ may be written as $\overline{H} = \lambda_L \hat{\mathbf{L}} \hat{\mathbf{L}} + \lambda_M \hat{\mathbf{M}} \hat{\mathbf{M}} + \lambda_N \hat{\mathbf{N}} \hat{\mathbf{N}}$, where $\hat{\mathbf{L}}, \hat{\mathbf{M}}$ and $\hat{\mathbf{N}}$ are the eigenvectors of $\overline{H}$ with eigenvalues $\lambda_L = \frac{\overline{P} - \overline{S}}{2}, \lambda_M = \frac{-\overline{P} - \overline{S}}{2}$ and $\lambda_N = \overline{S}$ respectively. We choose the eigensystem such that $\overline{S}$ is the eigenvalue of largest magnitude and $\hat{\mathbf{L}}, \hat{\mathbf{M}}$ and $\hat{\mathbf{N}}$ form a right handed orthonormal system, $\hat{\mathbf{L}} \cdot (\hat{\mathbf{M}} \times \hat{\mathbf{N}}) > 0$.

The local field $\overline{H}$ can also be written as (Eq. (A.3))

$$\overline{H} = \overline{S} \left( \frac{3}{2} \hat{\mathbf{N}} \hat{\mathbf{N}} - \frac{1}{2} \right) + \frac{\overline{P}}{2} \left( \hat{\mathbf{M}} \hat{\mathbf{M}} - \hat{\mathbf{L}} \hat{\mathbf{L}} \right), \quad (10.19)$$

with $\mathbf{I}$ the identity. The argument in the exponential of Eqs. (10.16) and (10.17) is now given by

$$\overline{H}_{\alpha\beta}\sigma_{\beta\alpha} = \overline{S} \frac{3}{2} \left( \frac{3}{2} (N_{\alpha}n_{\alpha})^2 - \frac{1}{2} \right) + \frac{3}{4} \overline{P} \left( (M_{\alpha}n_{\alpha})^2 - (L_{\alpha}n_{\alpha})^2 \right) \quad (10.20)$$
We expand \( \hat{n} \) in the eigenframe of \( \overline{H} \):

\[
\hat{n} = \left( \hat{L} \cdot \hat{n} \right) \hat{L} + \left( \hat{M} \cdot \hat{n} \right) \hat{M} + \left( \hat{N} \cdot \hat{n} \right) \hat{N},
\]

which expressed in spherical coordinates with \( \hat{L}, \hat{M} \) and \( \hat{N} \) as basis is

\[
\hat{n} = \sin \vartheta \cos \phi \hat{L} + \sin \vartheta \sin \phi \hat{M} + \cos \vartheta \hat{N}.
\]

In this frame

\[
\hat{n} \hat{n} = \begin{pmatrix}
\cos^2 \varphi \sin^2 \vartheta & \frac{\sin 2 \varphi \sin^2 \vartheta}{2} & \cos \varphi \sin \frac{2 \vartheta}{2} \\
\frac{\sin 2 \varphi \sin^2 \vartheta}{2} & \sin^2 \varphi \sin^2 \vartheta & \sin \varphi \sin \frac{2 \vartheta}{2} \\
\cos \varphi \sin \frac{2 \vartheta}{2} & \sin \varphi \sin \frac{2 \vartheta}{2} & \cos^2 \vartheta
\end{pmatrix},
\]

and the interaction potential becomes

\[
\overline{H}_{\alpha \beta \sigma \beta \alpha} = \left( \frac{3}{2} \right)^2 \left( \cos^2 \vartheta \left( \overline{S} + \frac{P}{3} \cos 2 \varphi \right) - \frac{P}{3} \cos 2 \varphi \right) - \frac{3}{4} \overline{S}.
\]

This yields for the integral \( I^{(1)} \)

\[
I^{(1)}(H_{ij}) = -\frac{3}{4} \overline{S} + \ln \int_0^{2\pi} d\varphi \int_{-1}^1 dx \exp \left( \frac{9}{4} \left( x^2 \left( \overline{S} + \frac{P}{3} \cos 2 \varphi \right) - \frac{P}{3} \cos 2 \varphi \right) \right)
\]

with \( x = \cos \vartheta \). The canonical average in the potential \( \sigma_{\alpha \beta} \overline{H}_{\beta \alpha} \) for any function \( \xi \) evaluates to

\[
\langle \xi \rangle_{\overline{H}} = \frac{\int_0^{2\pi} d\varphi \int_{-1}^1 dx \xi(\phi, x) \exp \left[ \frac{9}{4} \left( x^2 \left( \overline{S} + \frac{P}{3} \cos 2 \varphi \right) - \frac{P}{3} \cos 2 \varphi \right) \right]}{\int_0^{2\pi} d\varphi \int_{-1}^1 dx \exp \left[ \frac{9}{4} \left( x^2 \left( \overline{S} + \frac{P}{3} \cos 2 \varphi \right) - \frac{P}{3} \cos 2 \varphi \right) \right]}.
\]

### 10.2.1 Co-diagonality

Claim: \( \langle \sigma_{ij} \rangle_{\overline{H}} \) and \( \overline{H}_{ij} \) are codiagonal.

One finds the following symmetries for \( I^{(1)} \) and \( I_{ij}^{(2)} \) respectively:
1. The integrals $I^{(1)}$ and $I^{(2)}_{ij}$ are even in $\overline{P}: I(\overline{P}) = I(-\overline{P})$

2. The average of any function $\xi(\varphi, x)$ vanishes if $\xi$ is odd in $x$, i.e., $\xi(\varphi, x) = -\xi(\varphi, -x)$

3. The average $\langle \xi(\varphi, x) \rangle$ vanishes if $\xi$ is odd in $\varphi$ and periodic over $\pi$, i.e., $\xi(\varphi, x) = -\xi(-\varphi, x)$ and $\xi(\varphi + \pi, x) = \xi(\varphi, x)$

$$\int_{-1}^{1} dx \int_{0}^{2\pi} d\varphi \xi(\varphi, x) \exp \left( \frac{9}{4} \left( \frac{1}{3} x^2 + \frac{P}{3} (x^2 - 1) \cos 2\varphi \right) \right) = \int_{-1}^{1} dx \exp \left( g \left( x^2 \right) \right) \int_{-\pi}^{\pi} d\varphi \xi(\varphi, x) \exp \left( f \left( x^2 \right) \cos 2\varphi \right) = 0 \quad (10.27)$$

4. $\langle \xi \rangle$ vanishes if $\xi(\phi + 2\pi, x) = \xi(\phi, x)$ and $\xi(\phi + \pi, x) = -\xi(\phi, x)$

$$\int_{-1}^{1} dx \exp \left( g \left( x^2 \right) \right) \int_{0}^{2\pi} d\varphi \xi(\varphi, x) \exp \left( f \left( x^2 \right) \cos 2\varphi \right)$$

$$= \int_{-1}^{1} dx \exp \left( g \left( x^2 \right) \right) \times$$

$$\left( \int_{0}^{\pi} \xi(\varphi, x) + \int_{\pi}^{2\pi} \xi(\varphi, x) \right) \exp \left( f \left( x^2 \right) \cos 2\varphi \right) d\varphi$$

$$= \int_{-1}^{1} dx \exp \left( g \left( x^2 \right) \right) \times$$

$$\left( \int_{0}^{\pi} \xi(\varphi, x) + \int_{0}^{\pi} \xi(\varphi + \pi, x) \right) \exp \left( f \left( x^2 \right) \cos 2\varphi \right) d\varphi = 0 \quad (10.28a)$$

These symmetries imply that the off-diagonal elements in Eq. (10.23) vanish:

$\langle n_1 n_2 \rangle = \langle \sin^2 \varphi \sin^2 \theta \rangle$ vanishes because $\sin 2\varphi$ is odd in $\varphi$ and periodic over $\pi$.

$\langle n_1 n_3 \rangle$ and $\langle n_2 n_3 \rangle$ vanish because $\cos \phi$ and $\sin \phi$ have the symmetry given in point 4. This proves that $\langle \sigma_{ij} \rangle$ is co-diagonal with $\overline{H}_{ij}$. 

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10.2.2 Parametrization

Instead of using the parameters $\overline{P}$ and $\overline{S}$ to generate the interpolation table we chose to write the pair $(\overline{S}, \overline{P}/\sqrt{3})$ in polar coordinates [52]:

$$\overline{r} \cos \overline{\Psi} = \overline{S} \quad \text{and} \quad \overline{r} \sin \overline{\Psi} = \frac{\overline{P}}{\sqrt{3}}. \quad (10.29)$$

The interaction potential is then written as

$$\overline{H}_{\alpha\beta\gamma\rho} = g (\overline{r}, \overline{\Psi}) \left( x^2 + (x^2 - 1) \sqrt{3} \tan \overline{\Psi} \cos 2\varphi \right) - \frac{1}{3} g (\overline{r}, \overline{\Psi}) , \quad (10.30)$$

with $g \equiv \frac{2}{3} \overline{r} \cos \overline{\Psi}$. The final procedure is then: for a set of pairs $g$ and $\overline{\Psi}$ determine the functions $I^{(1)}$ and $I^{(2)}$ in the diagonal frame of $\overline{H}_{ij}$.

10.2.3 Determining $\overline{r}, \overline{\Psi}$ from $\overline{H}$

We define $\overline{S}$ to be the eigenvalue of the largest magnitude of $\overline{H}_{ij}$. This implies that $\overline{\Psi} \in [-\pi, \pi] \cup \left[ \frac{5}{6}\pi, \frac{7}{6}\pi \right]$, if the sign of $\overline{r}$ is chosen positive (Fig.10.1). Instead we may restrict $\overline{\Psi}$ to $[-\frac{\pi}{6}, \frac{\pi}{6}]$ and permit $\overline{r}$ to have arbitrary sign. One can express a relationship between $(\overline{r}, \overline{\Psi})$ and $\overline{H}$ as

$$\text{Tr} \overline{H}^2 = \frac{3}{2} \overline{r}^2 \quad \quad (10.31a)$$

$$\text{Tr} \overline{H}^3 =\frac{3}{4} \left[ \overline{S} \left( \overline{S}^2 - \overline{P}^2 \right) \right] = \frac{3}{4} \overline{r}^3 \left[ \cos^3 \overline{\Psi} - 3 \cos \overline{\Psi} \sin^2 \overline{\Psi} \right] = \frac{3}{4} \overline{r}^3 \cos 3\overline{\Psi}. \quad (10.31b)$$
Figure 10.1: Visualizing the relationship between $\bar{S}$, $\bar{P}$ and $\bar{r}$ and $\bar{\Psi}$ respectively. Left: The eigenvalues may be interpreted as the projections of a symmetric star of three vectors onto the horizontal axis. Right: The largest eigenvalue changes from $\lambda_3$ (solid line) to $\lambda_1$ (dashed line). This illustrates that $\Psi \in [-\pi/6..\pi/6] \cup [\pi/6..\pi/3] \cup [5\pi/6..\pi]$ if $\bar{r} > 0$.

Since $|\bar{\Psi}| \leq \frac{\pi}{6}$ it follows that $\cos 3\bar{\Psi} \geq 0$. This implies that the sign of $\bar{r}$ is determined by the sign of $\text{Tr} \bar{H}^3$. One can therefore write

\[
\bar{r} = \text{sign} \left( \text{Tr} \bar{H}^3 \right) \sqrt{\frac{2}{3} \text{Tr} \bar{H}^2} \tag{10.32a}
\]

\[
\cos 3\bar{\Psi} = \frac{2 \text{Tr} \bar{H}^3}{\bar{r} \text{Tr} \bar{H}^2} \tag{10.32b}
\]

\[
\bar{\Psi} = \frac{1}{3} \arccos \left( \frac{2 \text{Tr} \bar{H}^3}{\bar{r} \text{Tr} \bar{H}^2} \right) \tag{10.32c}
\]
Figure 10.2: Free energy surface at $T = T_{NI}$ for the Maier-Saupe tensor potential

10.2.4 Implementation

We evaluate the traceless integral $I_{ij}^{(2)} = \langle \sigma_{ij} \rangle_{\mathbf{H}}$ in its diagonal frame. Therefore only two components of $I_{ij}^{(2)}$ as well as $I^{(1)}$ are needed to tabulate.

\[
I_{11}^{(2)} = \langle \sigma_{11} \rangle_{\varphi, \psi} = \frac{3}{2} \left( \langle 1 - x^2 \rangle_{\varphi, \psi} \cos^2 \varphi \right)_{\varphi, \psi} - \frac{1}{2} \\
I_{33}^{(2)} = \langle \sigma_{33} \rangle_{\varphi, \psi} = \frac{3}{2} \langle x^2 \rangle_{\varphi, \psi} - \frac{1}{2} \\
I^{(1)} = \ln \int \exp \left( \sigma_{\alpha\beta} \overline{H}_{\beta\alpha} \right) d^2 \sigma \\
= -\frac{1}{3} g + \ln \int_{-1}^{1} dx \int_{0}^{2\pi} d\varphi \exp \left( g \left( x^2 + (x^2 - 1) \sqrt{3} \tan \overline{\Psi} \cos 2\varphi \right) \right)
\]

where the average $\langle \cdot \rangle_{\varphi, \psi}$ is defined by Eqs. (10.17) and (10.30). These functions are tabulated for a range of values $g$ and $\overline{\Psi}$. The integrals are not well defined for large
values of the exponent, so we tabulate only for $g \in [-7.36, 7.36]$. These values are precalculated and stored in a file. For example, fig. 10.2 shows the values for the free energy of a pure, homogenous liquid crystal, $\beta F = -I^{(1)}$, at the nematic-isotropic transition temperature. The simulation program subsequently reads these tables and initializes a 2-d spline fitting subroutine.\footnote{We are using the Fortran package fitpack, which is available (2003) at http://gams.nist.gov. (Coded 1987 by Alan Kaylor Cline, distributed by Pleasant Valley Software, 8603 Altus Cove, Austin, TX 78759, USA)} At each time step the evaluation for $I^{(2)}_{ij}$ and $I^{(1)}$ proceeds then as follows:

1. Determine the unitary transform $U$, for which $U^T \cdot H \cdot U$ is diagonal.

2. Calculate $g$ and $\Psi$ from $H$ (the eigenvalues are available from the previous step).

3. Determine $I^{(1)}$, $I^{(2)}_{11}$ and $I^{(2)}_{33}$ by spline-interpolation, and $I^{(2)}_{22} = -\left(I^{(2)}_{11} + I^{(2)}_{33}\right)$.

4. Transform $I^{(2)}_{ij}$ back into the lab-frame, $I^{(2)}_{ij} = U_{i\alpha}I_{\alpha\beta}U_{j\beta}$.

10.3 Dynamic scalings

10.3.1 Structure factor

Assuming an isotropic medium and a dielectric tensor $\varepsilon_{ij}(\mathbf{r}) = (\varepsilon_h + \Delta \varepsilon(\mathbf{r})) \delta_{ij}$, with $\varepsilon_h$ the average over the scattering volume of $\varepsilon$. A static light scattering experiment measures the structure factor of the field $\Delta \varepsilon(\mathbf{r})$, i.e., the Fourier transform of the pair-correlation function of $\Delta \varepsilon$

$$S(q) = \mathcal{F}_q \int_V \Delta \varepsilon(\mathbf{r}') \Delta \varepsilon^*(\mathbf{r}'+\mathbf{r}) \, d^3\mathbf{r}' ,$$

(10.34)
with $\mathcal{F}_q g (r)$ the Fourier transform of $g (r)$

$$
\mathcal{F}_q g \equiv \frac{1}{V} \int g (r) \exp (i q \cdot r) \, d^3 r.
$$

(10.35)

The shell average, $S(q)$, of the structure factor is defined as the average over a spherical shell $q < |q| < q + dq$ of the structure factor

$$
S(q) = \frac{1}{4\pi q^2} \int_{q < |q'| < q + dq} S(q') \, d^3 q'
$$

(10.36)

and is commonly used as a measure of the distribution of length scales in the system.

### 10.3.2 Scaling hypothesis and choice of length

The scaling hypothesis states that for sufficiently long times, i.e., when the system is in the asymptotic scaling regime, the dynamics of a phase ordering system is characterized by a single length, taken to be $L(t)$

$$
S(q, t) \simeq L^\alpha(t) G(qL(t))
$$

(10.37)

where $G$ is a time independent shape function and $\alpha$ some exponent. Under the assumption that the scaling hypothesis holds, the knowledge of the shape function at some time $t$ may be used to extract information about dynamic behavior of $L(t)$. One may give the dimensional argument that any dynamic length $\lambda(t)$ that we can construct from $G$ must be a multiple of $L(t)$, because $L(t)$ is the only dynamic length in the problem. A different argument is given here, which also shows a method to construct various lengths from $G$:

A functional $F_f$ maps a function $f$ to a real number $a$. Examples of functionals are: a) the first location of the maximum of $f$ in some interval $I$, $x_{\text{max}}$ =

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\{x \in I \mid f(x) < f(x') \ \forall x' \in I \text{ and } x < x'\}, b) \text{ the value of } f \text{ at some location } x_0, c) \text{ some constant value } c. \text{ We consider functionals for which}

\[ F_{f(\lambda x)} = \frac{a_f}{\lambda}, \tag{10.38} \]

where \(a_f\) is a constant that depends on the choice of \(f\). A family of such functionals is given by

\[ F_{f(x)}^{m,n} = \sqrt[\lambda]{(x^n)_m} = \left( \frac{\int x^n f^m(x) \, dx}{\int f^m(x) \, dx} \right)^{\frac{1}{n}}, \tag{10.39} \]

which can easily be seen by performing the transformation \(f(x) \to f(\lambda x)\):

\[ F_{f(\lambda x)}^{m,n} = \left( \frac{\int x^n f^m(\lambda x) \, dx}{\int f^m(\lambda x) \, dx} \right)^{\frac{1}{n}} = \left( \frac{\int u^n f^m(u) \, du}{\int f^m(u) \, du} \right)^{\frac{1}{n}} = \frac{1}{\lambda} \left( \frac{\int u^n f^m(u) \, du}{\int f^m(u) \, du} \right)^{\frac{1}{n}}, \tag{10.40} \]

and if \(f\) has a non-degenerate global maximum, the location of the maximum of \(f\) is given by \(\lim_{m \to \infty} \langle x \rangle_{f_m}\). We apply this family of functionals to the structure factor, \(F_{S_{(q,L)}}^{m,n} = \sqrt[\lambda]{(q^n)_{S_{(q,L)}}}\), which maps the structure factor to a wave number \(q_{m,n}(t) = q_{m,n}(0)L_0/L(t)\). Obviously, any such number can be chosen to determine the dynamic behavior of \(L(t)\).

Assuming the scaling hypothesis holds, we may take any length extracted from the structure factor as \(L\). On the other hands, for a system exhibiting multiscaling different length scales grow at different rates and the shape function does change with time. Such a system can not be characterized by a single length scale. One such system, a high dimensional conserved order parameter, was investigated by Coniglio and Zannetti [53], who found that here the shape function could be characterized by two lengths: the position of the maximum in the shape function and the width of
Figure 10.3: Left: center cross section through a phase separating system. Right: shell averaged structure factor of this field.

its peak. However, these two lengths would only differ by a logarithmic term of the time, the difference in shape function experimentally barely noticable.

Experimentally, the wavenumber $q_{\text{max}}$ for which $S(q)$ attains its maximum is typically measured. Numerically, however, $q_{\text{max}}$ cannot be determined accurately due to the discretization errors, unless the system is very large. Fig. 10.3.

illustrates this: the peak of the structure factor is not very smooth for the numerical evaluation on a $32 \times 32 \times 32$ grid. The maximum will be determined by locally fitting a parabola around its suspected location. Unlike using a functional like $q_{m,n}$ defined above this choice only uses a fraction of the number of points of $S$. The position of the maximum will also be more accurate when the structure factor will be taken as the average over a large number of numerical experiments with different
initial conditions. This may be computationally very expensive, however. Instead of using $q_{\text{max}}$, a typical measure for $L(t)$ in numerical simulations is to take the first moment of $q$ weighted by the structur factor, $q_{1,1} \equiv \langle q \rangle_{S(qL)}$. Of course, should the scaling hypothesis not hold, the scaling of $q_{1,1}(t)$ may differ from that of $q_{\text{max}}(t)$, recorded in experimental observations, albeit this difference may be weak as in the case described by Coniglio and Zannetti.

10.3.3 Numerical evaluation of $S(q)$

The structure factor is efficiently determined using the Wiener-Khinchin theorem, which states that the Fourier transform of the autocorrelation function of a function $g(r)$ equals the power spectrum of $g$

$$S(q) = \mathcal{F}_q \left\{ g(r) g(r + r') \right\} d^3 r' = |\mathcal{F}_q g|^2.$$

The Fast Fourier Transform (FFT) takes time $O(N \ln N)$ [54], $N$ being the number of nodes on the finite difference grid, while evaluating the autocorrelation function directly would take $O(N^2)$.

10.3.4 Caveats

When evaluating the moments $q_{m,n}$ for numerical experiments one needs to consider the following caveats: 1) Any moment $q_{n,m} = \sqrt{\langle q^n \rangle_{S_m}}$ of $q$ can only be used if $q^n S^m(q)$ vanishes sufficiently fast for large $q$, such that $q^n S^m(qL)$ is negligible for $q > q_N$, where $q_N = \frac{1}{2\Delta}$ is the Nyquist frequency and $\Delta$ the lattice spacing, otherwise the integral in Eq. (10.39) cannot be extended to infinity. (If the integral is over a finite extent, the scaling property in Eq. (10.38) is violated.) 2) In order to reduce
numerical round off it is advisable to integrate only up to a cut-off value $q_{\text{cut}}$, beyond which $q^n S^m$ is negligible.
Chapter 11

Problems in numerical simulations

Numerical integration of the dynamic equations using a cubic grid and using a forward-time centered-difference estimate for the time and spatial derivatives is straightforward. However, some problems should be noted.

11.1 Time step

The time step must be taken sufficiently small such that the simulation remains stable. The magnitude of this time step can be found by linear stability-analysis. In general, this will require a linear expansion of the order parameter fields $Q_{ij}$ and $\phi$ about the current state of the system. As a first approximation we may consider just the fourth derivative term arising in the dynamic equation of the conserved order-parameter. However, due to the complexity of the system, it was not feasible to get beyond this estimate. Instead we resorted to “trial and error,” where the program would adjust the timestep downward as soon as the volume fraction $\phi$ was leaving the domain $\phi \in (0..1)$. For a system without nematic ordering this would typically only adjust in the first few steps of the program and then run stable. For systems where nematic ordering would be induced by the phase separation, subsequent downward-corrections would take place, because the equilibrium liquid-crystal volume-fraction for high-order regions would become close to one (c.f. phase diagram in figure 9.6).
Figure 11.1: Numerical freezing for a grid that does not sufficiently resolve the smallest length occurring in the system. This simulation was done without nematic order parameter (Cahn-Hilliard). The scaling exponent in the first 3000 time units was 0.29 and completely stops after 60000 units. Compare this to the Cahn-Hilliard simulation in figure 12.10, where the scaling exponent is 0.335 and the coarsening does not stop after over 100000 units (the time units are the same in both simulations).

11.2 Node distance

The spatial discretization of the field must be taken sufficiently small such that the shortest length-scale occurring in the problem can be resolved. If the discretization is too coarse, the domain growth “freezes” after a while. This was pointed out by Castellano and Glotzer [55]. Figure 11.1 shows such a system. In principle, to eliminate such artifacts, simulations would need to be carried out for various discretization parameters until no more change in the scaling behavior occurs. In
Figure 11.2: Finite size effect for a volume fraction $\phi = 0.4$: because the numerical system is finite, the observed equilibrium configuration for a phase separating system is two regions separated by a straight interface.

practice, it takes a long time to carry out the simulations for a three-dimensional field. We carried out one such comparison, without nematic ordering, and found that the smallest acceptable discretization was $\Lambda/h \approx 0.17$, where $\Lambda^2$ is a coefficient of a gradient term in the dynamic equations, and $\Lambda$ is basically a molecular length, while $h$ is the distance between two nodes on the discrete grid. However, a well-defined interface appears to be a suitable indicator for a good discretization as well. (Observe the difference between figures 12.10 and 11.1.) Thus, we would visually inspect the later-stage concentration field and determine the viability of the simulation, adjusting the lattice width if necessary.
11.3 Finite-size effects

The numerical simulation is performed on a field of finite size. While the size of any physical system is necessarily limited, this size may be magnitudes larger than the field used for numerical simulation. The physical boundary is also of a different nature than the boundary used in simulation: in the former case, the boundary interacts with the enclosed material, while in the later the boundary is usually an artifact introduced to model a larger system, in particular when using periodic boundary conditions. Consider a simulation without nematic ordering. The total volume of the minority phase is its volume fraction $\phi$ times the volume of the system

$$V = \phi L^3,$$  \hspace{1cm} (11.1)

where we assume that the system is a cube of size $L^3$. States that minimize the total surface area of are: either a sphere, a cylinder or a pair of two parallel planes. Since the enclosed volume of these shapes must be the total volume of the minority phase, we can relate the surface area to the volume fraction. The respective volumes are given by

$$\frac{4\pi}{3} r_{\text{sphere}}^3 = \pi r_{\text{cylinder}}^2 L = L^2 d_{\text{plane}} = \phi L^3$$  \hspace{1cm} (11.2)

where $r_{\text{sphere}}$ and $r_{\text{cylinder}}$ are the radii of sphere and cylinder, respectively, and $d_{\text{plane}}$ is the separation of the two parallel planes.

$$r_{\text{sphere}} = \left(\frac{3}{4\pi\phi}\right)^{1/3} L, \quad r_{\text{cylinder}} = \sqrt{\frac{\phi}{\pi}} L, \quad d_{\text{plane}} = \text{arbitrary}$$  \hspace{1cm} (11.3)
Figure 11.3: Equilibrium interface shapes for a system with periodic boundary conditions (no nematic order parameter), ignoring energy cost of interface curvature.

Inserting these into the definitions for the respective surface areas yields

\[
\frac{A_{\text{plane}}}{2L^2} = 1 \tag{11.4}
\]

\[
\frac{A_{\text{sphere}}}{2L^2} = 2\pi \left( \frac{3}{4\pi} \phi \right)^{2/3} \approx 2.418\phi^{2/3} \tag{11.5}
\]

\[
\frac{A_{\text{cylinder}}}{2L^2} = \pi \sqrt{\frac{\phi}{\pi}} \approx 1.7725\phi^{1/2} \tag{11.6}
\]

The graphs of these surface areas are shown in figure 11.3.

The solution that minimizes the total surface area of the interface separating two phases given a volume fraction are: two parallel planes if \( \phi > 0.317 \), a cylinder for \( 0.154 < \phi < 0.317 \) and a sphere for \( \phi < 0.154 \). These shapes are the final shapes in the simulation for the given volume fractions if curved interfaces cost the same.
as flat ones. For a positive cost for curved interfaces, the sphere and cylinder will appear at lower volume fractions.
Chapter 12

Simulation results

12.1 Simplifications

We consider the dynamic equations (7.63), page 155, with the generalized forces given in tables 6.1 and 6.3, the local field given in table 6.2 and notation in table 6.4 (page 134 to 136). We perform the numerical integration of the dynamic equations with some significant simplifications.

- A binary, incompressible mixture of components $A$ and $B$.

- All terms containing $\langle \sigma^{B}_{ij} \rangle$, or $Q^{B}_{ij}$ are set to zero. In general, however, even if material $B$ does not exhibit a bulk nematic phase, such can be induced by the presence of concentration gradients.

- The polarizability anisotropy of material $B$ is negligible, assumed to be zero.

- The molecular volume is the same for both materials. This molecular volume is taken to be the reference volume $v_{\text{ref}}$.

- The reference temperature $T_{\text{ref}}$ is chosen to be the nematic pseudo-critical temperature $T_{AA}^{*}$ of material $A$. 

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Furthermore, the only term where the nematic order parameter couples directly to the concentration field gradient is in the effective field, and is of the form

\[
\frac{T_c}{T} s_\sigma \Lambda^2 \left( 1 + \sqrt{u^A / u^B} \right) \alpha^A_a \left[ \phi_{ij} \right]^* .
\]  (12.1)

It is mainly this term that is responsible for aligning the director with respect to the concentration field. We found that for reasonable choices of the parameters that the direction of the director would not be affected by the presence of a concentration gradient. Because our treatment does not include the anisotropy of steric interactions (we only consider the isotropic part of the pair-distribution function), it is expected that the the coupling between director and concentration gradients will be incorrect. We will therefore add a factor “\( f \)” to (12.1), enhancing the coupling of director to concentration field. To make clear that the factor is arbitrary and does not result from the presented theory, we put in in quotation marks. This factor, including its sign, ensures that all possible degrees of coupling to the interface are possible. A discussion about surface anchoring energies is for example given by Yokoyama [56].

With these assumptions, tables 6.2, 6.3, 6.1 and 6.4 simplify to tables 12.4, 12.2, 12.1 and 12.3, shown on the next pages.

The parameters used in all following simulations are summarized in table 12.1.
\[ \frac{\delta F'}{\delta Q_{ij}^A} (r) = \sum c_k f_k (r) \]

<table>
<thead>
<tr>
<th>k</th>
<th>( c_k )</th>
<th>( f_k (r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \frac{10}{3} )</td>
<td>( \phi_r^A \phi_{ij\gamma}^A \Delta_{ij\gamma}^A )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{10}{3} \Lambda_{AA}^2 )</td>
<td>( -\frac{11}{14} \phi_{ij\gamma}^A \left( (Q_{ij}^A \phi^A)_{\alpha\gamma</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{10}{3} \Lambda_{AA}^2 )</td>
<td>( \frac{12}{14} \phi_{ij\gamma}^A \left( \left( (Q_{ij}^A \phi^A)_{\alpha\gamma</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{10}{3} \Lambda_{AA}^2 )</td>
<td>( \frac{11}{14} \phi_{\alpha\gamma</td>
</tr>
</tbody>
</table>

Table 12.1: Generalized force \( \frac{\delta F'}{\delta Q_{ij|\gamma}^A} \) in an incompressible, binary mixture, simplified form.

\[ \frac{\delta F'}{\delta \phi_{ij\gamma}^A} = \sum_k c_k f_k (r) \]

<table>
<thead>
<tr>
<th>k</th>
<th>( c_k )</th>
<th>( f_k (r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( T/T_{AA}^* )</td>
<td>( \ln \phi^A - \ln (1 - \phi_{ij\gamma}^A) )</td>
</tr>
<tr>
<td>2</td>
<td>( 4T_{c}/T_{AA}^* )</td>
<td>( -\phi_{ij\gamma}^A )</td>
</tr>
<tr>
<td>3</td>
<td>( 20 \left( s_{\alpha\beta} \Lambda_{r}^2 + s_{\gamma} \Lambda_{r}^2 \right) T_c/T_{AA}^* )</td>
<td>( -\phi_{\alpha\gamma</td>
</tr>
<tr>
<td>4</td>
<td>( T/T_{AA}^* )</td>
<td>( -\ln \int \exp \left( \sigma_{\alpha\beta} H_{\beta\alpha}^A (r) \right) d^2 \sigma )</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{10}{3} )</td>
<td>( \phi_{ij\gamma}^A Q_{\alpha\gamma</td>
</tr>
<tr>
<td>6</td>
<td>( -4\alpha_{\alpha\gamma\beta\gamma}^A s_{\gamma} \Lambda_{r}^2 T_c/T_{AA}^* )</td>
<td>( \left( \phi_{ij\gamma}^A (\sigma_{\alpha\beta}^A)^{(A)}<em>{\beta\gamma\gamma} \right)</em>{\alpha\gamma</td>
</tr>
<tr>
<td>7</td>
<td>( \frac{10}{3} \Lambda_{AA}^2 )</td>
<td>( Q_{\alpha\gamma</td>
</tr>
<tr>
<td>8</td>
<td>( \frac{10}{3} \Lambda_{AA}^2 )</td>
<td>( \frac{11}{14} \left( \phi_{ij\gamma}^A Q_{\alpha\gamma}^A \right)_{\gamma\gamma</td>
</tr>
</tbody>
</table>

Table 12.2: Generalized force on \( \phi_{ij\gamma}^A \) in an incompressible, binary mixture, simplified form.
\begin{tabular}{|c|l|}
\hline
$F'$ & reduced free energy, $v_A F/k_B T_{AA}^*$ \\
\hline
$\alpha_{\parallel}/\alpha_{\perp}$ & larger/smaller eigenvalue of the molecular polarizability \\
\hline
$\bar{\alpha}^X$ & average molecular polarizability $\left(2\alpha_{\perp}^X + \alpha_{\parallel}^X\right)/3$ \\
\hline
$\alpha_{\parallel}^A$ & relative polarizability anisotropy of material $A$, $\left(\alpha_{\parallel}^A - \alpha_{\perp}^A\right)/\bar{\alpha}^A$ \\
\hline
$(h\nu)_{XY}$ & quantum-mech. oscillator-strength of pair $X - Y$ (London theory) \\
\hline
$A_{XY}$ & interaction parameter for the pair $X - Y$, $\frac{3}{2} (h\nu)_{XY} \bar{\alpha}^X \bar{\alpha}^Y / (4\pi\varepsilon_0)^2$ \\
\hline
$u_{XY}$ & a characteristic energy of the pair $X - Y$, $\frac{4\pi}{15} A_{XY} / v^X v^Y$ \\
\hline
$\langle \sigma_{ij}^A \rangle^{(A)}$ & the canonical average of $\sigma_{ij}^A$ in the field $H_{ij}^A$ \\
\hline
$\Delta_{ij}^A$ & $Q_{ij}^A - \langle \sigma_{ij}^A \rangle^{(A)}$ \\
\hline
$v^A$ & molecular volume of material $A$ (same as $B$) \\
\hline
$(\lambda_{XY}^L)^{L-3}$ & moment of the pair-distribution function, $(3 - L) \int_0^\infty g_{XY}(r) r^{L-4} dr$ \\
\hline
$\Lambda_{AA}^2$ & $(\lambda_{0}^{AA} / \lambda_{2}^{AA})^3$ \\
\hline
$\overline{\Lambda}_\sigma$ & $\left(3v^A / \sqrt{2k_B T_c}\right) \left|u_{AA}/\lambda_{2}^{AA} - u_{AB}/\lambda_{2}^{AB}\right|$ \\
\hline
$\overline{\Lambda}_\tau$ & $\left(3v^A / \sqrt{2k_B T_c}\right) \left|u_{BB}/\lambda_{2}^{BB} - u_{AB}/\lambda_{2}^{AB}\right|$ \\
\hline
$s_\sigma; s_\tau$ & $\text{sign}(u_{AA}/\lambda_{2}^{AA} - u_{AB}/\lambda_{2}^{AB})$, $\text{sign}(u_{BB}/\lambda_{2}^{BB} - u_{AB}/\lambda_{2}^{AB})$ \\
\hline
$T_{AA}^*$ & nematic pseudo-critical temperature of pure $A$–system \\
\hline
$T_c$ & crit. temperature for a phase-separating system w/o nematic order \\
\hline
\end{tabular}

Table 12.3: Definition of terms used in $\delta F'/\delta Q_{ij}^A$, $\delta F'/\delta \rho^A$ and effective field $H_{ij}^A$, simplified form.
\[ H_{ij}^A(r) = \sum c_k f_k(r) \]

| \[ \frac{10}{3} T_{AA}^*/T \] | \[ \phi_{ij}^A Q_{ij}^A \] |
| \[ \frac{10}{3} (T_{AA}^*/T) \left\{ \frac{6}{5} (T_c/T_{AA}^*) \right\} s_{\gamma} \bar{\alpha}_d \alpha_d^A f^* \] | \[ \phi_{ij}^A \] |
| \[ \frac{10}{3} (T_{AA}^*/T) \Lambda_{AA}^2 \] | \[ \frac{11}{14} \phi_{ij}^A Q_{ij}^A - \frac{12}{14} \left[ Q_{ij}^A \phi_{ij}^A \right] \] |

Table 12.4: Effective field \( H_{ij}^A \) in a binary, incompressible mixture; simplified form.

<table>
<thead>
<tr>
<th>ref.</th>
<th>fig.</th>
<th>( \frac{\Lambda_{AA}^2}{h^2} )</th>
<th>( s_{\sigma} \bar{\Lambda}_d^2 / h^2 )</th>
<th>( s_{\tau} \bar{\Lambda}_\tau^2 / h^2 )</th>
<th>“( f^* )”</th>
<th>( T / T_{AA}^* )</th>
<th>( \Gamma )</th>
<th>( \alpha_d^A )</th>
<th>( \phi_0 )</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>12.11</td>
<td>0.1212</td>
<td>0.03672</td>
<td>-0.01272</td>
<td>-19.608</td>
<td>0.82</td>
<td>10</td>
<td>1/3</td>
<td>0.4</td>
<td>64</td>
</tr>
<tr>
<td>02</td>
<td>12.8</td>
<td>0.1212</td>
<td>0.07272</td>
<td>n/a</td>
<td>100.02</td>
<td>0.82</td>
<td>n/a</td>
<td>1/3</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>03</td>
<td>12.10</td>
<td>n/a</td>
<td>0.0160</td>
<td>0</td>
<td>n/a</td>
<td>0.82</td>
<td>n/a</td>
<td>n/a</td>
<td>0.4</td>
<td>64</td>
</tr>
<tr>
<td>04</td>
<td>12.13</td>
<td>0.0808</td>
<td>0.0216</td>
<td>-0.0056</td>
<td>19.608</td>
<td>0.82</td>
<td>10</td>
<td>1/3</td>
<td>0.4</td>
<td>64</td>
</tr>
<tr>
<td>05</td>
<td>12.9</td>
<td>0.1212</td>
<td>0.07272</td>
<td>n/a</td>
<td>-166.67</td>
<td>0.82</td>
<td>n/a</td>
<td>1/3</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>06</td>
<td>11.2</td>
<td>n/a</td>
<td>0.0160</td>
<td>0</td>
<td>n/a</td>
<td>0.82</td>
<td>n/a</td>
<td>n/a</td>
<td>0.4</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 12.5: Simulation parameters for the dynamic equations:

\[ Q_{ij}^{t+ \tau} = Q_{ij}^t + \Gamma Q (\delta F' / \delta Q_{ij})_{ij}, \quad \phi_{ij}^{t+ \tau} = \phi_{ij}^t + \Gamma_{ij} \nabla \cdot (\phi (1 - \phi) \nabla F'/\delta \phi) \]

with \( \delta F' / \delta Q_{ij} \) and \( \delta F'/\delta \phi \) given in tables 12.1 and 12.2.
12.2 Eigenvalue exchange in a strongly deformed system

In a hybrid nematic cell the director anchors parallel to one surface and perpendicular to the opposite surface (figure 12.1). Palffy-Muhoray, Gartland and Kelly [15] (PGK) have investigated this system using a free energy density of the form

\[ \mathcal{F} = \frac{1}{2} A \text{Tr} \, Q^2 + \frac{1}{3} B \text{Tr} \, Q^3 + \frac{1}{4} C \text{Tr} \, Q^4 + \frac{1}{2} L Q_{\alpha \beta \gamma} Q_{\alpha \beta \gamma} \]  

(12.2)

and found that apart from the solution where the director pretilt \( \theta \) varies linearly with distance to the surface, \( \theta = \pi / 2 \cdot z \), an additional solution is given where the eigensystem remains fixed and the eigenvalues of \( Q \) exchange positions. They found that for strong deformations, or a very thin cell, the eigenvalue-exchange solution is the only one. It is here of interest to perform simulations on a hybrid cell: first, this allows us to test the program. Second, like the nematic liquid crystal encapsulated in a spherical droplet, it represents a geometry that requires the complete tensor representation. Third, it is relevant that the eigenvalue-exchange mode exists, because in a phase-separating system, the initial state of the system may consist of tiny droplets, which therefore form a strongly deformed system.

12.2.1 Simulation

We perform simulated annealing on a system with the generalized forces given by tables 12.1, 12.2 and 12.4. The system has the following geometry: the nematic liquid crystal is held between two parallel plates that extend to infinity and are separated by a distance \( d \). The \( \hat{x} \)-axis is taken to be along the normal of the plates. We assume that the system varies only along the \( \hat{x} \)-axis, with interval ends at \( x_0 \) and \( x_1 \) – i.e., we do not permit solutions that are periodic along any axis perpendicular to \( \hat{x} \). We
use the following boundary conditions: At both ends the anchoring is infinite, the nematic order parameter $Q_{ij}$ is uniaxial, and the scalar order parameter $S$ is fixed to the equilibrium value of a homogenous system at the given temperature, which we set below $T_{NI}$, the nematic-isotropic transition temperature ($T_{NI} \approx 1.10097$). At $x_0$ the director is parallel to the surface, at $x_1$ it is perpendicular. We take the $\hat{y}$-axis as the direction of the director at $x_0$. The director in the bulk can in principle have a component along $\hat{z}$, but in practice this was not observed for any late-stage configuration. Thus when presenting the results, we represent the orientation of the director by the polar angle $\theta$ only, where $\cos \theta = \hat{x} \cdot \hat{N}$ and $\hat{N}$ is the director. For a pure liquid crystal the volume fraction $\phi^A$ is one, and the dynamic equations become

$$\frac{\delta F}{\delta Q_{ij}^A} = \frac{10}{3} \left\{ Q_{ij}^A - \langle \sigma_{ij} \rangle_{H_{ij}^A} - \frac{11}{14} \Lambda_{AA}^2 Q_{ij,aa}^A + \frac{12}{14} \Lambda_{AA}^2 [Q_{io,ij}]^\# \right\},$$

(12.3)

Figure 12.1: A hybrid cell - the director is anchored homeotropically on one side and parallel on the other. Top: strong deformation keeps the eigenframe constant, but the eigenvalues exchange positions. Bottom: weak deformation leads to rotation of the director.
where \([\cdot]^{\#}\) denotes traceless, symmetric projection, and the local field is given by

\[
H_{ij}^A = \frac{10 T^*}{3 \bar{T}} Q_{ij}^A.
\]  

(12.4)

The second gradient-term in 12.3 for a one-dimensional system that only varies along \(\hat{x}\) is given by

\[
Q_{\alpha,\alpha j} = \begin{cases} 
Q_{xx,xx} & i = j = x \\
0 & \text{otherwise}
\end{cases}.
\]  

(12.5)

PGK use parameters \(a \equiv A/C, b \equiv B/\sqrt{6}C\) and \(d^2 C/L\), where \(a\) is essentially temperature (\(a = 0\) corresponding to the nematic pseudo-critical temperature \(T^*\)) and \(L/d^2 C\) is the strength of the deformation. Because the dynamic equation (12.3) does not employ a power series expansion, we cannot directly compare it to those derived from Eq. (12.2). In fact, for a pure liquid-crystal system the only adjustable parameters in (12.3) are reduced temperature and system size in units of molecular length (which is approximately the same as \(\Lambda_{AA}\)). We thus only present qualitative results. In the following graphs we define an absolute value of \(Q_{ij}\) as \(|Q| \equiv \sqrt{\left(\frac{2}{3}\right) Q_{\alpha \beta} Q_{\beta \alpha}}\), which is the same as the parameter \(r\) introduced in section 10.2.2 and is a measure of total order.

First, we performed simulations for the free energy density (12.2) used by PGK for various parameters, demonstrating the different modes of deformation. These are shown in figures 12.2 through 12.4. Then we perform analogous simulations for the dynamic equation (12.3), whose results are displayed in figures 12.5 through 12.7.
Figure 12.2: Late stage configuration for a hybrid cell with the free energy by PGK: rotational mode. For sufficiently large cell the director pretilt $\theta$ varies linearly throughout the cell and the order parameter $S$ stays constant. No biaxiality is observed.

Figure 12.3: Hybrid cell with the free energy by PGK: rotational mode for strong deformation. For a cell of intermediate width, the director pretilt $\theta$ deviates from varying linearly throughout the cell. The order parameter $S$ slightly decreases in the bulk, and significant biaxiality $P$ is observed.
Figure 12.4: Hybrid cell with the free energy by PGK: eigenvalue exchange mode. For a narrow cell, the director pretilt stays constant, except at the center, where the eigenvector associated with the largest eigenvalue changes position. The order parameter $S$ varies strongly and becomes negative in the center of the cell. The biaxiality $P$ is significant, but vanishes in the center.

Figure 12.5: Late stage configuration for a hybrid cell, dynamic equations (12.3): rotational mode. Unlike the rotational mode for the PGK free-energy, the director pretilt slightly deviates from linear variation.
Figure 12.6: Hybrid cell with dynamic equation (12.3): rotational mode for strong deformation. Unlike PGK, Fig. 12.3, the configuration is not symmetric with respect to the center of the cell.

Figure 12.7: Hybrid cell, dynamic equations (12.3): eigenvalue exchange mode. The result is similar to that of PGK, Fig. 12.4, but not symmetric about the center.
12.2.2 Results and discussion

Figures 12.5 through 12.7 qualitatively display the modes predicted by PGK. However, in all cases there is a deviation from the symmetry of the PGK solution: The rotational mode Fig. 12.5 deviates slightly from linear variation in the pretilt angle $\theta$, the other modes are not symmetric about the center of the cell. Of course, PGK implement the deformational energy using a one-constant approximation, while the dynamic equation (12.3) contains two distinct elastic terms $\frac{11}{14}\Lambda_{AA}^2 Q_{ij,\alpha\alpha}$ and $-\frac{12}{14}\Lambda_{AA}^2 [Q_{i\alpha,\alpha\alpha}]^\#$. (We find that omitting the second term does indeed yield a symmetric configuration.) If only the director is considered, however, both terms are the same in our geometry: the de Gennes elastic terms are given by

$$F_{\text{de Gennes}}^{\text{elastic}} = \frac{1}{2} L_1 Q_{ij,\gamma} Q_{ij,\gamma} + \frac{1}{2} L_2 Q_{ij,\gamma} Q_{ij,\beta},$$  \hspace{1cm} (12.6)

and for constant $S$ and $P$, these relate to the Oseen-Frank elastic free energy by [57]

$$K_{11} = K_{33} = L_1 + \frac{L_2}{2} \hspace{1cm} (12.7)$$

$$K_{22} = L_1. \hspace{1cm} (12.8)$$

The generalized force on $Q_{ij}$ using this free energy, on the other hand yields

$$\frac{\partial F_{\text{de Gennes}}^{\text{elastic}}}{\partial Q_{ij}} = -L_1 Q_{ij,\alpha\alpha} - L_2 [Q_{i\alpha,\alpha\alpha}]^\# \hspace{1cm} (12.9)$$

and therefore, in our case

$$K_{11}/K_{22} = \frac{11 - 6}{11} = \frac{5}{11}. \hspace{1cm} (12.10)$$

Thus the twist elastic coefficient $K_{22}$ is about twice as large in our dynamic equations as the splay- and bend-term ($K_{11}$ and $K_{33}$), respectively, while in the one-constant
approximation by PGK $L_2 \equiv 0$ and thus

$$K_{11} = K_{22} = K_{33}. \quad (12.11)$$

However, the late-stage configuration in all cases exhibits no twist deformation - the director stays in the $\hat{x} - \hat{y}$ plane everywhere and does not vary along $\hat{z}$. Thus the value of $K_{22}$ is irrelevant. The reason that the configurations for Eq. (12.3) do not exhibit the same spatial symmetry must then be due to the fact that the order parameter $S$ and $P$ vary throughout space.

Finally, we remark that for low temperatures in the eigenvalue-exchange mode, Fig. 12.7, the order parameter $S$ becomes negative in the center, rather than "melting" into the isotropic phase. This can be understood by considering that, in the underformed state and below then nematic pseudo-critical temperature, the free energy has a local minimum for negative order parameter $S$ (c.f., Fig. 9.2, page 175 and Fig. 9.3, page 177). Here the order parameter decreases the free energy by moving into a state that corresponds to a local free energy minimum in the undeformed state, while reducing the cost of the gradient terms in the free energy.

12.3 Fixed spherical concentration field

The following numerical experiments are performed with a fixed concentration field. The concentration field is created the following way: first an arbitrary concentration field of spherical symmetry is initialized and let relax to equilibrium. Next a nematic order parameter field is initialized and let relax, but this time the concentration field is held constant. This permits us to observe the behavior of the director in a model droplet more closely. The alignment preference of the director with respect to the
droplet interface is essentially determined by the $\phi_{ij}$-term in the local field $H_{ij}$, table 12.4. A positive sign leads to preferred alignment perpendicular to the concentration gradient (parallel to the surface) and a negative sign to alignment parallel to the concentration gradient (perpendicular to the surface). We will call the situations “parallel” and “homeotropic” coupling, respectively.

12.3.1 Bipolar director configuration

Figure 12.8 shows the late stage configuration for preferred parallel coupling in three orthogonal cross-sections through the center of the droplet. The parameters for this simulation are given in table 12.1, reference-number 02.

12.3.2 Radial director configuration

Figure 12.9 shows the late stage configuration for preferred homeotropic coupling for different times. The simulation parameters are given in table 12.1, reference-number 05. Here the director field was initially homogenous. A ring defect appears first at the surface and contracts towards decreasing radius until it collapses to a radius smaller than the finite difference cell. Depending on various parameters of the system (temperature, elastic constants, strength of the surface coupling) the system can evolve either towards a single isotropic core (a purely radial configuration), a “split core,” with two isotropic cores or a biaxial ring defect. Gartland and Mkaddem [13] have performed a stability analysis on these situations and determined that the radial configuration is always unstable for sufficiently low temperature. Kralji Virga and Žumer [14] have shown that the ring defect attains maximum biaxiality at the
center of the torus.

12.4 Simulations

12.4.1 Cahn-Hilliard model

Figure 12.10 shows a simulation with the nematic order parameter held zero, corresponding to the limit of a Cahn-Hilliard free energy. The parameters for this simulation are given in table 12.1, reference number 03. The scaling exponent is approximately 1/3. The domains are predominantly spherical but slightly deformed due to the attractive interaction between liquid-crystal droplets.

12.4.2 Homeotropic coupling

Figure 12.11 shows the evolution of a phase separating binary mixture with homeotropic coupling of the director to the nematic-isotropic interface. The parameters for this simulation are given in table 12.1, reference number 01. The dynamic scaling of the domain size is shown in figure 12.12. Note the cross-over from a growth exponent of about 1/2 to one of about 1/3. This slow down may be attributable to collective motion of defects.

12.4.3 Parallel coupling

Figure 12.13 shows the respective dynamics for parallel coupling of the director to the nematic-isotropic interface. The parameters for this simulation are given in 12.1, reference number 04. The top left image shows the dynamic scaling of the domain size, which is about 0.4 for all times (the very late stages may be affected by the finite size of the simulation field).
Figure 12.8: Simulation with fixed spherical concentration field, coefficient of $\varphi_{ij}$ in the local field $H_{ij}$ positive. Top left: concentration profile through the center of the sphere. Top right to bottom right: order parameter field for three orthogonal cross sections through the center of the sphere.
Figure 12.9: Simulation with fixed spherical concentration field, coefficient of $\varphi_{ij}$ in the local field $H_{ij}$ negative. Top left to bottom right: order parameter field of a cross section through the center of the sphere for increasing times.
Figure 12.10: Simulation without nematic order parameter. Top right: scaling behavior. Top left to bottom left: cross section of the concentration field for three times (marked by arrows in scaling plot); $\varphi$ is volume fraction of liquid crystal, red regions are l.-c. rich.
Figure 12.11: Evolution of a nematic binary mixture: homeotropic coupling.
Figure 12.12: Dynamic scaling of the domain size for the simulation in Fig. 12.11.

The arrows reference the points in simulation-time of the respective snapshots.
Figure 12.13: Evolution of a nematic binary mixture: parallel coupling.
Part II

Viscous Fingering in Shear Thinning Fluids
Chapter 13

Overview

This chapter gives a bird’s eye view of the contents of the second part of this dissertation. This part describes experimental work on viscous fingering in a radial Hele-Shaw cell using a shear thinning fluid. Chapter 14 introduces Hele-Shaw experiments as a hydrodynamic analog to the problem of dendritic growth in solidification. We remark on experiments in liquid crystal experiments that had led to the suggestion that shear thinning can cause dendritic fingers, not only surface tension anisotropy, which is the currently accepted mechanism for dendritic growth in solidification. In chapter 15 we describe some experimental considerations, in particular the required thickness of glass plates for the radial Hele-Shaw cell. In chapter 16 we introduce the phenomenological description of shear thinning fluids, which introduces experimentally accessible parameters that are used for comparison with simulation. In chapter 17 we describe the material that we chose for our experiments, and why. We also present the viscosity function that we have measured for this material. In chapter 18 we describe in detail the experimental setup used. In chapter 19 we introduce an algorithm used to characterize the shape of the tip of the dendritic fingers. In chapter 20 we describe the experimental procedure followed and present the result of the experiments and discuss them.
Chapter 14

Introduction

In a Hele-Shaw experiment a fluid is contained in the narrow gap between two parallel plates[58]. Hele-Shaw originally demonstrated experimentally that under these conditions the flow is governed by Laplace's equation and therefore can be treated theoretically analogous to electrostatic problems. Hele-Shaw experiments, in which one fluid drives a second one, exhibit interesting fingering patterns. If a fluid displaces an immiscible fluid of higher viscosity, an initially linear interface (in a rectangular setup) is unstable and will form a finger of a characteristic width of $1/2$ the channel width. This is known as the Saffman-Taylor instability[59]. In a radial geometry, instead a discrete number of fingers form and exhibit characteristic patterns. For example, figure 14.1 shows the characteristic pattern for the propagating front for a Newtonian fluid driven by air. In particular, for Newtonian fluids the fingers grow until the radius of curvature at the front exceeds a limiting value and then split. The branched fingers grow again, until they split again, and so on.

Hele-Shaw experiments serve as a hydrodynamic analog for the solidification problem. Here, they played historically an important role in verifying the role of surface tension anisotropy as being the critical ingredient to describe dendritic growth in solidification. The latter was a long standing problem, going back as far as to a paper by J. Kepler on the growth of snowflakes. A significant step was made by
Ivantsov [60], who showed that a stationary solution to the problem of a growing needle crystal was given in two dimensions by a parabola, or a paraboloid of revolution in three dimensions. The condition for existence of this solution fixes the product of tip-radius and propagation velocity as a function of dimensionless undercooling. Specifically, the undercooling is defined as

$$\Delta = \frac{T_m - T_\infty}{Lc_p^{-1}},$$

where $T_m$ is the melting temperature of the bulk, $T_\infty$ the temperature in the liquid phase far from the interface, and $L/c_p$ — the ratio of latent heat of the solid-liquid transition to heat capacity — a suitable temperature unit. Then the Ivantsov existence condition is given by

$$\Delta = 2\sqrt{Pe} \exp(Pe) \int_{\sqrt{Pe}}^{\infty} \exp(-t^2) \, dt,$$
with
\[ P_e = \frac{\rho_{\text{tip}} u}{2D} \] \hfill (14.3)

the Péclet number, and \( D \) is the diffusivity. Unfortunately, the Ivantsov solution only fixes the product \( \rho u \), but cannot determine either one individually, leaving the problem of wavelength selection open. Furthermore, the Ivantsov solution is unstable for arbitrarily small wavelength perturbations. The selection problem was not satisfactorily solved until the mid 1980’s, when it was shown by Kessler, Koplik and Levine [61] that introducing surface tension anisotropy to the problem creates a singular perturbation, with the result that a denumerably infinite set of solutions arises, only one of which – the fastest growing one – is stable. This theory is also known as the microscopic solvability theory. Subsequently experiments in Hele-Shaw cells were carried out, where anisotropy was imposed by etching the surface of the cell, that verified that introducing surface tension anisotropy leads to dendritic fingering[62].

(One should mention that Xu [63] claims to have developed a superceding, dynamic theory, which he calls “Interfacial Wave Theory”. At the time of this writing this theory appears to have found little acceptance, yet.)

Buka, Palffy-Muhoray and Rácz have performed Hele-Shaw experiments in nematic liquid crystals, in which they observed dendritic fingers. They propose that the origin of dendritic fingers is due to flow-induced viscosity anisotropy, rather than surface tension anisotropy. Since for liquid crystals the anisotropy of viscosity and surface tension are experimentally hard to separate, a system was needed without surface tension anisotropy that also exhibits flow-induced viscosity anisotropy:
shear-thinning materials. Kondic, Shelley and Palffy-Muhoray developed a theory for viscous fingering in shear-thinning fluids [64], and performed simulations [65] that show that shear-thinning alone can lead to dendritic viscous fingering. The present work was originally intended to verify these predictions.
Chapter 15

Experimental considerations

15.1 Darcy's law in parallel-plate geometries

For flow subject to Darcy's law, the velocity field is the gradient of a potential and the problem can be treated by potential theory: the original experiments by Hele-Shaw [58] exhibit this fact, where he compares the flow-lines of water through a narrow gap with results from two-dimensional electromagnetic theory. The fact that this kind of flow is governed by Darcy's law implies that the pressure field is determined by Laplace's equation, which enables us to use it as a hydrodynamic analog for the solidification problem.

Darcy's law for flow in porous media states that the fluid velocity is proportional to the permeability $\kappa$ of the medium

$$u(r) = \frac{\kappa}{\eta} (f_b - \nabla p),$$  \hspace{1cm} (15.1)

where $\eta$ is shear-viscosity, $f_b$ are body-forces, usually gravitation, and $\nabla p$ is an externally applied pressure gradient. For horizontally constrained flow, then

$$u(r) = -\frac{\kappa}{\eta} \nabla p.$$  \hspace{1cm} (15.2)

This section demonstrates that incompressible flow through a narrow parallel gap is governed by Darcy's law with a permeability of $\kappa = b^2/12$.

We consider incompressible ($\nabla \cdot u = 0$) flow between parallel plates, arranged

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horizontally to eliminate the effect of gravitational forces. The viscosity is assumed to be constant. The Navier-Stokes equation for such a system is given by

\[ \rho \frac{D}{Dt} \mathbf{u} = - \nabla p + \eta \Delta \mathbf{u}. \]  
(15.3)

For sufficiently low Reynolds numbers, the kinetic term on the left-hand side can be neglected as well, yielding

\[ \nabla p = \eta \Delta \mathbf{u}. \]  
(15.4)

We now consider the following geometry (Fig. 15.1): two parallel plates whose surface normal is along \( \hat{e}_x \) and separated by a vertical gap \( b \). The plates extend to infinity along \( \hat{e}_y \). The flow is linear along \( \hat{e}_x \) (\( u_x = u_y = 0 \) and therefore \( u = |\mathbf{u}| = u_x \)) and not periodic along \( \hat{e}_y \) (symmetry then requires \( \partial_y = 0 \)). The last condition is not self-evident, but we take it as experimental fact: a salient observation made by Hele-Shaw [58] was that flow through a narrow gap does not exhibit sinusoidal motion. Equation (15.4) for the \( y \) and \( z \) components are

\[ \partial_y p = \partial_z p = 0 \]  
(15.5)

from which immediately follows that \( p \) is a function of \( x \) only, and the \( x \)-component of (15.4) yields

\[ \frac{d}{dx} p(x) = \eta \left( \partial_x^2 + \partial_z^2 \right) u(x, z). \]  
(15.6)
The continuity equation is given by

\[ \partial_z u(x, z) = 0, \]  
(15.7)

thus \( u \) is a function of \( z \) only

\[ u = \Phi(z), \]  
(15.8)

and the momentum-balance equation (15.4) becomes

\[ \frac{d}{dx} p = \eta \frac{d^2}{dz^2} u, \]  
(15.9)

which can be integrated along \( dz \), yielding

\[ u(z) = \alpha + \beta z + \frac{1}{2\eta} \left( \frac{d}{dx} p \right) z^2. \]  
(15.10)

The coefficients \( \alpha \) and \( \beta \) are determined by the boundary-conditions. If we assume no slip boundary conditions, then \( u(-b/2) = u(b/2) = 0 \), yielding

\[ \beta = 0 \]  
(15.11)

\[ \alpha = -\frac{1}{2\eta} \left( \frac{d}{dx} p \right) \left( \frac{b}{2} \right)^2 \]  
(15.12)

and a velocity profile

\[ u(y) = \frac{1}{2\eta} \frac{p_x b^2}{b} \left( \left( \frac{y}{b} \right)^2 - \frac{1}{4} \right). \]  
(15.13)

The gap averaged velocity is given by

\[ \bar{u} = \frac{1}{b} \int_{-b/2}^{b/2} u(y) \, dy = \frac{b}{2\eta} \left( \frac{d}{dx} p \right) \left\{ -\frac{1}{4} b + \frac{b}{12} \right\} \]  
(15.14)

and Darcy's law in this geometry reads

\[ \bar{u}(x) = -\frac{b^2}{12\eta} \nabla p(x). \]  
(15.15)
Equation (15.15) is for flow of purely rectangular geometry. However, we can always choose a local frame \((\hat{e}_\zeta, \hat{e}_\eta, \hat{e}_\zeta)\) in which the velocity is parallel to \(\hat{e}_\zeta\). We assume that for incompressible flow between parallel plates the velocity vector remains parallel to the plates everywhere. Then we can choose the frame \((\hat{e}_\zeta, \hat{e}_\eta, \hat{e}_\zeta) = (\hat{x}, \hat{y}, \hat{z})\), with \(\hat{x}\), \(\hat{y}\) and \(\hat{z}\) as above. Finally, the pressure gradient is assumed to be along the velocity vector (this will not in general hold for liquid crystals). Then the same argument as above applies whenever the in-plane curvature of the constant-pressure surface is sufficiently small such that setting \(\partial_y = 0\) is a good approximation (small-gap limit). We arrive at Darcy's law for flow of a Newtonian, incompressible fluid through a narrow gap, given by

\[
\bar{u}(r) = -\frac{b^2}{12\eta} \nabla p(r),
\]  

(15.16)

which holds for sufficiently small Reynolds's numbers (required for non-sinusoidal flow) and a flow profile, for which the radius of curvature \(R\) of the surfaces of constant pressure is sufficiently large. (In particular, \(R\) must be much larger than the gap width \(b\), so that \(\partial_y \ll \partial_z\).) For an incompressible fluid \(\nabla \cdot \bar{u} = 0\), therefore, for incompressible flow through a narrow gap, the pressure field obeys Laplace's equation, \(\nabla^2 p = 0\).

### 15.1.1 Radial flow

Given that incompressible flow through a narrow parallel gap is governed by Eq. (15.16), we now turn our attention to radial flow. We use cylindrical coordinates \((\hat{r}, \hat{\varphi}, \hat{z})\) and consider purely radial flow, where \(\mathbf{u} = u_r \hat{r}\). The continuity equation in cylindrical
coordinates reads
\[ \frac{1}{r} \frac{\partial}{\partial r} (ru_r) = 0. \] (15.17)

For \( r \neq 0 \) this implies that
\[ ru_r = \Phi(z), \] (15.18)

where \( \Phi \) is a function of \( z \) only. The gap average of \( u_r \) is given by
\[ \bar{u}_r = \frac{1}{rb} \int_{-b/2}^{b/2} \Phi(z) \, dz = \frac{c}{r}, \]

where \( c \) is a constant. As before, the Navier-Stokes equations for the \( \varphi- \) and \( z- \) coordinate imply that \( p \) is a function of \( r \) only. We assume that (15.16) holds, thus
\[ -\frac{b^2}{12\eta} \frac{dp}{dr} = \frac{c}{r}. \] (15.19)

The constant \( c \) can be determined from boundary conditions. Integrating from \( r_0 \) to \( r_1 \) yields
\[ -\frac{b^2}{12\eta} \left(p(r_1) - p(r_0)\right) = c \ln \frac{r_1}{r_0}. \] (15.20)

If \( p_0 \equiv p(r_0) \) and \( p_1 \equiv p(r_1) \) are known, then
\[ c = \frac{b^2}{12\eta} \frac{p_0 - p_1}{\ln r_1/r_0}. \] (15.21)

In particular, setting \( r = r_1 \) in (15.20) the pressure as a function of position can now be expressed as
\[ p(r) = p_0 - (p_0 - p_1) \ln \frac{r}{r_0}. \] (15.22)
15.2 Plate bending

Originally, I performed experiments using a circular Hele-Shaw cell made from 1/4” window pane, because such glass is easily available. When experiments showed that dendritic fingers could be observed in dilute Xanthan solution, but only at high shear-rates, the question arose whether the plates would significantly bend and therefore distort the quantitative analysis of the finger shape. In this section we show that a plate of thickness 0.25” and radius of the order of 10 cm bends significantly under conditions that in dilute Xanthan solution yield viscous fingers of dendritic shape. This bending causes the gap at the center of the plates to expand to double its original size. We then show that plate bending can be reduced to less than five percent of change in the original gap, by using plates of an aspect ratio of radius over thickness less than six.

A circular plate of radius $R$ and thickness $h$ is clamped at the circumference and subject to pressure $p$ applied to one side. In the limit of a thin plate ($h/R << 1$), the (small) displacement $\zeta$ normal to the plate at distance $r$ from the center is given by [66]

$$\zeta_{rr} = \frac{3}{16} k_{\text{mat}} p \frac{R^4}{h^3} \left( 1 - \left( \frac{r}{R} \right)^2 \right)^2,$$

(15.23)

where $k_{\text{mat}}$ is a material constant, given by

$$k_{\text{mat}} = \frac{(1 - \sigma^2)}{E},$$

(15.24)

with material parameter $E$ the modulus of extension (Young’s modulus) and $\sigma$ the Poisson ratio. The displacement is given by Eq. (15.23) for a plate under homogenous load. We are interested, however, in an inhomogenous pressure of the following form:
A circular air bubble, with center at \( r = 0 \) and radius \( r_0 \) is under pressure \( p_0 \), while the pressure decays logarithmically between \( r_0 \) and the perimeter of the Hele-Shaw cell at \( r_1 \) according to Eq. (15.22). Instead of solving the complete problem for an inhomogeneously loaded plate, we use the solution of the homogeneously-loaded plate problem to find a lower limit for the plate-displacement. The force \( df \) acting on an area element \( r \cdot r + dr \) of the plate is given by

\[
\frac{f}{2\pi} = \left( p_{\text{inside}} - p_{\text{outside}} \right) 2\pi r dr
\]

where \( p_{\text{outside}} \) is the atmospheric pressure, which is pressing inward and \( p_{\text{inside}} \) is the driving pressure, given by Eq. (15.22), which presses outward. The total force acting outward is the integral of this over the whole plate, where we note that \( p_{\text{outside}} \equiv p_1 \):

\[
\frac{f}{2\pi} = \int_0^{r_0} (p_0 - p_1) r dr + \int_{r_0}^{r_1} \left( p_0 - (p_0 - p_1) \frac{\ln r}{r_0} - p_1 \right) r dr
\]

\[
= \frac{1}{2} \frac{p_0 - p_1}{2 \ln r_1 / r_0} \left( 1 - \left( \frac{r_0}{r_1} \right)^2 \right) \].

(15.27)

If we now assume that this total force is distributed homogeneously over the plate surface, then the pressure is given by

\[
p = \frac{f}{\pi r_1^2} = \frac{(p_0 - p_1)}{2 \ln r_1 / r_0} \left( 1 - \left( \frac{r_0}{r_1} \right)^2 \right)
\]

(15.28)

and entering this into (15.23) yields for the lower bound \( \zeta^* \) of the displacement

\[
\zeta^*_{r} = \frac{3}{16} k_{\text{max}} \frac{(p_0 - p_1)}{2 \ln R / r_0} \left( 1 - \left( \frac{r_0}{R} \right)^2 \right) \frac{R^4}{h^3} \left( 1 - \left( \frac{r}{R} \right)^2 \right)^2.
\]

(15.29)

It is clear that distributing the force such that more force is applied towards the perimeter should yield less bending, because the force has less leverage close to the boundary.
Young’s modulus for glass is between 40 and 90 GPa, the Poisson ratio between 0.19 and 0.28 [67]. The range of possible values of \( k_{\text{mat}} \) is therefore

\[
k \in \left[ \frac{1 - \sigma_{\text{min}}^2}{E_{\text{max}}} \cdots \frac{1 - \sigma_{\text{max}}^2}{E_{\text{min}}} \right] = [1.071 \cdot 10^{-11} \cdots 2.304 \cdot 10^{-11}] \text{ Pa}^{-1} \tag{15.30}
\]

The original glass plates had a radius of \( R = 12 \text{ cm} \) and a thickness \( h = 0.25\text{"} \). For such plates, the lower limit \( \zeta^* \) of the displacement at the center of the cell per 10 kPa applied pressure is

\[
\zeta^* = \frac{k_{\text{mat}}}{10^{-11} \text{ Pa}^{-1}} \frac{p}{10^4 \text{ Pa}} 10^4 10^{-11} \frac{3}{16} (12 \cdot 10^{-2})^4 1 \frac{1 - \frac{r_0}{r_{\text{mm}}}}{2} \left( \frac{1}{120} \right)^2 \ln \frac{120}{r_0/r_{\text{mm}}} \tag{15.31}
\]

\[
= \frac{k_{\text{mat}}}{10^{-11} \text{ Pa}^{-1}} \frac{p}{10^4 \text{ Pa}} 7.59\mu\text{m} \frac{1 - \frac{r_0}{r_{\text{mm}}}}{2} \left( \frac{120}{r_0/r_{\text{mm}}} \right)^2 \tag{15.32}
\]

and twice this for the change in gap. In particular, consider a gap of 50\( \mu\text{m} \) and a bubble with \( r_0 = 5\text{mm} \), then

\[
\frac{b_{\text{bent}}}{b_{\text{rest}}} \geq 1 + \frac{2\zeta^*}{50\mu\text{m}} \tag{15.33}
\]

where

\[
\frac{2\zeta^*}{50\mu\text{m}} \in [1.071\ldots2.304] \frac{p}{10^4 \text{ Pa}} 0.096 \tag{15.34}
\]

Thus for each meter of water column applied pressure (\( \approx 10 \) kPa) the gap in the center changes at least by ten percent. At applied pressures of the order of one atmosphere (\( \approx 100 \) kPa), the gap changes to about twice its width at rest. Conversely, we seek a condition such that the gap changes less that five percent, for a spacing as small as 19\( \mu\text{m} \). Hence we require that

\[
0.05 = \frac{2\zeta^*}{19\mu\text{m}} \geq \frac{1}{9.5\mu\text{m}} \frac{3}{16} k_{\text{mat}} \frac{(p_0 - p_1)}{2 \ln R / r_0} \left( 1 - \left( \frac{r_0}{R} \right)^2 \right) \frac{R^4}{h^3} \tag{15.35}
\]
The parameter $k_{\text{mat}}$ is mostly beyond our control. (Fortunately, the thick glass plates that we require – telescope blanks or optical flats – are typically made from fused silica, which is very rigid and yields $k_{\text{mat}}$ values at the low end of the available range.) We also require sufficiently high shear rates to observe dendritic fingers, but need a tip velocity slow enough that we can capture a sequence of interface images. Experimental experience (for the case of dilute solution of Xanthan) tells us that for a gap of the order of tens of micrometers, the pressure we need is on the order of one atmosphere. We assume that the lowest shear-rate at which we can observe dendrites is given. The shear rate is approximately $\dot{\gamma} \approx u_\tau/b$. With Darcy’s law we find that

$$\dot{\gamma} \approx \frac{b}{12\eta} \nabla p.$$  \hspace{1cm} (15.36)

If we were to increase the gap $b$, the pressure that we need to apply for the same shear rate decreases. However, at the same time the flow-velocity $u_\tau$ would increase. This may make it virtually impossible to observe the interface evolution. We can also not make $b$ too large, because then the thin-gap limit used to derive Darcy’s law fails. Assuming that $r_0 = 1\ \text{mm}$ and $R \approx 10\ \text{cm}$ yields a condition for the aspect ratio of the plates

$$\left(\frac{R}{h}\right)^3 < 9.5\mu m \frac{16}{3} \cdot \frac{0.05}{10^{-11}\text{Pa}^{-1}} \frac{1}{10^5\text{Pa}} 2 \ln \frac{R/\text{mm}}{R}$$  \hspace{1cm} (15.37)

$$\frac{R}{h} = (233)^{1/3} = 6.15.$$  \hspace{1cm} (15.38)

Glass plates of the size $R \approx 10\text{cm}$ and a ratio $R/h$ about 6 are commercially available as optical flats, although they are expensive. (An 8" flat was available, at the time of this writing, for about $2000 per piece: for example from Edmund Industrial Op-
tics, 101 East Gloucester Pike, Barrington, NJ 08007-1380; www.edmundoptics.com.) Another option is to polish two telescope blanks to flatness. An inexperienced person will need about 1-2 months to do this for two eight inch blanks, working full time. While not required, one will not achieve the quality of an optical flat in this time frame. In either case, one will need to drill a hole in the center of one of the finished plates, which may break it.
Chapter 16

Shear thinning

Hele-Shaw experiments by Buka, Palfy-Muhoray and Rácz [68] and Buka and Palfy-
Muhoray [69] using nematic liquid crystals showed dendritic viscous fingers. In these
papers the authors claimed that viscosity anisotropy caused the appearance of den-
dritic finger morphologies, rather than surface tension anisotropy, which is the cur-
rently accepted mechanism for dendritic growth in solidification. However, since
liquid crystals necessarily also exhibit surface tension anisotropy, the origin of den-
dritic fingers in these experiment may be disputed. Kondic, Shelley and Palfy-
Muhoray (KSP) [65] subsequently demonstrated numerically that dendritic fingers
are possible in shear-thinning systems without surface-tension anisotropy. A goal of
the present work was to verify these findings experimentally. This chapter introduces
the Cross-model for shear thinning fluids, which was used by KSP, and shows how
the relevant parameters can be determined.

Cross [70] introduced the rheological model function for the shear-rate dependence
of non-Newtonian fluids

\[ \eta(\dot{\gamma}) = \eta_0 \frac{1 + \alpha (\tau \dot{\gamma})^m}{1 + (\tau \dot{\gamma})^m}, \]

(16.1)

where \( \dot{\gamma} \) is the shear rate, \( \tau \) a characteristic relaxation time, \( \eta_0 \) the viscosity in the
limit of vanishing shear and \( \alpha \) a parameter, which is less than one for shear-thinning
and greater than one for shear-thickening fluids. Figure 16.1 shows the graph for this

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Figure 16.1: Shear rate dependence of viscosity (Cross function).

function for various parameters. Cross [71] shows that for linear polymers and their solutions, the exponent $m$ is a function of polydispersity and is strictly less than one, except at monodispersity, where it reaches unity. He presents the empiric formula

$$m = \left( \frac{\overline{M}_n}{\overline{M}_w} \right)^{1/5},$$

(16.2)

where $\overline{M}_n$ is the number-averaged and $\overline{M}_w$ the weight-averaged molecular weight,\(^1\) and $\overline{M}_w/\overline{M}_n$ is called the "polydispersity-index."

The characterization of shear thinning fluids is complicated by several aspects. First, viscosity is determined by measuring the force on two surfaces which move relative to each other, where the test fluid is contained between these. However, since the viscosity is shear-rate dependent, the velocity profile is *a-priori* unknown, except in some simple geometries, where the shear rate is constant throughout the

---

\(^1\)Simply defined as $\overline{M}_n = \sum n_i m_i / \sum n_i$ and $\overline{M}_w = \sum m_i^2 / \sum m_i$, where $n_i$ is the number of molecules with mass $m_i$.\)
fluid. Technically realizable is the cone-plate geometry.

Figure 16.2: Principle of a cone-plate viscometer. One measures the torque required to rotate the cone at a constant speed. The vertex of the cone is in the surface of the plate, the fluid is held by surface tension between cone and plate.

The Cross function, however, extends over six order of magnitude of shear rate and only a small interval of this range is accessible to cone-plate measurements. It is possible to determine the viscosity by measuring the flow rate through a capillary tube. We note however the following complications:

- The boundary condition at the capillary walls is in general a slip boundary condition [72].

- Entrance effects are not negligible [73][74].

- The velocity profile in the capillary tube is unknown.
A procedure for determining the viscosity as a function of shear rate is given by Astarrita and Marrucci [72]. It requires measuring the flow rate as a function of applied pressure for different capillary diameters and lengths. This procedure is in general needed, if one wants to determine the complete shear-rate function $\eta(\dot{\gamma})$. However, we assume that this function is given by Eq. (16.1). Thus our procedure will be to use a cone-plate viscometer to determine a part of $\eta(\dot{\gamma})$ and capillary measurements for the limits of viscosity at very low shear rates, $\eta_0$, and very high shear rates, $\eta_\infty$. We assume that the shear rate grows monotonously from the center of the capillary to the walls. Then it is clear that $\eta_0$ can be determined directly by using Hagen-Poiseuille’s law, because the shear rate everywhere is less than that at the wall and thus the fluid can be considered Newtonian for sufficiently slow flow. At high shear rates, however, the shear rate decreases from very high values at the capillary wall to zero in the center, and therefore the viscosity attains all values between $\eta_0$ and $\eta_\infty$. In particular, Kondic, Palffy-Muhoray and Shelley [64] suspect that the appearance of a slip-boundary condition for shear-thinning fluids is due to non-uniqueness of the mapping between shear-stress and shear-rate, which occurs for certain values of the parameter $\alpha$ and $m$. If we take this point of view, then if we show that this condition cannot occur for our set of parameters $\alpha$ and $m$, we may ignore the slip-layer boundary condition. Finally, if the flow rate is sufficiently high, the shear rate is high through most of the capillary, except for a thin column in the center that we may neglect. In fact, we expect that asymptotically the apparent viscosity will become a constant.
16.1 Uniqueness of shear-rate as a function of shear stress

We repeat here the argument by Kondic, Palffy-Muhoray and Shelley [64] to determine the condition that guarantees that the shear rate can be uniquely expressed as a function of shear stress. In their paper, however, they give a value for the minimum value of $\alpha$ based on an exponent $m$ that is not in agreement with experiment.

In fact, because $\eta$ should be expressible as an even function of the shear rate, they assume incorrectly that this exponent should be 2, which is basically never observed for linear polymers [70].

They start from the Navier-Stokes equation for incompressible flow ($\nabla \cdot \mathbf{u} = 0$) of a generalized Newtonian fluid and ignoring body forces,

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla \cdot (2\eta \mathbf{S}), \quad (16.3)$$

where $\mathbf{S}$ is the rate-of-strain tensor, $S_{ij} = (u_{i,j} + u_{j,i})/2$. The inertial term is subsequently ignored. Since the viscosity is a function of spatially varying shear rate

$$\frac{1}{2} \nabla p = (\nabla \eta) \cdot \mathbf{S} + \eta \nabla \cdot \mathbf{S}. \quad (16.4)$$

In particular, consider the case of rectangular flow, $\mathbf{u} = u \hat{x}$ and $\partial_x = \partial_y = 0$ (see figure 15.1 on page 240.) Here all element of $S_{ij}$ vanish except $S_{13} = S_{31} = \frac{1}{2} du/dz$

and

$$\frac{dp}{dz} = \frac{d\eta}{dz} \frac{du}{dz} + \eta(z) \frac{d^2 u}{dz^2}. \quad (16.5)$$

However, $\eta$ is a function of $z$ only due to its dependency on shear rate $\eta(z) = \eta(u_z(z))$, therefore

$$\frac{dp}{dz} = \left( u_z \frac{d\eta}{du_z} + \eta(z) \right) \frac{d^2 u}{dz^2} \equiv \eta^{eff}(z) \frac{d^2 u}{dz^2}, \quad (16.6)$$
where they define an effective viscosity $\eta^{\text{eff}}$. Finally, they show that $\eta^{\text{eff}} > 0$ is a sufficient condition for finding $\eta(z)$ in terms of applied pressure $dp/dz$. We now show that this condition implies that

$$\alpha > \left( \frac{1 - m}{1 + m} \right)^2. \quad (16.7)$$

With $\dot{\gamma} \equiv u_z$, define $x \equiv \tau \dot{\gamma}$, with Eq. (16.1) the effective viscosity is given by

$$\frac{\eta^{\text{eff}}}{\eta_0}(x) = x \frac{d}{dx} \frac{1 + \alpha x^m}{1 + x^m} + \frac{1 + \alpha x^m}{1 + x^m} \quad (16.8)$$

$$= \frac{1 + (1 + \alpha + m (\alpha - 1)) x^m + \alpha x^{2m}}{(1 + x^m)^2}. \quad (16.9)$$

A negative effective shear rate may exist only if $\eta^{\text{eff}}$ ever vanishes. Conversely, $\eta^{\text{eff}}$ is never negative if

$$1 + (1 + \alpha + m (\alpha - 1)) x^m + \alpha x^{2m} = 0 \quad (16.10)$$

has no (real) solution for $x^m$, i.e.,

$$D(\alpha) \equiv (1 + \alpha + m (\alpha - 1))^2 - 4\alpha < 0. \quad (16.11)$$

We conveniently define

$$\tilde{D}(\alpha) \equiv \frac{D(\alpha)}{(1 + m)^2} = \alpha^2 - 2 \frac{1 + m^2}{(1 + m)^2} \alpha + \left( \frac{1 - m}{1 + m} \right)^2 \quad (16.12)$$

and solve for the root of $\tilde{D}(\alpha) = 0$, which yields $\alpha = 1$ and

$$\alpha = \alpha_{\text{crit}} \equiv \left( \frac{1 - m}{1 + m} \right)^2. \quad (16.13)$$

The function $\tilde{D}(\alpha)$ is a convex-up parabola, therefore $D(\alpha) < 0$ for $\alpha_{\text{crit}} < \alpha < 1$. The condition $D(\alpha) < 0$ implies that the effective viscosity cannot become negative.
for any shear rate $x = \tau \dot{\gamma}$. Thus, for shear-thinning fluids that behave according to (16.1), the shear rate can be uniquely expressed as a function of shear stress, as long as

$$\alpha > \alpha_{\text{crit}} \equiv \left( \frac{1 - m}{1 + m} \right)^2,$$

(16.14)

and we may ignore slip conditions as long as $\alpha > \alpha_{\text{crit}}$, assuming that the presence of a slip-layer at the boundary is due to non-uniqueness of the mapping between shear stress and shear rate.
Chapter 17

Material: choice and parameters

Preliminary experiments that we have performed, using a dilute solution of polyethylene oxide (PEO) in water, did not reveal any dendritic fingers. Figure 17.1 shows a characteristic example of these experiments (This particular experiment was done with a solution of 0.9% of PEO, molecular weight $2 \cdot 10^6$, in water. The cell gap was 19 $\mu$m, the initial bubble radius $r_0 = 0.7$ mm, the cell size 12 cm and the applied pressure 291 cm H$_2$O. The parameters of the Cross function, Eq. (16.1), were $\alpha = 0.07$, $m = 0.67$ and $\eta_0 = 125$ mPa s. The dimension of the image is about 6 cm x 6 cm.) A defining characteristic of dendritic fingers is that tip-splitting is suppressed. Figure 17.1 does therefore not show dendritic fingers, although the fingers have sidebranches, simlar to typical dendritic fingers. For Hele-Shaw experiments in a similar system, see Kawaguchi, Makino and Taki [75]. Bonn and Meunier [76] have shown that viscous fingers are widened if the sheared fluid exhibits strong normal stresses (increased pressure due to shear). In the same paper they compare the behavior of PEO, with strong normal stresses, to that of Xanthan, with negligible normal stresses, and found that for the latter the finger-widening disappears. For this reason, we chose to perform experiments using a dilute solution of Xanthan instead of PEO.

PEO is a flexible, linear polymer. Xanthan, on the other hand, occurs in aqueous
solution as stiff helixes[77]. We used Rhodigel Xanthan gum of molecular weight 2·10⁶, that was generously provided to us by R. T. Vanderbilt Company, Inc.

17.1 Viscosity function

I prepared a solution of 0.05 weight percent Xanthan in de-ionized water. Figure 17.2 shows the measured viscosity of this solution vs. the applied shear rate. The low shear-rate part of the viscosity (Cross) function (16.1) were determined with a Brookfield low-viscosity cone-plate rheometer, model LV-III. The high shear rate part was determined by performing capillary measurements with a capillary, 25 cm long, a nominal diameter of 432μm and held at constant temperature of 20.0°C using water cooling. The applied pressure ranged between 50 and 400 kPa, yielding flow rates between 0.21 and 1.04 grams per second. The Reynolds number $Re = \bar{u}ar/\eta$ can be expressed for this capillary as $Re = 2941 \cdot \bar{m} [g/s]/\eta [mPa.s]$. The viscosity for water at 20°C is $\eta_{H_2O} = 1.002 mPa.s$. The critical Reynolds number
for pipe-flow is $Re_{\text{crit}} = 2300$. Thus the capillary measurements yield an increasing apparent viscosity for very high shear rates, because of the disruption of laminar flow conditions. The parameters $\alpha, m, \text{and } \eta_0$ were adjusted by hand to find the best apparent fit for figure 17.2, assuming that $\eta_\infty$ is given by the lowest apparent viscosity. The resulting parameters are $\alpha = 1/48, m = 0.60$ and $\tau = 0.4 \text{s}$. The condition for zero slip-velocity, Eq. (16.14), yields that $\alpha > 1/16$ guarantees that no slip occurs at the boundary. This is violated here and hence the procedure given in Astarrita and Marruci [72] should be applied for determining the high-shear viscosity. The cone-plate data indicates that the true high-shear viscosity must be below 2 mPas, while a lower bound is given by the viscosity of water of about 1 mPas.

![Diagram of viscosity function for 0.05 percent Xanthan in water.](image)

**Figure 17.2:** Visosity function for 0.05 percent Xanthan in water.
Chapter 18

Experimental setup

18.1 Dark-field illumination

In our experiment we want to observe the moving interface between air and a dilute polymer solution in water. We want to acquire images of sufficiently quality such that the interface geometry can be readily evaluated, in particular the radius of the tip of dendritic fingers and the interface velocity.

Unfortunately, the width of the interface is very thin (the order of the gap size - 50\( \mu \text{m} \) and less), and the interface moves very fast (on the order of 1 m/s). The fast moving interface causes the image of the interface to be smeared out due to the finite time that the camera shutter is open. On the other hand, the image of the interface is very faint, therefore either a strong light source or a longer shutter-time is required to be able to observe the interface at all. In either case, the image quality will deteriorate due to stationary objects (e.g., parts of the interface or the hole where air is injected into the cell, but in particular the tube connecting the injection-hole of the cell to the air-source). Those stationary objects will appear very bright, while the tip will appear very faint. Also, if we wish to use a digital camera, its dynamic range will determine the faintest object that we can resolve. While (expensive) cameras with a dynamic range of 16 bit (48 dB) and more are available, these are typically slow-scan cameras, which would permit the acquisition of only a single frame per experiment.
An alternative approach is to use a stroboscope. The duration of a stroboscopic flash is very short, of the order of 10 microseconds, which corresponds to a shutter time of 1/100000 s, unmatched by any commercial camera. Instead of acquiring images frame by frame, we hold the shutter open and only trigger the stroboscope, which results in a sequence of well-defined interfaces in the same image. We still need to solve the problem of how to illuminate the interface with a stroboscope such that outside influences are minimized. Fortunately, a method exists that is particularly well-suited for the imaging of faint interfaces: dark-field illumination (DFI).

In DFI one observes only the light that is (forward-) scattered at refractive-index inhomogenities, like at an air-water interface, and attempts to blend out all other light sources from the surroundings. The scatterer then effectively becomes the light source, which is imaged onto a camera (figure 18.1). Finally, we wish the illumination to be as omnidirectional and homogenous as possible, in order to acquire images whose interfaces exhibit uniform brightness.

For our Hele-Shaw experiment I built a special box for this purpose (figure 18.4). This box is large enough to accommodate the Hele-Shaw cell, which has a diameter of 20.3 cm and a height of 7 cm, it accommodates the stroboscope (EG&G machine vision strobe, MVS 5410-01) and the camera. The stroboscope is chosen for the features that it has a sufficiently strong light output (1 Joule per flash) at a sufficiently high repetition rate (up to 200 Hz). The stroboscope can be triggered externally, which makes it possible to have a calibrated time-interval between each flash. This can be done in various ways - I used an available oscilloscope as the trigger-device.
Figure 18.1: Principle of dark-field illumination. The object is placed in front of an absorbing, black background and light is incident obliquely from the far side of the medium. An inhomogeneity in the optical density causes forward-scattering of light. The scatterer effectively becomes a light source.

Figure 18.2: Cross section of the darkfield-illumination box.
As the camera I used a digital camcorder in progressive-scan (i.e., non-interlaced) mode (Canon Optura). This camera acquires images at the video rate of 30 frames per second. Most images were taken with a strobe frequency of 120 Hz, leading to four interfaces per frame.

The top of figure 18.4 shows a half-exploded view of a cross-section of the box, the bottom shows the assembled box (the cover for the hatch of the top tier is removed). The box is separated into three tiers, which, for reference, we label 1 through 3 from bottom to top, two adjacent tiers are separated by plates with a hole in the center. The purpose of the bottom tier (1) is to transform the light from the stroboscope into a homogenous, omnidirectional light source. It has an opening to the right hand side, which accommodates the stroboscope’s light-output. The stroboscope is placed on a table of height 10 cm, which is not shown. (The table is necessary for access to the stroboscope connections, which are located at its bottom.) The interior of the tier is painted white, as is the underside of the separating plate between tier one and two. The purpose of the second tier (2) is twofold. Firstly, it provides the dark background for the dark-field illumination: a ring cut from black felt is placed on top of a glass plate (window glass, 1/8” thickness). Secondly, it further enhances the circular symmetry of the incoming light: a collar cut from white cardboard is placed on the perimeter of the circular opening. The collar has approximately the same height as the distance between the bottom and the top separating plates of this tier. The interior of the second tier is not painted. The purpose of the third tier is to accommodate the Hele-Shaw cell. The interior of this tier is painted black, including
the top of the separator plate between tier one and two and the bottom of the top plate. The circular hole between the second and third tier is slightly larger than the cell-diameter. A cover from black cardboard with a sufficiently small hole is therefore placed on the separator plate (not shown in Fig. 18.4). This setup permits a certain degree of freedom in choosing the cell-diameter. Also, the cardboard cover can easily be replaced. This facilitates cleaning, which is necessary since some fluid ejects out of the Hele-Shaw cell during each experiment. Finally, the top cover has a hole through which the camera is pointed into the box. A neutral-density filter is placed on the camera lens, reducing reflection of light from the lens onto the Hele-Shaw cell and back onto the lens.

18.2 Cell assembly

The Hele-Shaw cell consist of two glass plates with diameter 8” and thickness of about 1.25”. A hole of diameter 1.4mm is drilled in the center of one of the plates. The plates are clamped together with two aluminum rings, on which eight screws are placed at

![Image of assembled darkfield-illumination box]

Figure 18.3: Photograph of the assembled darkfield-illumination box.
Figure 18.4: Dark-field illumination box
equidistant locations. Plastic spacers of with a thickness of the desired gap size are placed at the perimeter of the cell at the location of the screws. (Fig. 18.5 and 18.7)

18.2.1 Handling of the plates

The flat side of the plates is very vulnerable to scratches. In particular, when assembling the Hele-Shaw cell great care must be taken not to get dust particles between the plates, which may scratch the plates when they are moved against each other during disassembly. When not in use, the flat side of the plates should always be covered to avoid the accumulation of dust.

18.2.2 Drilling a hole

The Hele-Shaw assembly requires a hole in the center of one of the glass plates. Diamond drills of various sizes are available from jewelers. Before drilling the hole one needs to know how the fluid is injected. In our case we are using syringe needles
Figure 18.6: Structure of the borehole, through which air is injected into the cell (hole diameter exaggerated).

of diameter 18 Gauge (0.05” diameter) x 1.5” length, which are easily available. Plastic tubing of the right inner diameter (Tygon flexible plastic tubing, “microbore tubing,” formula S-54-HL, I.D. 0.04”, wall thickness 0.015”) is pulled over the needle and connected to a pressure reservoir. The pointed side of the needle is better suited for attaching and detaching tubing. The needle is glued into the hole, with the pointed side outward. The hole on the gap-side should not need to be as large as the needle diameter: the needle will sit on the brim where both holes meet (figure 18.6).

When drilling a hole all the way through glass, there is a great danger that a piece of glass chips away on the far side of the drill. It is safer to drill two holes from opposing sides that join together in the center. It is absolutely essential that the drill can be moved vertically in a controlled fashion and does not have play - hand drills, or bench presses for electronic equipment (which have too much play) are not suited. Because of the high cost of the plates, in money or time, it is highly recommended to practice with cheap 1/4” window glass before attempting to drill through the plates.
I used a bench-press drill set at the highest rpm settings. (The manufacturer of the drills recommended 10000 rpm, which were not available at the bench press). I marked the center of the plate on one side with permanent marker. The glass plate was placed on a wooden support plate and fastened with clamps, placing wooden spacers for protection of the plate between glass surface and clamp. A washing bottle with water was used to squirt water in regular intervals at the hole. This provide the necessary cooling and acts as lubricant. Also, it flushes away glass dust. I drilled in several stages. The first stage was to drill a guide hole, which is much thinner than the final hole. I moved the drill slowly, pushing it in a few millimeters at a time and pulling it out again, flushing between presses. The guide hole was drilled as deep as possible, without completely cutting through to the other end. The glass plate was removed, flushed thoroughly of glass dust, cleaned and dried. Next, I marked the spot exactly on the other end of the guide hole and repeated the procedure from the other side of the plate, until the holes met. One needs to be careful to actually hit the painted mark with the drill. The procedure was then completed by widening the

Figure 18.7: Photographs of the assembled Hele-Shaw cell.
Figure 18.8: Interference rings in the assembled Hele-Shaw cell when illuminated with a fluorescent light bulb. This can be used to verify that the cell is assembled correctly such that the gap is radially symmetric.

guide holes to the desired size.

18.2.3 Assembling and filling the Hele-Shaw cell

The plates are washed and dried, and plastic spacers, cut to about 1.5 cm squares, are placed on the bottom plate. The other plate is placed on top without touching the bottom cell. One needs to take care that the generated air flow does not blow away the spacers. The aluminum rings that are used to clamp the cells are placed on the perimeter and screwed together lightly. Finally, the screws are tightened evenly, opposing screws first - for example in the sequence 1,5,7,3,6,2,4,8, given that they labeled 1-8 in clockwise order. A fluorescent light bulb can help visualize the radial symmetry of the gap: because the spectrum of these lightbulbs contains characteristic lines, if the light is obliquely incident one can observe the interference rings caused by multiple reflections in the gap (size 19-50 μm) (Fig. 18.8).
The cell is assembled correctly if the density of interference lines is radially symmetric. Next the test fluid is injected into the gap. First, plastic tubing connects the needle attached to the Hele-Shaw cell (1) to another needle (2), which will later be attached to a syringe filled with the fluid. One then fills the syringe with fluid (about 2 cm³ are required for a 50 μm gap) and attaches it to needle 2. The fluid is injected slowly and carefully. If one injects too quickly, two things may happen. First, the interface may lag at certain places, causing air-bubbles and second, for solution of some polymers, the polymeric strands may rupture. Next, one disconnects the tubing filled with test fluid and attaches clean tubing, which will be used to pump air into the gap. One then connects a glass syringe (which glides more easily than a plastic syringe and is therefore easier to control) to the tubing. One pushes this syringe very carefully in order to press air into the gap, such that it just forms a circular ring around the inlet. Finally, one closes the tubing with a clamp. The cell is now ready for transport and can be placed into the illumination box.

18.2.4 Disassembling the Hele-Shaw cell

Disassembling the Hele-Shaw cell starts by unfastening the screws evenly as they were fastened before. One needs to take especially care that the screws are not loosened too quickly: This will cause splitting at the outside edges of the cell. The right-hand photo in figure 18.7 shows such splitting in the top plate, which occurred during unfastening of the screws. The capillary forces hold the plates together tightly, but it is possible to slide them carefully against each other, until they separate. If necessary, one may inject water into the cell gap, which makes the plates glide
more easily. The plates are then flushed with water, cleaned with glass-cleaner and dried.

18.3 Pressure apparatus

The Hele-Shaw experiment can be driven either by constant applied pressure or constant applied flow rate. The simulations done by Kondic, Shelley and Palffy-Muhoray [65] were performed for constant applied pressure. Figure 18.9 shows the principle by which our pressure apparatus operates. (Note that the presence of valve $v_1$ is somewhat redundant. This valve was perceived to seal better than the solenoid valve for long periods of observation.) This setup permits both driving conditions. The syringe pump (Sage Instruments model 341) works by pushing a plate at a constant speed $u_{\text{syringe}}$ against the piston of a syringe, therefore creating a constant-flow condition. Very slow flows are possible, but the highest flow rate is essentially limited by the maximum accepted syringe size (for this particular model.

![Figure 18.9: Schematic of the pressure apparatus.](image-url)
the limit is 0.21 cm³ per second for a 50 cm³ syringe.) The Hele-Shaw experiment can be driven under constant flow conditions by simply keeping valve \( v_1 \) in figure 18.9 closed. Constant pressure conditions are based on the idea to quickly connect a pressure reservoir to the lines leading to the Hele-Shaw cell. The volume of the reservoir is much larger than the volume of the cell gap plus the volume of the lines connecting the reservoir to the cell. First, with valves \( v_1 \) and \( v_2 \) closed, but \( v_3 \) open, an external pump increases pressure in the reservoir, until the pressure is above the desired pressure \( p_0 \). The pressure is measured with a differential pressure transducer (AutoTran series 600 low range differential pressure transducer, connected to a digital multimeter), whose low pressure side is opened to atmosphere. Then valve \( v_3 \) is closed and the vent valve \( v_2 \) opened to let out air until the pressure is close to the desired value. The high pressure side of the system is now ready. When the Hele-Shaw cell is first connected to the apparatus, the piston of the syringe is still free, i.e., the plate of the syringe pump does not yet touch the syringe piston. Thus there is no pressure applied to the cell. The syringe-pump is then turned on at high speed setting, until the plate almost touches the piston, at which time the speed is set to low. Now the image displayed on the camera is monitored continuously, until the air-bubble reaches the desired initial radius. At this point, one switches on the solenoid valve, starting the experiment.
Chapter 19

Fitting a parabolic finger: the generalized linear least squares problem

We need to evaluate the curvature at the tip of the parabolic finger. Since these parabolas are randomly oriented in space, we need a procedure that fits a randomly oriented parabolic curve through selected points on the finger interface. We show a procedure that minimizes the distance between measured points and an estimated surface in the least squares sense. Unlike common curve fitting, where distance is measured only between the measured and estimated value of dependent coordinates \( (e.g., y_{\text{measure}}(x) \text{ and } y_{\text{estimated}}(x)) \), here the distances are measured normal to the estimated surface. The following section follows Deming [78].

**Notation:** Some variables are distinguished by the number of indices they carry or the location of the index. Thus \( F^1, F^1 \) and \( F^{ij} \) have different meanings.

We consider a model described by \( \nu \) equations in \( d \) unknowns \( x_1...x_d \) and \( q \) parameters \( \alpha_1...\alpha_q \)

\[
F^h(x_1,...,x_d;\alpha_1,...,\alpha_q) = 0 \quad h = 1,...,\nu
\]  

(19.1)

We want to determine the parameters \( \alpha_1,...\alpha_q \) from experimental data.

Say, one has \( n \) measured values \( \bar{X}^1,...,\bar{X}^n \). Then one has values \( \bar{x}^1,...,\bar{x}^n \), called “estimated values”, to each data point and any given set of parameters \( \bar{\alpha} \) that lie on the hypersurface given by the constraint (19.1), which lie closest to the measured values. (It is in principle possible that to a given data point \( \bar{X}^k \) more than
one point with the same distance exist on different locations of the surface (19.1); such cases are ignored here.) This means that the square of each residual

\begin{align}
\bar{r}^i & \equiv \bar{X}^i - \bar{x}^i, \quad i = 1, \ldots, n \\
(\bar{r}^i)^2 & \equiv (X_1^i - x_1^i)^2 + \cdots + (X_d^i - x_d^i)^2
\end{align}

(19.2) (19.3)

is a minimum for any given set \( \bar{\alpha} \). We use now as a measure of the distance of the data set to the estimated surface the sum of all these residuals (normal distances to the surface). The best set of parameters is given when

\[ S(\{\bar{r}^i\}, \bar{\alpha}) = \sum_{i=1}^{n} w_i |\bar{r}^i|^2 \]

(19.4)

is simultaneously a minimum for both \( \{\bar{r}^i\} \) and \( \bar{\alpha} \) (The \( \{\} \) imply the set of all \( \bar{r}^i \)). The coefficients \( w_i \) correspond to the weight of a measurement. Note that the \( \{\bar{r}^i\} \) depend implicitly via the constraints on the \( \bar{\alpha} \). Note also that the estimated values lie always on the point of the surface with the least distance to the conjugate measured values. The above equation can be written slightly more general if we permit to assign different weights for different variables within the same measurement.

\[ S(\{\bar{r}^i\}, \bar{\alpha}) = \sum_{i=1}^{n} \sum_{j=1}^{d} w_j^i (\bar{r}_j^i)^2 \]

(19.5)

At this point it is useful to mention that the following procedure will require that an approximation for derivatives in the constraint functions is evaluated. This means an initial guess for the parameters will be required in general, since the constraint functions are not known \textit{ab initio}. The procedure will then yield a better estimate for the parameters and can be repeated if necessary. For this reason, we define residuals
\( \tilde{\eta} \) for the parameters analogously to the ones for the variables.

\[
\tilde{\eta} = \tilde{A} - \tilde{\alpha},
\]

(19.6)

where we denote the initial guess with \( \tilde{A} \) and the resulting estimated parameter values with \( \tilde{\alpha} \).

For convenience we now define the sets of data points and parameters as a single vector:

\[
\tilde{X} \equiv (\tilde{X}^1, \ldots, \tilde{X}^n) = ((X_1^1, \ldots X_d^1), (X_1^2, \ldots, X_d^2), \ldots (X_1^n, \ldots X_d^n))
\]

(19.7)

\[
\tilde{\zeta} \equiv (\tilde{x}^1, \ldots, \tilde{x}^n)
\]

(19.8)

\[
\tilde{r} \equiv (\tilde{r}^1, \ldots, \tilde{r}^n) = \tilde{X} - \tilde{\zeta}
\]

(19.9)

\[
\tilde{E} = (\tilde{X}, \tilde{A})
\]

(19.10)

\[
\tilde{R} = (\tilde{r}, \tilde{\alpha})
\]

(19.11)

\[
\tilde{Q} = (\tilde{r}, \tilde{\eta})
\]

(19.12)

**Normal Equations**

We want to enforce the constraints independently for \( n \) estimated values \( \tilde{x}^k, k = 1, \ldots, n \). Thus we seek to minimize the sum of the weighted residuals subject to the constraints

\[
G(\tilde{R}) \equiv \sum_{s,t} w_{st} (r_{st}^k)^2 + \sum_{i=1}^r \sum_{j=1}^n \lambda_{ij} F^i (\tilde{x}^j, \tilde{\alpha})
\]

(19.13)

with respect to \( (\tilde{r}, \tilde{\alpha}) \). The \( \lambda \)'s depend, of course, on the point on the surface to be evaluated. This requires as many \( \lambda \)'s as points. Another point of view is that we are going to linearize the constraint equation locally, thus creating \( n \) local tangent
planes, each of which is going through an estimated value. We have now a total of \( n\nu \) constraint equations:

\[
F^{ij}(\xi, \alpha) = F^i(\bar{x}^j, \bar{\alpha}) = 0. \tag{19.14}
\]

Each constraint corresponds to some measurement \( j \), i.e., any derivative with respect to a variable from a different measurement \( l \), \( l \neq j \), vanishes:

\[
\frac{\partial F^{ij}}{\partial x_k^l} = \delta_{lj} \left( \frac{\partial F^i}{\partial x_k} \right)_{|\bar{x}^j}, \tag{19.15}
\]

where \( \delta_{ij} \) is the Kronecker delta. We express the derivatives in terms of the residuals and get

\[
\frac{\partial F^{ij}}{\partial r_k^l} = \frac{\partial F^{ij}}{\partial x^a_k} \frac{\partial x^a_k}{\partial r_k^l} = \delta_{lj} \left( \frac{\partial F^{i}}{\partial x^\alpha} \right)_{|\bar{x}^j} \frac{\partial x^\alpha_k}{\partial r_k^l}
\]

\[= -\delta_{lj} \delta_{ak} \left( \frac{\partial F^i}{\partial x^\alpha} \right)_{|\bar{x}^j} = -\delta_{lj} \left( \frac{\partial F^i}{\partial r_k} \right)_{|\bar{x}^j} \tag{19.16}\]

for the derivative with respect to the residuals of the values, and

\[
\frac{\partial F^{ij}}{\partial \alpha_k} = \left( \frac{\partial F^i}{\partial \alpha} \right)_{|\bar{x}^j} \tag{19.17}
\]

\[
\frac{\partial F^{ij}}{\partial \theta_k} = -\left( \frac{\partial F^i}{\partial \alpha} \right)_{|\bar{x}^j} \tag{19.18}
\]

for the derivative with respect to the residuals of the parameters.

A possible minimum for \( G \) is found by setting its gradient to zero:

\[
\nabla_R G = \nabla_{(\xi, \alpha)} G = 0
\]

\[
\frac{\partial}{\partial r_k^l} G((\bar{r}, \bar{\alpha})) = \sum_{s,t} 2w^s_d r^s_d \delta_{sk} \delta_{tl} + \lambda_{ij} \frac{\partial F^{ij}}{\partial r_k^l}
\]

\[= 2w^l_k r^l_k - \sum_{i,j} \lambda_{ij} \delta_{lj} \left( \frac{\partial F^i}{\partial x_k} \right)_{|\bar{x}^j}
\]

\[= 2w^l_k r^l_k - \lambda_{\alpha l} \left( \frac{\partial F^\alpha}{\partial x_k} \right)_{|\bar{x}^l} \tag{19.19}\]
or

\[ r_k' = \frac{\lambda_{\alpha k}}{2 w_k} \left( \frac{\partial F^\alpha}{\partial x_k} \right) \bigg|_{\tilde{\xi}} \]  

(19.20)

and

\[
\frac{\partial G}{\partial \alpha_k} = \sum_{i,j} \lambda_{ij} \frac{\partial F^{ij}}{\partial \alpha_k} \\
= \lambda_{\beta \gamma} \left( \frac{\partial F^\beta}{\partial \alpha_k} \right) \bigg|_{\tilde{\xi}}. 
\]  

(19.21)

This gives us \( nd + p \) equations, while the data points yield \( nd \) and the parameters \( p \) estimated values to solve for. The introduced Lagrange multipliers are an additional \( n\nu \) unknowns, and the \( n\nu \) constraint equations make the system complete.

Now we linearize the constraints in the residuals:

\[ 0 = F^{ij}(\tilde{\xi}) = F^{ij}(\tilde{\xi} - \tilde{Q}) \]

\[ \approx F^{ij}_{\tilde{\xi}} - \nabla_{\xi} F^{ij}_{\tilde{\xi}} \cdot \tilde{Q} + \text{higher orders of } \tilde{Q} \]

\[ \Rightarrow F^{ij}_{\tilde{\xi}} \approx \nabla_{\xi} F^{ij}_{\tilde{\xi}} \cdot \tilde{Q} \]

\[ = \sum_{k,l} \left( \frac{\partial F^{ij}}{\partial x_k} \right)_{\tilde{\xi}} r_k' + \left( \frac{\partial F^{ij}}{\partial \alpha} \right)_{\tilde{\xi}} \theta_\beta \]

\[ = \sum_{k,l} \delta_{ij} \left( \frac{\partial F^i}{\partial x_k} \right)_{\tilde{\xi}} r_k' + \left( \frac{\partial F^i}{\partial \alpha} \right)_{\tilde{\xi}} \theta_\beta \]

\[ = \left( \frac{\partial F^i}{\partial x_\alpha} \right)_{\tilde{\xi}} r_\alpha' + \left( \frac{\partial F^i}{\partial \alpha} \right)_{\tilde{\xi}} \theta_\beta \]  

(19.22)

Inserting (19.20) into (19.22) yields

\[ F^{ij}_{\tilde{\xi}} = \sum_{s=1}^\nu \sum_{t=1}^d \frac{1}{2 w_{ij}} \left( \frac{\partial F^i}{\partial x_t} \right)_{\tilde{\xi}} \left( \frac{\partial F^s}{\partial x_t} \right)_{\tilde{\xi}} \lambda_{sj} + \left( \frac{\partial F^i}{\partial \alpha} \right)_{\tilde{\xi}} \theta_\beta \]

\[ = \sum_{s=1}^\nu \left( L_{ij} \lambda_{sj} + K_{j\beta}^i \theta_\beta \right). \]  

(19.23)
Together with (19.21), this is the linear system we want to solve.

So far we have evaluated all derivatives in the point given by the estimated values, \( \bar{x}^j \). But we don’t know them unless the system has been solved. Thus we estimate the derivatives by evaluating them in the measured points instead. Similarly, we need to evaluate them for the initial guess for our parameters, \( \bar{\alpha} \), instead of the parameters for which we solve, \( \bar{\alpha} \). The estimated values for \( L^i_\beta \) and \( K^i_{jk} \) are given by

\[
L^i_\beta \approx \sum_{t=1}^d \frac{1}{2w_t^2} \left( \frac{\partial F^s}{\partial x_t} \right)_{\bar{x}^i, \bar{\alpha}} \left( \frac{\partial F^s}{\partial x_t} \right)_{\bar{x}^i, \bar{\alpha}}
\]

\[
K^i_{jk} \approx \left( \frac{\partial F^l}{\partial \alpha_k} \right)_{\bar{x}^i, \bar{\alpha}}
\]

(19.24)

(19.25)

Obviously this works best when the derivatives don’t change strongly close to the measured points. In other words, we expect the error to be larger where the curvature of the hypersurface is large.

We write the system to be solved once more to have it in one place:

\[
\begin{align*}
F^{ij}_{\bar{x}} &= \sum_{s=1}^\nu L^i_\beta \lambda^{ij} + K^i_{j\beta} \xi_\beta \quad i = 1 \ldots \nu, j = 1 \ldots n \\
0 &= K^{-\alpha}_{\beta k} \lambda_\alpha \quad k = 1 \ldots q
\end{align*}
\]

In order to visualize the structure of this system we define vectors

\[
(j) \bar{F} = (F^{ij}, \ldots, F^{\nu j})
\]

and \((j) \bar{\lambda} = (\lambda_{1j}, \ldots, \lambda_{\nu j})\).

The system can then be written as

\[
(j) \bar{F} = (j) A \cdot (j) \bar{\lambda} + (j) B \cdot \bar{\xi}
\]

\[
\bar{\xi} = (\beta) B^T \cdot (\beta) \bar{\lambda}
\]

(19.26)

(19.27)
with

\begin{align}
(j)A_{kl} & \equiv L_{jl}^{k} \\
(j)B_{kl} & \equiv K_{jl}^{k}
\end{align}

(19.28)

(19.29)

and the upper left index in brackets denotes the number of measurement. Equations (19.26) and (19.27) are known as the normal equations. We can write them as a vector-matrix equation:

\[
\begin{pmatrix}
(1)\vec{F} \\
(2)\vec{F} \\
\vdots \\
(n)\vec{F}
\end{pmatrix}
= \begin{pmatrix}
(1)\vec{A} & 0 & \ldots & 0 \\
0 & (2)\vec{A} & 0 & \ldots & 0 \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & \ldots & 0 & (n)\vec{A}
\end{pmatrix}
\begin{pmatrix}
(1)\vec{B} \\
(2)\vec{B} \\
\vdots \\
(n)\vec{B}
\end{pmatrix}
= \begin{pmatrix}
(1)\vec{\lambda} \\
(2)\vec{\lambda} \\
\vdots \\
(n)\vec{\lambda}
\end{pmatrix}
\begin{pmatrix}
(1)\vec{x} \\
(2)\vec{x} \\
\vdots \\
(n)\vec{x}
\end{pmatrix}
\]

(19.30)

The dimension of the submatrices are \(\nu \times \nu\) for the \(\vec{A}\)'s and the zeroes in the upper left partition, \(\nu \times q\) and \(q \times \nu\) for the \(\vec{B}\)'s and \(\vec{B}^T\)'s respectively and \(q \times q\) for the zero matrix in the lower right partition. The complete matrix has thus a dimension of \((n\nu + q) \times (n\nu + q)\).

The matrix and the left hand vector contain only known quantities. Inverting the matrix and multiplying the equation from the left with its inverse yield the right hand vector in the unknowns. The \(\lambda\)'s give us the residuals for the measured values by applying equation (19.20).

\[
r_k^{(j)} = (j)\vec{\lambda} \cdot \frac{1}{w_k} \left( \frac{\partial F}{\partial x_k} \right)_{\vec{x}^j} 
\]

(19.31)
Having found the residuals we get the estimated values for variables and parameters.

\[ \hat{\alpha} = \bar{A} - \bar{q} \]  
\[ \hat{x}^j = \bar{X}^j - \bar{r}^j \]  

This procedure gives better approximations for the parameters, \( \hat{\alpha} \), than our initial guess, \( \bar{A} \), and also better approximations for the estimated values \( \hat{X}^j \).

\[ A_{\text{new}} = \hat{\alpha} \]  
\[ X^j_{\text{new}} = \hat{x}^j \]  

One can repeat this procedure with these better approximations. By definition, the estimated values lie on the hypersurface given by equation (19.1), i.e., entering them in the constraint function will give exactly zero. The vectors \( \langle j \rangle \bar{F} \) in Eq. (19.23) are, however, evaluated using a guess for the estimated value. If the system is solved exactly, the guess and the estimated value are the same. Thus one can use the length of the left hand vector of equation (19.30) as a measure of convergence: If its length becomes smaller with each iteration, until some numerical round-off condition is reached, the procedure converges. On the other hand, once the length of \( \{ \langle j \rangle \bar{F} \} \) is vanishingly small, the parameter set minimizes \( G(\bar{R}) \) in Eq. (19.13).

**Examples**

**Parabola**

The constraint equations for a general parabola are:

\[ F^1(x, y; a, b, c, d, e, f) = ax^2 + bxy + cy^2 + dx + ey + f = 0 \]  
\[ F^2(a, b, c) = 4ac - b^2 = 0 \]
This is a system consisting of 2 constraint equations ($\nu = 2$), 6 parameters ($q = 6$) and 2 variables ($d = 2$):

$$\hat{\alpha} = (a, b, c, d, e, f) \quad (19.38)$$

$$\bar{x}^j = (x^j, y^j) \quad (19.39)$$

We also need the $A$ and $B$ matrices for the normal equations:

$$^{(j)}A_{kt} = \sum_{t=1}^{d} \frac{1}{2w_t^2} \left( \frac{\partial F^k}{\partial x_t} \right)_{\bar{x}^j, \bar{\alpha}} \left( \frac{\partial F^l}{\partial x_t} \right)_{\bar{x}^j, \bar{\alpha}} \quad (19.40)$$

$$^{(j)}B_{kt} = \left( \frac{\partial F^k}{\partial x_t} \right)_{\bar{x}^j, \bar{\alpha}} \quad (19.41)$$

The derivatives are given by:

$$\left( \frac{\partial F^1}{\partial x}, \frac{\partial F^1}{\partial y} \right)_{\bar{x}^j, \bar{\alpha}} = (2ax^j + by^j + d, 2cy^j + bx^j + e) \quad (19.42)$$

$$\left( \frac{\partial F^1}{\partial a}, \frac{\partial F^1}{\partial b}, \frac{\partial F^1}{\partial c}, \frac{\partial F^1}{\partial d}, \frac{\partial F^1}{\partial e}, \frac{\partial F^1}{\partial f} \right) = (x^2, xy, y^2, x, y, 1) \quad (19.43)$$

$$\left( \frac{\partial F^2}{\partial x}, \frac{\partial F^2}{\partial y} \right) = (0, 0) \quad (19.44)$$

$$\left( \frac{\partial F^2}{\partial a}, \frac{\partial F^2}{\partial b}, \frac{\partial F^2}{\partial c}, \frac{\partial F^2}{\partial d}, \frac{\partial F^2}{\partial e}, \frac{\partial F^2}{\partial f} \right) = (4c, -2b, 4a, 0, 0, 0) \quad (19.45)$$

Thus the system of normal equations becomes Eq. (19.30) with submatrices

$$^{(j)}F = \begin{pmatrix} a(x^j)^2 + bx^jy^j + c(y^j)^2 + dx^j + ey^j + f \\ 4ac - b^2 \end{pmatrix} \quad (19.46)$$

$$^{(j)}A = \begin{pmatrix} \frac{1}{2w_i} (2ax^j + by^j + d)^2 + \frac{1}{2w_j} (2cy^j + bx^j + e)^2 & 0 \\ 0 & 0 \end{pmatrix} \quad (19.47)$$

$$^{(j)}B = \begin{pmatrix} (x^j)^2 & x^jy^j & (y^j)^2 & x^j & y^j & 1 \\ 4c & -2b & 4a & 0 & 0 & 0 \end{pmatrix} \quad (19.48)$$
Circle

A circle has only a single constraint equation:

\[ F^1(x, y; x_0, y_0, a) = (x - x_0)^2 + (y - y_0)^2 - a = 0 \]  \hspace{1cm} (19.49)

\[ \tilde{a} = (x_0, y_0, a) \]  \hspace{1cm} (19.50)

\[ \tilde{x}^j = (x^j, y^j) \]  \hspace{1cm} (19.51)

The derivatives with respect to data and parameters are given by

\[ \left( \frac{\partial F^1}{\partial x}, \frac{\partial F^1}{\partial y} \right) = (2(x - x_0), 2(y - y_0)) \]  \hspace{1cm} (19.52)

\[ \left( \frac{\partial F^1}{\partial x_0}, \frac{\partial F^1}{\partial y_0}, \frac{\partial F^1}{\partial a} \right) = (-2(x - x_0), -2(y - y_0), -1) \]  \hspace{1cm} (19.53)

thus the normal equations are given by Eq. (19.30) with submatrices

\[ (j)^{\tilde{F}} = ((x^j - x_0)^2 + (y^j - y_0)^2 - a) \]  \hspace{1cm} (19.54)

\[ (j)^{\tilde{A}} = \left( \frac{x^j - y_0}{w_1^j} + \frac{y^j - y_0}{w_2^j} \right) \]  \hspace{1cm} (19.55)

\[ (j)^{\tilde{B}} = (-2(x^j - x_0), -2(y^j - y_0), -1) \]  \hspace{1cm} (19.56)
Chapter 20

Experiments and results

20.1 Preparing and Performing

20.1.1 Making the calibration circles

The distances in the images of the viscous finger interfaces were determined relative to a calibration image of concentric circles, which would correspond to radii 1cm, 2cm, etc.. First, I printed a pattern of circles of radii exactly 1cm, etc. onto paper, which I then copied onto overhead transparency. Then I printed similar circles that were to be placed on top of the cell, and therefore needed to be adjusted for parallax. I placed the transparency with the exact pattern between both cell plates and the parallax-adjusted pattern on top of the top plate. Looking through the camera I decided if the circles of both patterns exactly coincided, and adjusted the radii of the top patterns accordingly. After a few steps of adjustment, the top and bottom circles were not distinguishable, and I kept the resulting transparency for calibration.

20.1.2 Performing the experiment

The cell was filled as described in section 18.2.3, and placed in the illumination box. The stroboscope was turned on and set to the desired frequency, using the highest available setting for the intensity (1 Joule per flash for frequencies less than 200 Hz).

Next, the focus and macro of the camera was changed until the focus was onto the inlet, hence in the plane of the gap, and the field of view covered and area of about

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7.5 cm × 10 cm. At the same time, the location of the cell was adjusted to place the inlet into the center of the image. A transparency with a calibration pattern, an image of concentric circles, was placed onto the cell, centered about the gap, and an image of it taken. Next, the center of the top of the cell was covered with black permanent marker; in order to reduce the apparent brightness of the inlet, increasing the available contrast for the images of the moving interface. The pressure tubing, which connects to the inlet, was attached to the pressure apparatus. Compressed air was used to blow off some remaining dust particles from the top surface of the cell surface, otherwise these would later appear as detracting speckles in the images. The access hatch of the illumination box was closed. The exposure time and aperture of the camera were adjusted for best contrast. At this time the camera was set to recording a movie, in progressive scan mode. The clamp was removed from the pressure tubing and the syringe pump started. As soon as the bubble began entering the cell, the solenoid valve to the pressure reservoir was opened. Finally, the solenoid valve was turned off and the recording was stopped.

20.2 Evaluating

20.2.1 Image processing

The duration for each experiment, in terms of a camera frame-rate of 30 per second, was from one to several frames. Each frame was captured to an image file and processed with non-distorting operations (inverting, changing intensity level distribution, changing gamma, etc.) in order to increase available contrast. In particular, all presented images are negatives, where the interface appears black, instead of white
as in the original picture. The images presented here are further processed by joining several frames into the same image. (A typical strobe frequency was 120 Hz, thus a single frame could only accommodate four interfaces.)

20.2.2 Characterizing interface shape

I wrote a program, which permits to fit a parabola to each finger, based on the fitting procedure given in chapter 19. This program first loads the image of the calibration circle, and one enters specified points along the horizontal and along the vertical axis with a pointing device (mouse). Next, one loads an image of the fingering interfaces. For each finger one selects several (about 10) points on the interface, close to the tip. The parameter of the fitted parabola are then stored in a file. In particular, the data contains the tip-radius and the distance of the tip to the center of the cell, as well as the location of the vertex of the tip (c.f. figure 20.1).

![Figure 20.1](image)

Figure 20.1: An example for the fitting of a dendritic finger to a parabola. The small squares on the interface indicate the manually selected points for which the parabola was adjusted.
20.3 Parameters

20.3.1 Material

All the experiment presented here were performed using a solution of 0.05% Xanthan (Rhodigel food grade Xanthan gum, molecular weight = 2·10⁶ dissolved in deionized water.) The shear-thinning properties (i.e., the parameters \(\tau, m, \eta_0\) and \(\alpha\) in the Cross function (16.1)) of this solution were determined by cone-plate and capillary measurements as described in section 17.1 to be \(\tau = 0.4\) s, \(m = 0.6\), \(\eta_0 = 62\) mPa s, \(\alpha = 1/48\). The surface tension is estimated to be similar to that of water, \(\sigma_{\text{fluid}} \approx \sigma_{\text{H}_2\text{O}} = 73\) mN/m [67].

20.3.2 Dimensionless groups \(\mathcal{W}e\) and \(Ca\)

Kondic, Shelley and Palffy-Muhoray [65] use the following definitions for the capillary and Weissenberg numbers \(Ca\) and \(\mathcal{W}e\), respectively:

\[
Ca = \frac{12\eta_0 \dot{R}_0 R_0^2}{\sigma b^2} \tag{20.1}
\]

\[
\mathcal{W}e = \frac{\tau \dot{R}_0}{b} \tag{20.2}
\]

where \(\eta_0\) and \(\tau\) are parameters in the Cross function (16.1), \(R_0\) the radius of the circular bubble when the pressure is turned on, \(\dot{R}_0\) the initial radial propagation velocity of the interface, \(\sigma\) is the surface tension, \(b\) the cell gap. For radial flow between parallel plates, the relation between gap-averaged velocity and pressure gradient is given by Darcy’s law (15.16), with a pressure field given by Eq. (15.22), thus

\[
\dot{R}_0 = \frac{b^2}{12\eta_0} \nabla p = \frac{b^2}{12\eta_0} \frac{\Delta p}{R_0 \ln R_1/R_0}, \tag{20.3}
\]
where $R_1$ is the radius of the Hele-Shaw cell, $\Delta p = p(R_0) - p(R_1)$, is the applied pressure and $\eta_0$ is the initial viscosity, before pressure is applied. Inserting this into the definitions for $Ca$ and $We$ yields

$$Ca = \frac{1}{\sigma} \frac{R_0}{\ln R_1/R_0} \Delta p$$  \hspace{1cm} (20.4)

$$We = \frac{\tau}{12 \eta_0 R_0 \ln R_1/R_0} \Delta p = \left( \frac{\tau \sigma}{12 \eta_0} \right) \frac{b}{R_0^2} Ca$$  \hspace{1cm} (20.5)

When creating the initial bubbles of a radius larger than the radius of the inlet, the interface would soon become off-center and not circular. Therefore, all experiments were performed with the same initial radius $R_0 = 0.7\text{mm}$. Table 20.1 shows the parameters for all experiments.

20.4 Results

20.4.1 Interface evolution

Figures 20.5 and 20.6 show the interface evolution for various applied pressures for a 50 $\mu$m gap, and figure 20.7 shows the same for a gap of 19 $\mu$m. In both series one can see the transition from Newtonian morphology to dendritic as the pressure increases.

Figure 20.2 demonstrates that the observed dendrites behave such that the product of radius of curvature at the tip and the velocity is proportional to the driving force. For each experiment in figure 20.2 the data points are stacked in a column, but it is not clear if there is a trend or the data points are random. Figure 20.3 reveals that the ratio $pb^2/rv$, tends to be smaller for later stages of the finger development. This ratio has dimension of a viscosity. It is interesting to note that there appears
to be a lower bound on this viscosity of about 10 mPa.s. Figure 20.4 shows that the
propagation velocity for low applied pressure first decreases, then increases and for
high applied pressure increases.

It is expected that the tip velocity increases, because the pressure gradient is
higher when the tip moves closer to the cell edge.

20.5 Conclusion

I have demonstrated experimentally that radial Hele-Shaw experiments in a dilute
solution of Xanthan in water exhibit stable dendritic fingering for high shear rates. To
best of my knowledge, this is the first observation of dendritic fingers in shear thinning
fluids, without any additional imposed anisotropy. (A closely related phenomenon

![Dendritic fingers - Ivantsov relation](image)

Figure 20.2: Tip radius times velocity as function of driving force, showing that \( ur \)
is proportional to the driving force \( pb^2 \).
<table>
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Table 20.1: Parameters for the Hele-Shaw experiments.
Figure 20.3: Plotting the ratio of driving force and the product \( rv \) versus distance from the center reveals that this ratio becomes more defined at later stages of finger development.

has been observed, however: viscous finger narrowing in a rectangular Hele-Shaw cell, using a dilute solution of polystyrene in dioctyl phthalate\([79]\). The main feature of the system here presented, is that anisotropy (viscosity or other) is introduced only dynamically, and neither present intrinsically (like in liquid crystals\([68]\) or solids), not extrinsically (as in grooves cut into the Hele-Shaw cell\([62]\) or the Couder-bubble experiment\([80]\).)

The original goal to perform experiments that can directly be compared to the simulation by Kondic, Shelley and Palffy-Muhoray (KSP)\([65]\) has not been attained: parameters, for which dendritic fingers are predicted are \( Ca=240, \ We=0.20 \) and
Figure 20.4: Velocity as a function of distance from the center. Each set of connected points corresponds to one finger, while each different symbol denotes a different experiment.

\( Ca = 480, \ We = 0.15 \). The capillary numbers of the experiments here presented are of the same orders of magnitude; however, the Weissenberg numbers are at least 2000 times larger. We turn our attention to equation (20.4) in order to determine which parameters may lead us into the parameter space of the simulation. The gap width \( b \) cannot be reduced much further, because even at \( 19 \mu m \), it becomes difficult to perform reproducible, clean experiments, and the acquired images are difficult to evaluate. It may be possible to change the initial radius \( R_0 \); however, the larger \( R_0 \), the more difficult it is to create a circular bubble. Also, to decrease \( We \) by a factor
Figure 20.5: Viscous fingers for a dilute Xanthan solution. Gap=50 μm. Applied pressure from top left to bottom right is 16.61, 21.51, 32.35, 42.51, 52.95, 60.13 kPa.
Figure 20.6: Viscous fingers for a dilute Xanthan solution, gap=50 μm, applied pressure from top left to bottom right is 73.06, 75.29, 82.05, 91.01, 98.52, 107.1 kPa.
Figure 20.7: Viscous fingers for a dilute Xanthan solution, gap=19 μm, applied pressure from top left to bottom right is 42.11, 61.95, 70.47, 99.12 kPa.

2000, $R_0$ would need to change from 0.7 mm to 3.1 cm, which is almost beyond the observed area. Finally, in order to observe the interface evolution for a sufficiently long time, such an experiment could only be performed with a cell much larger than 8” diameter.

The surface tension $\sigma$ does not vary too much for different materials. Therefore the best choice is to change either the concentration, in order to increase $\eta_0$, which will also lead to a small shear thinning parameter $\alpha$. Ideally, however, one wishes
to bring the system into a region for which the uniqueness between shear-stress and shear-rate is guaranteed. Assuming that $m \approx 2/3$, this requires that $\alpha > 1/16$. The remaining parameter one may be able to control is the relaxation time $\tau$. This relaxation time is assumed to be the largest characteristic time of the eigenmodes of a macromolecule (Zimm relaxation time [81]), which corresponds to collective re-orientation of the whole molecule. Apparently, choosing Xanthan with a smaller molecular weight should decrease $\tau$.

In addition, the Cross-function parameter in the simulation by KSP given as $m = 2$, and $\alpha = 0.15$. While $\alpha$ can relatively easily be changed by adjusting the concentration, the parameter $m$ cannot be expected to be greater than one for usual materials.

Since our experimental parameters are not even close to the parameter space selected by KSP, the experiments do neither support nor contradict their result. The underlying mechanism for dendritic behaviour may be different. In particular, one may speculate that the reorientation of rod-like Xanthan actually does create anisotropy of the surface tension, which, rather than (the also present) viscosity anisotropy, enables dendritic growth.
Appendix A

A.1 Useful identities

Some of the following identities are used in multiple places and gathered here for the convenience of having a point of reference.

The definitions of $Q$ and $\sigma$ are

$$Q = \frac{S - P}{2} \hat{L} \hat{L} - \frac{S + P}{2} \hat{M} \hat{M} + S \hat{N} \hat{N} \tag{A.1}$$

$$\sigma = \frac{3}{2} \hat{\mathbf{n}} \hat{\mathbf{n}} - \frac{1}{2} I, \tag{A.2}$$

with $I$ as the identity, $\hat{L}, \hat{M}$ and $\hat{N}$ the eigenvectors of $Q$ and $\hat{\mathbf{n}}$ the molecular long axis. Then, using $I = \hat{L} \hat{L} + \hat{M} \hat{M} + \hat{N} \hat{N}$ one can easily show that

$$Q = S \left( \frac{3}{2} \hat{N} \hat{N} - \frac{1}{2} I \right) + P \frac{\left( \hat{L} \hat{L} - \hat{M} \hat{M} \right)}{2}. \tag{A.3}$$

The contraction of $\sigma$ with $Q$ can be expressed as

$$\sigma_{\alpha\beta} Q_{\alpha\beta} = \frac{3}{2} S \left( \frac{3}{2} \left( \hat{\mathbf{n}} \cdot \hat{\mathbf{N}} \right)^2 - \frac{1}{2} \right) + \frac{3}{4} P \left( \left( \hat{L} \cdot \hat{\mathbf{n}} \right)^2 - \left( \hat{M} \cdot \hat{\mathbf{n}} \right)^2 \right). \tag{A.4}$$
A.2 Double tangent construction: invariance under addition of a linear term

The double tangent construction is invariant under the addition of a linear term. The convexification line, $g(\phi) = m\phi + t$ has the property that $\mathcal{F}(\phi) \geq g(\phi) \forall \phi \in D_\phi$ and equality only for the tangent points, $p_-$ and $p_+$. Adding a linear term to $\mathcal{F}$ yields

$$\hat{\mathcal{F}}(\phi) = \mathcal{F}(\phi) + m'\phi$$

$$\hat{g}(\phi) = g(\phi) + m'\phi$$

therefore

$$\hat{\mathcal{F}}(\phi) - m'\phi \geq \hat{g}(\phi) - m'\phi$$

with equality only for the tangent points, and finally

$$\hat{\mathcal{F}} \geq \hat{g}(\phi)$$

and equality only for the tangent points.

A.3 Isotropic integrals

We have encountered isotropic integrals of the form

$$I_{i_1...i_n} \equiv \int_\Omega r_{i_1}...r_{i_n} d^2\mathbf{r}, \quad (A.5)$$

where $r_i = \mathbf{r} \cdot \mathbf{e}_i$ is the $i^{th}$ component of the unit vector $\mathbf{r}$ and the integral is over all orientations, i.e., over the $D-$dimensional unit-sphere. It is clear that the terms for odd $n$ identically vanish

$$I_{i_1...i_n} = 0 \text{ for } n \text{ odd.} \quad (A.6)$$
For three dimensions one can show that

\begin{align}
I_0 &= 4\pi \\
I_{ij} &= 4\pi \frac{1}{3} \sum_{\Pi(ij)} \delta_{ij} \\
I_{ijkl} &= 4\pi \frac{1}{15} \sum_{\Pi(ij,kl)} \delta_{ij}\delta_{kl} \\
I_{ijklmn} &= 4\pi \frac{1}{105} \sum_{\Pi(ij,kl,mm)} \delta_{ij}\delta_{kl}\delta_{mn},
\end{align}

where \( \Pi(ij, kl) \) etc is the set of all pair-wise distinct permutations. (One can show this by performing all the integrals explicitly, or by using an enumeration approach as given in reference [82], reducing the number of integral to evaluate.) Writing the isotropic integrals explicitly yields

\begin{align}
I_0 &= 4\pi \\
I_{ij} &= 4\pi \frac{1}{3} \delta_{ij} \\
I_{ijkl} &= 4\pi \frac{1}{15} (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})
\end{align}

\begin{align}
I_{ijklmn} &= 4\pi \frac{1}{105} \left\{ \delta_{ij} (\delta_{kl}\delta_{mn} + \delta_{km}\delta_{ln} + \delta_{kn}\delta_{lm}) \\
&+ \delta_{ik} (\delta_{jl}\delta_{mn} + \delta_{jm}\delta_{ln} + \delta_{jn}\delta_{lm}) + \delta_{il} (\delta_{jk}\delta_{mn} + \delta_{jm}\delta_{kn} + \delta_{jn}\delta_{km}) \\
&+ \delta_{im} (\delta_{jl}\delta_{kn} + \delta_{jk}\delta_{ln} + \delta_{jn}\delta_{kl}) + \delta_{in} (\delta_{jl}\delta_{km} + \delta_{jk}\delta_{lm} + \delta_{jm}\delta_{kl}) \right\} 
\end{align}

\section*{A.3.1 Van-der-Waals kernel}

When evaluating the kernel due to Van-der-Waals interaction we defined a tensor

\begin{align}
J_{ijkl} = (3r_i r_k - \delta_{ik})(3r_i r_j - \delta_{ij})
\end{align}
and its symmetric, traceless projection, respectively

\[ K_{ijkl} = P_{ij\alpha\beta} J_{\alpha\beta kl} \]  \hspace{1cm} (A.11)

where the projection operator is defined by

\[ P_{ijkl} = \frac{\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}}{2} - \frac{1}{3} \delta_{ij}\delta_{kl}. \]  \hspace{1cm} (A.12)

We note the symmetries \( K_{ijkl} = K_{klij} \) and we define two additional isotropic integrals

\[ \Omega_{ijkl} \equiv \int K_{ijkl} d^2 \hat{r} \]  \hspace{1cm} (A.13)

\[ \Omega_{ijklmn} \equiv \int K_{ijklmn} r_m r_n d^2 \hat{r} \]  \hspace{1cm} (A.14)

We are going to express \( \Omega_{ijkl} \) and \( \Omega_{ijklmn} \) in terms of the isotropic integrals. First we write \( K_{ijkl} \) explicitly

\[ K_{ijkl} = \left( \frac{\delta_{\alpha\beta} \delta_{ij} + \delta_{\alpha\beta} \delta_{ij}}{2} - \frac{1}{3} \delta_{ij}\delta_{\alpha\beta} \right) \left( 9r_\alpha r_\beta r_k r_l - 3r_\alpha r_k r_\beta r_l - 3r_\beta r_k r_\alpha r_l + \delta_\alpha \delta_\beta \right) . \]  \hspace{1cm} (A.15)

Considering each term in the projector separately we get:

\[ \frac{\delta_{\alpha\beta} \delta_{ij}}{2} J_{\alpha\beta kl} = \frac{9}{2} r_i r_j r_k r_l - \frac{3}{2} r_i r_k r_\beta r_l - \frac{3}{2} r_j r_k r_\alpha r_l + \frac{1}{2} \delta_{ik}\delta_{jl} \]  \hspace{1cm} (A.16a)

\[ \frac{\delta_{\alpha\beta} \delta_{ij}}{2} J_{\alpha\beta kl} = \frac{9}{2} r_i r_j r_k r_l - \frac{3}{2} r_j r_k r_\alpha r_l - \frac{3}{2} r_i r_k r_\beta r_l + \frac{1}{2} \delta_{ij}\delta_{kl} \]  \hspace{1cm} (A.16b)

\[ -\frac{1}{3} \delta_{ij}\delta_{\alpha\beta} J_{\alpha\beta kl} = -3\delta_{ij} r_k r_l + \delta_{ij} r_k r_l + \delta_{ij} r_k r_l - \frac{1}{3} \delta_{ij}\delta_{kl} = -\delta_{ij} r_k r_l - \frac{1}{3} \delta_{ij}\delta_{kl} , \]  \hspace{1cm} (A.16c)

thus the kernel integrals are given by

\[ \Omega_{ijkl} = 9I_{ijkl} - \frac{3}{2} I_{ik}\delta_{jl} - \frac{3}{2} I_{jl}\delta_{ik} - \frac{3}{2} I_{jk}\delta_{il} - \frac{3}{2} I_{il}\delta_{jk} \]

\[ + \frac{1}{2} \delta_{ik}\delta_{jl} I_0 + \frac{1}{2} \delta_{jk}\delta_{il} I_0 - \frac{1}{3} \delta_{ij}\delta_{kl} I_0 - \delta_{ij} I_{kl} \]  \hspace{1cm} (A.17)
and
\[
\Omega_{ijklmn} = 9I_{ijklmn} - \frac{3}{2}I_{ikmn}\delta_{jl} - \frac{3}{2}I_{jlmn}\delta_{ik} - \frac{3}{2}I_{jkmn}\delta_{il} - \frac{3}{2}I_{ilmn}\delta_{jk} + \frac{1}{2}\delta_{ik}\delta_{jl}I_{mn} + \frac{1}{2}\delta_{jk}\delta_{il}I_{mn} - \frac{1}{3}\delta_{ij}\delta_{kl}I_{mn} - \delta_{ij}I_{klmn},
\]
respectively. Next we express the kernel integrals in Kronecker deltas. This is easily done for $\Omega_{ijkl}$:
\[
\frac{\Omega_{ijkl}}{4\pi/3} = \frac{9}{5} (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{3}{2} (\delta_{ik}\delta_{jl} + \delta_{jl}\delta_{ik} + \delta_{jk}\delta_{il} + \delta_{il}\delta_{jk}) + \frac{3}{2}\delta_{ik}\delta_{jl} + \frac{3}{2}\delta_{jk}\delta_{il} - \delta_{ij}\delta_{kl} - \delta_{ij}\delta_{kl}.
\]

We tabulate the terms

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{ij}\delta_{kl}$</th>
<th>$\delta_{ik}\delta_{jl}$</th>
<th>$\delta_{il}\delta_{jk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>terms in $\Omega_{ijkl}$</td>
<td>$\frac{9}{5} - 1 - 1$</td>
<td>$\frac{9}{5} - \frac{3}{2} - \frac{3}{2} + \frac{3}{2}$</td>
<td>$\frac{9}{5} - \frac{3}{2} - \frac{3}{2} + \frac{3}{2}$</td>
</tr>
<tr>
<td>total</td>
<td>$-\frac{1}{5}$</td>
<td>$\frac{3}{10}$</td>
<td>$\frac{3}{10}$</td>
</tr>
</tbody>
</table>

thus
\[
\frac{\Omega_{ijkl}}{4\pi/15} = 3 \left( \frac{\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}}{2} - \frac{1}{3}\delta_{ij}\delta_{kl} \right) = 3P_{ijkl}.
\]

The sixth rank kernel integral is a bit more involved:
\[
\frac{\Omega_{ijklmn}}{4\pi/15} = 9I_{ijklmn} - \frac{3}{2}I_{ikmn}\delta_{jl} - \frac{3}{2}I_{jlmn}\delta_{ik} - \frac{3}{2}I_{jkmn}\delta_{il} - \frac{3}{2}I_{ilmn}\delta_{jk} - \frac{3}{2}\delta_{ik}\delta_{jl}I_{mn} - \delta_{ij}I_{klmn} - \delta_{ij}I_{klmn} - \delta_{ij}I_{klmn} + \frac{5}{2}\delta_{ik}\delta_{jl}I_{mn} - \frac{5}{2}\delta_{jk}\delta_{il}I_{mn} - \frac{5}{2}\delta_{ij}\delta_{kl}I_{mn} - \delta_{ij}(\delta_{kl}\delta_{mn} + \delta_{km}\delta_{ln} + \delta_{kn}\delta_{lm}).
\]
Here too we tabulate all terms (each permutation picks up a term $\frac{9}{7}$ in the $I_{ijklmn}$ term)

<table>
<thead>
<tr>
<th>term in $\Omega_{ijklmn}$</th>
<th>term in $A_{\alpha\beta\gamma\lambda} \Omega_{ij\alpha\beta\gamma\lambda}$</th>
<th>factor in $I_{ijklmn}/(4\pi/15)$</th>
<th>factors in table A.22</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{ij}\delta_{kl}\delta_{mn}$</td>
<td>$\delta_{ij}A_{\alpha\alpha\beta\beta}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{5}{3} - 1$</td>
<td>$-\frac{29}{21}$</td>
</tr>
<tr>
<td>$\delta_{ij}\delta_{km}\delta_{ln}$</td>
<td>$\delta_{ij}A_{\alpha\beta\alpha\beta}$</td>
<td>$\frac{9}{7}$</td>
<td>$-1$</td>
<td>$\frac{2}{7}$</td>
</tr>
<tr>
<td>$\delta_{ij}\delta_{kn}\delta_{lm}$</td>
<td>$\delta_{ij}A_{\alpha\beta\beta\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-1$</td>
<td>$\frac{2}{7}$</td>
</tr>
<tr>
<td>$\delta_{ik}\delta_{jl}\delta_{mn}$</td>
<td>$A_{ij\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$\frac{5}{2} - \frac{3}{2} - \frac{3}{2}$</td>
<td>$\frac{11}{14}$</td>
</tr>
<tr>
<td>$\delta_{ik}\delta_{jm}\delta_{ln}$</td>
<td>$A_{ia\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{ik}\delta_{jn}\delta_{lm}$</td>
<td>$A_{io\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{il}\delta_{jk}\delta_{mn}$</td>
<td>$A_{ija\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$\frac{5}{2} - \frac{3}{2} - \frac{3}{2}$</td>
<td>$\frac{11}{14}$</td>
</tr>
<tr>
<td>$\delta_{il}\delta_{jm}\delta_{kn}$</td>
<td>$A_{ai\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{il}\delta_{jn}\delta_{km}$</td>
<td>$A_{ai\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{im}\delta_{jl}\delta_{kn}$</td>
<td>$A_{\alpha\alpha\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{im}\delta_{jn}\delta_{kl}$</td>
<td>$A_{aa\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$0$</td>
<td>$\frac{9}{7}$</td>
</tr>
<tr>
<td>$\delta_{in}\delta_{jl}\delta_{km}$</td>
<td>$A_{\alpha\alpha\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{in}\delta_{jk}\delta_{lm}$</td>
<td>$A_{\alpha\alpha\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$-\frac{3}{2}$</td>
<td>$-\frac{3}{14}$</td>
</tr>
<tr>
<td>$\delta_{in}\delta_{jm}\delta_{kl}$</td>
<td>$A_{\alpha\alpha\alpha\alpha}$</td>
<td>$\frac{9}{7}$</td>
<td>$0$</td>
<td>$\frac{9}{7}$</td>
</tr>
</tbody>
</table>
The resulting kernel integral can be written as
\[
\frac{\Omega_{ijklmn}}{4\pi/15} = \frac{11}{7} \left( \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{li} - \frac{1}{3} \delta_{ij}\delta_{kl} \right) \delta_{mn} - \frac{6}{7} \delta_{ij}\delta_{kl}\delta_{mn} - 12\frac{1}{4} \left( \delta_{ik}\delta_{jn} + \delta_{jk}\delta_{in} - \frac{1}{3} \delta_{ij}\delta_{kn} \right) \delta_{lm} - 12\frac{1}{4} \left( \delta_{ik}\delta_{jm} + \delta_{jk}\delta_{im} - \frac{1}{3} \delta_{ij}\delta_{km} \right) \delta_{ln} - 12\frac{1}{4} \left( \delta_{il}\delta_{jn} + \delta_{jl}\delta_{in} - \frac{1}{3} \delta_{ij}\delta_{lm} \right) \delta_{km} - 12\frac{1}{4} \left( \delta_{il}\delta_{jm} + \delta_{jl}\delta_{im} - \frac{1}{3} \delta_{ij}\delta_{kn} \right) \delta_{km}
\]
(A.23)

A.3.2 Summary

We finally arrive at the following contractions of tensors with the isotropic and kernel integrals that appear in the gradient expanded version of the functional derivatives:
\[
\frac{A_{\ell_0}}{4\pi/15} = 15A
\]
(A.24)
\[
\frac{A_{\alpha\beta} I_{\alpha\beta}}{4\pi/15} = 5A_{\alpha \alpha}
\]
(A.25)
\[
\frac{A_{\alpha\beta} I_{\alpha\beta\gamma}}{4\pi/15} = (\delta_{ij} A_{\alpha \alpha} + A_{ij} + A_{ji})
\]
(A.26)
\[
\frac{A_{\alpha\beta\gamma} \lambda I_{\alpha\beta\gamma\lambda}}{4\pi/15} = (A_{\alpha\beta\beta} + A_{\alpha\beta\alpha} + A_{\alpha\beta\alpha})
\]
(A.27)
\[
\frac{A_{\alpha\beta} \Omega_{\alpha\beta\gamma}}{4\pi/15} = 3 \left( \frac{A_{ij} + A_{ji}}{2} - \delta_{ij} A_{\alpha\alpha} \right)
\]
(A.28)
\[
\frac{A_{\alpha\beta\gamma} \lambda \Omega_{\alpha\beta\gamma\lambda}}{4\pi/15} = 3 \left( A_{\alpha\beta\alpha} + A_{\alpha\beta\alpha} - A_{\alpha\alpha\beta} \right)
\]
(A.29)
\[
\frac{A_{\alpha\beta\gamma\lambda} \Omega_{\alpha\beta\gamma\lambda}}{4\pi/15} = 11\left\{ \frac{A_{\alpha\beta\gamma\lambda} + A_{\alpha\beta\gamma\lambda}}{2} - \frac{1}{3} \delta_{ij} A_{\alpha\alpha\beta\gamma} \right\} - \frac{6}{7} \delta_{ij} A_{\alpha\alpha\beta\gamma}
\]
(A.30)
\[
\begin{align*}
\frac{A_{\alpha\beta\gamma\lambda\mu\nu} \Omega_{\alpha\beta\gamma\lambda\mu\nu}}{4\pi/15} &= \\
\frac{11}{7} \left\{ A_{\alpha\beta\gamma\alpha\alpha\alpha} + 2 A_{\alpha\beta\gamma\alpha\alpha} - \frac{1}{3} A_{\alpha\alpha\beta\gamma\gamma} \right\} - 6 \frac{1}{7} A_{\alpha\alpha\beta\gamma\gamma} \\
- \frac{12}{7} \left\{ A_{\alpha\beta\gamma\alpha\alpha\alpha} + 2 A_{\alpha\beta\gamma\alpha\alpha} - \frac{1}{3} A_{\alpha\alpha\beta\gamma\gamma} \right\} - \frac{12}{7} \left\{ A_{\alpha\beta\gamma\alpha\alpha\alpha} + 2 A_{\alpha\beta\gamma\alpha\alpha} - \frac{1}{3} A_{\alpha\alpha\beta\gamma\gamma} \right\} \\
- \frac{12}{7} \left\{ A_{\alpha\beta\gamma\alpha\alpha\alpha} + 2 A_{\alpha\beta\gamma\alpha\alpha} - \frac{1}{3} A_{\alpha\alpha\beta\gamma\gamma} \right\} - \frac{12}{7} \left\{ A_{\alpha\beta\gamma\alpha\alpha\alpha} + 2 A_{\alpha\beta\gamma\alpha\alpha} - \frac{1}{3} A_{\alpha\alpha\beta\gamma\gamma} \right\}
\end{align*}
\]
(A.31)

### A.4 Phase-separation critical point

We consider a (reduced) free energy density of the form

\[
\beta \mathcal{F} = -\frac{a}{2} \frac{T_c}{T} \left( \phi - \phi_0 \right)^2 + \phi \ln \phi + s \left( 1 - \phi \right) \ln \left( 1 - \phi \right)
\]
(yielding a (reduced) chemical potential

\[
\mu(\phi) = -a \frac{T_c}{T} \phi + \phi \ln \phi - s \ln \left( 1 - \phi \right),
\]
(ignoring constant terms. At the critical point the first and second derivative of \( \mu \) vanish simultaneously and \( T = T_c \), when \( T_c \) is taken to be the critical temperature.

Then the first derivative yields

\[
\mu'_\phi = -a \frac{\phi_c (1 - \phi_c) + 1 + (s - 1) \phi_c}{\phi_c (1 - \phi_c)} \equiv 0
\]
(A.34)

and the second

\[
\mu''_\phi = \frac{(s - 1) \phi_c^2 + 2 \phi_c - 1}{\phi_c^2 (1 - \phi_c^2)} \equiv 0.
\]
(A.35)

Solving Eq. (A.35) for \( \phi_c \) yields

\[
\phi_c = -\left( \frac{1}{s - 1} \right) \pm \frac{\sqrt{s}}{s - 1} = \frac{\pm \sqrt{s} - 1}{s - 1},
\]
(A.36)
of which only the positive root is of interest, since \( \phi_c \in [0..1] \) and \( s > 0 \): for \( s > 1 \) because \( \phi_c > 0 \) and for \( s < 1 \) because \( \phi_c < 1 \), respectively. The volume fraction at the critical temperature is thus given by

\[
\phi_c = \frac{1 - \sqrt{s}}{1 - s} = \frac{1}{1 + \sqrt{s}},
\]

(A.37)

and we also have

\[
\phi_c (1 - \phi_c) = \frac{\sqrt{s}}{(1 + \sqrt{s})^2}.
\]

(A.38)

Inserting Eqs. (A.37) and (A.38) back into (A.34) yields

\[
a_c = (1 + \sqrt{s})^2.
\]

(A.39)

The solution is the same if we multiply the chemical potential by \( u \):

\[
\mu u = -au \phi + u \ln \phi - su \ln (1 - \phi).
\]

(A.40)

With \( a' = au \) and \( s' = su \) we write

\[
\frac{a'}{u} = \left(1 + \sqrt{\frac{s'}{u}}\right)^2.
\]

(A.41)

or

\[
a' = \left(\sqrt{u} + \sqrt{s'}\right)^2.
\]

(A.42)

Thus for a chemical potential of the form

\[
\mu = -a \frac{T_c}{T} \phi + u \ln \phi - s \ln (1 - \phi),
\]

(A.43)

where \( T_c \) is the critical temperature, the parameter \( a \) is given by

\[
a = (\sqrt{u} + \sqrt{s})^2
\]

(A.44)
A.5 Pseudo-critical point of the nematic-isotropic phase transition

We consider a dimensionless free energy density of a homogenous system of the form

$$F' = -\lambda_1(\phi) \ln \int \exp \left( \frac{c}{T} \phi \left( \sigma_{\alpha\beta} Q_{\alpha\beta} - \frac{1}{2} Q_{\alpha\beta} Q_{\alpha\beta} \right) \right) d^2 \sigma.$$  \hspace{1cm} (A.45)

with $\lambda_1(\phi)$ some arbitrary function, independent of $Q_{ij}$, and want to find how the value of $c$ relates to the nematic pseudo-critical temperature $T^*$. We assume that in a homogenous system without molecular biaxiality the equilibrium value for $P$ is zero. We write Eq. (A.45) using (A.4), ignoring biaxiality terms as

$$F' = -\lambda_1(\phi) \ln \int \exp \left( \frac{3}{2T} \phi \left( S P_2 (\cos \theta) - \frac{1}{2} S^2 \right) \right) \sin \theta d\theta d\phi$$  \hspace{1cm} (A.46)

$$= \lambda_1(\phi) \left( \frac{3}{4T} \phi S^2 - \ln \int_0^1 \exp \left( \frac{3}{2T} \phi S \left( \frac{3}{2} x^2 - \frac{1}{2} \right) \right) dx \right) + \text{const.}$$  \hspace{1cm} (A.47)

Expanding about $S = 0$ yields (ignoring the constant term) to quadratic order in $S$

$$F' \simeq \lambda_1(\phi) \frac{3}{4T} \phi \left( 1 - \frac{3}{10T} \phi \right) S^2 + O(S^3).$$  \hspace{1cm} (A.48)

Since the nematic pseudo-critical temperature $T^*$ is defined as the temperature where the coefficient of the quadratic term in the free energy density vanishes in a pure system ($\phi = 1$), it follows that

$$c = \frac{10}{3} T^*.$$  \hspace{1cm} (A.49)

On the other hand, we may be given a functional derivative of the free energy of the form

$$\frac{\delta F'}{\delta Q_{ij}} = \frac{\partial F'}{\partial Q_{ij}} = b \phi \lambda_2(\phi) \left( Q_{ij} - \langle \sigma_{ij} \rangle_{H_{ij}} \right).$$  \hspace{1cm} (A.50)
where $\lambda_2$ ($\phi$) is an arbitrary function of $\phi$, independent of $Q_{ij}$, and the canonical average of the molecular orientation is given by

$$
\langle \sigma_{ij} \rangle_{H_{ij}} = \frac{\int \sigma_{ij} \exp \left( b\phi \sigma_{\alpha\beta} Q_{\beta\alpha} \right) d^2\sigma}{\int \exp \left( b\phi \sigma_{\alpha\beta} Q_{\beta\alpha} \right) d^2\sigma},
$$

(A.51)

where $b$ is a parameter to be determined. Eq. (A.50) with (A.51) can be thought of being derived from a free energy density of the form

$$
\mathcal{F}_2' = -\lambda_2 (\phi) \ln \int \exp \left( b\phi \left( \sigma_{\alpha\beta} Q_{\beta\alpha|r} - \frac{1}{2} Q_{\alpha\beta|r} Q_{\beta\alpha|r} \right) \right) d^2\sigma,
$$

(A.52)

which is unique up to a function that does not depend on $Q_{ij}$. The functional derivative with respect to $Q_{ij}$ of the free energy (A.45), on the other hand is

$$
\frac{\partial \mathcal{F}_1'}{\partial Q_{ij}} = \lambda_1 (\phi) \frac{c}{T} \phi \left( Q_{ij} - \langle \sigma_{ij} \rangle \right)
$$

(A.53)

with

$$
\langle \sigma_{ij} \rangle = \frac{\int \sigma_{ij} \exp \left( \frac{c}{T} \phi \sigma_{\alpha\beta} Q_{\beta\alpha} \right) d^2\sigma}{\int \exp \left( \frac{c}{T} \phi \sigma_{\alpha\beta} Q_{\beta\alpha} \right) d^2\sigma}
$$

(A.54)

Comparing (A.54) with (A.51) yields

$$
b = \frac{c}{T} = \frac{10}{3} \frac{T^*}{T}.
$$

(A.55)

Note that only the coefficients of $\sigma_{\alpha\beta} Q_{\beta\alpha}$ in the canonical average are relevant. The factor in front of the term $Q_{ij} - \langle \sigma_{ij} \rangle$ cannot not affect the result, as the free energy can always be rescaled yielding a different factor, but the critical temperature must be independent of a rescaling of the free energy.
Bibliography


[10] M. Plischke and B. Bergerson, in Equilibrium Statistical Physics, 2nd ed. (World Scientific, Singapore, 1994), Chap. 3.8, this textbook gives the Maier-Saupe free energy in slightly different form: set $T^* = 2\rho U / 5\phi$ in Eq. (2.1) to arrive at their form.


