THE EFFECT OF SHEAR FLOW ON THE ISOTROPIC-NEMATIC TRANSITION IN LIQUID CRYSTALS

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In this thesis I will discuss the effects of shear flow on the Isotropic-Nematic phase transition in liquid crystals. Shear flow has dramatic orienting effects on the rod-like constituents of nematic liquid crystals, with the general effects of (1) *inducing* order in the high-temperature isotropic phase, and (2) dictating a direction of alignment for the low-temperature nematic phase. Shear flow also imposes a biaxial symmetry on *both* the high and low temperature phases, thereby changing the nature of the symmetry-breaking at the transition.

We develop coupled deterministic dynamical equations for the 5-component nematic order parameter and the fluid velocity, which may be considered generalizations of the Leslie-Ericksen and Navier-Stokes equations, respectively. We examine the stable stationary solutions to these equations to determine the nature of the non-equilibrium phases, and discuss the analogies and differences between this system and equilibrium systems. From *homogeneous* solutions we obtain a state diagram analogous to that of a Van der Waals fluid, including a two-state region and a discontinuous transition which terminates at a critical point. To resolve the question of the analog of the Maxwell construction to distinguish locally stable states, we construct stable *inhomogeneous* interfacial states. From an analysis of these states we determine a coexistence line and find exponents characterizing the shape of the coexistence curve and the interface thickness as the critical point is approached. We find *mean-field* critical behavior, and comment on the possibility of the analogs of spinodal decomposition and nucleation.

Finally, we develop a formalism for describing light scattering from biaxial steady state, and investigate the Gaussian level fluctuations about these states. In the vicinity of the critical point we find singular behavior analogous to critical opalescence of a simple fluid at its critical point. We also find anisotropic correlations at the critical point which reflect the manner in which shear flow suppresses fluctuations, as was found by Onuki and Kawasaki in their studies of a binary fluid under shear flow. We finish by commenting on the application of these ideas to lyotropic systems, and combining flow and magnetic field effects in the same system.

In memory of Emily Olmsted

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Chapter 1

Introduction

1.1 Motivation

Beginning largely with the work of Gibbs[1] near the turn of the century, and continuing until the present day with the ideas of Einstein,[2] Onsager,[3] Landau,[4] Kadanoff,[5] Wilson,[6] and many others, the study of equilibrium statistical mechanics has been very successful in explaining aspects of many of the systems in our world: gases, liquids, and solids; magnets; superconductors; other-worldly phenomena such as the cosmic background radiation; and even, some might argue, the behavior of neurons in the brain. However, much of the world around us is *not* in an equilibrium state. Many events involve a relaxation to equilibrium, such as the aftermath of an explosion and the resulting expansion of gas and heat. Still other systems are, and remain, driven from equilibrium, such as the ocean tides, water boiling on a stove, or a running engine.

Whether in equilibrium or not, one of the most vexing, curious, and, many would argue, important problems is how a system changes its qualitative state. For example, why can we have water and ice as manifestations of the same substance under different imposed conditions, and how may we define and distinguish these phases? In the answers to these questions we have found that, while nature is unpredictably diverse and subtle, it is also very well organized, and the study of one system invariably provides insights into others. A familiar example of this from statistical physics is the Ising model which, due to the hypothesis (experimentally verified, at least approximately) of universality, is a model for such seemingly different systems as a liquid-gas mixture near its critical point, as well as the magnet it was originally devised to mimic.[5]

In this thesis I will discuss the effect of shear flow on the Isotropic-Nematic (IN) transition of liquid crystals. This system weds the two concepts I have just mentioned; the IN transition is a well-studied equilibrium phase transition, and shear flow drives the system out of equilibrium. While there are many non-equilibrium systems that have been studied, there are several features that make nematics in shear flow a particularly interesting and attractive system:

1. The order parameter has several coupled degrees of freedom, some of which become apparent only in the presence of external fields, of which applied shear stress is an example. The presence of several degrees of freedom provides a rich environment for exploring different possible macroscopic states and transitions. In addition, fluctuations of individual modes of the order parameter may be conveniently isolated by polarized light scattering, allowing one to probe in detail the behavior of the fluctuations of the order parameter.

2. Shear flow brings the system out of equilibrium, which makes the problem a testing ground for methods of determining and understanding non-equilibrium states.

3. Shear flow has two effects which are very important. First, it provides advection, which distorts fluctuations. This has a profound effect on the evolution of fluctuations, favoring some over others, and can thus alter the nature of a critical point,[7] whose properties reflect the fluctuation behavior of the system.

4. The second effect is that shear flow actually *induces ordering* in the rod-like molecules that constitute the liquid crystal.[8–10] This point distinguishes nematics in shear flow from other systems which have been studied under shear flow, and is one of the main motivations for this study.

This combination of an external agent (the flow field) which can both induce order and drive the system out of equilibrium, and the multi-component order parameter of the nematic system, leads us to suspect that shear flow may induce a transition. If this is so, then the transition happens under non-equilibrium conditions, which means that we cannot investigate the problem using the standard methods of equilibrium statistical mechanics. Finally, we would like to know how, if such a transition occurs, it may resemble, or differ from, equilibrium transitions.

1.2 Outline

This thesis is organized as follows. In the remainder of this Introduction I will discuss the general problem of non-equilibrium phase transitions.

In Chapter 2 I will review and summarize the theory of equilibrium nematic liquid crystals and the IN phase transition.[11] The important points about the IN transition for our discussion are that the equilibrium transition is a *weak* first order transition (this will discussed in more detail below) and that the order parameter has several coupled internal degrees of freedom.

In Chapter 3 I will return to the subject of non-equilibrium physics, and try to clarify the important distinction between the role of shear flow as an ordering field, and the role of shear in influencing fluctuations, and indicate how these considerations apply to non-equilibrium systems such as various complex fluids under shear, binary fluids under shear, and a driven diffusive lattice gas.

In Chapter 4 I will review the conventional theory of the dynamics of nematic liquid crystals,[12] which is a theory for the coupled dynamics of the director field (defined below) and the fluid velocity field. I will argue that to effectively describe the transition under shear flow one needs to consider the dynamics of the *entire order parameter*, rather than the director field.[8,13,9] We will derive a particular dynamics which will be used henceforth, and discuss possible alternative approaches to the dynamics.[9,10,14,15]

The non-equilibrium phase diagram at the mean-field level (*i.e.* not allowing the system to explore any configurations besides the stationary ones) as determined by these dynamics will be discussed in Chapters 5 and 6. In Chapter 5 we will examine homogeneous stable steady states and find state structure reminiscent of that exhibited by the van der Waals (VdW) fluid.[16] We will pursue this analogy further in Chapter 6, where we will examine stable stationary *interfacial* (*i.e.* inhomogeneous) solutions to the dynamics, from which we can explore the issues state selection and critical behavior.

Chapter 7 presents a discussion of the role of Gaussian fluctuations in this non-equilibrium system in terms of prediction for light scattering experiments. This aspect of the thesis is related to work by Onuki and Kawasaki and others.[7,17] I will focus on two particularly interesting regimes: (1) the region near equilibrium, where we will examine how shear flow perturbs the equilibrium behavior, and (2) the region near the non-equilibrium critical point, where we will find anomalous scattering analogous to the critical opalescence found at a liquid-gas critical point.

Finally, in Chapter 8 I will briefly discuss possible extensions of this work to systems such as lyotropic liquid crystals,[18] the application of renormalization group techniques to gain an understanding the non-equilibrium critical point,[7] and speculate on the effects fluid flow and magnetic fields may have when they act *together* on nematics.

1.3 Non-Equilibrium Systems

1.3.1 Non-Equilibrium States

Non-equilibrium systems pose many difficult problems. While equilibrium statistical mechanics is founded on the assumption of maximum entropy,[4,19] which provides a variational principle with which to determine the equilibrium states, no equivalent general principle has been found for non-equilibrium systems. The procedure for finding equilibrium states is well-documented: one begins with a formal expression for the partition function for the system, and then uses whatever mathematical techniques are available to compute the effective free energy for the system, usually beginning with a mean-field theory and later improving, if possible, on that. The guiding rule one always follows is that an equilibrium state is that which maximizes the entropy of the system, correspondingly minimizing the appropriate free energy.[4] However, as entropy is being *produced* in a non-equilibrium system, one is certainly not justified in using a maximum entropy hypothesis for non-equilibrium systems.

Since non-equilibrium steady states may often take the form of stationary solutions to partial differential equations in space and time, many workers have discussed such states by the method of Lyapunov,[20,21] originally developed as a method for determining the mathematical stability of such solutions. I will not explain this method in detail, but the general idea is to try and construct a *Lyapunov functional* $\mathcal{L}$. The Lyapunov functional is constructed from the time-dependent quantities in the system (*e.g.* the fluid velocity and temperature field for the Rayleigh-Benard convection problem[21]) and must obey certain convexity properties. If $\mathcal{L}$ can be found, then the steady state is also stable. Because of its convexity properties the Lyapunov functional bears a resemblance to a non-equilibrium entropy, and has been exploited as such, most notably by Glansdorff and Prigogine,[20] to develop formal stability criteria for non-equilibrium steady states. The search for such a functional often involves searching for an 'effective free energy', *i.e.*, a functional whose variation with respect to the dynamical quantities will give the correct equations of motion. Many people have used this method to examine non-equilibrium problems which admit such a functional,[20,22,15] often attacking the reformulated problem with the same methods used in *equilibrium* statistical mechanics.

An alternative phenomenological approach to determining non-equilibrium states has been developed by Graham. This method involves introducing a generalized thermodynamic potential which is related to the Onsager-Machlup function of the system.[23]

1.3.2 Non-Equilibrium Phase Transitions

While our understanding of equilibrium phase transitions is fairly complete,* and the idea of universality in systems at critical points is generally accepted,[5,6,27] the same is not true for non-equilibrium phase transitions.[28,29] Non-equilibrium transitions occur in systems such as Rayleigh-Benard convection of fluids[30] and chemical reactions[31], where the transition is between *non-stationary* steady states that may be, *e.g.*, chaotic or oscillatory; and in systems such as complex fluids under flow[7] or a driven diffusive lattice gas,[32] where the nature of an equilibrium transition between homogeneous states is qualitatively changed by driving the system into a steady *stationary* non-equilibrium state. In the latter systems the non-equilibrium transition may occur between stable stationary states, and may reduce smoothly to the equilibrium transition as the external driving field is removed. In this way the non-equilibrium transition bears a strong resemblance to the equilibrium transition, and the study of these systems could be an important step towards the understanding of the more complex transitions further from equilibrium. We shall discuss this kind of non-equilibrium transition in this thesis. Of course, it is also possible that such a study will provide *no* insight into more complex systems, precisely because they are close related to equilibrium.

*Not *all* issues of equilibrium phase transitions have, of course, been resolved. First order transitions are still not well-understood,[24,25] and there are many delicate issues yet to be resolved when many fluctuating degrees of freedom come into play, as near the nematic-smectic A-smectic C point in liquid crystals.[26]

Chapter 2

The Isotropic-Nematic Transition

2.1 Nematic Liquid Crystals

Nematic phases are the simplest of the myriad liquid crystalline phases.[26,33–35] Liquid crystalline phases are often referred to as *mesophases* because they are intermediate between the familiar liquid and solid states of matter. The constituents of these systems are thus often referred to as *mesogens*. Nematic liquid crystals comprise rodlike mesogens either in a melt (thermotropic) or in solution (lyotropic), which undergo a transition upon cooling (thermotropic) or increasing the concentration (lyotropic) from a disordered isotropic state to a state with orientational order but positional disorder. I will discuss primarily thermotropics, for simplicity, but say a few words about lyotropics. Examples of such systems are N-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA),[33] a thermotropic system with molecules of length ~ 20Å, and the Tobacco Mosaic Virus in, *e.g.*, water (TMV),[18] a lyotropic system with mesogenic dimension ~ 1800Å. Other mesogenic phases include various *smectic* phases, in which nematically aligned rods also acquire a one-dimensional density wave, and can roughly be considered a layered structure; *cholesteric* phases, whose molecules have a particular handedness, or chirality, and hence align with an intrinsic twist; and phases consisting of other kinds of molecules, such as disc shaped or polymeric molecules.[26]

Nematic liquid crystals are distinguished experimentally by the defect structures seen in the nematic state, which look like a tangle of threads ($\nu\eta\mu\alpha$ is the Greek word for thread), and intense scattering of certain polarizations of light below the transition temperature which, consequently, is known as the 'clearing point'.[33] We will see that this scattering is due to low energy fluctuations in the director orientation resulting from the spontaneously broken rotational symmetry of the nematic state.

The salient aspect of a nematically ordered phase is the direction, on average, in which the rod-like molecules point. Although the molecules do not generally have an exact microscopic symmetry under head-to-tail exchange, it is an experimental fact that the nematic phase is indistinguishable from that obtained upon a rotation by π about an axis normal to the director. This is due to factors such as fast microscopic rotation of the molecules and the low energy cost to pack them regardless of sense. The result is that the statistically preferred orientation is specified by a headless unit vector $\pm\hat{\mathbf{n}}$, called the *director*.[33]

2.2 Order Parameter

While the presence of a director distinguishes the nematic phase from the isotropic phase, order in the system is not measured by the director. Let $\psi\{\boldsymbol{\nu}\}$ be the rod orientation distribution function for a uniform phase, where $\boldsymbol{\nu}$ is the unit vector denoting the molecular orientation. Any vector order parameter built from averages over $\boldsymbol{\nu}$ vanishes because of the head-tail symmetry mentioned above, *i.e.* $\psi\{\boldsymbol{\nu}\} = \psi\{-\boldsymbol{\nu}\}$. The next simplest choice for an order parameter is a tensor built from an average over the second moment of the orientational distribution function:[11,36]

$$Q_{\alpha\beta}(\mathbf{r}) = \frac{1}{N}\sum_{i=1}^{N}\left\langle(\nu^i_\alpha\nu^i_\beta - \tfrac{1}{3}\delta_{\alpha\beta})\,\delta(\mathbf{r}-\mathbf{r}^i)\right\rangle, \tag{2.1}$$

where the average is taken over $\psi\{\boldsymbol{\nu}^i\}$. The trace is subtracted to give $Q_{\alpha\beta} = 0$ in the isotropic state. This order parameter has five degrees of freedom, being a traceless and symmetric second-rank tensor. In general one may also consider higher moments of the distribution function,[34] but for most purposes $Q_{\alpha\beta}$ suffices.

If the equilibrium distribution of rod orientations is isotropic then $Q_{\alpha\beta}$ is zero, as may be easily verified. If the equilibrium state is uniaxially nematic the order parameter may be written generally as

$$Q_{\alpha\beta} = \tfrac{3}{2}S_1(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{2.2}$$

where the unit vector (or director) $\hat{\mathbf{n}}$ is the non-degenerate eigenvector of $Q_{\alpha\beta}$ and S_1 is the corresponding eigenvalue. The director indicates the uniaxial alignment and the amplitude S_1 indicates the degree of order. Since $\{\boldsymbol{\nu}^i\}$ are unit vectors, we see from eqs. (2.1) and (2.2) that $0 \leq |S_1| \leq 2/3$. The rod distribution is *discotic* if $Q_{\alpha\beta}$ has two positive eigenvalues, and conventional uniaxial (sometimes called *calamitic*) if $Q_{\alpha\beta}$ has one positive eigenvalue.

The uniaxial distribution is by far the most common in equilibrium systems. Most examples of equilibrium biaxial phases (in the absence of external fields) have been found in lyotropic mixtures such as potassium laurate/1-decanol/D_2O.[37−39] The more general biaxial state, which is the natural state in the presence of a biaxial field such as shear flow, may be written as[36]

$$Q_{\alpha\beta} = \frac{3S_1}{2}(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}) + \frac{S_2}{2}(m_\alpha m_\beta - l_\alpha l_\beta), \tag{2.3}$$

where $\hat{\mathbf{m}}$ is a second unit vector (or sub-director) denoting the asymmetry of the distribution of the rod orientations, S_2 is a second amplitude, and $\hat{\mathbf{l}} = \hat{\mathbf{n}} \times \hat{\mathbf{m}}$. While a uniaxial state has the symmetry of a cigar (nematic) or a frisbee (discotic), a biaxial state has the symmetry of a match box: there is a major alignment direction, given by $\hat{\mathbf{n}}$, and if one looks head-on down this axis one sees not a circle, as in the uniaxial state, but an ellipse with apogee and perigee along $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$ respectively. The biaxial state is specified by five parameters: the two amplitudes S_1 and S_2, two angles to specify the director $\hat{\mathbf{n}}$, and a third angle to specify the rotation angle of $\hat{\mathbf{m}}$ about $\hat{\mathbf{n}}$. The uniaxial state is specified by only three parameters, the magnitude S_1 and two angles to locate the director.

The order parameters S_1 and S_2 may also be written in terms of the rod orientation distribution function according to

$$S_1 = \langle\cos^2\theta - \tfrac{1}{3}\rangle = \langle\nu_z^2 - \tfrac{1}{3}\rangle \tag{2.4}$$

$$S_2 = \langle\sin^2\theta\cos 2\phi\rangle = \langle\nu_x^2 - \nu_y^2\rangle. \tag{2.5}$$

Here the z-axis is taken to be parallel to $\hat{\mathbf{n}}$, and the angle brackets denote an average over the probability distribution $\psi\{\boldsymbol{\nu}\}$.

Table 2.1: Characteristics of the I-N Transition within Landau-de Gennes theory (see Gramsbergen, *et al.*[40]).

Transition temperature	$T_{IN} = T^- + \dfrac{B^2}{27aC}$
Upper spinodal temperature	$T^+ = T^- + \dfrac{B^2}{24aC}$
Order parameter discontinuity	$\Delta S_1 = -\dfrac{2B}{9C}$
Order parameter for $T \leq T_{IN}$	$S_1 = S_o(T) = -\dfrac{B}{6C} + \left(\dfrac{4A}{3C}\right)^{1/2}$
Entropy jump	$\Delta S = \dfrac{aB^2}{27C^2}$

As the order parameter is a measure of the anisotropy in the system, it may be inferred from various physical measurements. A common example is optical birefringence measurements.[34] In a uniaxial aligned state light will experience two indices of refraction, n_{o} and n_{e}, depending on whether the polarization of the light is perpendicular or parallel to the director. Other examples are the anisotropy in the magnetic susceptibility tensor $\chi_{\alpha\beta}$, which will be discussed below,[33] and the dielectric tensor $\epsilon_{\alpha\beta}$, whose fluctuations may be probed by light scattering (see Chapter 7).

2.3 Landau-de Gennes Theory of the Isotropic-Nematic Transition

The IN transition is experimentally found to be a *weak* first order transition (S_1 is typically ~ 0.3), so we may obtain satisfactory results by assuming that the equilibrium free energy is given by minimizing a free energy density which is an expansion in the order parameter $Q_{\alpha\beta}$:[4,11]

$$f_{\mathrm{L}} = \tfrac{1}{2}A\, Q_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{3}B\, Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}C\big(Q_{\alpha\beta}Q_{\beta\alpha}\big)^2. \tag{2.6}$$

This is known as the Landau-de Gennes free energy density. Note the use of Einstein summation convention, which will be employed throughout this thesis. The cubic term is allowed because $Q_{\alpha\beta} \rightleftharpoons -Q_{\alpha\beta}$ is not a symmetry of the system, so we see that the mean-field transition can be first order.[4] A negative B gives the conventional uniaxial nematic state. The important temperature dependence is taken to reside in $A = a(T - T^-)$, while the variation of B and C with T is assumed to be unimportant and is neglected. Figure 2.1 shows the Landau-de Gennes free energy density as a function of the order parameter for various temperatures, At high temperatures the system is isotropic. At T^+ (upper spinodal temperature) a metastable ordered state develops, and at T_{IN} the two states have the same free energy and the transition occurs. For lower temperatures the isotropic state is metastable until T^- (lower spinodal temperature) is reached, at which it becomes unstable. For $B < 0$ the ordered state is the conventional nematic state, while for $B > 0$ the ordered state is discotic. Table 2.1 summarizes some useful information about the first order transition, within a Landau description.[40]

Figure 2.1: Landau-de Gennes free energy f_L versus order parameter S_1 for the isotropic-nematic transition.

2.4 Distortions and Fluctuations

In addition to the uniform Landau-de Gennes free energy density, we may also parametrize the free energy cost of spatial distortions.[41] This may be done in two limits. At temperatures well below the transition temperature T_{IN}, the system strongly resists variations in the magnitude of the order parameter (the free energy well is 'steep'), so we may limit discussion to variations in the direction of alignment. These distortions will be allowed in the long wavelength limit, since they are Goldstone modes.[42] The appropriate energy is given by the Frank free energy density, which is an expansion to quadratic order in gradients of the director $\hat{\mathbf{n}}(\mathbf{r})$:

$$f_F\{\hat{\mathbf{n}}\} = \tfrac{1}{2}K_1(\nabla\cdot\hat{\mathbf{n}})^2 + \tfrac{1}{2}K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \tfrac{1}{2}K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2. \tag{2.7}$$

Here K_1, K_2, and K_3 parametrize *splay*, *twist*, and *bend* deformations, respectively. This free energy is, by construction, invariant under simultaneous rotations of $\hat{\mathbf{n}}$ and spatial coordinates.

For temperatures near the transition temperature (indeed, we may consider the system to be slightly *above* T_{IN}), variations in amplitude may occur much more easily, since the free energy minimum is 'flatter'. In this case is more sensible to parametrize non-uniformities in the system by the entire order parameter $Q_{\alpha\beta}(\mathbf{r})$, which will incorporate both amplitude *and* orientational variations. To quadratic order in the order parameter and its gradients we may perform an expansion[36]

$$f_F\{Q_{\alpha\beta}\} = \tfrac{1}{2}L_1\,(\partial_\alpha Q_{\beta\gamma})^2 + \tfrac{1}{2}L_2\,(\partial_\alpha Q_{\alpha\beta})^2, \tag{2.8}$$

where L_1 and L_2 are analogs of the Frank constants. This is not the most general expansion; we have ignored surface terms and terms of the same order in gradients but higher order in $Q_{\alpha\beta}$, but for bulk properties and systems near T_{IN} (*i.e.* small $Q_{\alpha\beta}$) this form is adequate. Notice that, for $f_F\{Q_{\alpha\beta}\}$ and $f_F\{\hat{\mathbf{n}}\}$ to be consistent with the relationship between $Q_{\alpha\beta}$ and $\hat{\mathbf{n}}$ (eq. 2.2), there must be a correspondence between the sets $\{K_i\}$ and $\{L_i\}$. One finds

$$K_1 = K_2 = \tfrac{9}{4}(2\,L_1 + L_2)\,S_1^2, \qquad K_3 = \tfrac{9}{2}L_1 S_1^2. \tag{2.9}$$

It is interesting to note that spatial gradients decouple from the tensorial indices for $Q_{\alpha\beta}$ when the modulus L_2 vanishes. This is also known as the 'one-constant approximation', for if we set $K_1 = K_2 = K_3 = K$, we can perform an integration by parts and write the director version of the Frank free energy density as

$$f_F\{\hat{\mathbf{n}}\} = \tfrac{1}{2}K(\partial_\alpha n_\beta)^2 + \text{surface terms.} \tag{2.10}$$

This form of the free energy is invariant under separate rotations of space and $\hat{\mathbf{n}}$, *i.e.*, the symmetry group is now $O(3)\otimes O(3)$. At this level of approximation we expect many properties associated with spatial gradients to be isotropic, and many calculations can be extensively simplified while retaining the much of the physics of the anisotropic fluids. We will employ this approximation later in our calculations of steady state correlation functions in shear flow.

Using the Landau-de Gennes and Frank free energies, we can now calculate the correlations of various thermally fluctuating quantities. For simplicity we will consider the one-constant approximation, $L_2 = 0$. At temperatures slightly higher than T_{IN} the system is isotropic, but because of the weak first order transition there will generally be nematic fluctuations. These fluctuations will be small in this regime, so we may safely truncate the Landau expansion after the quadratic term. In terms of Fourier modes $Q_{\alpha\beta}(\mathbf{k})$, the free energy is

$$F = \int \frac{d^3k}{(2\pi)^3}\,\frac{1}{2}\left(a(T - T^-) + L_1 k^2\right) Q_{\alpha\beta}(\mathbf{k})Q_{\alpha\beta}(-\mathbf{k}), \tag{2.11}$$

where†

$$Q_{\alpha\beta}(\mathbf{k}) = \int \frac{d^3k}{(2\pi)^3} Q_{\alpha\beta}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.12}$$

The equilibrium fluctuations in the modes of order parameter are therefore

$$\langle Q_{\alpha\beta}(\mathbf{k})Q_{\lambda\rho}(-\mathbf{k})\rangle = \frac{k_BT}{a(T - T^-) + L_1k^2}(\delta_{\alpha\lambda}\delta_{\beta\rho} + \delta_{\alpha\rho}\delta_{\beta\lambda} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\lambda\rho}). \tag{2.13}$$

Here $\langle\mathcal{O}\rangle \equiv Z^{-1}\int\mathcal{D}Q\,\mathcal{O}\exp(-F/k_BT)$, where $\mathcal{D}Q$ is the measure for a functional integral over all independent modes of the order parameter and $Z \equiv \int\mathcal{D}Q\exp(-F/k_BT)$ is the partition function. From this Ornstein-Zernicke form one may identify a correlation length which grows as the transition is approached from above:

$$\xi^2(T) = \frac{L_1}{a(T - T^-)}. \tag{2.14}$$

The fluctuations are isotropic and diverge in the $k \to 0$ limit as T^- is approached.

Because $T_{IN} > T^-$, one expects a transition before this divergence occurs. Furthermore, this discussion is based on mean field theory, which is incorrect sufficiently near a critical point, as interactions between fluctuations invalidate the Gaussian approximation. Qualitatively, then, one might expect to see a departure from mean-field results as T^- is approached, provided T_{IN} is close enough to T^-. Light scattering experiments have roughly verified this picture, indicating behavior which deviates from mean-field behavior near T_{IN}.[43,44] However, experimental results are not conclusive, and there is still much disagreement about the critical nature of the transition, indeed, of weak first-order transitions in general.[40] In addition to the possibility of fluctuations controlled by a (fictitious) critical point at $T = T^-$, workers have considered the possibility of tricritical behavior.[45,46] The experimental data fit not only the simple Landau-de Gennes theory above, but also a free energy which includes a sixth order term, $E\left(\mathrm{Tr}\,\mathbf{Q}^2\right)^3$, which predicts tricritical behavior.[47]

†Note that, since $Q_{\alpha\beta}(\mathbf{r})$ is real, $Q^*_{\alpha\beta}(\mathbf{k}) = Q_{\alpha\beta}(-\mathbf{k})$.

2.5 Nematics in Magnetic Fields

Before addressing the non-equilibrium system of nematics in flow, it is helpful to examine the equilibrium system of nematics in a magnetic field.[40] The questions we ask are: (1) How does a magnetic field couple to the order parameter? (2) What is the effect of a field on the phase transition? It turns out that the phase diagram we will find for nematics in shear flow is superficially very similar to that for nematics in a magnetic field.

An anisotropic medium responds to a magnetic field with an anisotropic susceptibility,

$$M_\alpha = \chi_{\alpha\beta} H_\beta, \tag{2.15}$$

where $\mathbf{M}$ is the induced magnetization in an externally applied field $\mathbf{H}$. The susceptibility generally reflects the anisotropic nature of the material. If impurities are negligible and the magnetic interaction between the rods is also negligible,[33] then the order parameter describes all the tensorial properties of the system, Thus, we may decompose the tensor $\chi_{\alpha\beta}$ into scalar and traceless-symmetric pieces, according to

$$\chi_{\alpha\beta} = \chi_o\,\delta_{\alpha\beta} + \Delta\chi_{max}\,Q_{\alpha\beta}, \tag{2.16}$$

where $\Delta\chi_{max}$ is the magnitude of the susceptibility anisotropy in the completely ordered state. It is now straightforward to write the contribution to the free energy density $\delta f_{\mathrm{H}} = -\mathbf{M}\cdot\mathbf{H}$, and obtain the Landau-de Gennes free energy density for nematics in a magnetic field:

$$f = \tfrac{1}{2}A\,Q_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{3}B\,Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}C\big(Q_{\alpha\beta}Q_{\beta\alpha}\big)^2 - \Delta\chi_{max}H_\alpha Q_{\alpha\beta}H_\beta. \tag{2.17}$$

The behavior of the system in a magnetic field depends crucially on the sign of the susceptibility anisotropy $\Delta\chi_{max}$. Consider the application of a field $\mathbf{H}$ to a uniaxial system with $Q_{\alpha\beta} \sim (n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta})$. If $\Delta\chi_{max}$ is positive then the rods prefer to lie along the magnetic field, and the magnetic field simply enhances the uniaxial order. The slightest magnetic field induces some uniaxial order in the system, eliminating the possibility of a symmetry-breaking transition. The absence of symmetry breaking at a first-order transition implies that the line of first order transitions may end at either a critical endpoint or a multicritical point.[4] As modulated or other complicated phases are not expected, it is reasonable to anticipate a critical endpoint as the field is increased. For typical systems this critical field is estimated, within the Landau-de Gennes theory, to be $H_c \sim 10^3$ T.

If $\Delta\chi_{max}$ is negative the rods prefer to lie normal to an applied field, and the application of a field will induce a *discotic* uniaxial state in a system of rods at high temperatures. As there are now two orthogonal directions in the problem (the director and the magnetic field), one expects that at lower temperatures a *biaxial* phase will result, once the rods have aligned in the plane normal to $\mathbf{H}$. Hence the transition remains a symmetry-breaking transition, now occurring between biaxial and uniaxial rather than isotropic and nematic states. As the field is increased from zero the first order transition may eventually give way, at a tricritical point, to a continuous transition. Notice also that in the low temperature biaxial phase, where the rods are generally aligned normal to the field, there will be a single Goldstone mode corresponding to the arbitrary choice of nematic alignment within the plane. The magnetic-field–temperature phase diagram is summarized in fig. 2.2

The overall picture for $\Delta\chi_{max} > 0$ is that coupling to a sufficiently strong field conspires to cancel the cubic term in the Landau-de Gennes free energy density (eq. 2.17) at the critical point; physically, the magnetic field forces the transition to occur between phases of the same symmetry, and suppresses certain configurations of $Q_{\alpha\beta}$ as the field is increased, until the distinction between the two phases vanished as the critical endpoint. This is the general picture we also find for nematics in shear flow, though through quite different methods. Of course, there are several other differences in the nature of the transitions. The

Figure 2.2: Phase diagram for a nematic with $\Delta\chi_{max} > 0$ in a magnetic field. $\mathrm{N_{U+}}$ refers to conventional uniaxial states, $\mathrm{N_{U-}}$ refers to discotic states, and $\mathrm{N_B}$ refers to biaxial states. Note the critical point for positive fields and the tricritical point for negative fields. Solid lines represent first order transitions and broken lines represent continuous transitions. After Gramsbergen, *et al.*[40]

shear-induced transition is between *biaxial* states, while the field-induced transition leading to the critical endpoint is between *uniaxial* states; and we, as yet, know of no analog of the behavior for $\Delta\chi_{max} < 0$, where the transition is still a symmetry breaking transition and a tricritical point appears for large fields.

Chapter 3

Examples of Fluids and Complex Fluids in Shear Flow

Before addressing the subject of nematics under shear flow in detail, I will briefly discuss the effect of external driving fields on some equilibrium transitions, including the IN transition. There has been a growing interest in the effects of shear flow on critical behavior and phase transitions in fluids and complex fluids, beginning with the work of Onuki and Kawasaki in 1979.[7] An important motivation for these studies is the fact that shear flow introduces a new macroscopic time scale into the system: the inverse of the strain rate D. Fluctuations that have a smaller natural lifetime than this new time scale will not be affected, while those fluctuations with larger time scales should be affected—that is, destroyed by the advective nature of the flow. One then expects that the general effect of shear flow is to suppress fluctuations in the system, and this is indeed the case, as has been shown both experimentally[48] and theoretically.[7] We shall see that the manner in which fluctuations are suppressed, and the ramifications, differ depending on the nature of the equilibrium fluctuations in the system. A second motivation for these studies, and perhaps the paramount reason for our study, is that, in addition to the advective effect on fluctuations, shear flow can influence the *order* of the system. This suggests the possibility of flow-induced transitions into an ordered state.

3.1 Binary and Critical Fluids Under Shear

A seminal theoretical study of the effects of shear on the binary fluid near its critical point was published by Onuki and Kawasaki (OK) in 1979.[7] This was followed by the experimental studies of Beysens and coworkers in 1983 and 1984 which confirmed many of OK's predictions.[48] We may regard this system as a paradigm for the advective effects of shear on equilibrium critical phenomena. Let us consider the effect of flow on fluctuations. An equilibrium critical point is characterized, according to the scaling hypothesis,[49,50] by a diverging fluctuation correlation length, which means that at the critical point fluctuations occur on all length scales. Associated with each fluctuation of a particular wave number k is a characteristic time scale τ_k over which the fluctuation relaxes. However, shear flow introduces a new time scale $\tau_D = D^{-1}$ into the system, where D is the strain rate associated with the macroscopic motion of the system. This new time scale is a measure of how fast a disturbance may be advected away by the flow; if $\tau_D < \tau_k$, the fluctuation will be shorn away before it can decay. Since long wave length fluctuations have longer equilibrium relaxation times τ_k, the afflicted fluctuations are then the long wavelength ones, precisely those which characterize the critical behavior of the system. Hence, as the strain rate is increased the contribution of long wavelength fluctuations about the critical point is reduced, and one might expect to find *mean-field* instead of critical behavior at the transition; *i.e.*, the exponents characterizing the transition should have their mean-field values. In addition, the fact that shear flow frustrates the microscopic processes (*e.g.* van der Waals attraction) which induce the equilibrium critical point leads one to suspect that the critical temperature will be *reduced* in the presence of shear. These predictions were made by OK within a renormalization group (RG) calculation applied to the Fokker-Planck description of the dynamics and verified, along with other predictions, by Beysens, *et al.*[48]

3.2 The Isotropic-Lamellar Transition Under Shear

The Isotropic-Lamellar (IL) transition under shear has been studied by Cates and Milner (1989) and Marques and Cates (1990).[17] This system is a level of complexity higher than the binary fluid, and exhibits many of the same qualitative features as the IN transition under shear. The IL transition occurs in, *e.g.*, microemulsions and diblock copolymers;[51,52] and is a transition between an isotropic state and a one-dimensionally ordered, or layered, state. Such order is characterized by a density wave with a wave vector of magnitude k_o but arbitrary direction (neglecting boundary considerations). The mean-field equilibrium transition, as dictated by symmetry, is either second order or weakly first order; but strong fluctuations at the transition associated with the degeneracy in the direction of the ordering wave vector $\mathbf{k}_o$ have been predicted by Brazovskii (1975) to induce a first order transition.[53]

The effect of shear flow on this transition is similar to the binary fluid case, in that fluctuations are suppressed, but there are important differences. Shear flow will have the same effect on droplets of the ordered phase that fluctuate out of the isotropic phase, in that shear flow will generally destroy them if their lifetimes are long enough, thereby reducing their efficacy. But in addition, a special role is played by the lamellar nature of the ordered phase.[17] Fluctuations which form with layers normal to the flow direction will quickly disappear in flow, while fluctuations with layers parallel to the flow will be more likely to survive. Hence, shear flow will not only suppress droplets larger than a given size, as for the binary fluid, but will also limit the *class* of fluctuations which may occur and constrain the manifold of potential low temperature lamellar states. In contradistinction to the binary fluid case, the transition temperature in this case will *increase* in the presence of shear, since fluctuations which frustrate the equilibrium transition are suppressed by the flow. The nature of the transition was predicted by Cates and Milner, and by Marques and Cates, to crossover to mean-field behavior at sufficiently high shear rates. In the case where fluctuations in the choice of orientation of the layers (Brazovskii fluctuations) induce an equilibrium first order transition, shear flow was predicted to *suppress* these fluctuations in the limit of infinite shear gradient, to recover the mean-field *continuous* transition.[17]

3.3 The Nematic to Smectic-A Transition Under Shear

The Nematic to Smectic-A (NA) transition under shear flow has been studied in detail experimentally by Safinya and coworkers[54] (1990) and theoretically by Bruinsma and Safinya[55] (1991). The transition between the nematic and smectic states is similar to the IL transition, in that a one-dimensional density wave develops in the system. Here the density wave may be crudely envisioned as stacked layers of nematically-aligned rod-like molecules. Similar arguments about fluctuations apply as with the IL transition under flow: advective effects suppress long-wavelength fluctuations, and the layering direction is prescribed by the flow. Hence, we expect the transition temperature to increase in flow, and the behavior to be mean-field-like. We should also note that the nature of the equilibrium NA transition is controversial; theoretically it has been argued that, while symmetry predicts a continuous transition, the director fluctuations within the layers can induce a weak first order transition.[56] This weak first order transition has indeed been verified experimentally.[57]

The NA transition in shear flow has an additional complication due to the nematic order which is present in the nematic and smectic phases. We shall see that flow picks out a direction for nematic ordering,[12,58] as a magnetic field does for a magnet below its Curie temperature. However, a flowing nematic liquid crystal cannot undergo a transition to a smectic state in the same way as it does in equilibrium, with the layer normals parallel to the rod orientation specified by the nematic phase. This is because shear flow orients the rods roughly parallel to the flow, and we have seen in the discussion of the IL transition[17] that layers normal to the flow will be immediately destroyed by advection; stable smectic layering can only occur in layers which do not cut across streamlines. There will then be a crossover in the preferred rod orientation, which will flip from an alignment roughly parallel to the flow, in the nematic state, to an alignment normal to the shear plane, in the smectic state.[59,55] As a result, the phase diagram acquires much more structure as shear flow is introduced into the system.[54] An additional set of interesting predictions for the NA system under shear concerns the anisotropic viscosities of the fluid, the Leslie coefficients of the nematic fluid.

3.4 The Isotropic-Nematic Transition Under Shear

The Isotropic-Nematic (IN) under shear flow has been studied by several researchers, beginning with Hess[8](1976) and followed by Olmsted and Goldbart[9] (1990) and See, *et al.*[10] (1990). Thirumalai[60] (1986), Lee[15] (1987), and Wang and Gelbart[14] (1987) have studied the related problem of rods in elongational flow. As noted first by Hess, the propensity of the rod-like mesogens to order in shear flow causes the transition temperature to occur at a higher temperature in the presence of flow. At sufficiently high strain rates a transition no longer occurs and the state of the system remains smooth as the temperature is lowered. How does this occur, and how can we understand it in light of the other transitions in flow we have discussed?

The equilibrium transition at temperature T_{IN} is a symmetry-breaking transition to a *uniaxial* nematic state,[33] and has the Goldstone modes of director fluctuations accompanying the broken symmetry.[42] Shear flow has two important effects on the alignment. First, as mentioned, it *induces* order in the rods and selects a particular orientation. This must be distinguished from the NA and IL transitions, where flow affects the layering orientation, but not the magnitude of the order. Second, shear flow has a biaxial symmetry, and hence both the high and low temperature states of nematics in shear are biaxial, which renders the transition in flow a non-symmetry-breaking transition, reminiscent of the liquid-gas transition. This is in contrast to the IL, NA, and binary fluid transitions, where the nature of the symmetry-breaking at the transition is not affected by the flow. By analogy with other non-symmetry-breaking transitions, such as the liquid gas transition, it is reasonable to expect that, as the applied shear stress is increased, the discontinuous transition will terminate in a critical endpoint (although, in principle, multicritical points are possible). Further, because flow suppresses fluctuations which frustrate ordering of the system, we also expect the transition temperature to increase with increasing strain rate, as with the IL and NA transitions.

The general picture of this behavior has been show by previous workers.[8–10,14,15,60] Hess identified the basic characteristics of the non-equilibrium phase diagram in the shear-stress–temperature plane: an increasing transition temperature with increasing shear, and a suppression of a transition at a critical point for large enough strain rates. These features were also pointed out by Olmsted and Goldbart and by See, *et al.*, and by Thirumalai, by Lee, and by Wang and Gelbart for elongational flow.

There are several important distinctions among the systems we have briefly examined, and it is worthwhile to review them. The binary fluid has no internal order, and the advective action of flow on the fluctuations changes the critical behavior into mean-field behavior. The NA and IL transitions both have more internal structure than the binary fluid, namely a one-dimensional density wave. The effect of the flow is two-fold:

(1) fluctuations are advected away; and (2) the orientation of the density wave is constrained by the flow gradient direction, with the result being an increase in the transition temperature. The symmetry-breaking nature (isotropic to one-dimensional density wave) of these transitions is preserved under shear flow. The IN transition has even more internal structure, which couples *directly* to the flow gradient. Hence flow affects both the magnitude and direction of the order, as well as changing the symmetry of the transition. Its effect is to again raise the transition temperature, and to introduce a non-equilibrium critical point into the phase diagram.

3.5 The Driven Diffusive Lattice Gas

Another related system which has been studied recently is the driven diffusive lattice gas (DDLG).[32–62] This was proposed by Katz, *et al.*,[32] as a simple model of a non-equilibrium system whose behavior under an external driving field could provide insight into the general subject of non-equilibrium phase transitions. The system is a lattice gas with conserved particle number, whose particles are free to hop on the lattice, and an external field is imposed by requiring anisotropic jump rates. Jumps parallel to the field have a much higher probability than jumps perpendicular to the field, and periodic boundary conditions are imposed to achieve the steady state. In the absence of a field the phase diagram is spanned by temperature and average particle density per site. At half-filling the system segregates into high and low density regions at an Ising-class critical point, analogous to the binary fluid consolute point, at a critical temperature T_c. The properties of this continuous transition as the external field is increased have been studied via numerical simulations,[32] mean-field approximations,[62] and field-theoretic techniques.[61]

The general results are that the transition remains continuous in the external field and the critical temperature increases with increasing field, but the universality class and critical behavior are different from that of the equilibrium critical point. As with the binary fluid[7], correlations become highly anisotropic due to the applied field, and mean-field behavior is found.

Chapter 4

Dynamics of Nematic Liquid Crystals in Flow

Now we turn our attention to the details of nematics in shear flow. It is straightforward to see that non-uniform flow will have an effect on rodlike molecules, and hence nematic order. Consider figure 4.1, which shows two possible orientations of a rod in plane shear flow. The rod on the left is aligned across the flow, and consequently will experience a strong torque. The rod on the right, however, is parallel to the flow, and we would expect it to feel much less torque than the first rod. In this way we see that flow will strongly effect the ordering properties of the nematic comprising these rods. As with the Frank free energy, there are (at least) two interesting limits: (1) $T \ll T_{IN}$, where one can ignore variations in the amplitude of the order parameter; and (2) $T \sim T_{IN}$, where amplitude variations cost comparatively little free energy and must be included. We will first examine the Leslie-Ericksen (LE) theory for director dynamics,[12,63] which is universally used to describe the dynamics of nematics in flow for $T \ll T_{IN}$. We will see that this framework is inadequate for examining the dynamics near T_{IN}, where flow easily perturbs the uniaxial nematic order, and we will derive an alternative, rather more complex, dynamics for the entire order parameter $Q_{\alpha\beta}$.

4.1 Leslie-Ericksen Theory

As we have seen, flow affects the alignment of the director. Further, distortions in the alignment will act back on the velocity field, inducing stresses into the Navier-Stokes equation. LE theory describes the dynamics of the director $\hat{\mathbf{n}}$ in a general flow field, and is based on the assumptions of local equilibrium and a uniaxial nematic state with uniform *magnitude* of order. That is, effects of flow are considered inasmuch as they effect the alignment of the director for a uniaxial nematic. All other effects, such as an increase of the ordering or an introduction of biaxiality into the rod distribution, are assumed to cost so much energy as to be negligible. These assumptions apply far below T_{IN}.

The relevant variable are then the director field $\hat{\mathbf{n}}(\mathbf{r}, t)$ and the fluid velocity field $\mathbf{v}(\mathbf{r}, t)$. We will not give a derivation of the equations of LE theory. One may derive these equations by a procedure similar to that we use later to derive the dynamics of the entire order parameter coupled to the flow, in Chapter 5. The equations of LE theory comprise the evolution of the director, and the contribution of director and flow gradients to the viscous (*i.e.* irreversible or dissipative) fluid stress tensor.

Figure 4.1: Two possible orientations for rods in shear flow. The left hand rod will feel much more torque than the right hand rod, which is nearly aligned with the flow.

We first decompose the velocity gradient tensor into symmetric and anti-symmetric parts;[*]

$$\kappa^{[s]}_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha v_\beta + \partial_\beta v_\alpha), \tag{4.1}$$

$$\kappa^{[a]}_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha v_\beta - \partial_\beta v_\alpha), \tag{4.2}$$

$$\omega_\alpha = \tfrac{1}{2}\epsilon_{\alpha\beta\gamma}\,\kappa^{[a]}_{\beta\gamma} = \tfrac{1}{2}(\boldsymbol{\nabla}\times\mathbf{v})_\alpha, \tag{4.3}$$

where $\boldsymbol{\omega}$ is the vorticity of the fluid, and $\epsilon_{\alpha\beta\gamma}$ is the anti-symmetric Levi-Civita tensor. The evolution of the director $\hat{\mathbf{n}}$ is given by[12,33,63]

$$\dot{n}_\alpha \equiv (\partial_t + \mathbf{v}\cdot\boldsymbol{\nabla})n_\alpha = (\boldsymbol{\omega}\times\hat{\mathbf{n}})_\alpha + \frac{1}{\gamma_1}h_\alpha + \lambda\,\kappa^{[s]}_{\alpha\beta}\,n_\beta\,, \tag{4.4}$$

where the molecular field $\mathbf{h}$ is given by

$$h_\beta \equiv -\frac{\delta F}{\delta n_\alpha}, \tag{4.5}$$

Here F is the total Frank distortion free energy of the system, $F = \int_V f_F\,dV$, and the coefficients γ_1 and λ are transport coefficients.

The equation for the convective time-derivative $\dot{\hat{\mathbf{n}}}$ (eq. 4.4) has three pieces: $(\boldsymbol{\omega}\times\hat{\mathbf{n}})$ describes the rigid body rotation of the director in the velocity field, h_α/γ_1 describes the dissipative relaxation of the director

[*]For any tensor $T_{\alpha\beta}$ we will define the decomposition into its isotropic, symmetric and traceless, and anti-symmetric pieces by

$$T_{\alpha\beta} = T^{o}_{\alpha\beta} + T^{[s]}_{\alpha\beta} + T^{[a]}_{\alpha\beta},$$

$$T^{o}_{\alpha\beta} \equiv \frac{\delta_{\alpha\beta}}{3}T_{\sigma\sigma}, \quad T^{[s]}_{\alpha\beta} \equiv \tfrac{1}{2}(T_{\alpha\beta}+T_{\beta\alpha}) - T^{o}_{\alpha\beta}, \quad T^{[a]}_{\alpha\beta} \equiv \tfrac{1}{2}(T_{\alpha\beta}-T_{\beta\alpha}).$$

field due to distortions in $\hat{\mathbf{n}}$, and $A_{\alpha\beta}\, n_\beta$ represents the (non-dissipative) interaction of $\hat{\mathbf{n}}$ with a purely symmetric velocity gradient.

The fluid equation of motion is a generalized version of the Navier-Stokes equation:[33]

$$(\partial_t + \mathbf{v}\cdot\boldsymbol{\nabla})\, v_\alpha = \partial_\gamma\, \sigma_{\alpha\gamma}, \tag{4.6}$$

where

$$\sigma_{\alpha\beta} = \sigma^{i[s]}_{\alpha\beta} + \sigma^{i[a]}_{\alpha\beta} + \sigma^{d}_{\alpha\beta} - p\delta_{\alpha\beta}. \tag{4.7}$$

Here $\sigma^{d}_{\alpha\beta}$ is the elastic stress induced on the fluid by the nematic. This is reversible, and is due to the Frank free energy density. The anti-symmetric part of the irreversible (*i.e.* viscous or dissipative) stress tensor, $\sigma^{i[a]}_{\alpha\beta}$, is related to the dissipative torque in the system $\boldsymbol{\Gamma}$ through

$$\begin{aligned}
\Gamma_\lambda &= \epsilon_{\lambda\alpha\beta}\,\sigma^{i[a]}_{\alpha\beta} && (4.8)\\
&= (\mathbf{n}\times\mathbf{h})_\lambda. && (4.9)
\end{aligned}$$

Finally, the irreversible part of the stress tensor, $\sigma^{i[s]}_{\alpha\beta}$, is given by[12,33,63]

$$\begin{aligned}
\sigma^{i[s]}_{\alpha\beta} &= 2\nu_2\,\kappa^{[s]}_{\alpha\beta} + 2(\nu_1+\nu_2-2\nu_3)\, n_\alpha n_\beta\, n_\mu \kappa^{[s]}_{\mu\nu} n_\nu \\
&\quad + 2(\nu_3-\nu_2)\,(n_\alpha n_\mu \kappa^{[s]}_{\mu\beta} + n_\beta n_\mu \kappa^{[s]}_{\mu\alpha}) - \frac{\lambda}{2}(h_\alpha n_\beta + h_\beta n_\beta).
\end{aligned} \tag{4.10}$$

The Onsager transport coefficients ν_1, ν_2, ν_3, and γ_1 have dimensions of viscosity, and λ is a dimensionless kinetic coefficient. The transport coefficients are combinations of the so-called Leslie coefficients $\{\alpha_i\}$. There are several versions of these equations for $\dot{\hat{\mathbf{n}}}$ and $\sigma^{i[s]}_{\alpha\beta}$, and several equivalent definitions of the transport coefficients, which can lead to some confusion in the literature. I will not explain these different conventions,[33] but note that there are always five independent coefficients. Table 5.2 summarizes the relations among different versions of the transport coefficients in LE theory. Henceforth we will refer to any coefficient or combination of coefficients arising in LE theory as a 'Leslie' coefficient. The minus sign in front of λ in eq. (4.10) is required in order to satisfy the Onsager reciprocity relations[64] (note the λ appears in the evolution equation for $\hat{\mathbf{n}}$, eq. (4.4), with a positive sign).

The irreversible stress is very complicated. It contains the usual viscosity term found in the Navier-Stokes equation for a simple incompressible fluid $(2\,\nu_2\,\kappa^{[s]}_{\alpha\beta})$, complicated interactions of the director with flow gradients, and a contribution from gradients in the director field $(h_\alpha n_\beta + h_\beta n_\beta)$. An important feature of the LE equations is that, within the constraints of (1) local equilibrium, (2) linear departure from total equilibrium, and (3) a unit vector for the director, equations (4.4) and (4.10) are *exact*. They involve an expansion in powers of $\hat{\mathbf{n}}$ which terminates, because $\hat{\mathbf{n}}$ is a unit vector. This is not a feature of the dynamical equations for $Q_{\alpha\beta}$ which will be derived later.

As we will be interested in the non-equilibrium steady states of the nematic in shear flow, we will present the steady-state conditions for the director in uniform shear, $\mathbf{v} = D\,y\,\hat{\mathbf{x}}$, within LE theory.[12,58] The stationary condition is

$$\dot{n}_\alpha = (\boldsymbol{\omega}\times\hat{\mathbf{n}})_\alpha + \frac{1}{\gamma_1} h_\alpha + \lambda\,\kappa^{[s]}_{\alpha\beta}\, n_\beta = 0. \tag{4.11}$$

Since stress can only be applied at the boundaries, the bulk torque must also be zero:

$$\boldsymbol{\Gamma} = \hat{\mathbf{n}}\times\mathbf{h} = 0. \tag{4.12}$$

Enforcing this condition for simple shear flow $\mathbf{v}(\mathbf{r}) = D\,y\,\hat{\mathbf{x}}$ and assuming a form for the director $\hat{\mathbf{n}} = \cos\theta\,\hat{\mathbf{x}} + \sin\theta\,\hat{\mathbf{y}}$, we find a simple expression for the alignment of the director in shear flow:

$$\cos 2\theta = \frac{1}{\lambda}, \tag{4.13}$$

where θ is the angle between the director and the flow velocity (see fig. 4.2). The kinetic coefficient λ may be expressed as a ratio of rotational viscosities. Note that for $|\lambda| < 1$ there is no stable aligned state. The resulting time-dependent states are the so-called 'tumbling states', and will not be discussed further.[65]

4.2 Limitations of Leslie-Ericksen Theory

LE theory provides an adequate hydrodynamic description of nematics in flow but, as noted, it is only valid when the amplitude can be assumed to be uniform and only the director may vary. Recall that uniform shear flow dictates a preferred alignment for the director and thus for the molecules. We therefore may expect that in an *isotropic* state, applied shear flow will have an ordering effect, however slight, since each rod will feel a torque unless it is at the equilibrium angle, $\theta = (1/2)\cos^{-1}(\lambda^{-1})$. So, the assumption that the magnitude is unperturbed by the flow does not hold near the transition temperature.

Another drawback of applying LE theory to nematics in shear flow is that shear flow has an intrinsic biaxial symmetry, whereas LE theory assumes that the only relevant dynamics are those of the director and that the system remains uniaxial. Again, this consideration manifests itself only near T_{IN}, where flow-ordering effects are comparable with or larger than the thermodynamic ordering effects which prefer a uniaxial state.

One may therefore view nematics in shear flow as a system with two competing ordering effects. Equilibrium thermodynamics favors a low temperature uniaxially ordered state, while shear flow induces a biaxially ordered state. At low temperatures the thermodynamics effects dominate, with the flow effects acting only to select the orientation of $\hat{\mathbf{n}}$; but near T_{IN} the two ordering effects must be considered equally. To do this we have developed a hydrodynamic theory for the entire order parameter $Q_{\alpha\beta}(\mathbf{r}, t)$ and fluid velocity $\mathbf{v}(\mathbf{r}, t)$.

4.3 Irreversible Hydrodynamics of Nematics in Flow

Following the standard prescription of linear (in departure from equilibrium) irreversible thermodynamics,[66,29] we will derive equations of motion for the order parameter field $Q_{\alpha\beta}(\mathbf{r}, t)$ and the incompressible velocity field $\mathbf{v}(\mathbf{r}, t)$. An incompressible fluid velocity is a proper hydrodynamic variable, as it is conserved and therefore 'slow.' Slow variables result from either conservation laws (mass, momentum, *etc.*) or broken symmetries (long wavelength Goldstone modes), and relax over time scales much longer than those characterizing microscopic processes.[42] The order parameter $Q_{\alpha\beta}(\mathbf{r}, t)$ is not entirely a proper slow variable, but is a linear combination of slow modes and fast variables. In equilibrium the slow modes are director fluctuations (Goldstone modes). Because shear flow *explicitly* breaks the symmetry to a biaxial state, there are no Goldstone modes in shear flow. Nevertheless, we expect there to be order parameter modes that are 'almost slow' and relax over intermediate time scales. This assumption is further strengthened by the behavior of the fluctuation modes as the critical point is approached. We shall see that near the non-equilibrium critical point a slow new mode emerges which is a linear combination of the independent modes of $Q_{\alpha\beta}$. Hence, to allow for a unified description which encompasses the equilibrium Goldstone modes and the new slow mode at the critical point, we will treat the dynamics of the entire order parameter.

The procedure we follow is based on de Gennes' derivation of LE theory,[33] which in turn follows the general framework of classical linear irreversible thermodynamics, as discussed, *e.g.*, by de Groot and Mazur.[66] The steps are:

Figure 4.2: Geometry of the order parameter in stationary alignment. The director $\hat{\mathbf{n}}$ lies at an angle θ with respect to $\hat{\mathbf{x}}$ in the shear plane $(\hat{\mathbf{x}} - \hat{\mathbf{y}})$, and the subdirector $\hat{\mathbf{m}}$ may also be taken to lie in the shear plane. The z-axis is out of the page.

(1) From the local conservation laws and the assumption of local thermodynamic equilibrium (LTE), calculate the entropy production in the system in terms of the relevant quantities in the system, including $Q_{\alpha\beta}$. LTE means that we can define local thermodynamic quantities as an average over a length scale large with respect to microscopic lengths and small with respect to the length scales of typical gradients characteristic of the non-equilibrium processes.[3,29] These quantities are then assumed to obey standard thermodynamic relations.

(2) Identify the relevant thermodynamic forces and fluxes in the system from the conjugate pairs that appear in the entropy production. Different choices of fluxes and forces may be convenient for different applications.[33]

(3) Assume that the system is 'close' to equilibrium so that we may expand the fluxes linearly in the forces.

(4) From the resulting force-flux relations we use conservation laws to obtain the equations of motion for $Q_{\alpha\beta}(\mathbf{r},t)$ and $\mathbf{v}(\mathbf{r},t)$.

Entropy production can be understood as the conversion of long wavelength energy into small scale microscopic motion, which in statistical mechanics is represented by heat. Energy is put into the nematic under shear flow via, *e.g.*, the work done at the boundaries (we will not consider external potentials acting on the bulk), and is converted into heat, which may flow out of the system. By using the thermodynamic relations that follow from the assumptions of LTE, we can arrive at a form for the rate at which this entropy is produced in the bulk. An important assumption of LTE is that local thermodynamic quantities may be defined over sufficiently large length scales so as to maintain a clear separation between these long wavelength quantities, which constitute a thermodynamic description, and the short wavelength quantities which define entropy. In addition to the requirement that the thermodynamic quantities be defined on long length scales compared to microscopic variables, these variables must be defined over *small* scales compared to the length scales which characterize the gradients associated with the dissipative forces (*e.g.* ∇T, ∇v, etc.). The assumptions of LTE therefore break down when the gradients are so severe that *microscopic* scales are needed to obtain gradual variations.

The largest velocity gradients we will consider in this work are of order $\nabla v \sim 10^5\,\mathrm{s}^{-1}$, which corresponds to a time scale of $10\,\mu$s. From the speed of sound in nematics ($v_s \sim 10^5\,\mathrm{cm/s}$), one obtains a characteristic length scale of 1 cm, which is much longer that any microscopic length scale. Hence we remain within the domain of validity of LTE.

We have also made the assumption that the independent variables are local versions of *equilibrium* quantities, such as temperature, pressure, and density, and that the dissipative fluxes relax quickly. This need not be the case, as with the dissipative stress tensor in certain polymer systems.[67,68] 'Generalized irreversible thermodynamics' has been devised as a way of handling this type of issue (as well as others), where a modified version of the local equilibrium hypothesis is adopted in which the non-equilibrium entropy is a function of the dissipative fluxes as well as intensive thermodynamic quantities.[69]

4.3.1 Calculation of Entropy Production

To derive the entropy production we follow de Gennes' procedure.[33] We will assume that temperature variations relax faster than variations in $Q_{\alpha\beta}(\mathbf{r},t)$ and $\mathbf{v}(\mathbf{r},t)$, and calculate the entropy production from the rate of change in the free energy of a fluid of nematogens in an arbitrary flow field:

$$\frac{dF}{dt} \equiv \dot{F} = \dot{E} - T\dot{S}. \tag{4.14}$$

Energy, being a conserved quantity, can only be transported through the surface (in the absence of external long-range forces). However, the entropy S can change by both transport through the surface and by production in the bulk. Hence we may find the entropy production θ by identifying the volume integral in $\dot{F}$,

$$\dot{F} = \int_\Sigma j^{\mathrm{E}}_\gamma \, d\Sigma_\gamma \; - \; T \int_\Sigma j^{\mathrm{S}}_\gamma \, d\Sigma_\gamma \; - \; T \int_V \theta \, dV \tag{4.15}$$

where $\mathbf{j}^E$ and $\mathbf{j}^S$ are, respectively, the energy and entropy fluxes through the surface. Here $d\Sigma_\gamma$ is the surface element normal to r_γ. For the free energy of the system in flow we include, in addition to the Landau-de Gennes and Frank free energy densities in terms of $Q_{\alpha\beta}$ and its gradients, the kinetic energy of the fluid:

$$F = \int_V \left\{ \tfrac{1}{2}\rho |\mathbf{v}(\mathbf{r},t)|^2 + f_L + f_F \right\} \, dV, \tag{4.16}$$

where ρ is the uniform density of the fluid. The fluid is assumed to be incompressible:

$$\boldsymbol{\nabla} \cdot \mathbf{v}(\mathbf{r},t) = 0, \tag{4.17}$$

and obeys the equation of motion

$$\rho \left(\partial_t + \mathbf{v} \cdot \nabla \right) v_\alpha(\mathbf{r},t) = \partial_\beta \, \sigma_{\beta\alpha}(\mathbf{r},t) \, , \tag{4.18}$$

where $\sigma_{\beta\alpha}(\mathbf{r},t)$ is the stress tensor. Note that, according to this definition, the stress tensor is only specified up to an additive function whose divergence vanishes.

To calculate the rate of change of the free energy we examine the behavior of F under, separately, a local change in the order parameter, and a material distortion of the fluid which leaves the form of $Q_{\alpha\beta}$ invariant. Any change in the system may be decomposed into these independent changes.

1. *Variation in order parameter.* We first consider the variation $Q_{\alpha\beta}(\mathbf{r}) \to Q_{\alpha\beta}(\mathbf{r}) + \delta Q_{\alpha\beta}(\mathbf{r})$, which must preserve the traceless and symmetric character of $Q_{\alpha\beta}$. Introducing Lagrange multipliers $\kappa(\mathbf{r})$ for tracelessness and $\boldsymbol{\mu}(\mathbf{r})$ for symmetry, we obtain the equilibrium conditions

$$\frac{\delta F}{\delta Q_{\alpha\beta}(\mathbf{r})} + \kappa(\mathbf{r}) \, \delta_{\alpha\beta} + \mu_\nu(\mathbf{r}) \, \epsilon_{\nu\alpha\beta} = 0. \tag{4.19}$$

We solve for the multipliers by separately contracting this set of equations with $\delta_{\alpha\beta}$ to obtain κ and with $\epsilon_{\lambda\alpha\beta}$ to obtain $\boldsymbol{\mu}$. Substituting the resulting expressions back into (4.19), we find the set of conditions

$$H^{[s]}_{\alpha\beta} = 0, \tag{4.20}$$

where

$$H_{\alpha\beta} \equiv -\frac{\delta F}{\delta Q_{\alpha\beta}} \tag{4.21}$$

is the local molecular field, analogous to the field $\mathbf{h}$ in LE theory (eq. 4.5). Equation (4.20) is the equilibrium condition for the nematic. The change in free energy due to a variation in $Q_{\alpha\beta}$ is then

$$\delta F_Q = -\int_V H^{[s]}_{\alpha\beta} \, \delta Q_{\alpha\beta} \, dV. \tag{4.22}$$

2. *Material Distortion.* Now we consider a distortion of the material which preserves the value of the order parameter:

$$\mathbf{r} \to \mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r}), \qquad Q'_{\alpha\beta}(\mathbf{r}') = Q_{\alpha\beta}(\mathbf{r}). \tag{4.23}$$

Under this variation the term $\left(Q'_{\alpha\beta}(\mathbf{r}')-Q_{\alpha\beta}(\mathbf{r})\right)\partial F/\partial Q_{\alpha\beta}$ vanishes, and the change in the free energy comes about from inducing a change in the gradients of $Q_{\alpha\beta}(\mathbf{r})$, resulting from non-uniformities in the deformation $\mathbf{u}(\mathbf{r})$. Hence,

$$\delta F'_{\mathbf{u}} = \int_V dV\, \frac{\delta F}{\delta\, \partial_\gamma Q_{\alpha\beta}} \left(\partial'_\gamma Q'_{\alpha\beta}(\mathbf{r}') - \partial_\gamma Q_{\alpha\beta}(\mathbf{r})\right). \tag{4.24}$$

Now we use $\partial'_\gamma Q'_{\alpha\beta}(\mathbf{r}') = \partial_\lambda Q_{\alpha\beta}(\mathbf{r})\left[\delta_{\lambda\gamma} - \partial_\gamma u_\lambda(\mathbf{r}) + \mathrm{O}\left((\partial u)^2\right)\right]$ to write

$$\partial'_\gamma Q'_{\alpha\beta}(\mathbf{r}') - \partial_\gamma Q_{\alpha\beta}(\mathbf{r}) = -\partial_\gamma u_\lambda(\mathbf{r})\, \partial_\lambda Q_{\alpha\beta}(\mathbf{r}). \tag{4.25}$$

At this stage we have not yet enforced the incompressibility condition for the fluid. This is accomplished by introducing another multiplier, the pressure p arg, via $F_p = F - \int_V dV\, p(\mathbf{r})\boldsymbol{\nabla}\cdot\mathbf{u}(\mathbf{r})$. Incorporating this constraint into eq. (4.24), we find the total change in F upon an incompressible distortion to be

$$\delta F_{\mathbf{u}} = \int_V (\sigma^d_{\alpha\beta} - p\,\delta_{\alpha\beta})\,\partial_\alpha u_\beta\, dV\,, \tag{4.26}$$

where

$$\sigma^d_{\alpha\beta} \equiv \pi^\alpha_{\rho\mu}\,\partial_\beta Q_{\rho\mu}, \tag{4.27}$$

$$\pi^\gamma_{\alpha\beta} \equiv -\frac{\delta F}{\delta \partial_\gamma Q_{\alpha\beta}}. \tag{4.28}$$

Here $\sigma^d_{\alpha\beta}$ is the distortion stress tensor, often called the Ericksen stress. It comprises elastic stresses induced in the fluid (via the Frank energy) by distortions of the nematic order.

Finally, to compute the total time rate-of-change of the free energy, $\dot{F}$, we must add the time rate-of-change of the kinetic energy:

$$\frac{d}{dt}\int_V \tfrac{1}{2}\rho\, v^2\, dV = \int_V \rho\, v_\alpha\, \partial_t v_\alpha\, dV = \int_V v_\alpha\, \partial_\beta\, \sigma_{\alpha\beta}\, dV \tag{4.29}$$

$$= \int_\Sigma d\Sigma_\alpha\, \sigma_{\alpha\beta}\, v_\beta - \int_V \sigma_{\alpha\beta}\, \partial_\beta\, v_\alpha\, dV \tag{4.30}$$

where we have used the equation of motion for the fluid (eq. 4.18). Next we express the total stress tensor $\sigma_{\alpha\beta}$ as the sum of a reversible (*i.e.* elastic) piece, $\sigma^r_{\alpha\beta}$, and an irreversible (*i.e.* dissipative or viscous) piece, $\sigma^i_{\alpha\beta}$, *viz.*

$$\sigma_{\alpha\beta} = \sigma^r_{\alpha\beta} + \sigma^i_{\alpha\beta}, \tag{4.31}$$

where

$$\sigma^r_{\alpha\beta} = \sigma^d_{\alpha\beta} - p\,\delta_{\alpha\beta}. \tag{4.32}$$

Using eqs. (4.15), (4.22), (4.26), and (4.30), we find the rate of change of the total entropy of the system to be

$$\begin{aligned} T\dot{S} &= \int_\Sigma j^S_\gamma\, d\Sigma_\gamma + T\int_V \theta\, dV \\ &= \int_\Sigma \left(j^E_\gamma - \sigma_{\alpha\beta}\, v_\beta\right)\, d\Sigma_\gamma + \int_V \left(\sigma^i_{\alpha\beta}\,\partial_\beta v_\alpha + H^{[s]}_{\alpha\beta}\,\dot{Q}_{\alpha\beta}\right)\, dV. \end{aligned} \tag{4.33}$$

It is possible to stop here and identify, *e.g.*, $\sigma^i_{\alpha\beta}$ and $\dot{Q}_{\alpha\beta}$ as the dissipative fluxes and $\partial_\beta v_\alpha$ and $H^{[s]}_{\alpha\beta}$ as the dissipative forces, but a more physical choice will become apparent if we separate the stress $\sigma^i_{\alpha\beta}$ into symmetric and anti-symmetric pieces, and examine the behavior of the system under a rigid-body rotation. We will see that invariance of the system under this rotation (which cannot change the total free energy) will enable us to identify the internal torques acting in the system, and hence to develop a more physical description of the dissipative processes in the system.

4.3.2 Invariance Under Rotation: Torque Balances

The free energy of the system is invariant under rigid body rotations, which is responsible for the conservation of angular momentum. We will calculate the variation of the free energy under such a rotation and obtain a condition which, together with conservation of angular momentum, will lead to an expression for the dissipative torque in the system due to the internal structure of the fluid. This relation will then enable us to choose a physically appealing set of forces and fluxes from the entropy production.

Consider a rotation of the coordinates and a concomitant rotation of the tensor order parameter $Q_{\alpha\beta}$. We emphasize that the 'internal' (tensorial indices) and 'external' (cartesian indices) spaces are the same space here, and do not transform independently. An infinitesimal rotation by an arbitrary angle $|\boldsymbol{\omega}|$ about the axis $\hat{\boldsymbol{\omega}}$ induces the following variations in $\mathbf{r}$ and $Q_{\alpha\beta}$:

$$\begin{aligned} \delta r_\alpha &= u_\alpha = \epsilon_{\alpha\beta\gamma}\,\omega_\beta\, r_\gamma && (4.34)\\ \delta Q_{\alpha\beta} &= \omega_\mu\,(\epsilon_{\mu\alpha\gamma}\,Q_{\gamma\beta} + \epsilon_{\mu\beta\gamma}\,Q_{\alpha\gamma}). && (4.35)\end{aligned}$$

The change in the free energy under this rotation is given by

$$\delta F = \int_V \left(\sigma^r_{\alpha\beta}\,\partial_\alpha u_\beta + \frac{\partial f^{[s]}}{\partial Q_{\alpha\beta}}\,\delta Q_{\alpha\beta} + \frac{\partial f^{[s]}}{\partial\,\partial_\gamma Q_{\alpha\beta}}\,\delta\partial_\gamma Q_{\alpha\beta}\right) dV, \tag{4.36}$$

where f is the total free energy density and $\sigma^r_{\alpha\beta}$ is the reversible stress tensor. Now we use the following:†

$$\begin{aligned} H^{[s]}_{\alpha\beta} &= -\frac{\delta F^{[s]}}{\delta Q_{\alpha\beta}} && (4.37)\\ &= -\frac{\partial f^{[s]}}{\partial Q_{\alpha\beta}} + \partial_\gamma \frac{\partial f^{[s]}}{\partial\,\partial_\gamma Q_{\alpha\beta}} && (4.38)\\ &= -\frac{\partial f^{[s]}}{\partial Q_{\alpha\beta}} - \partial_\gamma \pi^{\gamma[s]}_{\alpha\beta}. && (4.39)\end{aligned}$$

Inserting the variations $\mathbf{u}$ and $\delta Q_{\alpha\beta}$ (eqs. 4.34 and 4.35) into eq. (4.36), we find

$$\begin{aligned}\delta F = \int_V \omega_\lambda \Big\{ \sigma^r_{\alpha\beta}\,\epsilon_{\alpha\beta\lambda} &- (H^{[s]}_{\alpha\beta} + \partial_\gamma\,\pi^{\gamma[s]}_{\alpha\beta})(\epsilon_{\lambda\alpha\rho}\,Q_{\rho\beta} + \epsilon_{\lambda\beta\rho}\,Q_{\alpha\rho})\\ &- \pi^{\gamma[s]}_{\alpha\beta}\,\partial_\gamma\,(\epsilon_{\lambda\alpha\rho}\,Q_{\rho\beta} + \epsilon_{\lambda\beta\rho}\,Q_{\alpha\rho})\Big\}\,dV. \end{aligned}\tag{4.40}$$

Now we note that the parameter $\boldsymbol{\omega}$ is both arbitrary and spatially uniform, and that the variation in free energy must be zero for such a rotation. We can identify a total differential in the last term and obtain the following condition, which must hold at all times:

$$\int_V \epsilon_{\lambda\alpha\beta}\,(\sigma^r_{\alpha\beta} + Q_{\alpha\rho}\,H^{[s]}_{\rho\beta} - H^{[s]}_{\alpha\rho}\,Q_{\rho\beta})\,dV = \int_\Sigma \epsilon_{\lambda\alpha\beta}\,(\pi^{\gamma[s]}_{\alpha\rho}\,Q_{\beta\rho} - Q_{\alpha\rho}\,\pi^{\gamma[s]}_{\beta\rho})\,d\Sigma_\gamma. \tag{4.41}$$

†The expressions (4.38) and (4.39) follow from our expression of the free energy in terms of $Q_{\alpha\beta}$ and its gradients. Note also that an integration by parts and neglect of the surface term is implicit in the definition of $H^{[s]}_{\alpha\beta}$ according to eq. (4.38).

Another useful form of this identity which gives more insight into its physical meaning results upon integrating the first term on the left hand side by parts (we can write $\epsilon_{\lambda\alpha\beta} = \epsilon_{\lambda\rho\beta}\,\delta_{\alpha\rho} = \epsilon_{\lambda\rho\beta}\,\partial_\alpha r_\rho$ and integrate) to obtain

$$\int_V \epsilon_{\lambda\alpha\beta}\,(r_\alpha\,\partial_\rho\sigma^r_{\beta\rho} + H^{[s]}_{\alpha\rho}\,Q_{\rho\beta} - Q_{\alpha\rho}\,H^{[s]}_{\rho\beta})\,dV = \int_\Sigma \epsilon_{\lambda\alpha\beta}\,(r_\alpha\,\sigma^r_{\beta\gamma} + Q_{\alpha\rho}\,\pi^{\gamma[s]}_{\beta\rho} - \pi^{\gamma[s]}_{\alpha\rho}\,Q_{\beta\rho})\,d\Sigma_\gamma. \tag{4.42}$$

This equation expresses a balance between torques applied at the surface and torques in the bulk. The first term in the volume integral is the bulk orbital torque in the system, *i.e.*, that due to center of mass motion of the fluid. The second two terms comprise the bulk torques due to the internal structure of the fluid. Recalling that $H^{[s]}_{\alpha\beta}$ is zero in equilibrium, there can evidently be no equilibrium bulk torques due to the internal degrees of freedom. The first term in the surface integral is the torque applied at the boundary of the system; recall that $\sigma_{\alpha\beta}\,d\Sigma_\beta$ is the force applied at the surface. The last two terms are surface torques applied to the internal degrees of freedom; this could result if, *e.g.*, some twist which did not influence the center-of-mass motion of the rods was applied to the molecules at the surface. Finally, we stress that the above remarks refer only to *elastic* torques in the system, and that the relation (4.41) holds at all times, whether or not the system is in equilibrium.

4.3.3 Identification of Torques

Remembering our program to separate the dissipative stress into symmetric and anti-symmetric pieces, we may use the torque balance equation (eq. 4.41) to identify the anti-symmetric part of the dissipative stress tensor. We begin by considering the total torque $\mathbf{\Gamma^{app}}$ exerted on the system. This has contributions from: (1) torques exerted by the *total* stress tensor at the surface: (2) torques exerted by external fields which couple to the bulk (we will ignore these); and (3) torques exerted on the order parameter field at the surface. We will assume that no dissipation is induced at the surface (strong-anchoring condition), so that the contribution to (3) is the surface integral in eq. (4.41).[33] Assembling these torques we find that $\mathbf{\Gamma^{app}}$ is given by

$$\Gamma^{app}_\lambda = \int_\Sigma \epsilon_{\lambda\alpha\beta}\,(r_\alpha\sigma_{\gamma\beta} + Q_{\alpha\rho}\,\pi^\gamma_{\beta\rho} - \pi^\gamma_{\alpha\rho}\,Q_{\beta\rho})\,d\Sigma_\gamma. \tag{4.43}$$

This torque must equal the time rate-of-change of the total angular momentum $\mathbf{L}$ of the system which, in general, includes both fluid center-of-mass and rod rotational contributions. However, we can ignore the spin contributions, because the product of the moment of inertia and typical rotational frequencies of the director is small compared to the fluid orbital angular momentum.[36] The rate of change of the angular momentum is therefore

$$\dot{L}_\lambda = \frac{d}{dt}\int_V (\mathbf{r}\times\rho\mathbf{v})_\lambda\,dV \tag{4.44}$$

$$= \int_V \epsilon_{\lambda\alpha\beta}\,r_\alpha\,\partial_\gamma\sigma_{\gamma\beta}\,dV \tag{4.45}$$

$$= \int_\Sigma \epsilon_{\lambda\alpha\beta}\,r_\alpha\,\sigma_{\gamma\beta}\,d\Sigma_\gamma - \int_V \epsilon_{\lambda\alpha\beta}\,\sigma_{\alpha\beta}\,dV, \tag{4.46}$$

where we have used the fluid velocity equation of motion and integrated by parts.

Equating $\dot{\mathbf{L}}$ to the total applied torque, eq. (4.43), we cancel a surface term and find

$$\int_V \epsilon_{\lambda\alpha\beta}\,\sigma_{\alpha\beta}\,dV = \int_\Sigma \epsilon_{\lambda\alpha\beta}\,(\pi^{\gamma[s]}_{\alpha\rho}\,Q_{\beta\rho} - Q_{\alpha\rho}\,\pi^{\gamma[s]}_{\beta\rho})\,d\Sigma_\gamma. \tag{4.47}$$

Recalling that that‡ $\sigma_{\alpha\beta} = \sigma^i_{\alpha\beta} + \sigma^d_{\alpha\beta}$ from eqs. (4.31) and (4.32), we substitute for $\sigma^d_{\alpha\beta}$ from eq. (4.41) and

‡Equality holds up to the pressure term $-p\,\delta_{\alpha\beta}$, which vanishes when contracted against $\epsilon_{\lambda\alpha\beta}$.

cancel the surface term on the right hand side, leaving

$$\int_V \epsilon_{\lambda\alpha\beta}\,\sigma^i_{\alpha\beta}\,dV = \int_V \epsilon_{\lambda\alpha\beta}\,(Q_{\alpha\rho}\,H^{[s]}_{\rho\beta} - H^{[s]}_{\alpha\rho}\,Q_{\rho\beta})\,dV. \tag{4.48}$$

Finally, the dissipative torque Γ_λ is defined by

$$\Gamma_\lambda = \epsilon_{\lambda\alpha\beta}\,\sigma^i_{\alpha\beta}, \tag{4.49}$$

whence, from eq. (4.48), we can identify this torque in terms of the order parameter by

$$\Gamma_\lambda = \epsilon_{\lambda\alpha\beta}\,(Q_{\alpha\rho}\,H^{[s]}_{\rho\beta} - H^{[s]}_{\alpha\rho}\,Q_{\rho\beta}). \tag{4.50}$$

Note, as mentioned before, that the torque $\mathbf{\Gamma}$ vanishes in equilibrium.

4.3.4 Identification of Entropy Production

After this rather lengthy digression we return to the expression for the entropy production, eq. (4.33), and elucidate an appealing set of forces and fluxes. First, we decompose the irreversible stress tensor $\sigma^i_{\alpha\beta}$ and the velocity gradient tensor $\partial_\alpha v_\beta$ into symmetric-traceless and anti-symmetric pieces.[§] The entropy production is then given by

$$T\theta = \sigma^{i[s]}_{\alpha\beta}\,\kappa^{[s]}_{\alpha\beta} + \sigma^{i[a]}_{\alpha\beta}\,\kappa^{[a]}_{\alpha\beta} + H^{[s]}_{\alpha\beta}\,Q_{\alpha\beta}. \tag{4.51}$$

Using eq. (4.48) for $\sigma^{i[a]}_{\alpha\beta}$, we rewrite this in the more compact form

$$T\theta = \sigma^{i[s]}_{\alpha\beta}\,\kappa^{[s]}_{\alpha\beta} + H^{[s]}_{\alpha\beta}\,K_{\alpha\beta}. \tag{4.52}$$

The flux $K_{\alpha\beta}$ conjugate to the molecular field $H^{[s]}_{\alpha\beta}$ is defined by

$$K_{\alpha\beta} \equiv \dot{Q}_{\alpha\beta} - \left(\kappa^{[a]}_{\alpha\gamma}\,Q_{\gamma\beta} - Q_{\alpha\gamma}\,\kappa^{[a]}_{\gamma\beta}\right), \tag{4.53}$$

and may be physically interpreted as the rate of change of the order parameter relative to the fluid motion. From this expression we can understand the sources of dissipation in the fluid. There is dissipation associated with a velocity gradient in the fluid, just as in an isotropic fluid, and there is also dissipation if the order parameter is rotating relative to the rotation of the fluid, *i.e.*, friction between the rods and the fluid motion.

4.3.5 Irreversible Forces and Fluxes and Equations of Motion

The next step in obtaining the equations of motion is to identify the forces and fluxes in the system and perform the Onsager expansion.[66] While there is no unique prescription for determining which to call forces and which to call fluxes, we have found it convenient to choose $\kappa^{[s]}_{\alpha\beta}$ and $H^{[s]}_{\alpha\beta}$ as the forces and $\sigma^{i[s]}_{\alpha\beta}$ and $K_{\alpha\beta}$ as the fluxes. Expanding the fluxes to linear order in the forces we obtain the relations

$$\sigma^{i[s]}_{\alpha\beta} = \Lambda^{[1]}_{\alpha\beta\lambda\rho}\,\kappa^{[s]}_{\lambda\rho} + \mathrm{M}^{[1]}_{\alpha\beta\lambda\rho}\,H^{[s]}_{\lambda\rho} \tag{4.54}$$

$$K_{\alpha\beta} = \mathrm{M}^{[2]}_{\alpha\beta\lambda\rho}\,\kappa^{[s]}_{\lambda\rho} + \Lambda^{[2]}_{\alpha\beta\lambda\rho}\,H^{[s]}_{\lambda\rho}. \tag{4.55}$$

[§]The isotropic part of the stress tensor in $T\dot{S}$ vanishes since the fluid is compressible, $\mathbf{\nabla}\cdot\mathbf{v} = 0$.

In accordance with the Onsager reciprocity relations, the transport coefficient matrices $\Lambda^{[i]}_{\alpha\beta\lambda\rho}$ and $\mathrm{M}^{[i]}_{\alpha\beta\lambda\rho}$ satisfy

$$\mathrm{M}^{[1]}_{\alpha\beta\lambda\rho} = -\mathrm{M}^{[2]}_{\lambda\rho\alpha\beta}, \quad \Lambda^{[i]}_{\alpha\beta\lambda\rho} = \Lambda^{[i]}_{\lambda\rho\alpha\beta}, \tag{4.56}$$

the minus sign arising because the forces $\kappa^{[s]}_{\alpha\beta}$ and $H^{[s]}_{\alpha\beta}$ transform differently under time-reversal.[66] As the fluxes are traceless and symmetric, the matrices also satisfy the constraints

$$\mathrm{M}^{[i]}_{\alpha\alpha\lambda\rho} = \Lambda^{[i]}_{\alpha\alpha\lambda\rho} = 0, \tag{4.57}$$

$$\mathrm{M}^{[i]}_{\alpha\beta\lambda\rho} = \mathrm{M}^{[i]}_{\beta\alpha\lambda\rho} = \mathrm{M}^{[i]}_{\alpha\beta\rho\lambda}\,, \tag{4.58}$$

$$\Lambda^{[i]}_{\alpha\beta\gamma\rho} = \Lambda^{[i]}_{\beta\alpha\gamma\rho} = \Lambda^{[i]}_{\alpha\beta\rho\gamma}\,. \tag{4.59}$$

Finally, the entropy production must satisfy the Second Law of Thermodynamics, namely,

$$T\theta = \Lambda^{[1]}_{\alpha\beta\gamma\rho}\,\kappa^{[s]}_{\alpha\beta}\,\kappa^{[s]}_{\gamma\rho} + \Lambda^{[2]}_{\alpha\beta\gamma\rho}\,H^{[s]}_{\alpha\beta}\,H^{[s]}_{\gamma\rho} \geq 0. \tag{4.60}$$

The transport matrices $\mathrm{M}^{[i]}_{\alpha\beta\lambda\rho}$ and $\Lambda^{[i]}_{\alpha\beta\lambda\rho}$ are general tensors built from the available tensors in the problem: $\delta_{\alpha\beta}$ and powers of $Q_{\alpha\beta}$. The order parameter $Q_{\alpha\beta}$ has three orientational and two amplitude modes (see discussion under eq. 2.3), and therefore has two scalar invariants, which may be taken to be $T_2 \equiv \mathrm{Tr}\,\mathbf{Q}^2$ and $T_3 \equiv \mathrm{Tr}\,\mathbf{Q}^3$, where $\mathrm{Tr}\,(\cdot)$ denotes the trace. This in turn implies that any polynomial $(\mathbf{Q}^n)_{\alpha\beta}$ may be written in terms of $\delta_{\alpha\beta}$, $Q_{\alpha\beta}$, $(\mathbf{Q}^2)_{\alpha\beta}$, and the two invariants. Hence to construct $\mathrm{M}^{[i]}_{\alpha\beta\lambda\rho}$ and $\Lambda^{[i]}_{\alpha\beta\lambda\rho}$ we may use the tensors $\delta_{\alpha\beta}$, $Q_{\alpha\beta}$, and $(\mathbf{Q}^2)_{\alpha\beta}$, scalars which may include arbitrary functions of T_2 and T_3, and we must respect the constraints (4.57-4.60). Because of the functions of T_2 and T_3, this expansion of the transport matrices does not generally close. This is in contrast to the case of director dynamics, the LE theory, in which one obtains similar expressions for the entropy production and forces and fluxes, with the unit vector $\hat{\mathbf{n}}$ replacing $Q_{\alpha\beta}$. An expansion of the stress and rate of change of $\hat{\mathbf{n}}$ closes because $\hat{\mathbf{n}}\cdot\hat{\mathbf{n}} = 1$, yielding the Leslie-Ericksen equations (eqs. 4.4-4.10). We are interested in the behavior of the system for $T \sim T_{IN}$, where $Q_{\alpha\beta}$ is small, so we will truncate the expansion of the transport matrices at a low order in $Q_{\alpha\beta}$ and its invariants. For example, an expansion to *linear* order yields

$$\begin{aligned} K_{\alpha\beta} &= \frac{1}{\beta_2}\,H^{[s]}_{\alpha\beta} + \beta_6\left\{Q_{\alpha\gamma}\,H^{[s]}_{\gamma\beta} + H^{[s]}_{\alpha\gamma}\,Q_{\gamma\beta} - \tfrac{2}{3}\delta_{\alpha\beta}\,\mathbf{H}^{[s]}\mathbf{:Q}\right\} \\ &\quad \beta_1\kappa^{[s]}_{\alpha\beta} + \beta_5\left\{Q_{\alpha\gamma}\,\kappa^{[s]}_{\gamma\beta} + \kappa^{[s]}_{\alpha\gamma}\,Q_{\gamma\beta} - \tfrac{2}{3}\delta_{\alpha\beta}\,\boldsymbol{\kappa}^{[s]}\mathbf{:Q}\right\} \end{aligned} \tag{4.61}$$

$$\begin{aligned} \sigma^{i[s]}_{\alpha\beta} &= \beta_3\kappa^{[s]}_{\alpha\beta} + \beta_4\left\{Q_{\alpha\gamma}\,\kappa^{[s]}_{\gamma\beta} + \kappa^{[s]}_{\alpha\gamma}\,Q_{\gamma\beta} - \tfrac{2}{3}\delta_{\alpha\beta}\,\boldsymbol{\kappa}^{[s]}\mathbf{:Q}\right\} \\ &\quad -\beta_1 H^{[s]}_{\alpha\beta} - \beta_5\left\{Q_{\alpha\gamma}\,H^{[s]}_{\gamma\beta} + H^{[s]}_{\alpha\gamma}\,Q_{\gamma\beta} - \tfrac{2}{3}\delta_{\alpha\beta}\,\mathbf{H}^{[s]}\mathbf{:Q}\right\} \end{aligned} \tag{4.62}$$

Higher orders in $Q_{\alpha\beta}$ may be included systematically. In the following, we have calculated the phase diagram obtained from the equations of motion with the Onsager coefficients expanded to *cubic* order in $Q_{\alpha\beta}$, and have found qualitatively the same results as for an expansion to *zeroth* order in $Q_{\alpha\beta}$. Henceforth, we will only consider the zeroth order expansion of the Onsager matrices. We can now write the equations of motion for the order parameter and fluid velocity by combining the expansion of the transport coefficients to zeroth order with the fluid equation of motion and the definition of $K_{\alpha\beta}$. Thus, we obtain

$$(\partial_t + \mathbf{v}\cdot\boldsymbol{\nabla})\,Q_{\alpha\beta} = \kappa^{[a]}_{\alpha\gamma}Q_{\gamma\beta} - Q_{\alpha\gamma}\kappa^{[a]}_{\gamma\beta} + \beta_1\kappa^{[s]}_{\alpha\beta} + \frac{1}{\beta_2}H^{[s]}_{\alpha\beta} \tag{4.63}$$

$$(\partial_t + \mathbf{v}\cdot\boldsymbol{\nabla})\,v_\alpha = \partial_\gamma\,\sigma_{\alpha\gamma}\,, \tag{4.64}$$

where

$$\begin{aligned}
\sigma_{\alpha\beta} &= \sigma^{i[s]}_{\alpha\beta} + \sigma^{i[a]}_{\alpha\beta} + \sigma^{d}_{\alpha\beta} - p\delta_{\alpha\beta} &(4.65)\\
\sigma^{i[s]}_{\alpha\beta} &= \beta_3 \kappa^{[s]}_{\alpha\beta} - \beta_1 H^{[s]}_{\alpha\beta} &(4.66)\\
\sigma^{i[a]}_{\alpha\beta} &= H^{[s]}_{\alpha\gamma} Q_{\gamma\beta} - Q_{\alpha\gamma} H^{[s]}_{\gamma\beta}, &(4.67)\\
\sigma^{d}_{\alpha\beta} &= -L_1\, \partial_\alpha Q_{\mu\nu}\, \partial_\beta Q_{\mu\nu} - L_2\, \partial_\beta Q_{\alpha\mu}\, \partial_\nu Q_{\nu\mu}. &(4.68)
\end{aligned}$$

The distortion contribution to the stress tensor, $\sigma^d_{\alpha\beta}$, has been calculated from the Frank free energy (eq. 2.8) and the definition for $\sigma^d_{\alpha\beta}$ (eq. 4.68). It is interesting to note that while the elastic stresses are generally not symmetric, they become symmetric in the one-constant approximation, when the modulus L_2 vanishes. Finally, the condition that $T\dot{\theta} \geq 0$ implies the constraints $\beta_3 > 0$ and $\beta_2 > 0$, and the minus sign in eq. (4.66) is chosen to satisfy the Onsager reciprocity relations.

4.3.6 Correspondence with Leslie-Ericksen Theory

The fluid velocity equation is a generalized Navier-Stokes equation with a stress tensor that reflects the intrinsic anisotropy of the fluid. The order parameter equation of motion is a generalization of the Leslie-Ericksen equation of motion for the director. Note that there are two Onsager coefficients with dimensions of viscosity, β_3 and β_2, and one dimensionless kinetic coefficient β_1. Our theory has three transport coefficients, while LE theory has five transport coefficients. We have fewer because we have truncated the expansion of the transport matrices at zeroth order in $Q_{\alpha\beta}$.

We can see the correspondence with LE theory by comparing, *e.g.*, the results from the linear expansion (eqs. 4.61 and 4.62) with LE theory. If we follow the assumptions of LE theory and assume the uniaxial form for the order parameter,

$$Q_{\alpha\beta} = \tfrac{3}{2}\, S_1\, (n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{4.69}$$

then we find that the symmetric part of the irreversible stress tensor (eq. 4.62) becomes

$$\sigma^{i[s]}_{\alpha\beta} = \tfrac{3}{2}\beta_4 S_1 (n_\alpha n_\mu \kappa^{[s]}_{\mu\beta} + n_\beta n_\mu \kappa^{[s]}_{\mu\alpha}) + (\beta_3 - \beta_4 S_1)\kappa^{[s]}_{\alpha\beta} + (-\frac{\beta_1}{3S_1} - \frac{\beta_5}{6})(n_\alpha h_\beta + n_\beta h_\alpha). \tag{4.70}$$

Here $\mathbf{h}$ is the molecular field for the director, in terms of the Frank energy $f_F\{\hat{\mathbf{n}}\}$, and we have neglected an isotropic contribution which can be absorbed into a redefinition of the pressure. Similarly, we can reduce the equation for $K_{\alpha\beta}$ (eqs. 4.53 and 4.61) to an equation for n_α by substituting for $Q_{\alpha\beta}$ with eq. (4.69) and contracting with n_β, giving

$$\dot{n}_\alpha = (\boldsymbol{\omega} \times \hat{\mathbf{n}})_\alpha + (\frac{2}{9\beta_2 S_1^2} + \frac{\beta_6}{9S_1})\, h_\alpha + (\frac{2\beta_1}{3S_1} + \frac{\beta_5}{3})\, \kappa^{[s]}_{\alpha\beta}\, n_\beta. \tag{4.71}$$

In obtaining this result we have enforced the condition that $\hat{\mathbf{n}}$ remain a unit vector. Comparing these two expressions with the LE equations, eqs. (4.4) and (4.10), we find the correspondences

$$\begin{aligned}
S_1 \lambda &= \tfrac{2}{3}\beta_1 + \tfrac{1}{3}\beta_5\, S_1 + \mathrm{O}(S_1^2) &(4.72)\\
\frac{S_1^2}{\gamma_1} &= \tfrac{2}{9}\beta_2 + \tfrac{1}{9}\beta_6\, S_1 + \mathrm{O}(S_1^2) &(4.73)\\
2\,(\nu_3 - \nu_2) &= \tfrac{3}{2}\beta_4\, S_1 + \mathrm{O}(S_1^2) &(4.74)\\
2\,\nu_2 &= \beta_3 - \beta_4\, S_1 + \mathrm{O}(S_1^2) &(4.75)\\
2\,(\nu_1 + \nu_2 - 2\,\nu_3) &= \mathrm{O}(S_1^2). &(4.76)
\end{aligned}$$

Notice that, in the absence of any nematic order, $2\nu_2$ reduces to precisely the viscosity found in the Navier-Stokes equation for a simple incompressible fluid. Notice also that the combination of Leslie coefficients $2(\nu_1 + \nu_2 - 2\nu_3)$ does not appear, to the order in $Q_{\alpha\beta}$ in which we have expanded the transport matrices. A straightforward calculation shows that keeping terms in the Onsager expansion to the next order in $Q_{\alpha\beta}$ yields a non-zero contribution to this combination of viscosities.

4.4 Flow Alignment in Steady Shear

As an application of these equations of motion we consider uniform flow alignment in shear flow, analogous to the alignment condition for the director within LE theory (eq. 4.13). Again we consider homogeneous flow,

$$\mathbf{v}(\mathbf{r}) = D\, y\, \hat{\mathbf{x}}, \tag{4.77}$$

and impose the stationary conditions

$$\dot{Q}_{\alpha\beta} = \kappa^{[a]}_{\alpha\gamma}\, Q_{\gamma\beta} - Q_{\alpha\gamma}\, \kappa^{[a]}_{\gamma\beta} + \beta_1\, \kappa^{[s]}_{\alpha\beta} + \frac{1}{\beta_2} H^{[s]}_{\alpha\beta} = 0. \tag{4.78}$$

As noted before, the torque vanishes, so

$$\Gamma_\alpha = \epsilon_{\lambda\alpha\beta}\, (H_{\alpha\rho}\, Q_{\rho\beta} - Q_{\alpha\rho}\, H_{\rho\beta}) = 0. \tag{4.79}$$

We assume that the $\hat{\mathbf{n}}$ lies in the shear plane (we will see later that this is indeed a stable configuration) and that the order parameter has the diagonal form ¶

$$\mathbf{Q}\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{z}}\} = \begin{pmatrix} S_1 & 0 & 0 \\ 0 & -\frac{1}{2}(S_1 + S_2) & 0 \\ 0 & 0 & -\frac{1}{2}(S_1 - S_2) \end{pmatrix}. \tag{4.80}$$

The director will be rotated at an angle θ with respect to the $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$ coordinate system defined by the flow (see fig. 4.2), so that the representation of the order parameter in this frame is

$$\mathbf{Q}\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\} = \mathbf{R}(\theta) \cdot \mathbf{Q}\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{z}}\} \cdot \mathbf{R}^{-1}(\theta)\,, \qquad \mathbf{R}(\theta) = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{4.81}$$

It is straightforward to contract eq. (4.78) with $Q_{\alpha\beta}$ and the Levi-Civita tensor and, making use of eq. (4.79), obtain the flow alignment condition for nematics in steady shear flow:

$$2\,\beta_1 \cos 2\theta = 3S_1 + S_2. \tag{4.82}$$

Using the correspondence between our coefficients and the Leslie coefficients, we see that in the uniaxial limit ($S_2 = 0$) this expression reduces to eq. (4.13). This correspondence between the alignment and the degree of biaxiality should be observable from, *e.g.*, birefringence measurements.

4.5 Alternative Formulations of the Dynamics

Our treatment of the dynamics is similar to that of Hess,[8] who also followed irreversible thermodynamics to arrive at the dynamical equations, and parallels Leslie-Ericksen theory.[12] It is similar in spirit and in

¶The expression $\mathbf{Q}\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{z}}\}$ signifies the representation of the tensor $\mathbf{Q}$ in the basis $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{z}}\}$.

practice to the approach to hydrodynamics discussed by Kadanoff and Martin[70] and by Martin, Parodi, and Pershan,[71] relying on thermodynamic relations to obtain dynamic equations for slow variables in the limits of weak non-equilibrium processes. I will briefly discuss other approaches to obtaining the dynamics for the order parameter. The two most common alternatives are the Poisson bracket approach, first stressed by Dzyhaloshinski and Volovik[72] and Volovik and Kats,[73] and developed further for complex fluids by Edwards and Beris;[74] and a more microscopic approach studied separately by Wang and Gelbart,[14] and See, *et al.*[10]

4.5.1 Poisson Bracket Method

The Poisson Bracket (PB) approach is similar in spirit to classical irreversible thermodynamics in that it deals only with the symmetries, conserved quantities, and broken symmetry variables of the system.[72] The time evolution of a quantity in a classical system is given by the PB of the quantity in question with the system Hamiltonian[75]. The PB is defined in terms of the canonical coordinates of the system, which include fast microscopic variables as well as slow macroscopic quantities such as the density and entropy. From the PB one obtains the reversible parts of the equations of motion for macroscopic quantities, while the irreversible parts are introduced as derivatives of a dissipative function, a scalar quantity which represents the entropy production and is constructed, much like the Onsager expansion, to respect the symmetries of the system and to be positive definite. The resulting equations are actually coupled equations of motion for the fast *and* slow variables in the system. While one usually assumes, for calculational purposes, that the fast variables relax quickly and may be ignored, a more correct formulation involves incorporating these fast variables into additive noise in the equations of motion for the macroscopic variables, hence rendering the equations of motion stochastic.[76,77] This procedure can be formally justified through the projection operator formalism of Nakajima and Zwanzig.[78] The advantage of using the PB approach is that it is a straightforward cookbook method; the disadvantage is that (this may reflect the author's inadequacies) the details can be tedious and sometimes obscure the physics of the actual dissipation mechanisms involved.

4.5.2 Microscopic Approach

Microscopic approaches to order parameter dynamics have been employed by See, *et al.*,[10] and Wang and Gelbart.[14] Like all microscopic approaches, they suffer from the flaw that they begin with a *model* of what is happening on microscopic length and time scales, and try to project up to hydrodynamic length and time scales. Unfortunately, we can only construct a microscopic model from, ultimately, macroscopic observations. The problems inherent in this reductionist approach are familiar from quantum electrodynamics, where the bare mass of the electron postulated in the Lagrangian is not the *observed* mass, but is adjusted to give the correct observed results.[79] In this case the procedure is very successful.

The ultimate goal is to solve for the orientational distribution function $\psi(\hat{\mathbf{u}},\mathbf{r},t)$, where $\hat{\mathbf{u}}$ is the unit vector indicating the orientation of the rod. Once an appropriate description of the dynamics of the distribution function has been found it is, in principle, a simple matter to obtain the order parameter dynamics by using the definition of the order parameter as an average of moments of $\hat{\mathbf{u}}$. Most of the work in this direction has been from Doi and coworkers,[10,80] who discuss a uniform distribution function $\psi(\hat{\mathbf{u}},t)$, and I will follow their discussions here. For a homogeneous flow field $v_\alpha = \kappa_{\alpha\beta}\, r_\beta$, Doi has proposed the following rotational diffusion equation:

$$\frac{\partial\psi}{\partial t} = D_r\mathbf{R}\cdot\left(\mathbf{R}\psi + \frac{\psi}{k_BT}(\mathbf{R}V_{scf})\right) - \mathbf{R}\cdot\left[\hat{\mathbf{u}}\times(\boldsymbol{\kappa}\cdot\hat{\mathbf{u}})\psi\right]. \tag{4.83}$$

Here $\mathbf{R}$ is the rotational operator $\mathbf{R} = \hat{\mathbf{u}}\times\partial/\partial\hat{\mathbf{u}}$, D_{r} is the rotational diffusion coefficient, and V_{scf} is a self-consistent field for the excluded volume potential. This is typically taken to be a Maier-Saupe potential,[81]

$$V_{scf} = -\tfrac{1}{6}U k_B T\,(3u_\alpha u_\beta - \delta_{\alpha\beta})\int d\hat{\mathbf{u}}'(3u'_\alpha u'_\beta - \delta_{\alpha\beta})\psi(\hat{\mathbf{u}}',t)\,, \tag{4.84}$$

where U is proportional to nbL^2, n is the concentration of the rods, b is the rod thickness, and L is the rod length. The first term in eq. (4.83) is analogous to the diffusion term in the Fokker-Planck equation,[82] and governs the relaxation of the system to equilibrium in the absence of flow. The main assumption lies in the second term. This is justified from the assumption that the rods follow the rotation of the flow and are convected like an ordinary particle: $\dot{u}_\alpha = (\mathbf{u}\cdot\boldsymbol{\nabla})\,v_\alpha = \kappa_{\alpha\beta}\,u_\beta$. Hence the angular velocity due to the interaction with the flow becomes $\boldsymbol{\omega} = \hat{\mathbf{u}}\times\dot{\hat{\mathbf{u}}}$, which results in the last term in eq. (4.83).[80] The order parameter equation of motion,[10] after averaging over $(3u_\alpha u_\beta - \delta_{\alpha\beta})$, is identical to our equation (4.61), with the correspondences

$$\beta_1 = \beta_5 = 1.0, \quad \frac{A}{\beta_2} = 2D_r(3-U), \quad \frac{B}{\beta_2} = -2D_r U, \quad \frac{B}{C} = -3.0, \quad \beta_6 = 0. \tag{4.85}$$

See, *et al.* consider a concentration-driven transition, so the term $(3-U)$ corresponds roughly to our $(T–T^-)$. The omission of the β_6 term in their version of the equations of motion indicates that this description may not represent a consistent expansion in the departure of the system from equilibrium, for if they retain the β_5 term, they should also retain the β_6 term, in accordance with our expansion, eq. (4.61). Using these equations, results qualitatively similar to many of the phenomena we will study later may be obtained with these equations, including the general structure of the phase diagram.[10] Some qualitative results that cannot be reproduced, however, are the instability to tumbling, which is known to occur when β_1 is sufficiently small and for sufficiently large strain rates;[65] determination of coexistence and state selection; and spatially varying properties, such as the interface profile between coexisting states and the wavelength dependence of the fluctuation spectrum. In principle one may address these problems by using the full rotational and *translational* diffusion equation[80] for $\psi(\hat{\mathbf{u}},\mathbf{r},t)$, and performing the averaging over moments of $\hat{\mathbf{u}}$ to obtain the fully inhomogeneous equations of motion. This problem has not been discussed in detail.

Chapter 5

Homogeneous States: Non-Equilibrium State Diagram

Our first task is to find the non-equilibrium phase diagram for a nematic undergoing shear flow.[8–10] The experimental apparatus commonly envisaged for such an experiment is a Couette cell, which consists of two coaxial cylinders with the gap between them filled with mesogens. For simplicity, we will consider plane shear flow, $\mathbf{v} = D\, y\, \hat{x}$, throughout this thesis, as depicted in fig. 5.1, but it seems reasonable to assume that the results will apply qualitatively to Couette cell experiments, at least for large cylinder radii and small gaps. Furthermore, the extension to arbitrary flows is simply a matter of computation.

5.1 Elongational Flow: A Potential Formulation

Before beginning our discussion of nematics in *shear* flow, we should mention the case of *elongational* flow, which has been discussed by Kramers[22] (1946), Thirumalai[60] (1987) and Lee[15] (1989). For elongational flow it is possible to construct an effective free energy $\mathcal{L}$, whose variation with respect to the order parameter, $\delta\mathcal{L}/\delta Q_{\alpha\beta}$, gives the correct order parameter equations of motion. For nematics in a *general* flow field this is not possible because of the specific form of the coupling to flow. Recall from eq. (4.63) that dissipation involves the motion of the order parameter relative to the rotation of the background fluid, necessitating the term

$$G_{\alpha\beta} = \kappa^{[a]}_{\alpha\gamma} Q_{\gamma\beta} - Q_{\alpha\gamma}\kappa^{[a]}_{\gamma\beta} \tag{5.1}$$

in the equation of motion for $Q_{\alpha\beta}$, where $\kappa^{[a]}_{\alpha\gamma}$ is the anti-symmetric velocity gradient tensor. Explicit calculation shows that $\partial G_{\alpha\beta}/\partial Q_{\lambda\rho} = -\partial G_{\lambda\rho}/\partial Q_{\alpha\beta}$, since $\kappa^{[a]}_{\alpha\beta} = -\kappa^{[a]}_{\beta\alpha}$, which violates the conditions of integrability of $G_{\alpha\beta}$ with respect to $Q_{\alpha\beta}$ (*viz.*, that there exists a function ψ such that $\partial\psi/\partial Q_{\alpha\beta} = G_{\alpha\beta}$), except for special flow fields for which $G_{\alpha\beta}$ vanishes. An example of such a flow field is elongational flow, $\mathbf{v}(\mathbf{r}) = D\,(-x\hat{\mathbf{x}}, -y\hat{\mathbf{y}}, 2z\hat{\mathbf{z}})$. The resulting functional, called a Kramers' potential after Henrik Kramers,[22] may then be minimized to find the states of the system. This is the approach used by Thirumalai,[60] Lee,[15] and Wang and Gelbart[14] to examine nematics in elongational flow, and yields a qualitatively similar phase diagram to the case of nematics in shear flow.

Figure 5.1: Coordinate system for planar Couette flow showing boundary plates and velocity field for a homogeneous phase.

5.2 General Flow

Because an 'effective free energy' for shear flow does not exist, our method for finding the non-equilibrium phases of the system will be to find the stable stationary states of the system from the dynamics, without resorting to a variational principle. The most general way to do this would be to augment the deterministic long-wavelength equations of motion for the order parameter and fluid velocity (eqs.4.63 and 4.65) with Langevin noise sources to account for the otherwise-neglected small-scale motion.[77] In an equilibrium system the strength of this noise is determined by the condition that an equilibrium distribution function be the static solution, which is the familiar fluctuation-dissipation theorem (FDT). One can then, in principle, transform the Langevin equation into an equivalent Fokker-Planck equation and solve for the stationary probability distribution function.[82]

The first problem with this method in a non-equilibrium system is the issue of the noise; *i.e.* the dynamics of the fast and small wavelength fluctuations. We know of no prescription equivalent to the FDT to determine the strength of the noise, so this choice is, to some extent, arbitrary. It seems reasonable, however, to choose a noise which reduces to that given by the FDT when the shear rate is turned off: this is equivalent to the statement that macroscopic flow does not affect the probability distribution of the small-scale fluctuations. This assumption is frequently used, often with favorable comparisons with experiment.[83] Nevertheless, it is a strong assumption and should be viewed with some scepticism.

The next problem is one of practicality. As the equations governing the order parameter are non-linear and, because of the biaxiality induced by the shear, involve many modes, it is a formidable to challenge to find the stationary states of the distribution function. As a first step, therefore, we will find the non-equilibrium phases by finding the stable stationary solutions to the equations of motion for $Q_{\alpha\beta}$ and $\mathbf{v}$ in the *absence* of noise. This may be regarded as the analog of a mean-field determination of the phase diagram, and should give us a qualitatively accurate description of the system. We will return to the subject of fluctuations in Chapter 7.

5.3 Stationary Conditions for Homogeneous States

We begin with the coupled differential equations for the order parameter and velocity field, eqs. (4.63-4.68). For homogeneous and stationary states these become coupled non-linear *algebraic* equations. We wish to find the solutions to these equations as functions of the temperature and either the applied stress or imposed strain rate (and for appropriate physical choices of material parameters such as the Landau and Leslie coefficients). It is calculationally easier to assume that the stress is *adjusted* to give a particular value of the strain rate, in which case we need only consider the order parameter equation of motion, eq. (4.63), and vary the temperature and strain rate. The velocity equation of motion is automatically satisfied since we assume a uniform state, which implies that $\partial_\alpha \sigma_{\alpha\beta} = 0$. We shall see later, when we discuss inhomogeneous states, that two states may coexist at the same applied stress, rather than at the same imposed strain rate, so it is perhaps more physical to evaluate the states as functions of the applied stress. This will be done later, but for the determination of homogeneous states it is sufficient to consider fixed strain rate.

Before outlining the detailed numerical scheme, we will examine the stationary condition $\dot{Q}_{\alpha\beta} = 0$ and $\dot{\mathbf{v}} = 0$. We choose the velocity field $\mathbf{v} = D\, y\, \hat{\mathbf{x}}$, whence

$$\boldsymbol{\kappa}^{[s]}\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\} = \frac{D}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad \boldsymbol{\kappa}^{[a]}\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\} = \frac{D}{2}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{5.2}$$

Let us choose as coordinate axes the triad $\{\hat{\mathbf{n}},\hat{\mathbf{m}},\hat{\mathbf{z}}\}$ and examine the stationary conditions in this basis. As we have seen (eq. 4.82), in steady state the director $\hat{\mathbf{n}}$ lies in the shear plane at an angle θ with respect to the fluid flow $\mathbf{v}$. The subdirector $\hat{\mathbf{m}}$ may also be taken to lie in the shear plane, orthogonal, by definition, to $\hat{\mathbf{n}}$. We must use the representations of the velocity gradient tensors in the $\{\hat{\mathbf{n}},\hat{\mathbf{m}},\hat{\mathbf{z}}\}$ basis, which are related to their representations in the $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ basis by an orthogonal transformation:

$$\mathbf{A}\{\hat{\mathbf{n}},\hat{\mathbf{m}},\hat{\mathbf{z}}\} = \mathbf{R}(\theta)\cdot\mathbf{A}\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}\cdot\mathbf{R}^{-1}(\theta). \tag{5.3}$$

and similarly for $\boldsymbol{\kappa}^{[a]}$. The rotation matrix $\mathbf{R}(\theta)$ specifies a rotation about the z-axis by an angle θ. Inserting these expressions into eq. (4.63), using the general form for $Q_{\alpha\beta}$, eq. (2.3), and expressing $H^{[s]}_{\alpha\beta}$ in terms of the variation of the Landau free energy density, we find the three stationary conditions

$$\begin{aligned}
\frac{\beta_1}{\beta_2} D\sin 2\theta &= \left[A + C(\frac{3S_1^2+S_2^2}{2})\right] S_1 + \frac{B}{2}(S_1^2 - \tfrac{1}{3}S_2^2) && (5.4)\\
\frac{\beta_1}{\beta_2} D\sin 2\theta &= \frac{1}{2}\left[A + C(\frac{3S_1^2+S_2^2}{2})\right](S_1 - S_2) - \frac{B}{12}(S_2^2 - 6S_1S_2 - 3S_1^2) && (5.5)\\
2\,\beta_1\cos 2\theta &= (3S_1 + S_2). && (5.6)
\end{aligned}$$

These conditions determine the magnitude of the amplitudes S_1 and S_2 and the orientation of $\mathbf{n}$ in the shear plane with respect to $\mathbf{v}$, as a function of the applied strain rate D and the temperature, which enters through $A = a(T - T^-)$.

5.4 Stable Stationary States

We have found the stationary states as a function of temperature and imposed strain rate for a fixed set of coefficients which are typical of low molecular weight thermotropic nematogens. It is convenient to perform calculations in terms of the dimensionless control parameters

$$\tau \equiv \frac{a(T-T^-)}{C} \qquad \text{and} \qquad \delta \equiv \frac{D\beta_2}{C}, \tag{5.7}$$

in terms of which the stationary conditions become

$$0 = \delta\left[\widehat{\kappa}^{[a]}_{\alpha\mu}\, Q_{\mu\beta} - Q_{\alpha\mu}\, \widehat{\kappa}^{[a]}_{\mu\beta} + \beta_1 \widehat{\kappa}^{[s]}_{\alpha\beta}\right] - \tau Q_{\alpha\beta} + \frac{B}{C}(\mathbf{Q}^2)_{\alpha\beta} - (\mathbf{Q}^3)_{\alpha\beta} - \frac{B}{3C}\,\delta_{\alpha\beta}\,\mathbf{Q}{:}\mathbf{Q}. \tag{5.8}$$

Here $\widehat{\kappa}^{[a]}_{\alpha\beta} = \kappa^{[a]}_{\alpha\beta}/D$ and $\widehat{\kappa}^{[s]}_{\alpha\beta} = \kappa^{[s]}_{\alpha\beta}/D$. In this form it is evident that the nature of the states is determined by the kinetic coefficient β_1, which is a ratio of rotational viscosities;[33] and the ratio of Landau parameters B/C, which is a measure of the weakness of the first order transition (recall that $\Delta S_1 = -2B/9C$). From typical values of the order parameter discontinuity at the equilibrium transition of, *e.g.*, MBBA, $\Delta S_1 \sim 0.27$, we have chosen $B/C = -1.2$ (see Table 2.1). For β_1 we have used 0.9, which is obtained from the examination of the correspondence with LE theory (eq. 4.72) and a typical value for λ (see Table 5.1).

To perform the numerical calculations we have used a fully general form for $Q_{\alpha\beta}$,

$$\mathbf{Q} = \begin{pmatrix} q_1 & q_3 & q_4 \\ q_3 & q_2 & q_5 \\ q_4 & q_5 & -q_1 - q_2 \end{pmatrix}, \tag{5.9}$$

and have used the $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$ coordinate axes coincident with the flow and its gradient. It is easiest to implement the conditions (5.8) as a vector equation:

$$f_i(\mathbf{q}) \equiv \partial_t\, q_i = 0, \qquad (i = 1, \ldots, 5). \tag{5.10}$$

Physical solutions must be stable with respect to fluctuations. Thus, if we parametrize $\mathbf{q}$ according to

$$\mathbf{q}(t) = \mathbf{q}^{(o)} + \boldsymbol{\eta}(t), \qquad \dot{\mathbf{q}}^{(o)} = 0, \tag{5.11}$$

then the fluctuation $\boldsymbol{\eta}(t)$ obeys the equation

$$\dot{\eta}_i = \left.\frac{\partial f_i}{\partial q_j}\right|_{\mathbf{q}=\mathbf{q}^{(o)}} \eta_j + \mathrm{O}(\eta^2). \tag{5.12}$$

The condition for stability with respect to small fluctuations is then that the matrix $\Theta_{ij} \equiv -\left.\partial f_i/\partial q_j\right|_{\mathbf{q}=\mathbf{q}^{(o)}}$ be positive definite, so that fluctuations will decay in time. As mentioned before, the equations of motion for $Q_{\alpha\beta}$ are non-integrable, in the sense that one cannot derive them from a functional $\mathcal{L}$ via $\partial_t Q_{\alpha\beta} = \delta\mathcal{L}/\delta Q_{\alpha\beta}$. This implies that the matrix Θ_{ij} is not symmetric. Hence, the eigenvalues of Θ_{ij} are generally complex, and the condition for stability is that the real part of all eigenvalues be positive.* We also point out that these states are stable with respect to small perturbations, or *locally* stable. We are not able, with this method, to make a statement about the *global*, or absolute, stability of particular solutions.

*Since M_{ij} is generally a real non-symmetric matrix, it is possible that it may not be diagonalizable. However, this may only occur when an accidental degeneracy of the eigenvalues of M_{ij} occurs, and then only if the dimension of the eigenspace of this degeneracy is smaller than the degree of degeneracy. This is rare in a matrix with so many free parameters. It is interesting to speculate on the physical consequences of such an accidental degeneracy, but we will leave this for now.

Figure 5.2: Stationary values for the the order parameter S_1 as function of dimensionless temperature τ, for $B = -1.2C$ and $\beta_1 = 0.9$, and a reduced strain rate of $\delta = .005$. Solid lines signify stable states and broken lines signify unstable states.

Having chosen physical values for the parameters β_1 and B/C, we have used the Newton-Raphson technique[84] to find numerically the roots to eq. (5.8) as a function of the control parameters τ and δ, and have evaluated the stability of these roots. Fig. 5.2 shows the stationary values for $Q_{\alpha\beta}$ plotted as a function of dimensionless temperature for a particular value of the dimensionless strain rate δ. Broken lines correspond to unstable states while solid lines correspond to stable states. We find stable configurations of the order parameter tensor to have two principal axes (director and sub-director) in the plane, and the third out of the plane. At high temperatures there is a single stable state available to the system, which is weakly ordered and has a high degree of biaxiality. In fact, we can readily solve the stationary conditions, eqs. (5.4-5.6), in the limit of weak shear, to find

$$\left.\begin{aligned} \theta &\simeq \frac{\pi}{4} - \frac{D}{4A\beta_2} = \frac{\pi}{4} - \frac{\delta}{4\tau} \\ S_1 &\simeq S_2 \simeq \frac{D\beta_1}{2A\beta_2} = \frac{\beta_1 \delta}{2\tau} \end{aligned}\right\} \qquad \begin{aligned} &T \geq T_{IN}(D) \\ &D \simeq 0. \end{aligned} \tag{5.13}$$

Here, and below, $T_{IN}(D)$ refers to a (presumed) transition temperature in the presence of flow. While the transition is now between biaxial states, we retain the same nomenclature (T_{IN}) for clarity and correspondence with the equilibrium IN transition.

As the temperature is reduced, a second stable state (as well as an additional unstable state) becomes available to the system, and at still lower temperatures this new state becomes the only stable state. This new state is well-ordered and nearly uniaxial, reflecting the dominance at low temperatures of the thermodynamic

Figure 5.3: Order parameter S_1 as a function of reduced temperature τ for branches containing the stable roots $Q_{\alpha\beta}$, for a range of values of the dimensionless shear rate and for $B = -1.2\,C$ and $\beta_1 = 0.9$: (a) $\delta = 0$, (b) $|\delta| < \delta^*$; (c) $|\delta| = \delta^*$; and (d) $|\delta| > \delta^*$. Unbroken lines correspond to linearly stable steady states, while broken lines represent unstable states.

effects. In the limit of small strain rate we can calculate the corrections to the order due to the flow:

$$\left.\begin{aligned} S_1 &= S_o(T) + r\,D \\ r &\simeq \frac{\beta_2}{S_o(B+6S_oC)}(4\beta_1^2 - 9S_o^2)^{1/2} \\ S_2 &\simeq -\frac{(B+6S_oC)\,r\,D}{2B} \end{aligned}\right\} \qquad \begin{aligned} &T \le T_{IN}(D) \\ &D \simeq 0, \end{aligned} \tag{5.14}$$

where $S_o(T)$ is the equilibrium (*i.e.* $D = 0$) value of the order parameter, given in Table 2.1, and the alignment angle is given by the condition (5.6). The role of shear flow at low temperatures is largely to dictate the orientation of the liquid crystal phase. In the intermediate regime, where there are two locally stable states, there is, from this analysis, no way to determine which, if either, of the two states is physically selected. However, we can say with certainty that at some point in this region (possibly the boundary) the system makes a discontinuous jump as the temperature is decreased, assuming that the system is stable with respect to states we have not considered, such as spatially modulated configurations. Hence we may suspect that the system will exhibit the non-equilibrium analog of a first order transition, leaving aside for the moment questions of hysteresis and metastability.

As the strain rate is increased we find the family of curves depicted in Fig. 5.3. For low strain rates the curves are topologically identical, depicting a high temperature ordered phase which gives way to a two-state region at lower temperatures, and a single well-ordered phase at still lower temperatures. However, for higher strain rates we find qualitatively different behavior. For dimensionless strain rates larger than a critical strain rate δ^*, the state of the system varies smoothly with temperature, and there is no transition. Finally, when the temperature is reduced *at* the strain rate δ^* we see that the system undergoes a continuous transition from the high to the low temperature states of the system that is nonetheless *non-analytic*, as the slope of the order parameter vs. temperature line diverges at the *non-equilibrium critical point*, (δ^*, τ^*).

5.5 Summary

Figure 5.4 shows the phase diagram as a function of dimensionless temperature and strain rate. From this figure and Fig. 5.3 we see that the nematic in shear displays many features reminiscent of the van der Waals fluid:[16]

- Both systems possess a discontinuous transition in the order parameter ($Q_{\alpha\beta}$ for the nematic, volume for the VdW fluid) as a field is increased (strain rate and pressure, respectively), which ends in a critical point.
- It is possible to go *smoothly* from one state within the two state region to the other by varying the external parameters to go *around* the critical point. This can be done because the the two states have the same symmetry: liquid and gas for the VdW fluid, and two biaxial states for the nematic.
- For a given reduced strain rate δ, there exist temperatures $T^+(\delta)$ and $T^-(\delta)$ between which strongly and weakly ordered states are both locally stable states of the system. This leads one to ask whether there is a temperature $T_{IN}(\delta)$, where $T^-(\delta) \leq T_{IN}(\delta) \leq T^+(\delta)$, at which the two states may coexist. Such a temperature would provide the analog of the coexistence line in the liquid-gas system, and the shaded region in Fig. 5.3 would then correspond to the coexistence region of a liquid-gas system. This issue will be explored in Chapter 5, where we will find coexistence of states at a common *stress*.
- The critical points of both systems exhibit singularities. At the liquid gas critical point the compressibility, $-V^{-1}\,\partial V/\partial P$, diverges. The compressibility is related to density fluctuations, which may be probed by light scattering experiments. This divergence signals the familiar phenomenon of critical opalescence. For the nematic in shear flow the quantity $\partial Q_{\alpha\beta}/\partial T$ diverges at the critical strain rate δ^*. It is reasonable, therefore, to expect observable critical behavior analogous to that seen in the liquid-gas system. This analogy will be pursued further in Chapter 7.

While there are many similarities between the two systems, we must bear in mind the profound differences, aside from the issue of equilibrium vs. non-equilibrium systems. The critical point in the nematic in shear is a result of the flow suppressing certain configurations in the 5-dimensional parameter space of the order parameter, while the fluid critical point involves a scalar order parameter. The role of increasing the pressure in the fluid is to decrease the exchange of entropy of dissociation (from liquid to gas) for the cohesive energy of the liquid. This latent heat vanishes, of course, at the critical point, where the states become the same and there is no entropy change at the transition. The transition in the nematic in shear takes place between different orientations of the order parameter; the difference between these states vanishes at the critical point. It is interesting to speculate on the analog of latent heat for the nematic.

Using typical numbers for MBBA, we find a critical strain rate of $D^* \sim 10^5\,\mathrm{s}^{-1}$ and a temperature shift of $T^* - T_{IN} \approx 0.5\,\mathrm{K}$. While the magnitude of this strain rate is near the experimentally obtainable limit and could make observation of the critical point difficult, systems with a larger viscosity β_2 would have more

Figure 5.4: Dimensionless strain-rate (δ) vs. dimensionless temperature (τ) state diagram for $B = -1.2\,C, \beta_1 = 0.9$, as determined from homogeneous states. The shaded region is the two-state region with two locally stable states; solid lines mark the limits of stability for the high and low temperature states; the center dot marks the equilibrium IN transition, and the outer dots locate the non-equilibrium critical points at $(\tau^*; \delta^*) \simeq (0.07914, 0.007961)$.

Figure 5.5: Isotherms in the pressure-volume phase diagram for the van der Waals fluid.

readily accessible critical strain rates. An example of such a system is the Tobacco Mosaic Virus (TMV),[18] which has rotational diffusion times one to two orders of magnitude higher than MBBA. This is a lyotropic system, *i.e.*, a *solution* of rods, which necessitates a slightly different theoretical treatment because of the presence of the solvent. These problems will be discussed briefly in Chapter 8.

To explore further the analogies between the non-equilibrium nematic under shear and the van der Waals fluid, and to gain more understanding about the nematic under shear, we must settle two further issues, neither of which can be determined from an analysis of homogeneous states (in contrast to the VdW fluid):

- How do we determine whether one or the other of the two stable states within the two-state region is selected? Further, is there a coexistence line in this region which plays the role of the line of first order transitions in the VdW fluid? The procedure for determining such a line in equilibrium systems is well-defined for mean-field theories via the Maxwell construction, *i.e.*, the equality of chemical potentials. How may we address this problem for our non-equilibrium system?
- What is the nature of the critical point? We have seen that the nematic in shear flow is singular at the critical point, but how does this singularity manifest itself, and what are the analogs of the equilibrium critical exponents?

To answer these questions we will examine *inhomogeneous* solutions to the equations of motion, which we pursue in the next chapter.

Table 5.1: Material Parameters for MBBA

Transition temperature	T_{IN}	46.0	$^\circ$C	a
Frank elastic constants	K_1	6.0×10^{-12}	J m^{-1}	d
	K_2	4.0×10^{-12}	J m^{-1}	d
	K_3	9.5×10^{-12}	J m^{-1}	d
	L_1	1.4×10^{-12}	J m^{-1}	b
Landau parameters	a	$1.35,\ 0.93 \times 10^5$	J m^{-3} $^\circ K^{-1}$	a,b
	$-B$	$2.66,\ 2.12 \times 10^6$	J m^{-3}	a,c
	C	$2.76,\ 1.78 \times 10^6$	J m^{-3}	a,c
	$T_{IN} - T^-$	$0.7, 1.0$	$^\circ$K	a,c
Order parameter jump	ΔS_1	0.21, 0.27		a,c
Leslie parameters	α_1 (25.0° C)	6.5	c Poise	e
	α_2 (43.0° C)	-19.0	c Poise	e
	α_3 (43.0° C)	-1.7	c Poise	e
	α_4 (43.0° C)	40.0	c Poise	e
	α_5 (43.0° C)	5.0	c Poise	e
	α_6 (43.0° C)	-12.3	c Poise	e
Alignment angle	θ (43.0° C)	17.5^o		e

[a] Y. Poggi, J. C. Filippini, and R. Aleonard, *Phys. Let.* **57A** (1976), 53.
[b] T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.* **30** (1973), 688.
[c] T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.* **25** (1970), 503.
[d] M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.***46** (1974), 617.
[e] C. Gähwiller, *Mol. Cryst. Liq. Cryst.* **20** (1973), 301.

Table 5.2: Relations among various Leslie coefficients

γ_1	$=$	$\alpha_3 - \alpha_2$	$2\eta_1$	$=$	$\alpha_3 + \alpha_4 + \alpha_6$
γ_2	$=$	$\alpha_6 - \alpha_5$	$2\eta_2$	$=$	$\alpha_4 + \alpha_5 - \alpha_2$
λ	$=$	$-\gamma_2/\gamma_1$	$2\eta_3$	$=$	α_4
$\tan^2\theta$	$=$	α_3/α_2	$2\nu_1$	$=$	$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + 2\alpha_5$
$\cos 2\theta$	$=$	$1/\lambda$	$2\nu_2$	$=$	α_4
$\alpha_6 - \alpha_5$	$=$	$\alpha_3 + \alpha_2$	$2\nu_3$	$=$	$\alpha_4 + \alpha_5 + \lambda\alpha_2$

Chapter 6

Inhomogeneous States: Coexistence, Selection, and Critical Behavior

6.1 Equilibrium State Selection and Coexistence

For comparison with our non-equilibrium system, let us first examine the procedure for determining the *equilibrium* state of a system near a first order transition.[16] As a concrete example we consider the van der Waals (VdW) fluid, whose homogeneous states are specified, at fixed particle number, by the pressure and temperature. The equilibrium states of a system are those which minimize the relevant free energy, or thermodynamic potential, of the system, whose choice depends on the variables help constant in the system (*e.g.* the Helmholtz free energy $F(T,V)$ or the Gibbs free energy $G(T,P)$). Unfortunately, this program is usually too difficult to carry out explicitly. Landau theory is an approximation to this scheme near continuous phase transitions, where it is assumed that the equilibrium free energy may be obtained by minimizing a properly constructed functional.[4] This functional is assumed to be an expansion in terms of the order parameter which obeys the symmetries of the system. While its use is not justified for first order transitions where the order parameter jumps at the transition, it is often assumed to be qualitatively correct when the discontinuity in the order parameter is small.

The order parameter for the VdW fluid is the liquid-gas density difference, which is small near the critical point. Figure 5.5 show isotherms in the pressure-volume plane obtained from the VdW equation of state,

$$V^3 + a\,(P,T)\,V^2 + b\,(P)\,V + c\,(P) = 0. \tag{6.1}$$

This equation was originally obtained using heuristic arguments concerning molecular interactions, but may also be considered to be the stationary condition $\partial G/\partial V$, for a Landau free energy G.[16] Notice the similarity, as noted in Chapter 5, of the VdW isotherms to the isoshears in the order parameter-temperature plane for the nematic under shear. Now we ask, given T, at what pressure P will we find two coexisting states? To determine the state of the system we must satisfy the conditions of equilibrium for two thermodynamic systems in contact with each other (the two systems being the liquid and gas phases). By 'contact' we mean that the systems may exchange heat and matter. In equilibrium, then, the temperatures, pressures, and chemical potentials of the systems must be the same:

$$T_l = T_g, \qquad p_l = p_g, \qquad \mu_l = \mu_g, \tag{6.2}$$

Figure 6.1: Isotherm in the pressure-temperature plane for a van der Waals fluid, showing the Maxwell equal-areas construction for liquid-gas coexistence. From Kittel and Kroemer.[87]

where the subscripts refer to the liquid and gas phases. For the VdW fluid we may use the Gibbs-Duhem relation,[16]

$$d\mu = -\frac{S}{N}\,dT + \frac{V}{N}\,dp, \tag{6.3}$$

to obtain the familiar Maxwell equal areas construction (see Fig. 6.1), which follows from

$$\mu_l - \mu_g = \int_l^g d\mu = \int_l^g \frac{V}{N}\,dp = 0. \tag{6.4}$$

From the Gibbs-Duhem relation we see that the chemical potential is the same as the effective potential per particle for the system at specified pressure and temperature. To see this we perform a Legendre transformation to obtain the Gibbs free energy $G(T, P, N)$,

$$G = E - TS + PV, \tag{6.5}$$

whose differential is

$$dG = -S\,dT + V\,dP + \mu\,dN, \tag{6.6}$$

which implies that $\mu = \partial G/\partial N$. Hence the Maxwell construction is equivalent to choosing the pressure at which, for a given isotherm, two states have the same free energy density. We also note that the Maxwell construction is only a heuristic construct, which in fact corrects the unphysical nature (lack of convexity) of certain solutions to VdW equation of state.[19]

6.2 State Selection and Coexistence out of Equilibrium

A general non-equilibrium system does not possess a prescription analogous to the Maxwell construction for determining the stable steady states, or phases, of the system. Even the prescription for determining the state of the system when only a single steady state exists is not as well defined. In equilibrium the state of the system follows from a variational principle, which in turn is a statement simply of the most probable state. It has been conjectured that non-equilibrium steady states obey a similar variational principle, namely, that of minimum entropy production.[20] This condition is obeyed by, *e.g.*, steady state heat flow in a system with open boundaries (to permit heat flow) and an applied temperature gradient.[66] However, the principle of minimum entropy production only asserts that the state of the system is a *local* minimum, in function space, of the entropy production.[66] It is not a criterion which may distinguish globally among different locally stable states of the system, as the Maxwell construction or minimization of the free energy does for equilibrium states. A second method often used to determine the states of a non-equilibrium system involves the use of an effective free energy to mimic the relaxation of the system. As we discussed in Chapter 5, it is possible to find an effective free energy only for special flows, such as elongational flows.

Since we cannot appeal to a variational principle to distinguish locally stable states, we will take a more pragmatic approach. At a given applied stress there is a range of temperatures for which there are two locally stable homogeneous states (see fig. 6.2). We wish to find which state, if any, is preferred at a particular temperature within this interval, and whether there is a temperature at which two states may coexist. To address this we will search for non-uniform solutions to the equations of motion which interpolate between configurations that are both locally stable states at a given temperature. By this somewhat brute-force method we will be able to determine not only a coexistence line which (we conjecture) corresponds to the analog of an equilibrium line of first order transitions, but also information about the mean-field critical behavior as the non-equilibrium critical point is approached.[85]

6.3 Interface Method for Determining Coexistence

6.3.1 Fixed Boundaries

While in Chapter 5 we chose, as is commonly done,[10,14,15] to examine the phase diagram in the strain-rate vs. temperature plane, a stable *inhomogeneous* steady state must have uniform *stress* across the system. Hence we will focus on the applied-stress vs. temperature plane in this chapter, and imagine the system to be sheared with an applied stress σ_{xy} at two boundary plates, as shown in fig. 5.1. It is straightforward to generalize our procedure for finding stable states at an imposed strain rate to the case of an applied shear stress σ_{xy}. This will be described in detail below. The result is a state diagram in the applied-stress–temperature plane analogous to the strain-rate–temperature phase diagram of Chapter 5, with a critical point at (σ^*, T^*), where σ^* is the critical applied shear stress.[†] Within the two-state region we find two locally stable homogeneous states (fig. 6.2). Our goal is to determine whether, for fixed applied stress, there is a temperature $T_{IN}(\sigma_{xy})$ which plays the role of the first-order transition temperature in an equilibrium system. If so, then for temperatures above $T_{IN}(\sigma_{xy})$ the system will select the weakly ordered state, while at temperatures below $T_{IN}(\sigma_{xy})$ the system will select the strongly ordered state. To address this question we imagine that the two plates impose boundary conditions such that the nematic adopts one of the two

[†] It is interesting to note that the critical temperature determined using fixed strain rate, T^*_D, is not the same as that determined at fixed stress, T^*_σ. This is because the manifold of stable states is different between the two cases, so that a stable solution at, *e.g.*, fixed strain rate, need not be stable at fixed stress. This difference is, however, largely academic in this case, since the system may physically only have coexisting states at fixed *stress*.

Figure 6.2: Order parameter vs. temperature for fixed applied stress. The branches labeled $Q^{+}_{\alpha\beta}(\sigma_{xy,T})$ and $Q^{-}_{\alpha\beta}(\sigma_{xy,T})$ are locally stable states. The shaded region is the two-state region, and the dotted line identifies a conjectured coexistence temperature.

homogeneous stable states at one plate, and the alternative state at the other. We will ignore boundary effects around the perimeter of the plates. With the order parameter thus specified, we will examine how the order parameter and strain rate vary from one plate to the other.

First we will discuss a familiar equilibrium problem in this language. Consider an Ising magnet in a small applied field h below its Curie temperature T_c. At a coarse-grained level the system free energy is postulated to minimize[50]

$$F = \int dV \Big\{ -\tfrac{1}{2} m\phi^2 + \tfrac{1}{4}\lambda\phi^4 - h\phi \Big\}, \tag{6.7}$$

where $m = m_o(T_c - T)$ and ϕ, which is a real scalar field, represents an average of the magnetization over a length scale large compared to the lattice and small compared to the system size. Based on the principle that the state of the system is that which minimizes F, we can characterize this system. In zero field ϕ chooses one of the values $\phi^{\pm} = \pm(m/\lambda)^{1/2}$ which minimize F. For a small positive field $h > 0$ and $T < T_c$, two local minima exist at $\phi^{\pm}(h)$, but the state $\phi^{+}(h)$ has the lower free energy and is the selected state. As the field is reduced a first order transition occurs at $h = 0$, where the free energies of the states $\phi^{\pm}(h = 0) = \phi^{\pm}$ are identical.

Now we will discuss an alternative method, generalizable to non-equilibrium systems, for determining the behavior of the stable states of the system for $T < T_c$ and general h. We would like to be determine, as we did above by minimizing the free energy, the transition field h_c and the selection behavior of the system for $h \neq 0$. Consider a finite-size one-dimensional system for the moment. Imagine that the order parameter is

Figure 6.3: Stable interface at a presumed coexistence temperature. $Q^{+}_{\alpha\beta}$ refers to the order of the high temperature state, and $Q^{-}_{\alpha\beta}$ refers to the order of the low temperature state.

specified to be $\phi^{+}(h)$ at one end of the system and $\phi^{-}(h)$ at the opposite end, necessitating an interface, or a 'kink', somewhere in the system. We will determine the coexistence field for this system by examining the behavior of this interface. For a positive field the $\phi^{+}(h)$ configuration costs less energy, so the interface will be pushed over to the $\phi^{-}(h)$ wall in order to minimize the total free energy; while the converse will happen for a negative field. Finally, for zero applied field the interface will lie in the middle of the system. This provides a simple numerical determination of the coexistence field ($h = 0$) and selection behavior ($\phi^{+}(h)$ for $h > 0$, $\phi^{-}(h)$ for $h < 0$). These arguments were made for a finite system; in an infinite system we should find similar results, with the exception that coexistence would be determined by translational invariance of the interface position, rather than location at the center.

Now we apply this procedure to the nematic under shear flow. For a given applied stress and a system with finite extent in the $\hat{\mathbf{y}}$ direction, we examine the behavior of the interface which interpolates between the two configurations, $Q^{+}_{\alpha\beta}(\sigma_{xy}, T)$ and $Q^{-}_{\alpha\beta}(\sigma_{xy}, T)$, which are the locally stable homogeneous states (fig. 6.3). We consider an applied boundary stress σ_{xy} which induces a velocity gradient $\partial v_x/\partial y = D(y)$ (see fig 5.1). Notice that, because the strain rate and the order parameter are related by the stress, they will vary together across the system. We will only consider states which vary normal to the interface, which ignores interesting phenomena such as capillary waves and instabilities on the interface. For fixed applied stress the homogeneous states are slightly more complicated to find than for fixed strain rate, because we must analyze both the order parameter and fluid velocity equations of motion. The stationary conditions now read (rewriting eqs. 4.63 and 4.65)

$$0 = \kappa^{[a]}_{\alpha\gamma} Q_{\gamma\beta} - Q_{\alpha\gamma}\kappa^{[a]}_{\gamma\beta} + \beta_1 \kappa^{[s]}_{\alpha\beta} + \frac{1}{\beta_2} H^{[s]}_{\alpha\beta} \tag{6.8}$$

$$0 = \nabla_\gamma \sigma_{\alpha\gamma}\, ; \qquad \sigma_{\alpha\beta} = \sigma^{i[s]}_{\alpha\beta} + \sigma^{i[a]}_{\alpha\beta} + \sigma^{d}_{\alpha\beta} - p\delta_{\alpha\beta} \tag{6.9}$$

where $H^{[s]}_{xy}$ is given in terms of $Q_{\alpha\beta}$ by

$$H^{[s]}_{\alpha\beta} = -AQ_{\alpha\beta} + BQ_{\alpha\gamma}Q_{\gamma\beta} - CQ_{\alpha\beta}\,\mathrm{Tr}\,\mathbf{Q}^2 - \frac{\delta_{\alpha\beta}}{3} B\,\mathrm{Tr}\,\mathbf{Q}^2, \tag{6.10}$$

and the various contributions to the stress tensor are given by eqs. (4.66-4.68). For a uniform state the distortion tensor $\sigma^{d}_{\alpha\beta}$ vanishes because it depends on gradients of $Q_{\alpha\beta}$. Furthermore, since $\sigma^{i[a]}_{\alpha\beta}$ is the

Figure 6.4: State diagram for nematics under shear. Axes are dimensionless applied stress s vs. dimensionless temperature τ. The shaded area is two state region, the center dot locates the equilibrium IN transition, and the outer dot identifies the critical point. For $B = -1.2C$, $\beta_1 = 0.9$, and $\beta_3 = 0.1$, the critical point is $(\tau^*_{;} s^*) \simeq (0.08168, 0.003795)$.

commutator of $Q_{\alpha\beta}$ and $H^{[s]}_{\alpha\beta}$ (see eq. 4.67) it also vanishes for uniform states. Hence we need only consider $\sigma^{i[s]}_{\alpha\beta}$, given by eq. (4.66), to find the following relation among the applied stress σ_{xy}, D, and $Q_{\alpha\beta}$:

$$\sigma_{xy} = \frac{D}{2}\beta_3 - \beta_1 H^{[s]}_{xy}. \tag{6.11}$$

Thus we may eliminate D from eq. (6.8) (it appears in $\kappa^{[s]}_{\alpha\beta}$ and $\kappa^{[a]}_{\alpha\beta}$) in favor of σ_{xy}, and search for the stable roots $Q_{\alpha\beta}\,(\sigma_{xy}, T)$ of eq. (6.8).

Thus we are able to obtain the stable steady states and the stress-temperature state diagram (fig. 6.4). Before proceeding with the interface solution, we note two interesting rheological consequences of the state diagram. First, we find that, for fixed stress, the state with the larger value of the order parameter in the two state region also has a larger strain rate than the stable state with weaker order. This implies that the effective viscosity $\eta \equiv \sigma_{xy}/\partial_y v_x$ of the well ordered state is smaller than that of the weakly ordered state. Hence, as the system makes a discontinuous jump in *order* somewhere in the two state region upon decreasing the temperature at fixed stress, it also makes a jump in the *strain rate*. Now imagine varying the stress at a fixed temperature between T_{IN} and T^* (that is, moving vertically through figure 6.4). Again, the system makes a jump somewhere within the two state region, accompanied by a jump in the strain rate. Hence we see that, for a given temperature T, $T_{IN} < T < T^*$, there will be a range of strain rates, corresponding to the jump mentioned above, which are *inaccessible* to the system in the form of stable homogeneous states. We will see that the system can nevertheless adopt these strain rates by 'phase-separating' into a mixture of the two stable states. This is analogous to a liquid-gas system phase separating according to the lever rule.[4]

6.3.2 Periodic Boundary Conditions

An alternative approach to determining coexistence is to impose periodic boundary conditions on the system and let it relax from arbitrary initial conditions. If there is a coexistence temperature $T_{IN}(\sigma_{xy})$, then the system should consistently relax to the weakly ordered state for $T > T_{IN}(\sigma_{xy})$, and to the strongly ordered state for $T < T_{IN}(\sigma_{xy})$. The exception to this is if the initial condition places the system in the basin of attraction for the locally stable state which, in the language of equilibrium systems, would be termed a metastable state. Another 'experiment' one can perform is prepare the system in a mixture of the two homogeneous stationary states and observe whether the evolution proceeds towards one state or the other. For example, half of the system could be prepared in the state $Q^+_{\alpha\beta}$ and half in the state $Q^-_{\alpha\beta}$, with the two interfaces interpolating smoothly between the states.

We have performed exploratory calculations using the first method (random initial conditions), and found behavior consistent with the results of the fixed boundary method. That is, we are able to find behavior consistent with a coexistence temperature $T_{IN}(\sigma_{xy})$, as described above. However, we have not investigated this in detail.

6.4 Results of Interface Method

The details involved in computing the stable interface are described in Appendix B. We have used the implicit Crank-Nicholson method[84] to find the stable interface profile, introducing a fictitious dynamics to govern relaxation to the proper profile. An important aspect of the method we have chosen is that, while it correctly finds the stable steady states, the dynamics of the relaxation are *fictitious* because we slave the velocity field dynamics to the order parameter by always imposing a uniform stress tensor. This ensures that $\partial_t \mathbf{v}(\mathbf{r}) = 0$ at all times during the relaxation. For the majority of our computations we have chosen the parameters $B/C = -1.2, \beta_1 = 0.9, \beta_3 = 0.1\beta_2$, and have used the approximation $L_1 = L_2 = L$. This choice of the ratio β_3/β_2 follows from the correspondences $\beta_2 \simeq 4\gamma_1/(9x^2)$ and $\beta_3 \simeq 2\nu_2$ (eq. 4.76) and typical experimental values for γ_1 and ν_2 (see tables 2.1 and 5.2). Experimentally, L_1 and L_2 are found to be roughly the same.[40,44] Again, we use dimensionless control parameters,

$$\tau \equiv \frac{a(T-T^-)}{C}, \qquad s \equiv \sigma_{xy}/C, \tag{6.12}$$

and scale length and time scales to dimensionless units according to

$$\bar{t} \equiv \frac{tC}{\beta_2}, \qquad \bar{y} \equiv y\left(\frac{C}{L_1}\right)^{1/2}. \tag{6.13}$$

The position of the interface is characterized by a 'kink' between the two stable configurations of the order parameter. Since the order parameter has many components, we will use the maximum of the distortion (*i.e.* Frank) free energy density as a scalar indicator of the kink position. As an exercise, we first performed this method on the ϕ^4 magnet and verified that we could determine the coexistence field and selection behavior at temperatures below the Curie point.

Using this method for the nematic in shear flow we have found a coexistence line in the applied-stress–temperature plane for system sizes (in dimensionless units) $64, 128$, and 256, with meshes containing, respectively, $80, 80$, and 160 points. Time steps were chosen in specific cases to efficiently find the stable states. For the larger systems, on the order of 10^5 time steps were needed to achieve the stationary configuration. Calculations were carried out on IBM RISC-6000 5400 and 320, and VAX DEC-6410 machines, using code adapted from *Numerical Recipes*.[84] Specific routines were developed to facilitate inversion of large sparse matrices.

Our algorithm to find the coexistence line was to iteratively correct the temperature for a given stress until a temperature was found which corresponds to a coexistence temperature, as discussed above. In weak shear flow, near the equilibrium IN transition, we found that the interface position was very sensitive to the temperature on either side of the transition. That is, a slight increase (or decrease) of the temperature from the (presumed) transition temperature would easily push the interface to one side or the other. Conversely, the system was not so temperature-sensitive near the non-equilibrium critical point, presumably because the two states are so similar; hence the accuracy with which we could determine the coexistence temperature for a given stress decreased as we neared the critical point. This technique is similar to a method used by Krug, *et al.*,[62] to find the coexistence line for the driven diffusive lattice gas. Using typical numbers for low molecular weight mesogens, we have found interface widths for small applied stress (*i.e.* near equilibrium) of a few 100Å, in reasonable agreement with what is expected experimentally.

6.4.1 Critical Behavior

Figure 6.5 shows interface profiles for the system of size 256, at reduced applied stresses of 0.0001, 0.0035, and 0.00377, which should be compared with the stress at the critical point, $(\tau^*, s^*) \simeq (0.08168, 0.003795)$. For small applied stress the interface is relatively sharp, while as the stress is increased, approaching the critical point, the interface broadens. This behavior is what we expect from an equilibrium system near a critical point, for which the width of the interface between the two phases grows as the critical point is approached, diverging like the correlation length. In equilibrium one expects the scaling law[5,49]

$$W \sim \xi \sim (T_c - T)^{-\nu}, \tag{6.14}$$

where ξ is the correlation length and T_c the equilibrium critical temperature. Within mean-field theory one expects the exponent $\nu = 1/2$. We do not yet have an explicit formulation for the correlation length, but if we suppose that it is indeed the only large length scale in the problem, and that the same kind of scaling applies as in equilibrium, then we expect a similar scaling law. Fig. 6.6 is a log-log plot of W vs. $(\tau - \tau^*)$, and indicates scaling similar to an equilibrium mean-field theory, with $\nu \simeq 0.51 \pm 0.01$. We have defined W as the width at half maximum in the Frank free energy, and verified that our results are robust with respect to this choice.

A second scaling law we can investigate concerns the shape of the coexistence curve in the vicinity of the critical point. Upon determining the coexistence temperature for a given applied stress we have also determined the order parameter of the coexisting phases, $Q^+_{\alpha\beta}$ and $Q^-_{\alpha\beta}$. In the VdW system, the density difference between the two states (which is the order parameter), scales as[16]

$$\rho_{\rm l} - \rho_{\rm g} \sim (T - T_c)^{\beta}, \tag{6.15}$$

where $\rho_{\rm l}$ and $\rho_{\rm g}$ are the densities of the liquid and gas phases and, within mean-field theory, $\beta = 1/2$. We must be careful in extending this type of scaling to the nematic because of the multi-component order parameter, $Q_{\alpha\beta}$. Such a relation only characterizes the behavior of the particular mode in the system which has a diverging correlation length at the transition. In equilibrium, within Landau mean-field theory, this critical mode is that mode whose quadratic coefficient in the effective free energy vanishes.[4] In a non-equilibrium system without an effective free energy we may define the critical mode as that mode whose fluctuations are long-lived at the critical point. Generally, for the nematic, this mode will be a complicated linear combination of the five independent degrees of freedom of $Q_{\alpha\beta}$:

$$\widehat{Q}_{\alpha\beta} = \sum_{i=1}^{5} \xi_i \, e^i_{\alpha\beta}, \tag{6.16}$$

Figure 6.5: Interface profiles for system size L=256 and reduced applied stresses of $0.0001, 0.0035$, and 0.00377, for parameters $B = -1.2C$, $\beta_1 = 0.9$, and $\beta_3 = 0.1$. The critical point is $(\tau^*, s^*) \simeq (0.08168, 0.003795)$.

where $\widehat{Q}_{\alpha\beta}$ is the slow mode and $\{e^1_{\alpha\beta}\}$ is a complete set of traceless-symmetric eigentensors (see Appendix A for a description of our parametrization of $Q_{\alpha\beta}$).

We may find this mode by examining the stability matrix Θ_{ij} for fluctuations away from the stable steady state, given by (eq. 5.12):

$$\dot{\xi}_i = -\Theta_{ij}\xi_j + \mathrm{O}(\xi^2), \tag{6.17}$$

where $\{\xi_i\}$ are the amplitudes of the fluctuations of the independent degrees of freedom $\{e^i_{\alpha\beta}\}$ of $Q_{\alpha\beta}$. The matrix Θ_{ij} is positive definite except at the critical point, where we find a single zero eigenvalue which corresponds to the slow mode. This critical mode corresponds to a combination of stretching the two amplitudes S_1 and S_2 and rotating the major director $\hat{\mathbf{n}}$ in the shear plane. For the $B = -1.2C, \beta_1 = 0.9$, and $\beta_3 = 0.1$, this massless mode is given by

$$\widehat{Q}_{\alpha\beta} = 0.402\, e^1_{\alpha\beta} + 0.283\, e^2_{\alpha\beta} + 0.871\, e^3_{\alpha\beta}. \tag{6.18}$$

The next step is to define how to measure the *approach* to the transition to extract the divergence, *i.e.*, the analog of $(\rho_l - \rho_g)|_{T\to T_c}$ along the coexistence line for the VdW system. As a *scalar* measure of the vanishing of the critical mode at the critical point we will use the magnitude of the projection of the order

Figure 6.6: $\log W$ vs. $\log(\tau-\tau^*)$ for the L=256. system. The straight line indicates the best fit, with an exponent $\nu \simeq .51 \pm 0.01$.

parameter discontinuity $Q^+_{\alpha\beta} - Q^-_{\alpha\beta}$ onto the soft mode, along the coexistence line. This projection is done implicitly in, *e.g.*, a Heisenberg magnet. In this case the magnetic field selects a particular direction for the magnetization, and it is the magnitude of the projection of the magnetization along the field whose behavior yields the exponent β.

The inner product for the set $\{e^i_{\alpha\beta}\}$ is defined by taking the trace, so we may expect to find the following scaling relation as the critical point is approached along the coexistence line:

$$\mathrm{Tr}\left[(\mathbf{Q}^+ - \mathbf{Q}^-)\cdot\widehat{\mathbf{Q}}\right] \sim (\tau^* - \tau)^\beta. \tag{6.19}$$

Figure 6.7 shows a log-log plot of the projected order parameter discontinuity vs. the deviation from τ^*. As with the exponent ν, we find behavior suggestive of classical mean-field behavior, with $\beta \simeq 0.51 \pm 0.01$.

Although classical mean-field behavior in a non-equilibrium system may be surprising, when we consider the system in light of the structure we find at the critical point it is not so surprising. In addition to the vanishing of the mass term of the critical mode at the critical point, we find that the quadratic and cubic coefficients of the contributions of the critical mode to the equations of motion vanish as well. Hence the mathematical structure is like a Landau theory for a scalar field at a critical point,[16] or like a simple fold catastrophe in catastrophe theory,[86] both of which predict so-called mean-field behavior (*i.e.* the exponents $\nu = 1/2$ and $\beta = 1/2$). It is also not unexpected because we have explicitly omitted fluctuations (having not

Figure 6.7: $\log \mathrm{Tr}\left[(\mathbf{Q}^{+}-\mathbf{Q}^{-})\cdot\widehat{\mathbf{Q}}\right]$ vs. $\log(\tau-\tau^{*})$ for the L=256. system. The straight line indicates the best fit, with an exponent $\beta \simeq .51 \pm 0.01$.

included noise in the dynamics to allow the system to explore configuration space), so we cannot expect to extract non-classical critical behavior from our analysis.

As a final comment on the singularities in the nematic under shear flow, we note that we find a *single* critical mode. This suggests that the system may have Ising-like critical behavior,[5] although this must remain a suggestion for the present. Recall that one of the important results of Onuki and Kawasaki's (OK) treatment of the binary fluid is that shear flow makes the transition mean-field in character.[7] In the binary fluid system the effect of shear is purely advective; *i.e.*, there is no order parameter which couples to the flow, either directly (as in the IN transition) or indirectly (as in the IL transition). To determine the universality class of the IN transition in shear flow requires an analysis of the fluctuations beyond the Gaussian level. We can conceive of two possibilities, although there are, of course, possibly more. The critical strain rate D^{*} sets a characteristic length scale l_{D}, corresponding to the size of that fluctuation which relaxes, in equilibrium, over the same time scale as $\tau_{D} = D^{-1}$. The work of OK for a binary fluid shows that for larger length scales the system is mean-field–like. If the critical strain rate is such that this l_{D} is extremely large (weak shear), then one might expect to observe not mean-field behavior, but critical behavior, possibly Ising-like. Conversely, if l_{D} is small (strong shear), we might expect to observe mean-field behavior.

Figure 6.8: Complete phase diagram in the reduced stress s vs. reduced temperature (τ) phase diagram for $B = -1.2\,C, \beta_1 = 0.9, \beta_3 = .1\beta_2$, and $L_1/C = L_2/C = 10^4\,\text{Å}^2$. The broken line is the coexistence line; The shaded region is the two-state region with two locally stable states; the solid lines mark the limits of stability for the high and low temperature states. The non-equilibrium critical point is $(\tau^*, s^*) \approx (0.081675, 0.0037950)$.

6.4.2 Coexistence Line and Phase Diagram

Figure 6.8 shows the phase diagram in the applied-stress vs. temperature plane, including the coexistence line obtained from the analysis of the interface solutions. This line interpolates smoothly between the equilibrium IN transition and the non-equilibrium critical point. We expect that a physical system could exhibit 'supercooling' (or 'superheating') whereby, for example, the high temperature state could be fixed at $T < T_{IN}(\sigma)$ for short times until a nucleation process initiated a transition to the well-ordered low temperature state. We also anticipate the analog of spinodal decomposition for either a temperature quench or a step in applied stress which takes the system completely across the two-state region. For a decrease in stress at fixed temperature, we also expect phase separation into regions of different magnitude of order and different stress, analogous to the phase separation of a fluid into a mixture of liquid and gaseous states as the pressure is reduced at fixed temperature.

We have now further established the correspondences between the IN transition undergoing shear flow and equilibrium systems such as a critical fluid. We have seen that there is a coexistence line ending in a critical endpoint, and that there are mean-field–like divergences at this endpoint. Table 6.1 shows a more complete comparison of the two systems. In the next chapter we will examine the critical point in more detail when we discuss light scattering experiments. There we will see the analog of critical opalescence for the nematic under shear flow.

Table 6.1: Analogies between the van der Waals fluid and nematics in shear flow.

Van der Waals Fluid	Nematic in Shear
Density ρ	Order parameter $Q_{\alpha\beta}$ or Strain rate D
Temperature T	Temperature T
Pressure p	Stress σ_{xy}
Coexistence line in $p-T$ plane	Coexistence line in $\sigma_{xy}-T$ plane
Phase separation into liquid and gas states on the coexistence line	Phase separation into regions with different strain rates.
Equilibrium critical point	Non-equilibrium critical point
$(\rho_{\mathrm{l}}-\rho_{\mathrm{g}}) \sim (T-T_c)^\beta$	$\mathrm{Tr}\left[(\mathbf{Q}^{+}-\mathbf{Q}^{-})\cdot\widehat{\mathbf{Q}}\right] \sim (T-T_c)^\beta$
Ising-like critical behavior	Shear flow probably alters critical behavior (as with Onuki and Kawasaki)
Critical opalescence	Anomalous light scattering for $k_x \to 0$ for critical mode $\widehat{Q}_{\alpha\beta}$

Chapter 7

Fluctuations in Nematics Under Shear Flow

The discussion thus far has centered around how to determine the analog of a mean-field phase diagram for nematics under shear flow. In this chapter we will discuss some of the consequence of the fluctuations about these mean-field states. We will focus on light scattering experiments, which provide one of the primary probes of fluctuations in nematics. Light is scattered by fluctuations in the dielectric tensor, which are in turn related to the order parameter tensor, and hence light scattering experiments can tell us about the nature of the order parameter fluctuations. We will describe a general program for analyzing Gaussian fluctuations about the stable stationary states of the system, and discuss in detail two regions of strain rates: (1) small strain rates, to see the perturbative effect on the equilibrium fluctuations; and (2) strain rates near the critical strain rate, where we will find anomalous scattering similar to critical opalescence in a fluid. We will see effects similar to those discussed in, for example, Onuki and Kawasaki's work on critical fluids in shear flow,[7] where the highly anisotropic correlations reflect the tendency of shear flow to suppress certain fluctuations. We must keep in mind, however, that while anomalous scattering occurs at all strain rates in the binary fluid, in the nematic under shear flow it only occurs near the specific *critical* strain rate; this is because a critical point occurs at all strain rates in the binary fluid, while it occurs at a single strain rate in the nematic.

Let us first discuss an important length scale in the problem. Consider a fluctuation of spatial extent L, with corresponding wave number scale $k \sim 2\pi/L$. In a flow field there are two stresses which act to suppress this fluctuation: (1) elastic stresses associated with the deformation of the order parameter (we consider the one-constant approximation),

$$\sigma_{elastic} \sim L_1 \nabla^2 Q_{\alpha\beta} \sim L_1 k^2 Q_{\alpha\beta} , \tag{7.1}$$

and (2) viscous stresses due to the flow gradient trying to advect the fluctuation,

$$\sigma_{viscous} \sim \beta_2 (\partial_y v_x) \sim \beta_2 D, \tag{7.2}$$

where β_2 is a viscosity and D the strain rate. (these are roughly the terms in the order parameter equation of motion, eq. 4.63.) These processes are of a comparable magnitude at a characteristic wave number,

$$k_D = \left(\frac{D\beta_2}{L_1}\right)^{1/2} . \tag{7.3}$$

Hence we expect to find qualitatively different behavior depending on the wave number of the fluctuation. For fluctuations with $k > k_D$ the elastic restoring forces should dominate and correlations between fluctuations should essentially retain their equilibrium form. However, for fluctuations with $k < k_D$, viscous forces dominate, and we expect to find behavior which reflects the symmetries and advective effects of the flow.

7.1 Elastic Light Scattering From Nematics

Elastic light scattering from a *uniaxial* nematic state has been discussed extensively by many workers.[43,44,88] However, since planar shear has a biaxial symmetry, we must discuss scattering from a *biaxial* state. Using the parametrization of $Q_{\alpha\beta}$ in terms of $\hat{\mathbf{n}}, \hat{\mathbf{m}}, S_1$, and S_2 (described in eq. 2.3), we expand an arbitrary fluctuation $\delta Q_{\alpha\beta}(\mathbf{r})$ in terms of a basis of tensors $\{e^i_{\alpha\beta},\ i = 1, \ldots, 5\}$ (see Appendix A) representing independent fluctuations, obtaining

$$\delta Q_{\alpha\beta}(\mathbf{r}) = \sum_{i=1}^{5} \xi_i(\mathbf{r})\, e^i_{\alpha\beta}\,. \tag{7.4}$$

The local value for the dielectric tensor for the anisotropic fluid is, generally, given by*

$$\epsilon_{\alpha\beta}(\mathbf{r}) = \bar{\epsilon}\,\delta_{\alpha\beta} + \mathcal{N}\, Q_{\alpha\beta}(\mathbf{r}) + \cdots\,. \tag{7.5}$$

The omitted terms refer to other tensorial quantities which may, in principle, affect the dielectric properties, such as temperature gradients $(\partial_\alpha T\, \partial_\beta T)$ or the fluid stress tensor $(\sigma_{\alpha\beta})$. We will assume that the contribution from the order parameter dominates that from any other source. Noting that $\bar{\epsilon}$ is a uniform scalar, we see that the fluctuations of the $\mathbf{k} \neq 0$ Fourier components of $\epsilon_{\alpha\beta}$ are proportional to the fluctuations of the order parameter, according to

$$\langle \delta\epsilon_{\alpha\beta}(\mathbf{k})\, \delta\epsilon_{\lambda\rho}(-\mathbf{k})\rangle = \mathcal{N}^2\, \langle \delta Q_{\alpha\beta}(\mathbf{k})\, \delta Q_{\lambda\rho}(-\mathbf{k})\rangle. \tag{7.6}$$

The overall factor $\mathcal{N}$ may be determined experimentally.

Now, the differential cross-section per solid angle for elastic light scattering at scattering wave vector $\mathbf{k}$ is related to the fluctuations in the dielectric tensor of the fluid by[90]

$$\frac{d\sigma}{d\Omega} = \frac{\omega^4}{16\pi^2 c^4}\, \langle \delta\epsilon_{\alpha\beta}(\mathbf{k})\delta\epsilon_{\lambda\rho}(-\mathbf{k})\rangle\, \hat{p}_\alpha\, \hat{p}'_\beta\, \hat{p}_\lambda\, \hat{p}'_\rho, \tag{7.7}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{p}}'$ are the polarization vectors of the incident and scattered light and ω is the frequency of the light. The angle brackets denote an appropriate average over the states of the system. In an equilibrium system this is an ensemble average with a Boltzmann weight for each state, or, equivalently, a time average. For our non-equilibrium systems we will define this to be an average over the noise and initial conditions. Naturally, results will depend on the choice of noise, for this choice reflects the freedom with which the system may explore various configurations.

Using eqs. (7.4), (7.6), and (7.7), it is straightforward to calculate the scattering cross-section in terms of the correlations $\langle \xi_i(\mathbf{k})\, \xi_j(-\mathbf{k})\rangle$. While the general expression is quite cumbersome, we will reproduce a few configurations here).

*We remark that for a biaxial state the tensor $Q_{\alpha\beta}$ has two scalar invariants for a biaxial state, and may therefore, in the proper basis, be represented as the sum of two orthogonal tensors, as in eq. (2.3). There may, in general, be different normalizations $\mathcal{N}$ and $\mathcal{N}'$ for the separate contributions of each of these tensors to $\epsilon_{\alpha\beta}$. We shall assume that $\mathcal{N} = \mathcal{N}'$ and note that this assumption is, in principle, experimentally testable.

(i) $\underline{\hat{\mathbf{p}} \perp \hat{\mathbf{z}},\, \hat{\mathbf{p}}' \perp \hat{\mathbf{z}};\, \hat{\mathbf{p}}\cdot\hat{\mathbf{n}} = \cos\theta,\, \hat{\mathbf{p}}'\cdot\hat{\mathbf{n}} = \cos\theta'}$—*Polarizations in the shear plane (see fig. 7.1)*:

$$\begin{aligned}\frac{d\sigma}{d\Omega} \quad \sim \quad & \Big\{ \tfrac{1}{6}\,\langle|\xi_1(\mathbf{k})|^2\rangle\,(2\cos\theta\cos\theta' - \sin\theta\sin\theta')^2 + \tfrac{1}{2}\,\langle|\xi_2(\mathbf{k})|^2\rangle\sin^2\!\theta\sin^2\!\theta' \\ & + \tfrac{1}{2}\,\langle|\xi_3(\mathbf{k})|^2\rangle\sin^2(\theta+\theta') + \langle\xi_2(\mathbf{k})\,\xi_3(-\mathbf{k})\rangle\sin(\theta+\theta')\sin\theta\sin\theta' \\ & + \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_3(-\mathbf{k})\rangle\sin(\theta+\theta')(2\cos\theta\cos\theta' - \sin\theta\sin\theta') \\ & + \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_2(-\mathbf{k})\rangle\sin\theta\sin\theta'\,(2\cos\theta\cos\theta' - \sin\theta\sin\theta') \Big\}.\end{aligned} \tag{7.8}$$

(ii) $\underline{\hat{\mathbf{p}} \perp \hat{\mathbf{m}},\, \hat{\mathbf{p}}' \perp \hat{\mathbf{m}};\, \hat{\mathbf{p}}\cdot\hat{\mathbf{n}} = \cos\phi,\, \hat{\mathbf{p}}'\cdot\hat{\mathbf{n}} = \cos\phi'}$—*Polarizations in the* **z**-**n** *plane*:

$$\begin{aligned}\frac{d\sigma}{d\Omega} \quad \sim \quad & \Big\{ \tfrac{1}{6}\,\langle|\xi_1(\mathbf{k})|^2\rangle\,(2\cos\theta\cos\theta' - \sin\theta\sin\theta')^2 + \tfrac{1}{2}\,\langle|\xi_2(\mathbf{k})|^2\rangle\sin^2\!\theta\sin^2\!\theta' \\ & + \tfrac{1}{2}\,\langle|\xi_4(\mathbf{k})|^2\rangle\sin^2(\theta+\theta') - \langle\xi_2(\mathbf{k})\,\xi_4(-\mathbf{k})\rangle\sin(\theta+\theta')\sin\theta\sin\theta' \\ & + \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_4(-\mathbf{k})\rangle\sin(\theta+\theta')(2\cos\theta\cos\theta' - \sin\theta\sin\theta') \\ & - \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_2(-\mathbf{k})\rangle\sin\theta\sin\theta'\,(2\cos\theta\cos\theta' - \sin\theta\sin\theta') \Big\}.\end{aligned} \tag{7.9}$$

(iii) $\underline{\hat{\mathbf{p}} \perp \hat{\mathbf{n}},\, \hat{\mathbf{p}}' \perp \hat{\mathbf{n}};\, \hat{\mathbf{p}}\cdot\hat{\mathbf{m}} = \cos\varphi,\, \hat{\mathbf{p}}'\cdot\hat{\mathbf{m}} = \cos\varphi'}$—*Polarizations normal to the director*:

$$\begin{aligned}\frac{d\sigma}{d\Omega} \quad \sim \quad & \Big\{ \tfrac{1}{6}\,\langle|\xi_1(\mathbf{k})|^2\rangle\cos^2(\varphi-\varphi') + \tfrac{1}{2}\,\langle|\xi_2(\mathbf{k})|^2\rangle\cos^2(\varphi+\varphi') \\ & + \tfrac{1}{2}\,\langle|\xi_5(\mathbf{k})|^2\rangle\sin^2(\varphi+\varphi') - \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_2(-\mathbf{k})\rangle\cos(\varphi-\varphi')\cos(\varphi+\varphi') \\ & - \tfrac{1}{\sqrt{3}}\,\langle\xi_1(\mathbf{k})\,\xi_5(-\mathbf{k})\rangle\sin(\varphi+\varphi')\cos(\varphi-\varphi') \\ & + \langle\xi_2(\mathbf{k})\,\xi_5(-\mathbf{k})\rangle\sin(\varphi+\varphi')\cos(\varphi+\varphi') \Big\}.\end{aligned} \tag{7.10}$$

(iv) $\underline{\hat{\mathbf{p}} = \hat{\mathbf{n}},\, \hat{\mathbf{p}}' \perp \hat{\mathbf{n}};\, \hat{\mathbf{p}}'\cdot\hat{\mathbf{m}} = \cos\varphi}$—*Polarizations normal to and parallel to* **n**:

$$\frac{d\sigma}{d\Omega} \sim \Big\{ \tfrac{1}{2}\,\langle|\xi_3(\mathbf{k})|^2\rangle\cos^2\varphi + \tfrac{1}{2}\,\langle|\xi_4(\mathbf{k})|^2\rangle\sin^2\varphi + \tfrac{1}{2}\,\langle\xi_3(\mathbf{k})\,\xi_4(-\mathbf{k})\rangle\sin 2\varphi \Big\}. \tag{7.11}$$

7.2 Steady State Correlations in Nematics Under Shear Flow

The next step is to evaluate the non-equilibrium correlations of the fluctuations, $\langle\xi_i(\mathbf{k})\,\xi_j(-\mathbf{k})\rangle$. To obtain these we begin with the equations of motion for the order parameter and the fluid velocity, eqs. (4.63-4.65). As we discussed in Chapter 6, while one may consider non-equilibrium states of the system at fixed *imposed strain rate* D or fixed *applied stress* $\sigma_{\alpha\beta}$, it is only under conditions of equal stress that two states may

Figure 7.1: Geometry for measuring critical mode via light scattering near the critical point. The polarization vectors $\hat{\mathbf{p}}$ and $\hat{\mathbf{p}}'$ lie in the shear plane, and the broken arrows denote the velocity field.

coexist. For the present discussion, however, we shall examine the critical point at imposed strain rate D. This makes the problem calculationally more tractable and, we believe, captures the essence of the physics.

As before, we consider plane shear flow $\mathbf{v}(\mathbf{r}) = D\, y\, \hat{\mathbf{x}}$. The stable steady states for non-zero shear have a director $\hat{\mathbf{n}}$ in the shear plane (canted at an angle with respect to the flow direction) and a sub-director $\hat{\mathbf{m}}$ also in the shear plane, reflecting the biaxial symmetry of shear flow (see fig. 4.2). The equations of motion for the fluctuation $\delta Q_{\alpha\beta}$ are found by expanding eqs. (4.63) about the steady state value for $Q_{\alpha\beta}$, which leads to a set of non-linear evolution equations for $\delta Q_{\alpha\beta}$. As a first step we will truncate these at linear order, hence treating the system at the non-equilibrium equivalent of the Gaussian level. We next introduce noise into these equations to allow the system to explore phase space. We may consider this noise to describe the interactions of the semi-macroscopic degrees of freedom ($Q_{\alpha\beta}$) with the hitherto neglected microscopic (fast) degrees of freedom. In principle one must work with the entire system of coupled equations of motion for the fluid velocity and order parameter, and treat both equations of motion as stochastic equations.[7] However, for the present discussion we will treat the velocity field as immutable, and only consider the dynamics of the order parameter.

After expanding $\delta Q_{\alpha\beta}$ according to eq. (7.4), projecting eqs. (4.63) onto the set $\{e^{i}_{\alpha\beta}\}$, and linearizing, we obtain the following equations of motion for the amplitudes $\{\xi_i\}$:

$$(\partial_t + Dy\partial_x)\,\xi_i(\mathbf{r},t) = -\frac{1}{\beta_2}\,\Theta_{ij}(\boldsymbol{\nabla})\,\xi_j(\mathbf{r},t) + \eta_i(\mathbf{r},t), \quad (i = 1,\ldots,5) \tag{7.12}$$

where

$$\Theta_{ij}(\boldsymbol{\nabla}) = -L_1\nabla^2\delta_{ij} + M_{ij}. \tag{7.13}$$

Notice that the *Frank matrix*, $-L_1\nabla^2\delta_{ij}$, is isotropic in $\mathbf{k}$-space. This is a consequence of the one-constant approximation (*i.e.* $L_2 = 0$; see the discussion in Section 2.4). The mass matrix M_{ij} has the block structure

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}^{(123)} & 0 \\ 0 & \mathbf{M}^{(45)} \end{pmatrix}, \tag{7.14}$$

where

$$\mathbf{M}^{(123)} = \left(\begin{array}{c|c|c} A + BS_1 + \frac{1}{2}C(9S_1^2 + S_2^2) & S_2\sqrt{3}\,(CS_1 - \frac{1}{3}B) & -\sqrt{3}\,\beta_2 D \\ \hline S_2\sqrt{3}\,(CS_1 - \frac{1}{3}B) & A - BS_1 + \frac{3}{2}C(S_1^2 + S_2^2) & \beta_2 D \\ \hline \sqrt{3}\,\beta_2 D & -\beta_2 D & A + \frac{1}{2}B(S_1 + S_2) + \frac{1}{2}C(3S_1^2 + S_2^2) \end{array}\right) \tag{7.15}$$

and

$$\mathbf{M}^{(45)} = \left(\begin{array}{c|c} A + \frac{1}{2}B(S_1 - S_2) + \frac{1}{2}C(3S_1^2 + S_2^2) & -\beta_2 D \\ \hline \beta_2 D & A - BS_1 + \frac{1}{2}C(3S_1^2 + S_2^2) \end{array}\right). \tag{7.16}$$

In this matrix the amplitudes S_1 and S_2 characterize the uniform stable steady state and depend on the Landau parameters A, B, and C, the transport coefficients β_1 and β_2, and the strain rate D (see eqs. 5.4-5.6).

Langevin noise sources $\eta_i(\mathbf{r},t)$ have been included in eq. (7.12) with a strength chosen to obey the fluctuation-dissipation theorem (FDT),[82]

$$\langle \eta_i(\mathbf{r},t)\,\eta_j(\mathbf{r}',t')\rangle = 2\,\beta_2\,\delta_{ij}\,\delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}'). \tag{7.17}$$

This choice of noise, by definition, ensures that in the *absence* of flow the stationary distribution function for the system will be given by the Boltzmann distribution.[82] This assumption, that the noise for a *driven* system obeys the same distribution as that for the same system *relaxing* to equilibrium, is non-trivial. However, there are examples where predictions based on the validity of the FDT for non-equilibrium steady states have been verified experimentally; an example is the series of light scattering experiments by Sengers and Law, for a fluid driven out of equilibrium by a steady state temperature gradient.[83]

First we examine the familiar uniaxial case in the absence of shear. In this case $S_2 = 0$ and $Q_{\alpha\beta} = (3S_1/2)(n_\alpha n_\beta - \delta_{\alpha\beta})$. The equilibrium conditions for the amplitude S_1 are $S_1 = 0$ ($T > T_{IN}$) and $S_1 = S_o(T)$ ($T < T_{IN}$, see Table 2.1), for which $\mathbf{M}$ reduces to the forms

$$\left.\begin{array}{lr} M_{ij} = A\,\delta_{ij}, & T > T_{IN} \\ M_{11} = -2A - \tfrac{1}{2}BS_o, \quad M_{22} = M_{55} = -\tfrac{3}{2}BS_o & T < T_{IN} \end{array}\right\} \tag{7.18}$$

with all other elements zero. The temperature-dependence of these matrix elements enters through the dependence of A and S_o on T. For $T < T_{IN}$ the elements $M_{33} = M_{44} = 0$, and we recover the Goldstone modes of director fluctuations, corresponding to $e^3_{\alpha\beta}$ and $e^4_{\alpha\beta}$ (see Appendix A); while for $T > T_{IN}$ we find the same value for all modes M_{ii}. Next we observe that shear couples the modes ξ_i by introducing off-diagonal terms into M_{ij}. Note also that M_{ij} is not symmetric for non-zero shear, which is a restatement of the fact that shear flow, unlike, *e.g.*, elongational flow, is non-potential. Furthermore, fluctuations in the shear plane (ξ_1, ξ_2, ξ_3) are decoupled from fluctuations out of the shear plane (ξ_4, ξ_5) at the Gaussian level.

Our goal is to calculate steady state correlations among the set $\{\xi_i\}$. Our calculation follows along the same line as the works of Onuki and Kawasaki[7], and subsequently Cates and Milner,[17] who investigated the effect of shear flow on, respectively, binary fluids and the isotropic-lamellar transition. The starting point is the statement that stationary correlations satisfy

$$\partial_t \langle \xi_i(\mathbf{k}, t) \xi_j(-\mathbf{k}, t)\rangle \equiv \partial_t\, \chi_{ij}(\mathbf{k}, t) = 0 \tag{7.19}$$

where the angle brackets now refer to an average over the noise distribution and initial conditions. We will define $\chi_{ij}(\mathbf{k})$ to be the stationary value of $\chi_{ij}(\mathbf{k}, t)$. From the stochastic equations of motion for $\xi_i(\mathbf{r}, t)$ and the properties of the noise distribution one may obtain the following Fokker-Planck equation for the probability distribution function $\mathcal{P}\Big(\{\xi_i(\mathbf{r})\}; t\Big)$,[82]

$$\partial_t\, \mathcal{P} = \int d^3r \frac{\delta}{\delta\xi_i(\mathbf{r})}\left\{\beta_2^{-1}\frac{\delta}{\delta\xi_i(\mathbf{r})} - \Big[D\, y\, \delta_{ij}\, \partial_x + \Theta_{ij}(\boldsymbol{\nabla})\Big]\, \xi_j(\mathbf{r})\right\}\mathcal{P}. \tag{7.20}$$

The time rate-of-change of averaged quantities is given by

$$\partial_t \langle \mathcal{O}\rangle = \int \mathcal{D}\xi\, \mathcal{O}\, \partial_t\, \mathcal{P}(\{\xi_i\}, t), \tag{7.21}$$

assuming that $\mathcal{P}$ is properly normalized. Here the measure $\mathcal{D}\xi$ refers to a functional integral over the independent degrees of freedom, namely the amplitudes $\{\xi_i(\mathbf{r})\}$. We insert the Fokker-Planck equation into eq. (7.21) and, enforcing the stationary condition (7.19), obtain the following differential equation which describes the stationary correlations $\chi_{ij}(\mathbf{k})$:

$$Dk_x \frac{\partial}{\partial k_y}\chi_{ij}(\mathbf{k}) - \Big(\Theta_{ik}(k)\, \chi_{kj}(\mathbf{k}) + \chi_{ik}(\mathbf{k})\, \Theta^{\mathrm{T}}_{kj}(k)\Big) = -2\,\beta_2\,\delta_{ij}. \tag{7.22}$$

Here Θ^{T}_{kj} denotes the transpose of Θ_{kj}.

This equation may be integrated to obtain $\chi_{ij}(\mathbf{k})$:

$$\begin{aligned} \chi_{ij}(\mathbf{k}) \;&=\; \frac{1}{\beta_2}\int_0^\infty dt\, \exp\Big\{-\frac{L_1}{\beta_2}\int_0^t ds f(\mathbf{k}, Dk_x s/2)\Big\} \\ &\quad\times\Big[\exp\Big\{-\frac{\mathbf{M}t}{2\beta_2}\Big\}\Big]_{ik}\Big[\exp\Big\{-\frac{\mathbf{M}^{\mathrm{T}}t}{2\beta_2}\Big\}\Big]_{kj}, \end{aligned} \tag{7.23}$$

Figure 7.2: Convection of fluctuations in shear flow. The left hand figure shows a fluctuation with $|k_x| \gg |k_y|$. Such a fluctuation is quickly suppressed by the flow. The figure on the right show a fluctuation with $|k_x| \ll |k_y|$. In this case the fluctuation is more robust under flow.

where $f(\mathbf{k}, p) \equiv k_x^2 + (k_y + p)^2 + k_z^2$. In obtaining this form we have used the fact that $\Theta_{ij}(k)\,\Theta_{jk}(k') = \Theta_{ij}(k')\,\Theta_{jk}(k)$ by virtue of the one-constant approximation to the Frank free energy (see eq. 7.13).

We next assume that, in order to simplify the expression for $\chi_{ij}(\mathbf{k})$, M_{ij} is diagonalizable† by a transformation matrix U_{ij}. In this case, M^{T}_{ij} is also diagonalizable, with the same set of eigenvalues, and we have:‡

$$\left[\mathbf{U}\mathbf{M}\mathbf{U}^{-1}\right]_{ij} = \left[\left(\mathbf{U}^{\mathrm{T}}\right)^{-1}\mathbf{M}^{\mathrm{T}}\mathbf{U}^{\mathrm{T}}\right]_{ij} = m_{(i)}\delta_{ij}. \tag{7.24}$$

We will refer to the quantities $\{m_i\}$ as the *masses* of the fluctuations. We introduce the identity matrix into eq. (7.23) via the realization $\delta_{ij} = (\mathbf{U}\mathbf{U}^{-1})_{ij}$. Performing the s integration in the exponential, we find the following:

$$\left[\mathbf{U}\boldsymbol{\chi}(\mathbf{k})\mathbf{U}^{\mathrm{T}}\right]_{kl} = \left[\mathbf{U}\mathbf{U}^{\mathrm{T}}\right]_{kl} J_{(kl)}(\mathbf{k})\,, \tag{7.25}$$

where

$$J_{kl}(\mathbf{k}) = \frac{1}{\beta_2}\int_0^\infty dt\,\exp\left\{-\frac{t(m_k + m_l + 2L_1 k^2)}{2\beta_2} - \frac{D^2t^2}{2}\frac{k_x k_y}{k_D^2} - \frac{D^3t^3}{12}\frac{k_x^2}{k_D^2}\right\} \tag{7.26}$$

and k_D is the natural wave vector scale set by the shear flow (eq. 7.3).

From the structure of $J_{kl}(\mathbf{k})$ we may immediately note that strong shear will exponentially damp the steady state correlations, except for wave vectors for which k_x=0. In this special case fluctuations are directed parallel to the streamlines of the flow; heuristically we do not expect these fluctuations to be destroyed, via advection, in shear flow. On the other hand, fluctuations with wave vectors which intersect streamlines (*i.e.* $k_x \neq 0$) will have their correlations greatly reduced (see Fig. 7.2). This is a general feature of fluctuations in shear flow, and is also seen in systems such as binary fluids,[7] the isotropic-lamellar transition,[17] and the nematic to smectic-A transition.[55]

†We remark that, since M_{ij} is a real non-symmetric matrix (see eqs. 7.14-7.15), a transformation matrix U_{ij} may, in principle, not exist. We shall assume that M_{ij} *is* diagonalizable, and note that a non-diagonalizable M_{ij} may happen only for rare accidental degeneracies.

‡We use the notation that indices enclosed in parentheses (as in $m_{(i)}\delta_{ij}$) are not to be summed over.

7.3 Scattering Near the Equilibrium Transition

Zero Strain Rate—We first examine the case of zero strain rate. In this case M_{ij} is already diagonal (see eqs. 7.18) so that $U_{ij} = \delta_{ij}$, and eq. (7.26) may be integrated exactly, yielding

$$\chi_{ij}(k)\Big|_{D=0} = \frac{2}{m_i + m_j + 2L_1 k^2}. \tag{7.27}$$

This is the familiar Ornstein-Zernicke form for scattering from a uniaxial nematic. Of particular interest are the correlations $\chi_{33} = \chi_{44} = 1/(L_1 k^2)$ for $T < T_{IN}$, which represent anomalous scattering due to director fluctuations. These may be most efficiently probed by considering, for example, polarizations $\hat{\mathbf{p}} = \hat{\mathbf{n}}$ and $\hat{\mathbf{p}}' \perp \hat{\mathbf{n}}$ whence, from eqs. (A.3) and (7.7),

$$\frac{d\sigma}{d\Omega}\Big|_{\substack{T<T_{IN}\\ D=0}} \sim \langle|\xi_3(\mathbf{k})|^2\rangle \sim \frac{1}{L_1 k^2} \quad . \tag{7.28}$$

For $T > T_{IN}$ all masses are identical (eq. 7.18), and we expect isotropic scattering of the form $d\sigma/d\Omega \sim \left(a(T-T^-) + L_1 k^2\right),^{-1}$ regardless of polarization.

Weak Shear Flow—Next we find the leading corrections to eq. (7.27) for small shear. For sufficiently small shear and wave number we may approximate the integral in eq. (7.26) by

$$\begin{aligned} J_{kl}(\mathbf{k}) \quad &\simeq \quad \frac{2}{m_k + m_l + 2L_1 k^2}\left[1 - \frac{4\,L_1^2\,|k_x|\,|k_y|\,k_D^2}{(m_k + m_l + 2L_1 k^2)^2}\right. \\ &\qquad \left. - \frac{4\,L_1^3\,k_x^2\,k_D^4}{(m_k + m_l + 2L_1 k^2)^3} \;+\; \cdots\right], \end{aligned} \tag{7.29}$$

for

$$\frac{|k_x|\,|k_y|}{k_D^2} \ll \frac{k^4}{k_D^4}, \qquad \text{and} \qquad \frac{|k_x|}{k_D} \ll \frac{k^3}{k_D^3}. \tag{7.30}$$

To find $\chi_{ij}(\mathbf{k})$ we must diagonalize the mass matrix M_{ij}, and then use the resulting transformation matrix U_{ij} to express the correlations $\chi_{ij}(\mathbf{k})$ as a sum of the contributions of the correlations of the eigenmodes $J_{kl}(\mathbf{k})$, using eq. (7.25). We will carry out this program in the limit of small strain rates D.

For $T < T_{IN}(D)$ the stationary conditions are given by eqs. (5.14): $S_1 = S_o(T) + rD$, with $S_2 \sim D$. The equilibrium value of the order parameter $S_o(T)$ is given in Table 2.1. With this we find

$$\mathbf{M} \;=\; \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathrm{O}(D^2); \tag{7.31}$$

$$\mathbf{M}^{(0)} \simeq \begin{pmatrix} -2A - \frac{1}{2}BS_o & 0 & 0 & 0 & 0 \\ 0 & -\frac{3}{2}BS_o & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{3}{2}BS_o \end{pmatrix}, \tag{7.32}$$

$$\mathbf{M}^{(1)} \simeq \begin{pmatrix} \mathbf{M}^{(1A)} & 0 \\ 0 & \mathbf{M}^{(1B)} \end{pmatrix}, \tag{7.33}$$

$$\tag{7.34}$$

where

$$\mathbf{M}^{(1A)} = +\begin{pmatrix} (B+9CS_o)\,rD & \sqrt{3}\,(CS_o-\frac{1}{3}B)\,S_2 & -\sqrt{3}\beta_2 D \\ \sqrt{3}\,(CS_o-\frac{1}{3}B)\,S_2 & -(B-3CS_o)\,rD & \beta_2 D \\ \sqrt{3}\beta_2 D & -\beta_2 D & \left(\frac{27AC}{2}\right)^{1/2} rD \end{pmatrix}, \tag{7.35}$$

$$\mathbf{M}^{(1B)} = \begin{pmatrix} \left(\frac{3AC}{2}\right)^{1/2} r\,D & -\beta_2 D \\ \beta_2 D & -(B-3CS_o)\,rD \end{pmatrix}. \tag{7.36}$$

Working to lowest order in D, we may diagonalize M_{ij} and find its eigenvectors, construct U_{ij}, and hence obtain the weak shear limit of, for example, the correlations within the set $\{\xi_4, \xi_5\}$:

$$\chi_{44}(\mathbf{k}) = J_{44}(\mathbf{k})\,, \tag{7.37}$$

$$\chi_{45}(\mathbf{k}) = -\frac{4\beta_2 D}{3BS_o}\Big[J_{44}(\mathbf{k}) + J_{45}(\mathbf{k}) + J_{55}(\mathbf{k})\Big]\,, \tag{7.38}$$

$$\chi_{54}(\mathbf{k}) = \chi_{45}(\mathbf{k})\,, \tag{7.39}$$

$$\chi_{55}(\mathbf{k}) = J_{55}(\mathbf{k})\,, \tag{7.40}$$

$$\tag{7.41}$$

where $J_{kl}(\mathbf{k})$ are as given in eq. (7.29), with

$$m_4 = \left(\frac{3AC}{2}\right)^{1/2} rD \tag{7.42}$$

$$m_5 = -\tfrac{3}{2}BS_o - (B-3CS_o)\,rD. \tag{7.43}$$

Using polarized light scattering one can choose suitable polarizations to isolate these modes. The most interesting point here is the shift in the mass of the Goldstone mode $\chi_{44}(\mathbf{k})$; it has acquired a mass proportional to the strain rate D (eq. 7.42). Note also that $\chi_{45}(\mathbf{k})\,\Big(=\chi_{54}(\mathbf{k})\Big)$ is now non-zero, to lowest order in the strain rate, and as we see from eqs. (7.29) and (7.38), is approximately a sum of three individual Ornstein-Zernicke forms, $(m_i + m_j + 2\,L_1\,k^2)^{-1}$. Performing the same calculations for the 3×3 sector yields qualitatively similar behavior, with a shift in the mass of the Goldstone mode $\chi_{33}(\mathbf{k})$ proportional to the strain rate, and shear-induced scattering in the off-diagonal modes $\chi_{ij}(\mathbf{k})\,, i\neq j$.

For $T \geq T_{IN}(D)$ we can perform a similar calculation. In this case $S_1 = S_2 \sim D$ (see eqs. 5.13) and the mass matrix becomes

$$\mathbf{M} = A\,\mathbf{I} + \mathbf{M}^{(1)}, \tag{7.44}$$

where I is the identity matrix and

$$\mathbf{M}^{(1)} = \begin{pmatrix} BS_1 & \frac{1}{\sqrt{3}}BS_1 & -\sqrt{3}\,\beta_2 D & 0 & 0 \\ \frac{1}{\sqrt{3}}BS_1 & -BS_1 & \beta_2 D & 0 & 0 \\ \sqrt{3}\,\beta_2 D & -\beta_2 D & 0 & 0 & 0 \\ 0 & 0 & 0 & BS_1 & \beta_2 D \\ 0 & 0 & 0 & \beta_2 D & -BS_1 \end{pmatrix}. \tag{7.45}$$

The effect of shear is, as with temperatures $T < T_{IN}(D)$, to give the diagonal modes an additional mass proportional to the strain rate, and induce correlations in the off-diagonal elements of χ_{ij}.

7.4 Scattering Near the Non-Equilibrium Critical Point

The eigenvalues of M_{ij} govern the time-dependence of the modes of $\delta Q_{\alpha\beta}$. For a stable steady state the matrix M_{ij} is positive definite, while an unstable state has one or more eigenvalues with negative real part. In the absence of flow we have seen the zero-modes corresponding to the Goldstone modes of director fluctuations. In the presence of shear flow these Goldstone modes no longer exist, and all eigenvalues have a positive real part. The exception to this situation is at the critical point, where there is a single zero-mode, corresponding to the critical mode (recall the discussion of Chapter 6). This mode is a combination of the modes $\{e^1_{\alpha\beta}, e^2_{\alpha\beta}, e^3_{\alpha\beta}\}$, and corresponds to simultaneously 'stretching' the order (changing both S_1 and S_2) and rotating the director $\hat{\mathbf{n}}$ in the shear plane, as can be seen from eqs. (A.3) and (A.4). We can also understand this physically. In the presence of shear the director lies in the shear plane at a particular angle. Consider a departure from this stationary alignment. A tilt of the rods *within* the shear plane will quickly be suppressed by the flow, which exerts a torque pulling it back. However, a tilt *out* of the shear plane will not be so strongly affected, so we expect more excursions out of the plane than in the plane. Hence the rod orientation distribution is biaxial. The non-equilibrium transition occurs between a state governed primarily by the flow (rather weakly ordered, biaxial) and a state governed primarily by the thermodynamics of the IN transition (strongly ordered, more uniaxial). These states differ by their amplitudes S_1 and S_2, and by the alignment of $\hat{\mathbf{n}}$ in the plane. At the critical point these states become identical, and the soft mode is thus a combination of the two amplitudes and the rotation of $\hat{\mathbf{n}}$ in the plane.

One may isolate the modes contributing to the critical mode by considering, for example, polarizations in the shear plane, for which, as we see from eqs. (A.3) and (7.8), fluctuations involving the amplitudes ξ_4 and ξ_5 do not contribute (see fig. 7.1). Near the critical point we may identify two distinct scattering behaviors, at large or small wave number limits compared to the characteristic wave number k^*_D.

Large Wave Vector Limit—For sufficiently small ratios k_x/k and for $k \gg k_D$ we may use eq. (7.29) to approximate the behavior of the correlations, $J_{kl}(\mathbf{k})$. The general form of a particular element of the susceptibility matrix is a sum over the correlations of the eigenmodes of the fluctuations, given by

$$\chi_{ij}(\mathbf{k}) = \Gamma_{ij,\,kl}\, J_{kl}(\mathbf{k}), \tag{7.46}$$

where $\Gamma_{ij,\,kl}$ is prescribed by eq. (7.25). As the critical point is approached this sum will be dominated at long wavelengths by the term

$$\Gamma_{ij\,00}\, J_{00}(\mathbf{k}) \sim \frac{1}{2\, m_0 + 2\, L_1\, k^2} \tag{7.47}$$

for all correlations χ_{ij} $(i, j = 1, 3)$, where m_0 is the (vanishing) mass of the critical mode. Hence we expect that in this wavelength regime, as the critical point is approached the system should behave qualitatively similarly to a critical fluid approaching its critical point, with the exception that observation of diverging fluctuations is now *polarization dependent*. For example, if we choose $\hat{\mathbf{p}}||\hat{\mathbf{m}}$ and $\hat{\mathbf{p}'}||\hat{\mathbf{z}}$, we find from eq. (7.10) that $d\sigma/d\Omega \sim \langle|\xi_5(\mathbf{k})|^2\rangle$, which is *not* divergent at the critical point. Note also from eq. (7.29) that for $k \gg k_D$ the scattering is isotropic in $\mathbf{k}$-space. This is the small wavelength limit, and matches the intuitive picture, proposed by Onuki and Kawasaki[7], that smaller fluctuations decay via thermodynamic relaxation before shear flow can act to suppress them. (Recall that within the one-constant approximation, equilibrium scattering properties are isotropic in $\mathbf{k}$-space, as discussed in Chapter 3).

Large Shear and Small Wave Vector— In the limit of large strain rates and small scattering wave numbers, we may compute the following corrections to $J_{kl}(\mathbf{k})$:

$$J_{kl}(\mathbf{k}) \quad = \quad \frac{(4/9)^{1/3}}{L_1(k_x\, k_D^2)^{2/3}} \left[\Gamma(\tfrac{1}{3}) - \Gamma(\tfrac{2}{3}) \left(\frac{3}{2}\right)^{1/3} \frac{(m_k + m_l + 2L_1 k^2)}{L_1(k_x\, k_D^2)^{2/3}} \right.$$

$$- (18)^{1/3} \frac{k_y}{(k_x\, k_D^2)^{1/3}} + \cdots \Bigg], \tag{7.48}$$

for

$$\frac{|k_x|}{k_D} \gg \frac{k^3}{k_D^3}, \qquad \frac{|k_y|^3}{k_D^3} \ll \tfrac{4}{9} \frac{|k_x|}{k_D}. \tag{7.49}$$

The correlations in this regime are strongly suppressed by the flow ($\chi_{ij}(\mathbf{k}) \sim D^{-2/3}$), are largely independent of the incident and scattering polarizations, and are strongly anisotropic. For a given critical strain rate the correlations diverge in the $k_x \to 0$ limit, which corresponds to fluctuations aligned *with* the flow, which are less susceptible to flow deformation (see fig. 7.2).

7.5 Discussion

To summarize, we find the following behavior from an analysis of the Gaussian correlations at the critical point: (1) polarization dependent divergent fluctuations, (2) anisotropic correlations at long wavelengths, and (3) isotropic scattering at small wavelengths. Figure 7.3 shows a plot of χ_{11} at the critical point, which exhibits the anisotropy at small wave vectors which gives way to an isotropic profile at large wave vectors.

We have shown that the effects of shear flow on the IN transition can be very dramatic near the critical point, inducing a variant of critical opalescence. The spatial anisotropy of the correlations reflects the role of shear flow in selecting certain fluctuations to destroy, a general feature that we saw is important for the binary fluid and isotropic-lamellar transitions. The polarization-dependence of the anomalous scattering, which we may refer to as an *internal* anisotropy, is a new feature not seen in the binary fluid or IL transitions, which have fewer degrees of freedom. This internal anisotropy follows directly from the additional role of shear flow, peculiar to the nematic system, as an *ordering* field which acts on particular degrees freedom within the five-dimensional order parameter space. This ordering field imposes biaxial nematic order on all phases of the nematic and, at a sufficiently strong fields, induces a continuous transition between configurations of the order parameter dictated by this biaxial symmetry. By the proper choice of polarization configurations, one may selectively probe fluctuations which will either exhibit divergences at the critical point, or remain smooth through the critical point.

Another difference between the behaviors of the nematic in shear and, *e.g.*, the binary fluid, is the observability of these effects. In principle, one may choose any strain rate desired to observe the fluctuations in the critical fluid, and therefore probe different wavevector regimes. In contrast, for a given nematic there is a *single* material dependent critical strain rate at which one may observe the divergent fluctuations. Hence, we may expect to find some materials for which the observable range of wave numbers lies in the isotropic limit; that is, the critical wave number for these materials corresponds to length scales much larger than optical length scales. Conversely, other materials may have a critical wave number at smaller length scales, so that light scattering probes may detect the anisotropy due to shear.

To examine this final point we will obtain a different expression for the critical wave number. The characteristic wave number at the critical point is

$$k_D^* = \left(\frac{D^* \beta_2}{L_1} \right)^{1/2}, \tag{7.50}$$

where D^* is the critical strain rate, β_2 is a viscosity, and L_1 characterizes the elastic energy of deformation of the nematic state. If we recall that the dimensionless strain rate δ and dimensionless temperature τ are

Figure 7.3: Scattering intensity at the critical point for the mode χ_{11}, for parameters $B = -1.2C$, and $\beta_1 = 0.9$. Wave vectors are plotted in dimensionless units, $\bar{k} = k\,\xi(\tau^*)\,\tau^{*1/2}$, where $\xi^2(T) = L/a(T-T^-)$ is the equilibrium correlation length.

given by

$$\delta = \frac{D\beta_2}{C}, \qquad \tau = \frac{A}{C}, \tag{7.51}$$

we see that the characteristic wave number at the critical point is determined by

$$k_D^* = \frac{1}{\xi(T^*)}\left(\frac{\delta^*}{\tau^*}\right)^{1/2}, \tag{7.52}$$

where $\xi(T^*) = (L_1/a(T-T^-))^{1/2}$ is the typical *equilibrium* correlation length associated with the mesogens at the *non-equilibrium* critical temperature (see the discussion in Section 2.4). The critical parameters τ^* and δ^* are functions of two parameters: the ratio B/C, which is a measure of the weakness of the first order transition ($\Delta S_1 = -2B/9C$; see table 2.1), and the dimensionless parameter β_1, which is a ratio of rotational viscosities and is approximately material-independent. Hence we may roughly say that the characteristic wave number at the critical point depends on the weakness of the equilibrium first order transition, and on the equilibrium correlation length at temperatures near the critical temperature.

For the parameters we have chosen, which are representative of low molecular weight systems with $\Delta S_1 \sim 0.3$, we have found a ratio $\delta^*/\tau^* \sim 0.1$ (see fig. 5.4). Using the typical experimental values[44] $\xi(T^*) \sim 150$Å, where we take $(T^*-T^-) \sim 1.0\,\mathrm{K}$, we find $k_D^* \sim 10^7\,\mathrm{m}^{-1}$. Typical scattering experiments have optical wavenumbers $k = 2k_o \sin(\theta/2)$, where $k_o \sim 10^7\mathrm{m}^{-1}$ and θ is the scattering angle. Hence we expect thermotropic materials to have critical wave numbers in the observable range, so one may expect to see the crossover from anisotropic critical scattering at long wavelengths to isotropic scattering at small wavelengths.

Chapter 8

Concluding Remarks

8.1 Summary

In our discussion of nematics under shear we have seen many close analogies with equilibrium systems, such as the van der Waals fluid, and similarities with other fluids under shear flow, paying particular attention to Onuki and Kawasaki's treatment of the binary fluid under shear flow. We have made several approximations and left out potentially interesting effects in the name of reducing the problem to a tractable one. I will finish this work by reviewing some of these approximations and omissions, and propose possible directions for further study.

In all of our discussions we have assumed smooth behavior as the strain rate is increased. That is, we have not allowed for transitions to other qualitatively different states, of which one can envision many. There are possibilities of dynamic instabilities to non-stationary steady states, the so-called tumbling states. Such transitions have been observed in some low molecular weight systems at strain rates above a critical strain rate.[65] There is also the interesting possibility of a transition to a tumbling state as the temperature is lowered. If we recall the alignment condition (eq. 4.82),

$$2\,\beta_1 \cos 2\theta = 3S_1 + S_2. \tag{8.1}$$

we see that for sufficiently large order, S_1 and S_2, this condition cannot be satisfied, and one does not expect to find a stationary steady state. This behavior has been seen by Gäwiller in measurements of the temperature dependence of the Leslie coefficients.[91]

There are also instabilities associated with shear flow. One example is Taylor-Couette instability[92], which occurs for simple fluids in Couette flow. It would be interesting to investigate how this instability is affected by the stresses induced on the fluid by the order parameter. Another shear instability is associated with the instability of layers sliding past each other, as has been discussed for smectics under shear.[93] This could have an effect on our interface calculation, where we allowed only those spatial variations normal to the direction of flow. Since our equations are highly non-linear, it is conceivable that capillary waves could be excited on the interface by the shear flow and quantitatively alter our coexistence results, by shifting the coexistence line, or qualitatively alter them, by eliminating the coexistence line.

In our discussion of the fluctuations near the critical point we have made at least three crucial assumptions. (1) We have introduced noise which obeys the fluctuation dissipation theorem. This is equivalent to the statement that non-equilibrium microscopic fluctuations have the same probability distribution that they do in equilibrium. This is a fundamental question about non-equilibrium systems, and is presently a very active and controversial subject of research.[23] (2) We have ignored fluid fluctuations at the critical point and concentrated solely on the order parameter equation of motion. This can be justified if the time scales associated with the decay of velocity fluctuations are much faster than those associated with the decay of order parameter fluctuations. In that case the fluid flow acts like noise and may be formally projected out[42] and included in the additive Gaussian noise, if memory effects may be neglected. While this may be true precisely *at* the critical point, where the critical mode is infinitely long-lived, it is probably not true in general, because the fluid velocity is conserved (assuming an incompressible fluid) and therefore relaxes in macroscopic time scales. Hence a proper treatment of the Gaussian level fluctuations would involve enlarging the space of fluctuating hydrodynamic quantities to include the fluid velocity, and solving the entire set of equations. This we leave for future study. (3) Finally, we have only treated fluctuations at the Gaussian level. This does not allow us to probe the critical behavior beyond mean-field theory. This will be discussed further below.

We have also not considered the effects of *defects* on dynamics. Nematics are known to cool with many topological defects if care is not taken,[33] and these defects are stable, in the sense that they will not decay. Inevitably, applied flow will induce defects into a sample which could conceivably, *inter alia*, serve as sources for nucleation in a quench across the non-equilibrium coexistence line, frustrate this line altogether, or have interesting effects such as renormalizing the transport properties.

8.2 Future Directions

In this final section I will briefly outline further directions of research in this area. I will discuss the extension to lyotropic liquid crystals, renormalization treatments to include non-linear contribution to the equations of motion for the fluctuations near the critical point, and the possibility of examining a system in conjunction with a magnetic field.

8.2.1 Lyotropic Systems

We have seen that the critical strain rates for thermotropic liquid crystals are very high, $D^* \sim 10^5\,\mathrm{s}^{-1}$. These strain rates are near the experimental limit, and are also high enough to make dynamic instabilities a serious issue, in that these instabilities could set in before the critical point is reached. Recalling the form for the dimensionless strain rate,

$$\delta = \frac{D\beta_2}{C}, \tag{8.2}$$

we see that a larger viscosity β_2 enables the critical point δ^* to be reached with smaller strain rates D. Ideal candidates are then mesogenic materials which have high viscosities. Lyotropic systems such as solutions of the Tobacco Mosaic Virus (TMV), which are molecules of length $\sim 1800\,\text{Å}$, have much higher viscosities than the smaller ($\sim 20\,\text{Å}$) low molecular weight thermotropic materials, and are known to be very sensitive to flow gradients.[18]

One problem with extending our dynamical treatment to lyotropics is that the solvent should be treated as an additional hydrodynamic variable, with its own dynamics. Also, in many systems the transition is both temperature and concentration dependent, and the specific volume discontinuity at the transition is not negligible, as it is for thermotropics. Hence there are regions in the temperature-concentration phase diagram in which phase coexistence occurs, because of the large concentration difference between isotropic and nematic phases, which introduces a new dimension to the problem. Finally, the order parameter discontinuity is usually larger in lyotropics ($\Delta S_1 \sim 0.5$ for TMV, compared to $\Delta S_1 \sim 0.3$ for MBBA);[18] which makes a Landau expansion less reliable.

As a first step in this direction, one may consider an effective free energy which describes a concentration-driven, rather than a temperature-driven, transition, which can be done most simply by replacing the Landau parameter $a(T-T^{-})$ by $a(c-c^{-})$, where c is the concentration. The dynamics that result from this approach are essentially those derived by See, *et al.*[10] However, this approach does not account for the sizeable discontinuity in the concentration of the two phases. In addition, their approach does not address the dynamics of the local concentration. Lee[15], Wang and Gelbart[14] and Thirumalai[60] also considered the transition to be concentration-dependent in their Kramers' potential formulation of the problem of nematics in elongational flow, but again, did not consider the explicit dynamics of the concentration.

A possible approach would be to write down a Landau free energy of *two* order parameters, one for the nematic order and one for the concentration. The coupling between these is very important. The next step is to obtain the coupled dynamics of the nematic order, fluid velocity, and local concentration, and analyze the problem from there. It is a challenging problem and, although difficult, could describe fascinating non-equilibrium behavior, from coexistence of non-equilibrium phases to very strong light scattering effects. An analogous problem is the effect of flow on concentration fluctuations in *polymer* solutions under shear, which has been studied recently by X. L. Wu, *et al.*[94]

8.2.2 Critical Phenomena

Our treatment of the critical point has been at the mean-field level. It would be desirable to obtain a scaling analysis of the critical point, perhaps following roughly the steps outlined by Onuki and Kawasaki in their treatment of the binary fluid. There are many questions one could ask, such as

- What is the universality class of the critical point? Is it mean-field, as with the binary fluid, or mean-field for certain material parameters and not for others (recall our discussion at the end of Chapter 7)?
- Although a single mode is present at the critical point, does the fact that it is a combination of amplitude and orientation fluctuations have any interesting effects? In particular, is the non-equilibrium critical point an Ising-like transition perturbed by shear, as the binary fluid is (because of the single mode), or something else?

The transition under shear flow is a transition that becomes, in the limit weak shear flow, an equilibrium first order transition. It is interesting to speculate about a transition under flow that, in the limit of weak flow, becomes an equilibrium critical point. Consider a parameter set that includes flow, temperature, and an applied magnetic field. Recall from our discussion in Chapter 3 that a magnetic field should induce an equilibrium critical point. Like fluid flow, the field-induced critical point is predicted to occur at fields at or above the experimental limit ($H_c \sim 1000\,\mathrm{T}$ for a system like MBBA). It would be interesting to consider a critical point induced by a combination of a magnetic field and an applied flow. One would expect that there exists a locus of critical points, probably a line, in the three-dimensional temperature-field-flow parameter space. Further, one can inquire whether the nature of the critical behavior changes as one moves along this line from a purely non-equilibrium critical point to an equilibrium critical point. This system could provide a unique opportunity to examine, in a controlled manner, the distinctions between equilibrium and non-equilibrium critical points. And, like the case of flow, some lyotropic systems have much higher susceptibilities because of their size, and may have magnetic critical points within experimental range. With that morsel I will close this discussion.

Appendix A

Order Parameter Decomposition

In this Appendix we outline the parametrization of the order parameter and its variation as used in this thesis. First we consider the order parameter for a general biaxial state,

$$Q_{\alpha\beta} = \frac{3S_1}{2}(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}) + \frac{S_2}{2}(m_\alpha m_\beta - l_\alpha l_\beta), \tag{A.1}$$

where $\hat{\mathbf{n}}$ is the director, $\hat{\mathbf{m}}$ is the sub-director which denotes the asymmetry in the distribution of rod orientations relative to $\hat{\mathbf{n}}$, and $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ form a right-handed orthonormal triad.[36] The amplitudes S_1 and S_2 parametrize the strength of ordering. Upon performing a variation in $Q_{\alpha\beta}$, it is possible to expand a fluctuation $\delta Q_{\alpha\beta}$ in a suitable basis of orthonormal traceless symmetric tensors:[88]

$$\delta Q_{\alpha\beta} = \sum_{i=1}^{5} \xi_i \, e^i_{\alpha\beta}, \tag{A.2}$$

where

$$\begin{aligned} e^1_{\alpha\beta} &= \sqrt{\tfrac{3}{2}}(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), & e^2_{\alpha\beta} &= \tfrac{1}{\sqrt{2}}(m_\alpha m_\beta - l_\alpha l_\beta), \\ e^3_{\alpha\beta} &= \tfrac{1}{\sqrt{2}}(n_\alpha m_\beta + m_\alpha n_\beta), & e^4_{\alpha\beta} &= \tfrac{1}{\sqrt{2}}(n_\alpha l_\beta + l_\alpha n_\beta), \end{aligned} \tag{A.3}$$

$$e^5_{\alpha\beta} = \tfrac{1}{\sqrt{2}}(m_\alpha l_\beta + l_\alpha m_\beta).$$

The basis $\{e^i_{\alpha\beta}\}$ satisfies orthonormality for tensors, defined by $e^i_{\alpha\beta} e^j_{\beta\alpha} = \delta^{ij}$. In obtaining this expansion we have kept variations to first order in $\delta\mathbf{n}$ and $\delta\mathbf{m}$, which implies $\hat{\mathbf{n}} \cdot \delta\mathbf{n} = \hat{\mathbf{m}} \cdot \delta\mathbf{m} = 0$, and enforced the conditions of orthonormality of $\{\hat{\mathbf{n}}, \hat{\mathbf{m}}, \hat{\mathbf{l}}\}$ under the variation. The amplitudes $\{\xi_i\}$ are related to the explicit variations in the order parameter by

$$\begin{aligned} \xi_1 &= \sqrt{\tfrac{3}{2}}\,\delta S_1, & \xi_2 &= \tfrac{1}{\sqrt{2}}\,\delta S_2, \\ \xi_3 &= \tfrac{3}{\sqrt{2}}(3S_1 - S_2)\,\hat{\mathbf{m}} \cdot \delta\mathbf{n}, & \xi_4 &= \tfrac{1}{\sqrt{2}}(3S_1 + S_2)\,\hat{\mathbf{l}} \cdot \delta\mathbf{n}, \end{aligned} \tag{A.4}$$

$$\xi_5 = S_2\sqrt{2}\,\hat{\mathbf{l}} \cdot \delta\mathbf{m}.$$

Note that ξ_1 and ξ_2 parametrize amplitude fluctuations, while ξ_3, ξ_4, and ξ_5 parametrize orientation fluctuations. $e^1_{\alpha\beta}$ is a fluctuation in which the order along the director increases; this is the standard amplitude fluctuation found in uniaxial nematics. $e^2_{\alpha\beta}$ denotes an increase in the asymmetry in the distribution about $\hat{\mathbf{n}}$, and is a measure of the biaxiality of the fluctuation. $e^3_{\alpha\beta}$ and $e^4_{\alpha\beta}$ are fluctuations in which $\hat{\mathbf{n}}$ tilts in either of the two directions available to it, and in the uniaxial state ($S_2 = 0$)* correspond to the Goldstone modes. $e^5_{\alpha\beta}$ is a rotation of the sub-director $\hat{\mathbf{m}}$ about $\hat{\mathbf{n}}$.

*One may also construct a uniaxial state formally by choosing $S_2 = 3S_1$. This corresponds to a discotic uniaxial state, and may be cast in a form with $S_2 = 0$ by a suitable redefinition of $\hat{\mathbf{n}}$.

Appendix B

Numerics for Interface Solution

In this Appendix I will discuss the details of setting up the numerics for finding the stable interface solution extending between the two configurations corresponding to the stable homogeneous solutions. We find the interface profile by considering a fictitious dynamics; that is, we let the order parameter configuration evolve according to the order parameter equation of motion, eq. (4.63), but constrain the fluid velocity to be stationary at all times. To do this we impose an external stress σ_{xy} and determine the velocity gradient by requiring the stress to be uniform across the system *at all times*, as given by eq. (6.9). This will not give the true dynamics of the system, but will recover the correct stable interface profile. Since we do not care, at this point, about the details of the dynamics, we are free to choose any method which will converge rapidly to the steady state. We have chosen an implicit Crank-Nicholson discretization scheme which rapidly converges even for large time steps, making the computations relatively less computer-intensive.[84]

As outlined in Chapter 4, we choose a particular basis for the order parameter $Q_{\alpha\beta}$ and rewrite the equations of motion for $Q_{\alpha\beta}$ interns of this basis. We have found it convenient to choose the following basis:

$$\mathbf{Q} = \begin{pmatrix} -2m_1 - \frac{2}{3}m_2 & m_3 & m_4 \\ m_3 & \frac{4}{3}m_2 & m_5 \\ m_4 & m_5 & 2m_1 - \frac{2}{3}m_2 \end{pmatrix}. \tag{B.1}$$

The virtue of this representation is that the contribution of the Frank free energy to the equations of motion, which involves gradient terms which make the interface profile a challenge, is diagonal in this basis. In our analysis of the homogeneous states we found that the stable stationary states have $m_4 = m_5 = 0$; hence we take them to be zero throughout the interface, and reduce our system of equations to three coupled PDE's. In this basis the equation of motion for $Q_{\alpha\beta}$ may be transformed to

$$\begin{aligned} \partial_t m_1 &= -Dm_3/4 - A\beta_2^{-1}m_1 + B\beta_2^{-1}(m_3^2/4 + 4m_1m_2/3) \\ &\quad -C\beta_2^{-1}(8m_1^3 + 8m_1m_2^2/3 + 2m_1m_3^2) - \beta_2^{-1}L_1\,\partial_y^2 m_1 \end{aligned} \tag{B.2}$$

$$\begin{aligned} \partial_t m_2 &= -(3Dm_3)/4 - A\beta_2^{-1}m_2 + 2B\beta_2^{-1}(m_1^2 - m_2^2/3 - m_3^2/8) \\ &\quad -C\beta_2^{-1}(8m_1^2m_2 + 8m_2^3/3 + 2m_2m_3^2) - (L_1 + \tfrac{4}{3}L_2)\,\partial_y^2 m_2 \end{aligned} \tag{B.3}$$

$$\begin{aligned} \partial_t m_3 &= -(\beta_1 D)/2 + D(m_1 + m_2) - A\beta_2^{-1}m_3 + 2B\beta_2^{-1}(m_1m_3 - m_2m_3/3) \\ &\quad -C\beta_2^{-1}(8m_1^2m_3 + 8m_2^2m_3/3 + 2m_3^3) - (L_1 + L_2)\,\partial_y^2 m_3 \end{aligned} \tag{B.4}$$

We have assumed the only spatial dependence is the variation normal to the interface, along $\hat{\mathbf{y}}$. The convective part of the equations of motion $(\mathbf{v} \cdot \boldsymbol{\nabla})$ drops out because we assume the stationary velocity profile is given by $\mathbf{v}||\hat{\mathbf{x}}$ everywhere. The terms with coefficients A, B, C arise from the Landau-de Gennes free energy, and the gradient terms are from the Frank free energy. The strain rate D appears in these equations, and must be solved for from the condition that the applied stress is uniform throughout the system in steady state.

The stress condition is given by

$$\sigma_{xy} = \sigma_{xy}^{i[s]} + \sigma_{xy}^{i[a]} + \sigma_{xy}^{d}, \tag{B.5}$$

where the stresses may now be calculated in terms of the $\mathbf{m}$ basis:

$$\begin{aligned} \sigma_{xy}^{i[s]} &= \beta_3 \kappa_{xy}^{[s]} + \beta_1 H_{xy}^{[s]} \\ &= \beta_3 D/2 - A\beta_1 m_3 + B\beta_1(2m_1m_3 - 2m_2m_3/3 - m_4m_5) \\ &\quad - C\beta_1(8m_1^2m_3 + 8m_2^2m_3/3 + 2m_3^3 + 2m_3m_4^2 + 2m_3m_5^2) \qquad \text{(B.6)} \\ &\quad + (L_1 + L_2)\,\partial_y^2 m_3 \\ \sigma_{xy}^{i[a]} &= H_{xi}^{[s]}\,Q_{iy} - Q_{xi}\,H_{iy}^{[s]} \\ &= L_2\left[2(m_1+m_2)\,\partial_y^2 m_3 - \tfrac{8}{3} m_3\,\partial_y^2 m_2\right] \qquad \text{(B.7)} \\ \sigma_{xy}^{d} &= -\,L_2\,\partial_y m_3\,\partial_y(\tfrac{2}{3}m_2 - 2m_1). \qquad \text{(B.8)} \end{aligned}$$

We may invert eq. (B.5) to find the strain rate $D(\mathbf{m}, \partial_y\mathbf{m}, \sigma_{xy})$, and substitute this into eqs. (B.2-B.4) to find the PDE's which describe the relaxation of the order parameter.

We solve for the interface profile by discretizing these coupled PDE's and placing the system on a mesh. We use the implicit Crank-Nicholson scheme to iterate the solution forward. Upon making the physically reasonable assumption $L_1 = L_2$ and the transformation to dimensionless time $\bar{t} \equiv tC/\beta_2$ and position $\bar{y} \equiv y(C/L)^{1/2}$, the interface is a function of the dimensionless parameters $s = \sigma_{sy}/C$, $\tau = A/C$, β_1, and β_3/β_2. We assume values for β_1 and β_3/β_2 in general agreement with experiments on low molecular weight materials, and examine behavior of the interface as we vary s and τ. In this way we are able to obtain the profiles discussed in Chapter 6.

I will give examples of the discretization scheme for representative terms in the equations of motion.* Consider a PDE of the form

$$\partial_t m_\alpha = f_\alpha(\mathbf{m}) + g(\mathbf{m})\partial_y^2 m_\alpha + h(\mathbf{m})\partial_y m_\alpha \partial_y m_2, \tag{B.9}$$

where $f_i(\mathbf{m}), g(\mathbf{m})$, and $h(\mathbf{m})$ are non-linear functions of $(\mathbf{m})$. We discretize in time and space with superscript n denoting a time index and subscript j denoting a space index. Greek indices refer to cartesian indices on the field $\mathbf{m}$.

$$\begin{aligned} \frac{m_{\alpha,j}^{n+1} - m_{\alpha,j}^{n}}{\Delta t} &= \tfrac{1}{2}\left[f_\alpha^{n+1} + f_\alpha^{n}\right]_j + \tfrac{1}{2}\left[(g(\mathbf{m})\partial_y^2 m_\alpha)^{n+1} + (g(\mathbf{m})\partial_y^2 m_\alpha)^{n}\right]_j \\ &\quad + \tfrac{1}{2}\left[(h(\mathbf{m})\partial_y m_\alpha \partial_y m_2)^{n+1} + (h(\mathbf{m})\partial_y m_\alpha \partial_y m_2)^{n}\right]_j . \end{aligned} \tag{B.10}$$

Next we calculate approximations to the terms in brackets on the right hand side:

$$\left[f_\alpha^{n+1} + f_\alpha^{n}\right]_j \simeq f_\alpha^n(\mathbf{m}_j^n) + \left.\frac{\partial f_\alpha}{\partial m_\beta}\right|_{\mathbf{m}_j^n} (m_{\beta,j}^{n+1} - m_{\beta,j}^{n}) + f_\alpha^n(\mathbf{m}_j^n), \tag{B.11}$$

$$\begin{aligned} \left[(g(\mathbf{m})\partial_y^2 m_\alpha)^{n+1}\right. &+ \left.(g(\mathbf{m})\partial_y^2 m_\alpha)^{n}\right]_j \simeq \\ & g(\mathbf{m}^n)(\partial_y^2 m_\alpha^n)_j + \left.\frac{\partial g_\alpha}{\partial m_\beta}\right|_{\mathbf{m}_j^n} (m_{\beta,j}^{n+1} - m_{\beta,j}^{n}) + g(\mathbf{m}^n)(\partial_y^2 m_{\alpha,j}^{n+1})_j, \end{aligned} \tag{B.12}$$

*We thank Fong Liu and Nigel Goldenfeld for explaining this method to us.

and

$$\Big[(h(\mathbf{m})\partial_y m_\alpha \partial_y m_2)^{n+1} \quad + \quad (h(\mathbf{m})\partial_y m_\alpha \partial_y m_2)^{n}\Big]_j \simeq \tag{B.13}$$

$$(\partial_y m_\alpha^{n+1})_j(\partial_y m_2^n)_j h(\mathbf{m}^n) + (\partial_y m_\alpha^n)_j(\partial_y m_2^{n+1})_j h(\mathbf{m^n})$$

$$+(\partial_y m_\alpha^n)_j(\partial_y m_2^n)_j \left.\frac{\partial h_\alpha}{\partial m_\beta}\right|_{\mathbf{m}_j^n} (m_{\beta,j}^{n+1} - m_{\beta,j}^n).$$

We take the following definitions for our finite differences:

$$(\partial_y m)_j \quad \equiv \quad \frac{m_{j+1} - m_{j-1}}{2\Delta y} \tag{B.14}$$

$$(\partial_y^2 m)_j \quad \equiv \quad \frac{m_{j+1} - 2m_j + m_{j-1}}{\Delta y^2}. \tag{B.15}$$

The PDE is iterated forward in time by solving for $\mathbf{m}_j^{n+1}$ in terms of $\mathbf{m}^n$:

$$\Gamma_{\alpha\beta,ij}\, m_{\beta,j}^{n+1} = V_{\alpha,i}\ , \tag{B.16}$$

where $\mathbf{\Gamma}$ is a matrix on both cartesian $(\alpha, \beta, \ldots)$ and discrete space $(i, j, \ldots)$ indices, and $\mathbf{\Gamma}$ and $\mathbf{V}$ are, generally, non-linear functions of $\{\mathbf{m}_i^n\}$.

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