

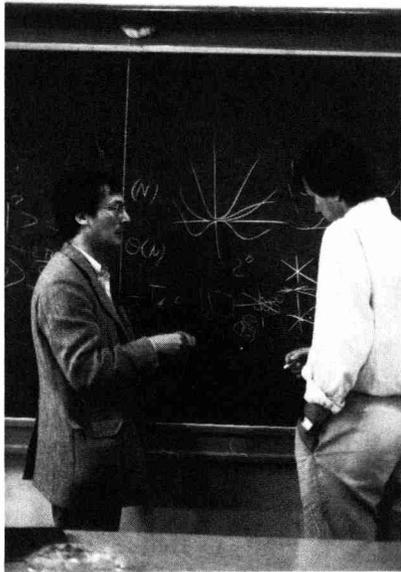
COURSE 9

**STATISTICAL MECHANICS
OF LIQUID CRYSTALS**

D. FRENKEL

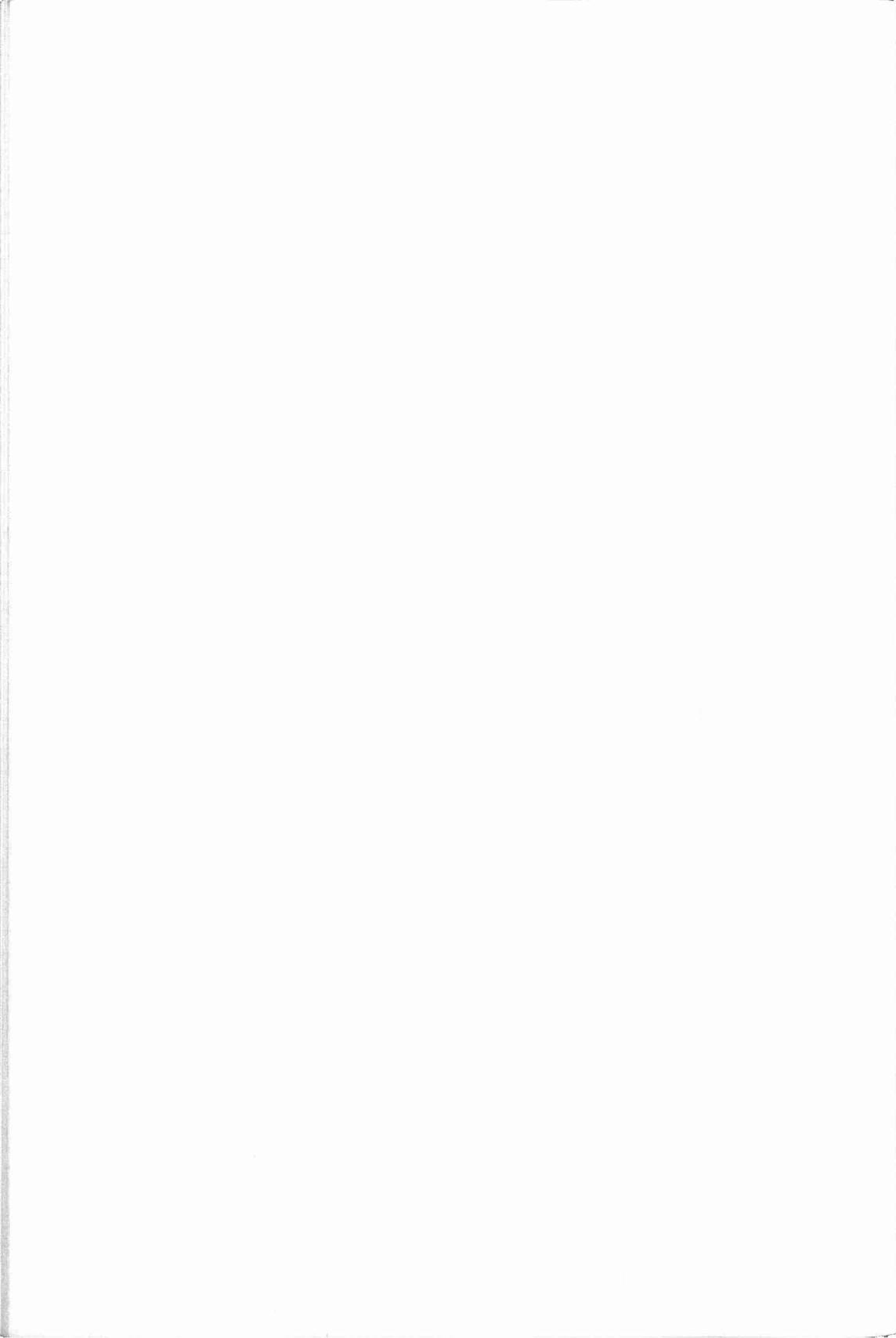
*FOM Institute for Atomic and Molecular Physics
P.O. Box 41883
1009 DB Amsterdam, The Netherlands*

*J. P. Hansen, D. Levesque and J. Zinn-Justin, eds.
Les Houches, Session LI, 1989
Liquides, Cristallisation et Transition Vitreuse/
Liquids, Freezing and Glass Transition
© Elsevier Science Publishers B.V., 1991*



Contents

1. Introduction	693
1.1. Liquid crystals	694
1.1.1. Nematics	696
1.1.2. Smectics	697
1.1.3. Columnar phases	698
1.1.4. Other phases	698
1.2. Statistical mechanics?	699
2. Nematics	700
2.1. Order parameters	700
2.2. Landau expansion	702
2.3. Mean field theory	704
2.4. Onsager model	710
2.4.1. Discussion	713
2.5. Computer simulation	715
2.6. Theoretical description	719
3. Elastic constants	720
4. Two-dimensional nematics	727
5. Smectics	733
5.1. Introduction	733
5.2. Landau theory	735
5.3. Mean-field theories	737
5.4. Hard-core models: beyond nematics	738
5.4.1. Parallel molecules	738
5.4.2. Theories of parallel hard-core systems	743
5.4.3. The effect of rotation	746
6. Conclusion	753
Appendix A. . Approximate solution of the Onsager model	754
Appendix B. . Cubatic order and the Onsager model	756
References	759



1. Introduction

The term ‘liquid crystal’ is commonly used to designate certain phases of (macro-)molecular substances. It is easiest to define liquid crystals by saying what they are not: they are not simple molecular liquids nor are they crystalline solids. Rather, they are characterized by some degree of order that is intermediate between that of a molecular crystal where the molecular centers-of-mass are arranged on a periodic lattice, and a ‘normal’ molecular liquid that has no long-range translational or orientational order. Just as with regular crystals, the name of a liquid crystalline phase (e.g., nematic, smectic, cholesteric etc.) is supposed to convey information about the nature of the phase. Unfortunately, a large number of liquid-crystalline phases were baptized before their structure was understood: hence their names usually tell us more about the visual appearance of these substances (e.g., ‘blue phases’) than about their symmetry.

Liquid crystals are quite common in nature, yet, even among physicists and chemists they are not widely known for what they are: the bridge between simple liquids and crystalline solids. Imagine constructing a molecular crystal from a molecular liquid via a step-by-step breaking of different symmetry elements of the liquid: first break the isotropy of the distribution of molecular orientations, then break translational invariance in one dimension, next impose two-dimensional bond-order, then break translational invariance in a second direction, and finally break the remaining translational invariance. To every intermediate stage in this stepwise freezing process there corresponds an existing liquid crystalline phase (although I do not know of any single substance that actually exhibits *all* degrees of ordering sketched above).

The previous paragraph shows that liquid crystals are important, at the very least conceptually. Why is it then that liquid crystals are not discussed in every high-school physics textbook. I tend to believe that it is due to a historical accident that predates the discovery of liquid crystals (in 1888 [1]) by some 22 centuries: if only Aristoteles had allowed for more elements than ‘earth, water, air and fire’, the western mind might have been more prepared to accept the existence of other phases than solids, liquids, gases and plasma.

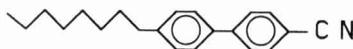
Statistical mechanics of liquid crystals is a topic so vast that entire books and conferences have been devoted to many of its subtopics. It is therefore impossible to give a balanced presentation of the subject in a few lectures and I shall not attempt to do so. What I wish to achieve in these lectures is something else. I shall discuss liquid crystals as a special case of 'simple liquids'. This is a hazardous undertaking because the (macro)molecules that form liquid crystal are usually far from simple. My aim is therefore to see how far we can strip down the molecular model for a liquid crystal without losing the essential physics. As in the theory of simple liquids almost all choices for the intermolecular potential of a liquid- crystal-forming molecule (a 'mesogen') lead to models that cannot be solved exactly. The outstanding exception being the Onsager model [2] that I shall discuss in some detail. All other 'exact' results come from computer simulations. I shall rely heavily on the results of such simulations to explain the physics of liquid crystals. For most liquid crystalline phases computer simulation data are lacking. This does not imply that it is totally obscure what feature of the intermolecular interactions makes them behave the way they do (although sometimes it is). However, my discussion (if any) of such phases will necessarily be much more superficial.

In my discussion of statistical-mechanical theories I shall try, as much as possible, to give examples that are sufficiently simple that they can be worked out with pencil and paper. Such simple theories are not necessarily the most accurate. My aim is more to show the structure of a particular class of theories than to present the most recent theoretical 'conquests'.

Finally I should mention that there is a very important area of liquid-crystal physics for which the precise molecular nature of the substance is largely irrelevant, namely the study of continuous phase-transitions. Over the last two decades many physicists have been attracted to this field, and for a good reason: the diversity of phases and phase-transitions in liquid crystals both in the bulk, in thin films and at interfaces gives rise to a wealth of interesting pretransitional phenomena. This branch of liquid-crystal physics has become one of the major testing grounds of modern theories of critical phenomena. However, I shall largely refrain from discussing this topic because it falls outside the scope of the 'molecular' approach that I intend to follow. Moreover, an excellent reprint collection has recently been published on this topic [3].

1.1. Liquid crystals

Originally, the word 'liquid-crystal' was used to designate a phase with some degree of order intermediate between a crystalline solid and an isotropic



P-OCTYL-P'-CYANOBIIPHENYL

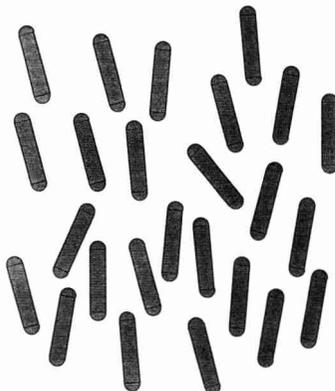
Fig. 1. Molecular structure of *p*-octyl-*p'*-cyanobiphenyl (8CB). This is a typical example of a thermotropic liquid-crystal forming molecule.

(i.e., orientationally disordered) liquid. There are dozens of distinct liquid-crystalline phases. It has proven useful (and, occasionally, misleading) to group these phases in 'families'. Below I shall name some of the main families. Before doing so, let us first consider what the building blocks of liquid crystals are. First of all, there are liquid crystals consisting of non-spherical organic molecules. A typical example of such a molecule is *p*-octyl-*p'*-cyanobiphenyl (8CB, for short, see fig. 1) that has both a nematic and a smectic phase. Transitions between these phases are most easily achieved by changing the temperature of the sample. For this reason, this class of materials is often referred to as 'thermotropic' liquid crystals.

A second class are the so-called 'lyotropic' liquid-crystals. Lyotropic systems are not pure substances but solutions of a non-spherical macromolecule or aggregate. Phase transformations are effectuated by changing the concentration of the non-spherical particles, or by changing the characteristics of the solvent (e.g., its ionic strength). An example of a lyotropic liquid crystal is a concentrated solution of the (rod-like) Tobacco Mosaic Virus (TMV).

Finally, liquid-crystalline order can occur in certain polymers. These have the prosaic name 'liquid-crystalline polymers' (LCP's). Usually, phase transitions in LCP's are induced by a temperature change. One way to synthesize LCP's is to attach molecules that form thermotropic liquid crystals at the end of a flexible side-chain ('spacer') that is tied to a polymer backbone. In practice, the dividing lines between thermotropics, lyotropics and LCP's are ill-defined.

Let us now consider the most important liquid-crystalline phases. It is convenient to distinguish the different phases, according to the form of the single-particle distribution function ρ_1 . In the most general case, ρ_1 is a function of the cartesian coordinates x, y, z specifying the position of the molecular center-of-mass and the orientational coordinate Ω that describes the molecular orientation: $\rho_1 = \rho_1(x, y, z, \Omega)$. In a crystalline solid ρ_1 is of this form. In contrast, in an isotropic fluid phase ρ_1 is equal to the number density ρ , independent of x, y, z and Ω . In liquid crystals, ρ_1 depends on some, but not all coordinates.



Nematic Liquid Crystal

Fig. 2. Schematic drawing of a 'snapshot' of the molecular configuration in a nematic liquid crystal

1.1.1. Nematics

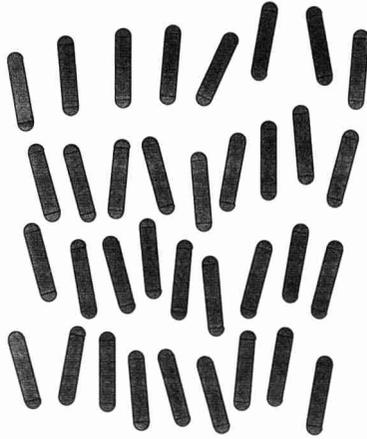
The simplest, and best known liquid-crystalline phase is the *nematic* phase. Nematics have no long-range positional order, hence ρ_1 does not depend on x, y or z . However, nematics do exhibit orientational order and, as a consequence, ρ_1 does depend on Ω :

$$\rho_1(x, y, z, \Omega) = \rho f(\Omega), \quad (1.1)$$

where $f(\Omega)$ denotes the normalized orientational distribution function. In normal nematics the orientational distribution function is axially symmetric around a preferred direction \mathbf{n} : the nematic *director*. The orientational distribution function is then only a function of $\cos \theta \equiv \Omega \cdot \mathbf{n}$. Moreover, molecules are equally likely to point parallel and anti-parallel to the director. Hence $f(\cos \theta) = f(-\cos \theta)$. Note that the latter property is not restricted to molecules with head-tail symmetry. In fact, many nematogens may even have a dipole moment along the molecular axis. Figure 2 shows an artist's impression of the molecular arrangement in a nematic liquid crystal.

In addition to the uniaxial nematics mentioned above, there also exist biaxial nematics in which the orientational distribution function does not have axial symmetry. All known biaxial nematics are either mixtures of rod-like and plate-like molecules or systems of molecules that have very different x, y and z dimensions (ruler-like).

Closely related to the nematic phase is the cholesteric phase. Like in nematics, the number density in cholesterics is independent of position.



Smectic Liquid Crystal

Fig. 3. Schematic drawing of a 'snapshot' of the molecular configuration in a smectic liquid crystal

However, the preferred molecular orientation is a function of position in one direction (say z): $f(\boldsymbol{\Omega}) = f(\boldsymbol{\Omega}(z))$. Cholesterics consist of chiral molecules. Near the transition to the isotropic phase, many cholesterics are known to transform into so-called 'blue-phases'. In the blue phases that are presently best understood, the orientational distribution function is a periodic function of all three cartesian coordinates. In some respects these phases behave as crystals [4].

1.1.2. Smectics

Proceeding one step in the direction from liquid to crystal, we arrive at the smectic phase. Of these there are close to 20. The single-particle distribution function of smectics is periodic in one spatial dimension:

$$\rho_1(x, y, z, \boldsymbol{\Omega}) = \rho(z, \boldsymbol{\Omega}) . \quad (1.2)$$

For convenience I have ignored the fact that, due to an accident in the nomenclature, one phase that happens to have cubic symmetry has been named smectic-D.

The simplest smectic phase is smectic-A. In smectic-A the orientational distribution of the molecules is axially symmetric and the direction of the symmetry axis (the director \mathbf{n}) is perpendicular to the smectic planes. A sketch of the molecular arrangement in a smectic-A phase is given in fig. 3.



Columnar Liquid Crystal

Fig. 4. Schematic drawing of a 'snapshot' of the molecular configuration in a columnar liquid crystal

Smectic-B has crystalline order in the planes and is maybe better described as a crystal with extremely anisotropic elastic constants. Hexatic-B is like smectic-B but for the fact that it has no long-range positional order in the planes but only long-range 'bond-order'. Smectic-C is like smectic-A but the director \mathbf{n} is tilted with respect to the plane-normal. Then there are a whole range of smectics with increasingly complex orientational and positional order. These I shall not discuss at all.

1.1.3. Columnar phases

Columnar phases are liquid crystals that consist of stacks ('columns') of disk-like molecules. These columns form a periodic two-dimensional array. But in the third direction the system has no long-range positional order. Hence the single-particle distribution function is of the form:

$$\rho_1(x, y, z, \boldsymbol{\Omega}) = \rho(x, y, \boldsymbol{\Omega}) . \quad (1.3)$$

Figure 4 shows an a possible molecular configuration in a columnar liquid crystal. A wide variety of distinct columnar phases exists. But, even more than with smectics, the experimental picture is still incomplete.

1.1.4. Other phases

The above summary of liquid-crystalline phases has been very sketchy: for a more detailed account I refer the reader to the books by de Gennes [5], Chandrasekhar [6], Priestley et al. [7], Luckhurst and Gray [8] and the more recent books by Vertogen and de Jeu [9] and Pershan [3]. Finally it should be stressed that even in these more recent books the list of known liquid-crystalline phases already incomplete: the number of known liquid-crystalline phases is growing every year. I suppose that this trend will

continue for some time because, when contemplating the number of *possible* liquid crystalline phases, the great surprise is not that so *many* are known in nature, but so *few*.

1.2. Statistical mechanics?

If this brief introduction to liquid-crystalline phases has achieved anything, it is probably that it has convinced the reader that liquid crystals are *not simple*. The building blocks are large (molecular weight 10^2 – 10^3), flexible and often polar organic molecules or still larger (bio-)polymers and aggregates. All these factors appear to make the study of the statistical mechanics of liquid crystals a messy and possibly futile project. Of course, the critical behaviour at continuous phase-transitions is only sensitive to the symmetry and not to the molecular details of the phases involved. However, these lectures are not about critical phenomena in liquid crystals but about the *molecular* statistical mechanics of such systems. Clearly, there is no point in attempting an accurate statistical mechanical description of, say, *p*-octyl-*p*'-cyanobiphenyl. My aim is different. I wish to demonstrate what we can learn by applying the machinery of statistical mechanics to the *simplest* molecular (as distinct from phenomenological) models that exhibit liquid-crystalline behaviour. There are two motives behind this approach. The first is that the study of simple models provides insight. The second is that a comparison between experiments (or computer 'experiments') and the predictions for simple model systems tells us something about the relevance of all 'complex' features that we have chosen to ignore in our model. Such a comparison may point the way to meaningful refinements of our model.

The starting point of our discussion should therefore be the 'ideal' liquid crystal. 'Ideal' model systems play a central role in many branches of statistical mechanics. An ideal model system may be loosely defined as a many-body system with a well defined Hamiltonian for which we can compute all equilibrium properties exactly. For gases the ideal reference system is (not surprisingly) the ideal gas. For crystalline solids, the harmonic lattice plays this role. Both models can be solved exactly, and the effect of non-ideality (intermolecular interactions in gases at finite density, anharmonic effects in warm solids) can be treated as a perturbation. For simple liquids the situation is more complicated. There is no 'ideal liquid' model that can be solved exactly. However, with the advent of the computer it has become possible to compute the properties of model fluids to any desired accuracy. In particular, the properties of the hard-sphere fluid have been simulated extensively, and it is the latter model that now plays

the role of the ideal simple liquid.

How about liquid crystals? Is there an exactly solvable ideal liquid crystal? For most liquid-crystalline phases the answer is: no. However, exactly 40 years ago Onsager published a paper in which he presented an exactly solvable ‘molecular’ model (namely a system of infinitely thin hard rods) that exhibits a transition from the isotropic to the nematic phase [2]. This model plays the role of the ideal nematic. In all other cases we have to turn to computer simulation to generate our ideal liquid-crystalline reference system.

In view of the scarcity of exact results for liquid crystals, it is not surprising that phenomenological descriptions play an important role in this field. Of particular importance are mean-field models (such as the one due to Maier and Saupe [10]) that are based on a molecular picture, and continuum descriptions where the free energy density of the system is expanded in powers of the appropriate order parameters (Landau theory). In the next section I shall describe these different approaches in the case of nematics, and I shall try to clarify the relation between them.

2. Nematics

In this section I describe different approaches to the statistical mechanical description of the nematic phase. My description of the nematic phase will be much more detailed than that of other liquid-crystalline phases. There are two reasons for this emphasis. First of all, the nematic phase has been studied more extensively than any other liquid-crystalline phase. And secondly, much of the discussion of models for nematics carries over, with minor modifications, to the discussion of other phases. First, however, I should introduce the concept of ‘order parameters’ that quantify the degree of liquid-crystalline order of a particular phase.

2.1. Order parameters

In an isotropic molecular liquid, the single particle distribution function ρ_1 is a constant. In an ordered system, such as a liquid crystal, ρ_1 depends on the molecular orientation Ω and possibly also on the center-of-mass coordinate \mathbf{r} . In a nematic, ρ_1 is a function of Ω only [see eq. (1.1)].

Although knowledge of ρ_1 suffices to determine the nature and degree of ordering in a liquid crystal, it is often convenient to be able to quantify the liquid-crystalline order with a few numbers rather than with a continuous

function. These parameters should have the property that they are non-zero if a particular type of ordering is present, and zero otherwise. In the case of the nematic phase a natural choice for these so-called *order parameters* results if we express the single-particle distribution function in orthogonal polynomials. As mentioned in section 1.1.1 the orientational distribution function $f(\boldsymbol{\Omega})$ in a uniaxial nematic depends only on the angle θ between the molecular orientation $\boldsymbol{\Omega}$ and the nematic director \mathbf{n} . Hence it is convenient to expand $f(\boldsymbol{\Omega} \cdot \mathbf{n})$ in orthogonal polynomials of $\cos \theta$ on the interval $[-1, 1]$, i.e., the Legendre polynomials. We can therefore write:

$$f(\cos \theta) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{4\pi} S_{\ell} P_{\ell}(\cos \theta) \quad (\ell \text{ even}). \quad (2.1)$$

In the isotropic phase all coefficients S_{ℓ} with $\ell > 0$ vanish. However, in the nematic phase the S_{ℓ} with $\ell = 2, 4, \dots$ are nonzero:

$$S_{\ell} = \int d\cos \theta d\phi f(\cos \theta) P_{\ell}(\cos \theta) = \langle P_{\ell}(\cos \theta) \rangle. \quad (2.2)$$

The quantities S_{ℓ} with $\ell \geq 2$ can therefore be used as a measure of the nematic order. Often the quantity $S_2 = \langle P_2(\cos \theta) \rangle$ is referred to as *the* nematic order parameter. Similarly, it is possible to define order-parameters that quantify smectic and columnar order by expanding the spatial variation of the single-particle density function ρ_1 in Fourier components. The amplitude of the Fourier component with the lowest non-zero wavevector that is commensurate with the periodicity of the density modulation is a measure for the smectic (columnar) order.

The definition of the nematic order parameters in eq. (2.2) is not entirely satisfactory for the following reason: S_{ℓ} is defined as the average of $P_{\ell}(\cos \theta)$, where θ is the angle between the molecular orientation vector \mathbf{u} (for convenience we consider axially symmetric molecules) and the nematic director \mathbf{n} . But the director is defined as the average alignment direction of the molecules in a nematic. In the absence of external forces the direction of \mathbf{n} is not known *a priori*. Hence eq. (2.2) suggest that in order to measure the order parameter, we should first determine the preferred alignment (i.e. we should already know if the sample is nematic) and only then can we measure the degree of nematic order.

Fortunately, it is possible to give a definition of S_2 that does not presuppose knowledge of \mathbf{n} . To see this, consider the expression for $\langle P_2(\mathbf{u} \cdot \mathbf{e}) \rangle$, where \mathbf{e} is an arbitrary unit vector:

$$\langle P_2(\mathbf{u} \cdot \mathbf{e}) \rangle = \frac{1}{N} \sum_{i=1}^N \mathbf{e} \cdot \left(\frac{3\mathbf{u}^i \mathbf{u}^i - \mathbf{I}}{2} \right) \cdot \mathbf{e}$$

$$\equiv \mathbf{e} \cdot \mathbf{Q} \cdot \mathbf{e}, \quad (2.3)$$

where \mathbf{I} is the second-rank unit tensor and the last line of eq. (2.3) defines the tensor order-parameter \mathbf{Q} . \mathbf{Q} is a traceless, symmetric second-rank tensor. Its eigenvalues correspond to the expectation values of $S_\alpha \equiv \langle P_2(\mathbf{u} \cdot \mathbf{e}_\alpha) \rangle$ for the three orthonormal eigenvectors \mathbf{e}_α . We now *define* the director \mathbf{n} to be the eigenvector of \mathbf{Q} that has the largest eigenvalue S . In a uniaxial nematic the other two eigenvalues must be equal. If we combine this with the fact that \mathbf{Q} is traceless, it follows that these eigenvalues must be equal to $-S/2$. In the nematic phase we can therefore rewrite the tensor order-parameter \mathbf{Q} as:

$$\mathbf{Q} = S \frac{3\mathbf{n}\mathbf{n} - \mathbf{I}}{2}. \quad (2.4)$$

We shall return to this expression in chapter 3 below. Note that it is in principle possible to have a biaxial tensor order parameter even if the molecules are uniaxial. However, I know of no example where a pure system of uniaxial molecules forms a biaxial nematic (for a discussion, see [11,12]).

2.2. Landau expansion

A convenient starting point to discuss the transition from the isotropic to the nematic phase (I-N transition) is to consider nematic ordering as a weak perturbation of the isotropic phase. Following Landau [13], we then assume that the free-energy difference between the nematic and isotropic phase may be expressed as a power series in the nematic order parameter \mathbf{Q} (see de Gennes [5]). Clearly, such an expansion of the free energy F may only contain rotationally invariant combinations of \mathbf{Q} . As \mathbf{Q} contains at most two independent eigenvalues (say S and $-S/2 - \Delta$), the most general expression for F would be a power series in S and Δ . Here we only consider transitions to the uniaxial nematic phase, and hence we only need to consider the case $\Delta = 0$. The more general case is important in the context of I-N transitions in the presence of external fields: it is discussed in ref. [12]. The leading terms in the expansion of F in powers of \mathbf{Q} are:

$$F = F_0 + A \operatorname{tr} \mathbf{Q}^2 + B \operatorname{tr} \mathbf{Q}^3 + C_1 (\operatorname{tr} \mathbf{Q}^2)^2 + C_2 \operatorname{tr} \mathbf{Q}^4 + \dots \quad (2.5)$$

If we only consider uniaxial fluctuations, we can use eq. (2.4) to express F in powers of S :

$$\begin{aligned} F &= F_0 + \frac{3}{2}AS^2 + \frac{3}{4}BS^3 + \frac{9}{4}(C_1 + C_2/2)S^4 + \dots \\ &\equiv F_0 + a(T - T^*)S^2 - bS^3 + cS^4 + \dots \end{aligned} \quad (2.6)$$

The last line in eq. (2.6) defines the coefficients a, b and c . Moreover, we have assumed that in the vicinity of the I–N transition the coefficient of A varies linearly with temperature, while b and c are varying slowly. It is important to note that the coefficient of the cubic term (b) is non-zero. This reflects the fact that a fluctuation with positive S (prolate orientational distribution function) is not equivalent to a fluctuation with opposite S (oblate orientational distribution function). The presence of a cubic term in eq. (2.6) implies that according to Landau–de Gennes theory, the isotropic–nematic transition in three dimensions should be first order.

In two dimensions the situation is different: there a change of sign of the order-parameter ($S = \langle \cos 2\phi \rangle$) can be effectuated by rotating the system over 90 degrees. Hence, in 2D fluctuations with S and $-S$ are equivalent and the free energy is a function of even powers of S only. If the coefficient of the quartic term is positive, Landau theory predicts a second order phase-transition in 2D. In fact, as we shall see in chapter 4, the situation in two-dimensional nematics is somewhat more complex.

In order to see what the Landau–de Gennes theory predicts for the I–N transition, it is convenient to write eq. (2.6) slightly differently (neglecting terms $O(S^5)$):

$$F - F_0 = \left[a(T - T^*) - \frac{b^2}{4c} \right] S^2 + cS^2 \left[S - \frac{b}{2c} \right]^2. \quad (2.7)$$

It is immediately obvious that the right-hand side of eq. (2.7) vanishes for $S = 0$ (of course) and for $S = b/(2c)$ at $T = T^* + b^2/(4ac)$. At the latter temperature the transition from the isotropic to the nematic phase occurs. At this transition temperature (T_{NI}) the order parameter jumps discontinuously from $S = 0$ to $S = b/(2c)$. For $T < T_{NI}$ the order parameter is found by computing the value of S where $(\partial F/\partial S) = 0$. This yields:

$$S(T) = \frac{3b}{8c} \left(1 + \sqrt{1 - \frac{8(T - T^*)}{9(T_{NI} - T^*)}} \right).$$

From eq. (2.6) we can derive expressions for all thermodynamic properties in the vicinity of the I–N transition. Although the Landau–de Gennes theory is very useful as a unified framework to describe different experiments on the isotropic–nematic transition, it should be stressed that the theory does not provide us with predictions for the magnitude of the coefficients a, b, c, \dots . That would require a molecular theory. Examples of such theories are discussed in the following sections. However, before proceeding it

is interesting to see if there is any *direct* evidence that the free energy in the vicinity of the I–N transition indeed behaves as predicted by eq. (2.6). One way to find out is to study spontaneous order-parameter fluctuations in the vicinity of the I–N transition, for instance by light-scattering [14]. The problem is that the form of the Landau expansion used in eq. (2.5) is only valid for fluctuations in a volume that is sufficiently small that variations of the order parameter over this volume can be ignored (i.e., the linear dimensions of this volume must be much smaller than the ‘correlation length’ for order-parameter fluctuations). Otherwise we must use the full expression for the Landau–de Gennes free energy, including gradient terms:

$$\begin{aligned}
 F = F_0 + \frac{2}{3}a(T - T^*)Q_{\alpha\beta}Q_{\beta\alpha} + BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} \\
 + C_1(Q_{\alpha\beta}Q_{\beta\alpha})^2 + C_2Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha} + \dots \\
 + \frac{L_1}{2}\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma} + \frac{L_2}{2}\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + \dots \quad (2.8)
 \end{aligned}$$

Order-parameter fluctuations are correlated over a distance of order $\xi = \sqrt{L_1/[a(T - T^*)]}$. In normal thermotropic liquid-crystals, this correlation length is at most a few tens of nanometers, even close to the I–N transition. In light scattering experiments, the scattering volume is certainly larger than λ^3 (where λ is the wavelength of the incident light). Typically, $\lambda=500$ nanometers. Hence, light-scattering probes many correlation volumes in which the fluctuations of S are uncorrelated. The central limit theorem then tells us that it is going to be very difficult to see anything but Gaussian fluctuations (for a discussion see [12]).

A more direct way to probe $F(S)$ is by computer simulation. With that technique we can study order-parameter fluctuations in systems containing a few hundred molecules [15]. Even in that case it is not always possible to ensure that the order-parameter fluctuations in the system are completely correlated. But now, at least, the non-Gaussian effects are clearly visible (see fig. 5). If we try to extract the behaviour of the expansion coefficients A and B from our simulations, we see that A does indeed go linearly to zero very near the transition point (see fig. 6). However, the (noisy) simulation data provide no support for the assumption that B varies little through the transition region. We shall return to eq. (2.8) in chapter 3.

2.3. Mean field theory

At this stage it is useful to recall the steps that led us to the Landau–de Gennes expansion for the free energy. First, we introduced the single-particle density function ρ_1 . Next, we argued that, for a uniaxial nematic,

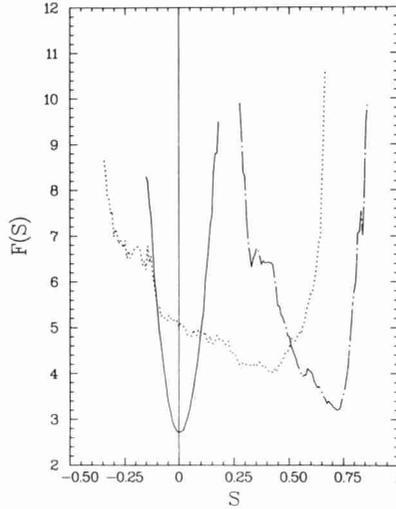


Fig. 5. ‘Landau’ free energy associated with nematic order-parameter fluctuations. The curves in the above figure were obtained by Monte Carlo simulations of infinitely thin hard platelets [15]. Drawn curve: low-density isotropic phase. Dotted curve: density just beyond the isotropic–nematic transition. Note that the minimum of $F(S)$ shifts to non-zero values of S . Dash-dot curve: high-density nematic. Now only small fluctuations around a non-zero average of S are possible.

ρ_1 may be expanded in a series of Legendre polynomials. We interpreted the coefficients of this expansion as ‘order parameters’ and then focused exclusively on the lowest non-trivial order parameter, i.e., $S \equiv \langle P_2(\mathbf{u} \cdot \mathbf{n}) \rangle$. Finally, we assumed that the free energy could be written as a power series in S_2 .

We know from density-functional theory (see the lectures of Oxtoby in this volume), that the free energy of a system is a unique functional of the single-particle distribution function. As ρ_1 for a uniaxial nematic is completely specified by the average density and all order parameters S_ℓ , it follows that F must be a unique functional of the set $\{\rho, S_\ell\}$. In the previous section we assumed that F could be approximated by a power series in S_2 . Here, we shall consider simple parametrizations of ρ_1 in terms of the order parameter S_2 . We find the stable phase by minimizing the free energy with respect to ρ_1 (strictly speaking we should consider the free enthalpy, but because the density jump at the I–N is small we ignore the distinction).

The mean-field theory for the I–N transition was first derived by Maier and Saupe [10]. Let me first present the Maier–Saupe theory in its ‘con-

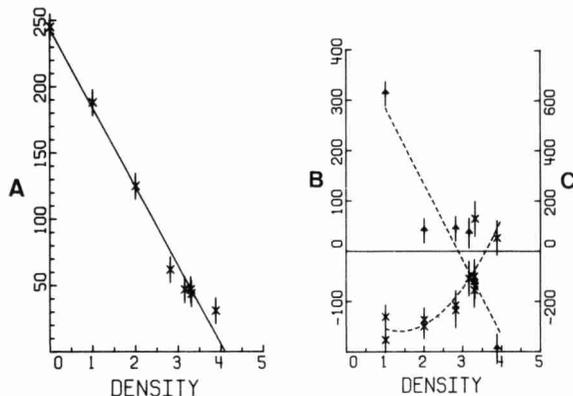


Fig. 6. Density-dependence of the coefficients of A (left), B (right, crosses) and C (right, triangles) of successive powers of S in the expansion of the free energy $F(S)$ of a system of thin hard platelets [15] (see text). Note that A goes to zero in the vicinity of the isotropic–nematic transition (as expected). In the vicinity of the I–N transition the coefficient B (and possibly C) exhibits a pronounced density dependence. This is contrary to the assumptions of the Landau theory of (almost) second-order phase transitions.

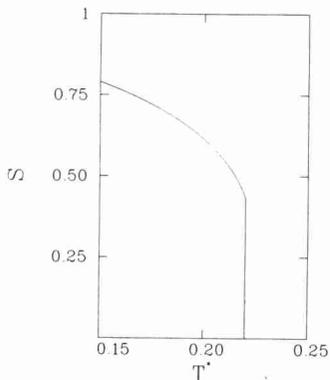


Fig. 7. Dependence of the nematic order parameter on the (reduced) temperature in the Maier–Saupe model (see text).

ventional' form (see e.g., ref. [5]). We write the single-particle distribution function $\rho_1(\boldsymbol{\Omega})$ as $\rho f(\boldsymbol{\Omega})$. We assume that the free energy $F(\rho, T)$ of a nematic liquid crystal can be written as a sum of three terms: 1) the free energy $F_I(\rho, T)$ of the isotropic liquid at the same density and temperature, 2) a term that reflects the loss in ideal-gas entropy due to the fact that in an orientationally ordered phase $f(\boldsymbol{\Omega})$ is no longer a constant: $\Delta F_{\text{id}} = kT \int \rho f(\boldsymbol{\Omega}) \log(4\pi \rho f(\boldsymbol{\Omega})) \, d\boldsymbol{\Omega}$ and 3) a term ΔF_{ex} that describes

the lowering of the excess free energy due to the orientational ordering. It is of course the latter term that contains all the interesting physics. Maier and Saupe considered the case where anisotropic dispersion interactions are the dominant ordering force. In that case, the leading contribution to ΔF_{ex} is of the form $\Delta U = -(U_2/2)S_2^2$. We then get the following expression for $F(\rho, T)$:

$$F(\rho, T) = F_1(\rho, T) + kT \int f(\boldsymbol{\Omega}) \log(4\pi\rho f(\boldsymbol{\Omega})) \, d\boldsymbol{\Omega} - \frac{U_2}{2} \left(\int f(\boldsymbol{\Omega}) P_2(\mathbf{n} \cdot \boldsymbol{\Omega}) \, d\boldsymbol{\Omega} \right)^2. \quad (2.9)$$

Next we minimize $F(\rho, T)$ with respect to $f(\boldsymbol{\Omega})$, with the constraint that f is normalized to 1. The variational equation has the following form:

$$\delta F(\rho, T) - \mu \int \delta f(\boldsymbol{\Omega}) \, d\boldsymbol{\Omega} = 0. \quad (2.10)$$

From eq. (2.10) we derive the following equation for f :

$$\log(4\pi f) = \mu - 1 + U_2 \langle P_2 \rangle P_2(\cos \theta). \quad (2.11)$$

The Lagrange-multiplier μ is fixed by the condition that $f(\cos \theta)$ is normalized:

$$f(\cos \theta) = \frac{\exp(w \cos^2 \theta)}{2\pi \int d \cos \theta \exp(w \cos^2 \theta)}, \quad (2.12)$$

where we have defined $w \equiv 3U_2 \langle P_2 \rangle / (2kT)$. Note that w still depends on the (as yet unknown) order-parameter $\langle P_2 \rangle$. This implicit dependence on $\langle P_2 \rangle$ can be resolved by imposing the self-consistency condition:

$$\langle P_2 \rangle = \frac{\int d \cos \theta P_2(\cos \theta) \exp(w \cos^2 \theta)}{\int d \cos \theta \exp(w \cos^2 \theta)}. \quad (2.13)$$

The reduced temperature kT/U_2 then follows, as: $kT/U_2 = 3\langle P_2 \rangle / (2w)$. Finally, the free energy follows from eq. (2.9). The transition from the isotropic to the nematic phase takes place at a reduced temperature $kT/U_2 = 0.22019 \dots$ where $F_1 = F_N$. At this temperature the order parameter jumps discontinuously from $S = 0$ to $S = 0.4289 \dots$ (incidentally, this is quite a reasonable value for the order-parameter of thermotropic nematics at the I-N transition). For $0.22019 > kT/U_2 > 0.2$ the isotropic phase is metastable. Below the latter temperature the isotropic phase is absolutely unstable. This is easily verified by expanding the free energy [eq. (2.9)] around $w = 0$. This very simple bifurcation analysis is a useful exercise. Figure 7 shows the order-parameter *vs* temperature diagram for the Maier-Saupe model.

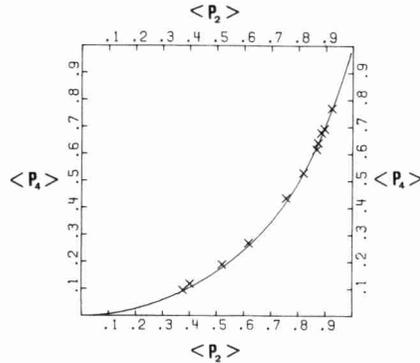


Fig. 8. Relation between the nematic order parameters $\langle P_2(\cos \theta) \rangle$ and $\langle P_4(\cos \theta) \rangle$ obtained by Monte Carlo simulation of thin hard platelets [15] (crosses) compared with the prediction of the Maier-Saupe theory (drawn curve).

The above presentation of the Maier-Saupe model contained no ‘molecular’ information, i.e., no attempt was made to justify the form of the free-energy function (eq. (2.9)). The reason is not that this form is difficult to justify. For instance, Maier and Saupe derived this mean-field model assuming that anisotropic dispersion forces are responsible for nematic ordering. Rather, the problem is that there are so *many* different intermolecular interactions that give rise to a ‘Maier-Saupe’-like free energy. As an illustration, consider the following example: we can employ the distribution function $f(\cos \theta)$ [eq. (2.12)] to compute the relation between $\langle P_2 \rangle$ and higher order-parameters, such as $\langle P_4 \rangle$. A plot of $\langle P_4 \rangle$ as a function of $\langle P_2 \rangle$ is shown in fig. 8. Also shown in this figure are the results of a computer simulation study of a system of infinitely thin, hard disks [15]. Clearly, the intermolecular interactions in this model system are totally different from the dispersion forces considered by Maier and Saupe. Still, the Maier-Saupe model does appear to account for the observed relation between $\langle P_2 \rangle$ and $\langle P_4 \rangle$. This forces us to think about mean-field models in more general terms.

A very elegant discussion of this problem was presented some years ago by Sluckin and Shukla [16]. These authors considered the isotropic-nematic transition in the context of density-functional theory. As the essential features of density-functional theory are discussed elsewhere in this volume, I shall limit myself to a brief sketch of the argument of ref. [16]. For simplicity I shall assume (unlike ref. [16]) that the density jump at the isotropic-nematic transition can be ignored. More precisely, I wish to compare the stability of isotropic and nematic states *at the same density*. Moreover, I shall consider the difference in Helmholtz free energy of the

isotropic and nematic phases $\Delta F \equiv F_N - F_I$ rather than the difference in grand potential $\Delta\Omega$ discussed in ref. [16]. Let us denote the density of the isotropic phase by ρ_I and the (orientation- dependent) density of the nematic phase by $\rho_N(\boldsymbol{\Omega}) \equiv \rho_I + \delta\rho_N(\boldsymbol{\Omega})$. The difference in Helmholtz free energy $\Delta F = F_N - F_I$ is expanded to second order in powers of $\delta\rho_N(\boldsymbol{\Omega})$:

$$\begin{aligned} \frac{\Delta F}{kT} &= \int d\mathbf{r} d\boldsymbol{\Omega} \rho_N(\boldsymbol{\Omega}) \log[\rho_N(\boldsymbol{\Omega})/\rho_I] \\ &\quad - \frac{1}{2} \int d\mathbf{r} d\boldsymbol{\Omega} d\mathbf{r}' d\boldsymbol{\Omega}' \delta\rho_N(\boldsymbol{\Omega}) \delta\rho_N(\boldsymbol{\Omega}') c_2(\mathbf{r}, \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}') + \dots, \end{aligned} \quad (2.14)$$

where we have used the fact that $\langle \rho_N \rangle = \langle \rho_I \rangle$. Next, we expand $\delta\rho_N$ in Legendre polynomials [see eq. (2.1)]:

$$\delta\rho_N(\boldsymbol{\Omega}) = \rho_I \sum_{\ell=2}^{\infty} \frac{2\ell+1}{4\pi} S_\ell P_\ell(\cos\theta) \quad (\ell \text{ even}).$$

Finally, we employ the fact that the two-body direct correlation function $c_2(\mathbf{x}, \mathbf{x}')$ (with $\mathbf{x} \equiv \{\mathbf{r}, \boldsymbol{\Omega}\}$) in the isotropic phase is translationally and rotationally invariant:

$$\begin{aligned} c_2(\mathbf{x}, \mathbf{x}') &= \sum_{\ell, \ell', \ell''} c_{\ell\ell'\ell''}(\Delta\mathbf{r}) \\ &\quad \times \begin{pmatrix} \ell & \ell' & \ell'' \\ m & m' & m'' \end{pmatrix} Y_{\ell m}(\boldsymbol{\Omega}) Y_{\ell' m'}(\boldsymbol{\Omega}') Y_{\ell'' m''}(\Delta\mathbf{r}), \end{aligned} \quad (2.15)$$

where $\Delta\mathbf{r} = \mathbf{r}' - \mathbf{r}$,

$$\begin{pmatrix} \ell & \ell' & \ell'' \\ m & m' & m'' \end{pmatrix}$$

is the Wigner 3J-symbol [17] and the $Y_{\ell m}$ represent spherical harmonics. Inserting equations (2.1) and (2.15) in eq. (2.14) and carrying out the integration over all angular variables, we obtain:

$$\frac{\Delta F}{kT} = \int d\mathbf{r} d\boldsymbol{\Omega} \rho_N(\boldsymbol{\Omega}) \log[\rho_N(\boldsymbol{\Omega})/\rho_I] - \frac{1}{2} \sum_{\ell} U_{\ell} S_{\ell}^2, \quad (2.16)$$

where we have defined U_{ℓ} as:

$$U_{\ell} \equiv \rho_I^2 \sqrt{\frac{2\ell+1}{4\pi}} \int_0^{\infty} c_{\ell\ell 0}(r) r^2 dr. \quad (2.17)$$

If we truncate equation (2.16) at the lowest order in ℓ , we recover the free-energy expression [eq. (2.9)] that formed the starting point of the Maier–Saupe theory. But now the coefficient of S_2^2 has a simple statistical mechanical interpretation: it is directly related to the integral of the function $c_{220}(R)$, and the latter function can be obtained from a spherical-harmonics expansion of the two-body direct correlation function of the isotropic fluid. Note however that, even if $c_2(\mathbf{r}, \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}')$ were known, eq. (2.16) would not be exact, because it is based on second-order density-functional theory. Only in the case of the Onsager model (see section 2.4 below) are higher order terms negligible.

Not surprisingly, the original version of the Maier–Saupe model can be recovered by assuming that for a weak, anisotropic dispersion interactions $U(\mathbf{x}, \mathbf{x}')$, $c_2(\mathbf{x}, \mathbf{x}')$ may be replaced by $-U(\mathbf{x}, \mathbf{x}')/kT$. For more details, the reader is referred to ref. [16].

After this long introductory discussion of approximate schemes to model the nematic phase, the reader is probably desperate for some hard facts. At first sight it would seem too much to expect any *exact* results. After all, even for atomic liquids there is not a single non-trivial model that can be solved exactly (in three dimensions). So how can we expect exact results for fluids consisting of non-spherical molecules. Fortunately, the situation is different. Liquid-crystal physics has its (almost) exactly solvable model. It was introduced by Onsager in 1942 (and published in 1949 [2]). In fact, Onsager did not bother to find the ‘exact’ solution (because it could not be obtained in closed form), but others have done so since [18,19]. In the next section, the Onsager model is briefly discussed.

2.4. Onsager model

The model that Onsager considered is a gas of thin, hard spherocylinders of length L and diameter D , in the limit that the ratio $L/D \rightarrow \infty$. We wish to compute the Helmholtz free energy of a system of N such rods as a function of density (ρ). There are several ways to do this. The simplest is to consider the cluster expansion of the free energy [20]. For an isotropic fluid, this expansion reads:

$$\frac{F}{NkT} = c(T) + \log \rho - 1 - \frac{\beta_1}{2} \rho - \frac{\beta_2}{3} \rho^2 + \dots, \quad (2.18)$$

where $c(T)$ is a constant that depends only on temperature and β_n are the irreducible Mayer cluster integrals [20]. The latter are related to the

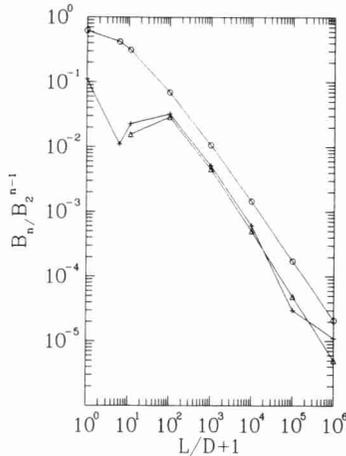


Fig. 9. Third (circles), fourth (triangles) and fifth (pluses) virial coefficients of hard spherocylinders as a function of the length-to-width ratio L/D . The n -th virial coefficient are expressed in units of the B_2^{n-1} . Note that these higher-order virial coefficients tend to zero as $L/D \rightarrow \infty$. The fourth virial coefficient is in fact negative for large L/D . The figure shows $-B_4/B_2^3$.

virial coefficients B_n by: $B_{n+1} = -n/(n+1)\beta_n$. In particular, for a hard-core fluid $-\beta_1 = v_{\text{excl}}$, where v_{excl} is the average excluded volume of two hard-core molecules. In what follows I shall omit all constants that are independent of density. We can now rewrite eq. (2.18) as:

$$\frac{F}{NkT} = \log \rho + \rho B_2 + \frac{B_3}{2B_2^2}(\rho B_2)^2 + \dots \quad (2.19)$$

Equation (2.19) allows as to evaluate F if: [1] The virial series for F converges rapidly and [2] The relevant virial coefficients are known. These restrictions usually limit the applicability of eq. (2.19) to the dilute gas phase. However, for the Onsager model the situation is different. The reason is that for a system of spherocylinders with $L/D \rightarrow \infty$ the contribution to eq. (2.19) of all virial coefficients beyond the second goes to zero. More precisely: Onsager showed that for large L/D the ratio $B_3/B_2^2 \approx \log(L/D)/(L/D)$. In addition, he *assumed* that the ratio B_n/B_2^{n-1} for $n > 3$ vanishes in the same limit. In fact, for purely geometric reasons it is indeed plausible that $B_3/B_2^2 \approx \log(L/D)/(L/D)$ while the leading contribution to B_n/B_2^{n-1} for $n > 3$ is proportional to D/L (this is left as an exercise to the reader). A quantitative measure of the first five virial coefficients of the spherocylinder system was obtained by computer simulation [21]. The result of these simulations is shown in fig. 9. The figure shows that, indeed, all higher virial coefficients tend to zero. However,

it also shows that quite long rods are needed before these higher order coefficients become negligible. In the limit $L/D \rightarrow \infty$, all higher-order terms in eq. (2.19) may be neglected at all finite densities ($\rho B_2 \ll L/D$).

Up to this point we have assumed that the system is isotropic. However, we should allow for the possibility that an orientationally ordered phase has a lower free energy. We shall therefore rewrite eq. (2.18) for a system with an arbitrary orientational distribution function $f(\boldsymbol{\Omega})$. In that case the single-particle density distribution is of the form: $\rho_1(\boldsymbol{\Omega}) = \rho f(\boldsymbol{\Omega})$.

$$F/(NkT) = \log \rho + \int d\boldsymbol{\Omega} f(\boldsymbol{\Omega}) \log(4\pi f(\boldsymbol{\Omega})) + \frac{\rho}{2} \int d\boldsymbol{\Omega} d\boldsymbol{\Omega}' f(\boldsymbol{\Omega}) f(\boldsymbol{\Omega}') v_{\text{excl}}(\boldsymbol{\Omega}, \boldsymbol{\Omega}') + O(\rho^2), \quad (2.20)$$

where $v_{\text{excl}}(\boldsymbol{\Omega}, \boldsymbol{\Omega}')$ is the pair-excluded volume of two spherocylinders with orientations $\{\boldsymbol{\Omega}, \boldsymbol{\Omega}'\}$. The orientation of a spherocylinder can be specified by a unit-vector $\hat{\mathbf{u}}$ along the molecular axis. $v_{\text{excl}}(\boldsymbol{\Omega}, \boldsymbol{\Omega}')$ is a function of the relative angle $\gamma = \arccos \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}'$:

$$v_{\text{excl}} = \frac{4}{3}\pi D^3 + 2\pi L D^2 + 2L^2 D |\sin \gamma|.$$

For large values of L/D the dominant term is $2L^2 D |\sin \gamma|$. In the same limit the average pair-excluded volume in the isotropic phase is $\langle v_{\text{excl}} \rangle_{\text{I}} = 2B_2 = \pi L^2 D/2$. We can now minimize F [eq. (2.20)] with respect to $f(\boldsymbol{\Omega})$. This leads to the following (non-linear) integral equation for f :

$$0 = \lambda + \log(4\pi f(\boldsymbol{\Omega})) + \rho B_2 \frac{8}{\pi} \int d\boldsymbol{\Omega}' f(\boldsymbol{\Omega}') |\sin \gamma|, \quad (2.21)$$

where λ is an, as yet undetermined, constant (Lagrange multiplier) that will be fixed by the condition that f is normalized. Onsager did not solve eq. (2.21) exactly but showed: [1] that the isotropic solution becomes unstable for $\rho B_2 \geq 4$ and [2] that a trial function for f of the form:

$$f(\cos \theta) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha \cos \theta)}{\sinh \alpha}$$

yields a strong first-order phase transition. Onsager's estimate of the densities of the coexisting phases is: $\rho_{\text{I}} B_2 = 3.3399$ and $\rho_{\text{N}} B_2 = 4.4858$. The 'exact' answers [18,19] are: $\rho_{\text{I}} B_2 = 3.2906$ and $\rho_{\text{N}} B_2 = 4.2230$. At coexistence, the value of the order parameter in the nematic phase is $\langle P_2 \rangle = 0.784$.

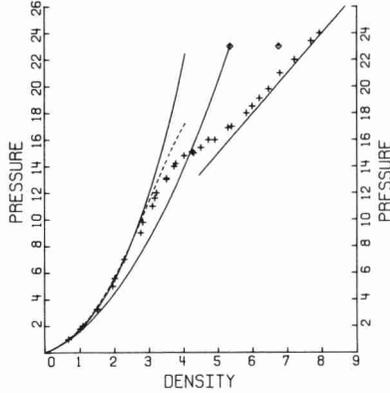


Fig. 10. Equation-of-state of a system of infinitely thin, hard platelets [15]. Monte Carlo results: crosses. Five-term virial series: dashed curve. For this model the Onsager assumption that virial coefficients higher than the second can be ignored leads to an incorrect prediction for the location of the isotropic–nematic transition (diamonds). For the meaning of the drawn curves, see ref. [15].

For a discussion of an approximate solution of the Onsager model, see Appendix A.

2.4.1. Discussion

In many respects, the system of thin hard rods is the ‘Ising model’ of liquid-crystal physics. It is certainly no coincidence that the 2D Ising model was also solved by Onsager. The existence of such an exactly solvable model for a liquid crystal confronts us with several questions. I shall name a few: [A] Is this the *only* exactly solvable model? [B] Is it a useful starting point for a ‘perturbation’ approach? and [C] How does it compare with the real world?

A. *Other exactly solvable models?* Let me begin with the first question. The Onsager model has been extended to mixtures of rods of different length [22]. However, it is my impression that the basic idea behind the model could be exploited in other directions. The essence is to make a model for a fluid of particles with proper volume v_0 and virial coefficients B_n , such that $v_0/B_2 \rightarrow 0$ and $B_n/B_2^{n-1} \rightarrow 0$. Thin hard rods are the simplest geometrical shape that yields such behaviour. However, one could consider ‘molecules’ consisting of two or more hard rods, assembled into rigid (or even non-rigid) objects with a ‘loop-free’ pair-excluded volume. For instance, of particular interest would be molecules of three perpendicular rods, joined at their mid-points. Such a model system will not (I suppose) form a nematic phase. Yet the pair-excluded volume does depend on the relative orientation of the

molecules in such a way that parallel alignment is favoured (although less strongly than in the case of rods). Hence at sufficiently high density such a system should be orientationally ordered, yet translationally disordered, i.e., a ‘cubatic’ liquid crystal (see Appendix B).

B. *Perturbation series?* The answer of the second question is very much a matter of words. One may take the point of view that the Onsager model is an example of a system where second-order density functional theory is exact. It is clearly interesting to apply density-functional theory to molecules with less extreme shapes. In that case one must go beyond second-order. This is certainly a worthwhile enterprise (see below). What is *not* advisable, is to simply assume that second-order density functional theory is also valid for other molecules. This is strikingly illustrated by the behaviour of a model system consisting of infinitely thin, hard platelets with diameter σ . This system is interesting because, at the level of the second-order theory, it is *identical* to the Onsager model. In particular, the pair-excluded volume v_{excl} equals $(\pi\sigma^3/2)\sin\gamma = (8/\pi)B_2\sin\gamma$. Hence, if all higher order terms could be ignored the I-N transition would be located at a reduced density $\rho_I\sigma^3 = 5.3345$ and $\rho_N\sigma^3 = 6.846$. In fact, Monte Carlo simulations [15] indicate that this prediction fails badly. The actual transition densities are at $\rho_I\sigma^3 = 4.04$ and $\rho_N\sigma^3 = 4.12$ (see fig. 10). The density jump at the transition is much smaller than in the Onsager model ($\sim 2\%$ instead of $\sim 30\%$) and the value of the nematic order parameter at coexistence is 0.3-0.4.

Finally, the Onsager model cannot be used as a reference system for a van der Waals-type perturbation theory. The reason is simple: in such a theory the effect of attractive interactions is to add a term $-a\rho$ to the free energy. In simple liquids this term is harmless because at any density it can be compensated by the (positive) excluded-volume contribution to the free energy. For the Onsager model this does not work. At high densities the hard-core contribution to the free energy goes as $3\log\rho$. Hence, at sufficiently high density the attractive term will always dominate and the system will collapse. Of course, this behaviour peculiar to systems of particles with zero volume.

C. *Real world?* The Onsager model was originally devised to model systems of rigid rod-like colloidal particles. This it does quite well (for a recent discussion, see [23]). There are several sources of discrepancy between the simple theory and experiment. Most important among these are the following:

(a) Real rod-like colloids are not completely rigid. This has a pronounced effect on the location of the I-N phase transition. Odijk [24] has studied the effect of flexibility on the location of the I-N transition and on the

properties of the nematic phase in the context of the Onsager model.

(b) The interaction potential between rod-like colloids is not really a hard-core. This point was already discussed by Onsager. More recently, Stroobants et al. [22] have analysed the effect of screened Coulomb interactions on the ordering transition in systems of rod-like colloids.

(c) In practice, the limit $L/D \rightarrow \infty$ is never achieved. In colloidal systems very large L/D values are possible, but for thermotropic liquid crystals the length-to-width ratio of the molecules is usually of the order $L/D = 4$. Hence, the Onsager model is of little value for thermotropic liquid crystals. Unfortunately, this has resulted in a distinct unpopularity of excluded volume models among researchers in the field of thermotropic liquid-crystals.

2.5. Computer simulation

What has been missing from the discussion thus far is the observation that most molecular liquids freeze rather than form a liquid crystal. In the case of the phenomenological Landau–de Gennes theory freezing does not occur because the possibility of solid order is not built into the form of the free energy expansion. Neither does the Maier–Saupe theory allow for the possibility of crystallization. In fact, the Maier–Saupe model might just as well describe orientational freezing of a plastic molecular crystal as nematic ordering of an isotropic molecular liquid. In the Onsager model there is no need to consider freezing because this is expected to take place at a much higher density than the I–N transition. More precisely, nematic ordering of thin hard rods takes place when $\rho_{\text{IN}}L^2D$ is of order 1. In contrast, freezing will take place when $\rho_f v_0 \propto \rho_f LD^2$ is approaching the value 1. Hence the ratio $\rho_f/\rho_{\text{IN}} \sim L/D$. Moreover, in the vicinity of the freezing point the Onsager model is no longer tractable because the higher-order virial coefficients are no longer negligible. Hence, if we wish to study the competition between liquid-crystal and crystal formation we must look for other models. In the absence of exactly solvable models, the only way to obtain ‘hard’ information is by computer simulation.

With computer simulation it is, in principle, possible to compute the properties of *any* model for a classical many-body system. The choice of the model is determined by the nature of the question that we wish to answer. In the present case we are interested in crystalline and liquid-crystalline ordering in simple models for molecular liquids. What is the most appropriate model? There is no unique answer to this question. Several mechanisms have been invoked to explain the onset of liquid crystalline ordering. Two of these I have already mentioned, namely: non-spherical excluded-volume

effects (Onsager), anisotropic attraction forces (Maier–Saupe). However, there are other factors that can play a role. For instance, for thermotropics, the tendency of molecules to form liquid crystals depends strongly on the nature of the flexible side-chains attached to the rigid core of the molecule [25], while the angle-dependence of the effective attractive forces depends on the shape of the non-spherical hard core of the molecule [26]. For lyotropics, molecular flexibility and polydispersity both have a pronounced effect on the tendency to form a liquid crystal. All these factors are real. However, it would be very unwise to try to take everything into account at once. It is inevitable that a choice is made between primary and secondary factors.

In the case of freezing of molecular liquids the situation is similar: attraction, repulsion and flexibility all play a role. For instance, we know that the presence of flexible side-chains in a molecule makes the formation of a molecular crystal entropically less favourable. Only for *atomic* liquids the picture is clear. Since the work of Alder and Wainwright [27] it is known that the freezing of atomic liquids is primarily an excluded volume effect. That does not imply that attractive forces do not affect the location of the freezing point (they do). But the structure of the coexisting phases is largely determined by the harsh repulsive interactions between the atoms. The effect of attraction can be considered a perturbation [28].

If freezing can be understood in terms of excluded volume effects alone, it is natural to ask how far we can push this idea in the case of liquid crystalline ordering. Our aim then is to study the simplest possible hard-core models that may form both crystalline and liquid-crystalline phases.

It should be noted that an alternative approach has been followed by Luckhurst and collaborators [29]. Following the pioneering work of Lebwohl and Lasher [30], these authors focused on the effect of anisotropic intermolecular interactions of the form $v_{ij} = -J_{ij}P_2(\cos\theta_{ij})$. The choice of the Lebwohl–Lasher model was inspired by the original justification of the Maier–Saupe theory in terms of anisotropic dispersion forces. However, the discussion in section 2.3 suggests that there are many possible mechanisms that lead to an effective interaction potential of this form. It should be noted that in simulations of models such as the one introduced by Lebwohl and Lasher it is assumed that the molecules are on a periodic lattice. In that case the ‘I–N’ transition may also be interpreted as a rotational order-disorder transition in a crystalline solid.

Computer simulations of hard-core models for two-dimensional liquid crystals were pioneered by Vieillard-Baron in the early seventies [31]. Vieillard-Baron also made much progress towards the study of three-dimensional model systems [32], but did not observe spontaneous nematic

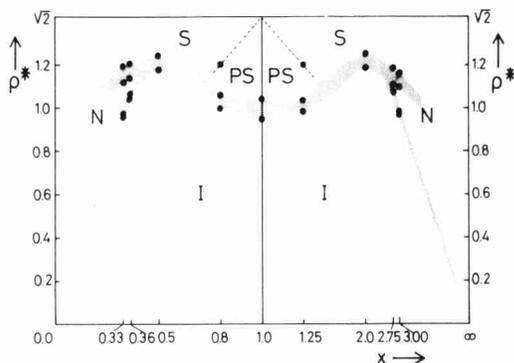


Fig. 11. 'Phase diagram' of a system of hard ellipsoids of revolution [33]. The ratio of the length of the semi-major to the semi-minor axis is denoted by x . The reduced density ρ^* is defined such that the density of regular close packing is equal to $\sqrt{2}$ for all x . The shaded areas indicate two-phase regions associated with a first-order phase transition. The following phases can be distinguished: **I**: Isotropic fluid. **S**: orientationally ordered crystalline solid. **PS**: Orientationally disordered ('plastic') crystal, and **N**: Nematic liquid-crystalline phase. The densities of coexisting phases at a first order phase transition (black dots) were computed in a free-energy calculation. Note that no stable nematic is possible for $0.4 < x < 2.5$.

ordering in 3D. The first systematic simulation study of a three-dimensional hard-core nematogen was performed by Frenkel and Mulder [33] who studied a system of hard ellipsoids-of-revolution for a range of length-to-width ratios.

The shape of hard ellipsoids of revolution is characterized by a single parameter, x , the ratio of the length of the major axis ($2a$) to that of the minor axis ($2b$): $x = a/b$. Prior to the simulations reported in ref. [33], the phase behaviour of hard spheroids was only known for a few special values of x , viz.: $x = 1$: hard spheres, which freeze at $2/3$ of close packing [34]. $x \rightarrow \infty$: thin hard needles, because this limit is equivalent to the Onsager's model. The latter system has a transition to the nematic phase at vanishing volume fraction. And $x \rightarrow 0$: thin hard platelets, which also form a low-density nematic [15].

The simulations of ref. [33] were performed for values of x between 3 and $1/3$. In order to locate all phase transitions, the absolute free energy of all phase was computed. Figure 11 shows how the stability of the different phases of hard ellipsoids depend on their length-to-width ratio. Four distinct phases can be identified, namely the low-density isotropic fluid, an intermediate-density nematic liquid crystalline phase, which is only stable if the length-to-width ratio of the ellipsoids is larger than 2.5 or less than

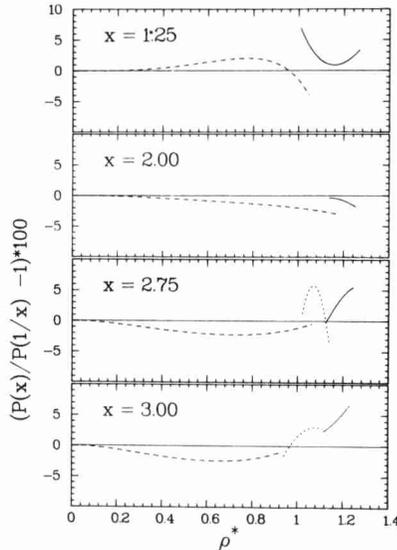


Fig. 12. Ratio of the pressure of a system of hard ellipsoids of revolution with inverse length-to-width ratios x and $1/x$. For the values of x studied in the Monte Carlo simulations of ref. [33] this ratio is very close to 1. In fact, for the isotropic phase (dashed curve), the difference from unity is less than 3%.

0.4, and a high-density orientationally ordered solid phase. In the case of weakly anisometric ellipsoids, an orientationally disordered solid phase was also observed. Perhaps the most striking feature of the phase diagram in fig. 11 is the near symmetry between the behaviour of oblate and prolate ellipsoids with inverse length-to-width ratios. In fact, this behaviour is also exhibited by the pressure (see fig. 12) which is also remarkably insensitive to the permutation of x and $1/x$. At low densities such behaviour is to be expected because the second virial coefficient $B_2(x)$ equals $B_2(1/x)$. However, no such relation holds between the third and higher virial coefficients. To give a specific example: in the limit $x \rightarrow \infty$ (the Onsager limit), $B_3/B_2^2 \rightarrow 0$, whereas for $x \rightarrow 0$ (hard platelets [15]) $B_3/B_2^2 \rightarrow 0.4447(3)$. For larger anisotropies than studied in the simulations of ref. [33] one should expect to see asymmetric behaviour in the location of the isotropic-nematic transition. It is doubtful, however, if the near symmetry of the melting line will be much affected. Strongly aligned rods and platelets follow the same equation of state ($P = 3\rho$) and a simple estimate of the melting point of very anisometric ellipsoids [35] suggests that in the limit $x \rightarrow \infty$ the symmetry between oblate and prolate ellipsoids is still present.

Another point to note about the phase transitions in the hard-ellipsoid

system is that for particles with $3 \geq x \geq (1/3)$ the relative density-jump at the I–N transition is much smaller than for the Onsager model. Typically, the density changes only by some 2% at the I–N transition. For technical details the reader is referred to ref. [33]. Hence the very large density discontinuity at the I–N transition in the Onsager model is peculiar to long rods and not to hard-core models in general.

2.6. Theoretical description

The numerical simulation of the phase diagram of hard ellipsoids of revolution provided theoreticians with an opportunity to compare analytical theories for the isotropic–nematic transition with ‘exact’ numerical data. Several rather different theoretical approaches have been tested in this way. Actually, this work was predated by the scaled-particle for the isotropic–nematic transition constructed by Cotter and Martire [36,37]. However, this scaled-particle theory was worked out for hard spherocylinders and could only be compared with simulation data for the isotropic phase.

The first statistical mechanical theory for the I–N transition in a fluid of hard ellipsoids was developed by Mulder [38] who followed the so-called ‘*y*-expansion’ approach of Barbooy and Gelbart [39]. Mulder found that the *y*-expansion led to a slight over-estimate of the pressure in the isotropic phase and that the isotropic–nematic transition was predicted to occur at too low a density. Moreover, the density-jump at this transition was predicted to be larger than observed in the simulations. However, the very symmetric appearance of the phase-diagram was well reproduced by the theory of ref. [38].

Subsequently, several authors have applied density-functional theory to the study of the isotropic–nematic transition of hard ellipsoids. The first such theory was formulated by Singh and Singh [40]. These authors also discussed the freezing transition of hard ellipsoids and used density-functional theory to estimate the stability of the plastic crystalline state. Subsequently, alternative density-functional theories for hard ellipsoids of revolution were presented by Baus et al. [41] and by Marko [42]. A good discussion of the relative merits of these theories can be found in the article by Colot, Wu, Xu and Baus [43].

A rather different approach was followed by Perera et al. [44]. These authors studied the generalization to convex hard-body fluids of the Percus–Yevick (PY) and Hypernetted Chain (HNC) integral equations that are known to be quite successful for simple fluids [20]. Perera et al. found that for hard ellipsoids of revolution the PY approach failed to predict the existence of a stable nematic phase. In contrast, the HNC theory yielded a

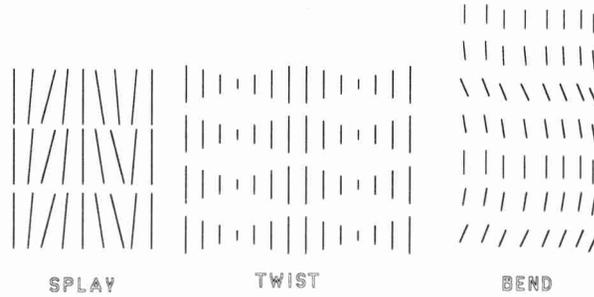


Fig. 13. Schematic representation of the splay, twist and bend deformations in a nematic liquid crystal. In the 'twist' case a rotation of the molecules out of the plane of the drawing is indicated by a shortening of the line-segments.

fair estimate of the location of the isotropic–nematic transition (or, to be more precise, of the density where the isotropic phase becomes mechanically unstable).

3. Elastic constants

Nematic liquid crystals are ordered liquids. This has interesting consequences for the mechanical properties of these materials. In particular, nematics exhibit elastic behaviour. To be precise, any attempt to deform the uniform alignment of the director in a nematic results in an elastic restoring force. The constants of proportionality between deformation and restoring force are known as the Frank constants. On basis of symmetry arguments it can be shown that in a uniaxial nematic there are 3 independent elastic constants (see e.g., [5]). Here I shall follow a 'derivation' of the expression for the deformation free energy of a nematic given by Ping Sheng and Priestley [45]. This derivation is not rigorous (it is even incorrect in that it predicts that the three elastic constants are not all independent). But it does provide insight in the physical meaning of the Frank constants.

Our starting point is the Landau–de Gennes expression for the free-energy density associated with order-parameter fluctuations in the *isotropic* phase: eq. (2.8) in section 2.2:

$$\begin{aligned}
 F = F_0 &+ \frac{2}{3}a(T - T^*)Q_{\alpha\beta}Q_{\beta\alpha} + BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} \\
 &+ C_1(Q_{\alpha\beta}Q_{\beta\alpha})^2 + C_2Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha} + \dots \\
 &+ \frac{L_1}{2}\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma} + \frac{L_2}{2}\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + \dots
 \end{aligned}$$

Using equation (2.4) in section 2.1:

$$\mathbf{Q} = S \frac{3\mathbf{nn} - \mathbf{I}}{2}$$

we can rewrite eq. (2.8) in terms of the *local* order parameter $S(r)$ and the *local* director $\mathbf{n}(r)$:

$$\begin{aligned} F = F_0 + \frac{1}{2}a(T - T^*)S^2(r) + \frac{3}{4}BS^3(r) + \frac{9}{4}[C_1 + C_2/2]S^4(r) \\ + \frac{9}{4}L_1S^2(r)\partial_\alpha n_\beta(r)\partial_\alpha n_\beta(r) \\ + \frac{9}{8}L_2S^2(r)[\nabla \cdot \mathbf{n}(r)]^2 + \frac{9}{8}L_2S^2(r)[\mathbf{n}(r) \times (\nabla \times \mathbf{n}(r))]^2 + \dots \end{aligned} \quad (3.1)$$

where the \dots include all terms that contain gradients of $S(r)$. We shall now simply assume that eq. (3.1) is also valid in the nematic phase. In particular, we assume that the magnitude of the order parameter is everywhere equal to the average order parameter S . In that case, the terms on the right-hand side of the first line of eq. (3.1) simply yield some constant c , while all the terms containing gradients of $S(r)$ can be neglected. In addition, we employ the relation:

$$\begin{aligned} \partial_\alpha n_\beta \partial_\alpha n_\beta = [\nabla \cdot \mathbf{n}]^2 + [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 \\ + [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 - \nabla \cdot [\mathbf{n}(\nabla \cdot \mathbf{n}) + \mathbf{n} \times \nabla \times \mathbf{n}]. \end{aligned}$$

Upon integration, the last term yields a surface contribution which can be neglected if we are only interested in bulk properties. Finally, we obtain:

$$\begin{aligned} F = c + \frac{9}{4}S^2(r)\{(L_1 + L_2/2)[\nabla \cdot \mathbf{n}(r)]^2 + L_1[\mathbf{n}(r) \cdot \nabla \times \mathbf{n}(r)]^2 \\ + (L_1 + L_2/2)[\mathbf{n}(r) \times \nabla \times \mathbf{n}(r)]^2\}. \end{aligned} \quad (3.2)$$

Equation (3.2) strongly resembles the usual expression for the deformation free-energy density in a nematic:

$$F = c + \frac{1}{2}\{K_1[\nabla \cdot \mathbf{n}(r)]^2 + K_2[\mathbf{n}(r) \cdot \nabla \times \mathbf{n}(r)]^2 + K_3[\mathbf{n}(r) \times \nabla \times \mathbf{n}(r)]^2\} \quad (3.3)$$

where K_1, K_2 and K_3 are, respectively, the Frank elastic constants for 'splay', 'twist' and 'bend'. The director patterns corresponding to typical long-wavelength periodic splay, twist and bend deformations are shown in fig. 13. I have chosen to display periodic director variations, because I find the drawing of splay, twist and bend deformations that one finds in

most publications rather misleading. According to eqs. (3.2) and (3.3): $K_1 = (9/2)S^2(L_1 + L_2/2)$, $K_2 = (9/2)S^2L_1$ and $K_3 = K_1$. This suggests that the Frank elastic constants are proportional to the square of the nematic order parameter, provided that the constants L_1 and L_2 do not vary strongly through the I-N transition. The prediction $K_1 = K_3$ is an artifact of the present derivation in which we only considered gradient terms of the second-order tensor order parameter. If higher rank order parameters are included in the expansion, all three elastic constants will in general be different [46].

Next consider how one should compute the Frank elastic constants. The most direct way is to evaluate the difference in free-energy per unit volume between a uniformly aligned nematic and the same substance under slowly varying deformation of a given type. On a molecular level, the effect of a variation of the director is to make the single-particle density $\rho f(\boldsymbol{\Omega})$ a function of position. The natural language to describe the effect of a variation in the single-particle density on the free energy is density-functional theory. In the limit of very slowly varying deformations the local density and structure of the nematic is not affected by the director deformation. Hence, while the local alignment axis \mathbf{n}' varies in space, the local orientational distribution function $f(\mathbf{n}' \cdot \mathbf{u})$ has the same functional form as $f_0(\mathbf{n} \cdot \mathbf{u})$ in the undeformed sample. Following Poniewierski and Stecki [47] in spirit (but not in notation), and expanding the free energy to second order in $(f - f_0)$

$$\begin{aligned} \frac{\Delta F}{kT} = & -\frac{1}{2}\rho^2 \int d\mathbf{r} d\boldsymbol{\Omega} d\mathbf{r}' d\boldsymbol{\Omega}' (f(\mathbf{r}, \mathbf{n}' \cdot \boldsymbol{\Omega}) - f_0(\mathbf{r}, \mathbf{n} \cdot \boldsymbol{\Omega})) \\ & \times (f(\mathbf{r}', \mathbf{n}' \cdot \boldsymbol{\Omega}') - f_0(\mathbf{r}', \mathbf{n} \cdot \boldsymbol{\Omega}')) c_2(\mathbf{r}, \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}'). \end{aligned} \quad (3.4)$$

Equation (3.4) is the starting point (in some cases *a posteriori* [48-50]) for most molecular theories of the Frank elastic constants. Note that the deformation free energy is invariant under a *global* rotation of the orientation of the director of the undeformed state. This allows us rewrite eq. (3.4) in the following way. We transform to new coordinates $\mathbf{R} \equiv (\mathbf{r} + \mathbf{r}')/2$ and $\Delta\mathbf{r} \equiv (\mathbf{r} - \mathbf{r}')$. We first perform the integration over $\Delta\mathbf{r}$ at fixed \mathbf{R} taking as the direction of the director of the uniform reference state the value of \mathbf{n} at \mathbf{R} . The distribution functions at \mathbf{r} and \mathbf{r}' is obtained by Taylor expansion:

$$\begin{aligned} f(\mathbf{n}(\mathbf{R} + \frac{\Delta\mathbf{r}}{2}) \cdot \boldsymbol{\Omega}) = & f(\mathbf{n}(\mathbf{R}) \cdot \boldsymbol{\Omega}) + \frac{\Delta\mathbf{r} \cdot \nabla_{\mathbf{R}}}{2} f(\mathbf{n}(\mathbf{R}) \cdot \boldsymbol{\Omega}) \\ & + \frac{1}{2} \left(\frac{\Delta\mathbf{r} \cdot \nabla_{\mathbf{R}}}{2} \right) \left(\frac{\Delta\mathbf{r} \cdot \nabla_{\mathbf{R}}}{2} \right) f(\mathbf{n}(\mathbf{R}) \cdot \boldsymbol{\Omega}) + O(\Delta^3\mathbf{r}). \end{aligned} \quad (3.5)$$

After partial integration, eq. (3.4) reduces to:

$$\frac{\Delta F}{kT} = \frac{1}{4}\rho^2 \int d\mathbf{R} d\Delta\mathbf{r} d\boldsymbol{\Omega} d\boldsymbol{\Omega}' f'(\mathbf{n} \cdot \boldsymbol{\Omega})f'(\mathbf{n} \cdot \boldsymbol{\Omega}') \\ \times [\Delta\mathbf{r} \cdot \nabla_R(\mathbf{n} \cdot \boldsymbol{\Omega})][\Delta\mathbf{r} \cdot \nabla_R(\mathbf{n} \cdot \boldsymbol{\Omega}')] c_2(\Delta\mathbf{r}, \boldsymbol{\Omega}, \boldsymbol{\Omega}'). \quad (3.6)$$

To compute a particular Frank constant we impose a director pattern that corresponds to a pure splay, twist or bend deformation. For instance, to compute K_1 we could choose:

$$\mathbf{n}(\mathbf{R}) = \hat{z} + \epsilon X \hat{x}$$

with ϵ small. For this deformation, $\nabla \cdot \mathbf{n} = \epsilon$ and $\Delta\mathbf{r} \cdot \nabla_R(\mathbf{n} \cdot \boldsymbol{\Omega}) = \epsilon \Delta x \Omega_x$. Hence,

$$K_1 = \frac{\rho^2 kT}{2} \int d\mathbf{R} d\Delta\mathbf{r} d\boldsymbol{\Omega} d\boldsymbol{\Omega}' \\ \times f'(\mathbf{n} \cdot \boldsymbol{\Omega})f'(\mathbf{n} \cdot \boldsymbol{\Omega}') \Delta^2 x \Omega_x^2 c_2(\Delta\mathbf{r}, \boldsymbol{\Omega}, \boldsymbol{\Omega}'). \quad (3.7)$$

As usual, the problem is that knowledge of the direct correlation function is required. In the Onsager model c_2 is known exactly (it is equal to $-v_{\text{excl}}(\mathbf{r}, \mathbf{r}', \boldsymbol{\Omega}, \boldsymbol{\Omega}')$). And for this model calculations of the elastic constants were performed approximately by Priest [48] and Straley [49], and essentially exactly by Poniewierski and Stecki [47] and Lee and Meyer [50]. For the Onsager model $K_1 = 3K_2$ [51]. Odijk has shown that in the Gaussian approximation (see section 2.4) very simple analytical expressions result for the elastic constants [51]:

$$K_1 = \frac{7c}{8\pi}, \quad K_2 = \frac{K_1}{3}, \quad K_3 = \frac{4c^3}{3\pi^2}, \quad (3.8)$$

where $c \equiv B_2\rho$. Equation (3.8) clearly shows that K_3 , the bend elastic constant, has a much stronger density dependence than K_1 and K_2 . The Gaussian approximation is particularly useful to estimate elastic constants in mixtures of hard-rods and in systems consisting of semi-flexible molecules. For more details, see [51–53].

In general, the direct correlation function in eq. (3.4) is not known and must be approximated. In models that stress the importance of long-range anisotropic interactions (i.e., the usual context of the Maier–Saupe model) the most logical choice is to write the anisotropic part of $c_2(r_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$ as $-U(r_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)/kT$ (see e.g., ref. [54]). Over the last two years there has

been much progress in the development of density-functional techniques to compute Frank elastic constants of hard-core nematics (see e.g., refs. [55–57,75]). The crucial point in these theories is to find an accurate representation of the direct correlation function.

In this context it would be highly desirable to have accurate simulation data on c_2 . Unfortunately, a simple method to ‘measure’ c_2 in a computer experiment seems to be lacking. However, it is possible to measure the Frank elastic constants themselves in a simulation (although, unfortunately, not very accurately). The method that is used to estimate the Frank elastic constants in a simulation is to measure the mean-square amplitude of certain director fluctuations. In spirit, this technique is identical to an experimental method to extract the value of K_i from the intensity of light scattered by director fluctuations (see e.g., ref. [5]).

Consider a nematic with the average director \mathbf{n}_0 along the z -axis. To first order, a fluctuation in the orientation of the director will be perpendicular to the director itself. This is so because the director is a unit vector: hence $\delta(\mathbf{n} \cdot \mathbf{n}) = 2\mathbf{n} \cdot \delta\mathbf{n} \approx 2\mathbf{n}_0 \cdot \delta\mathbf{n} = 0$. Therefore $\delta\mathbf{n}$ lies in the xy -plane. Let us now consider equation (3.3) in Fourier-transformed form:

$$F = c + \frac{1}{2V} \sum_{\mathbf{q}} \{K_1[\mathbf{q} \cdot \mathbf{n}(\mathbf{q})]^2 + K_2[\mathbf{n}_0 \cdot (\mathbf{q} \times \mathbf{n}(\mathbf{q}))]^2 + K_3[\mathbf{n}_0 \times \mathbf{q} \times \mathbf{n}(\mathbf{q})]^2\}. \quad (3.9)$$

It is convenient to transform to a different coordinate system in which the director fluctuations are decomposed in a component $n_2(\mathbf{q})$ perpendicular to \mathbf{q} and a component $n_1(\mathbf{q})$ perpendicular to both \mathbf{n}_0 and n_2 . Similarly, we decompose \mathbf{q} in components q_{\parallel} and q_{\perp} that are respectively parallel and perpendicular to \mathbf{n}_0 . With these definitions, equation (3.9) becomes:

$$F = c + \frac{1}{2V} \sum_{\mathbf{q}} \sum_{\alpha=1,2} |n_{\alpha}(\mathbf{q})|^2 (K_3 q_{\parallel}^2 + K_{\alpha} q_{\perp}^2). \quad (3.10)$$

Note that eq. (3.10) is a sum of quadratic terms. Equipartition dictates that the average contribution to the free energy of every quadratic degree of freedom is equal to $\frac{1}{2}kT$. Hence:

$$\begin{aligned} \langle |n_1(\mathbf{q})|^2 \rangle &= \frac{VkT}{K_3 q_{\parallel}^2 + K_1 q_{\perp}^2} \\ \langle |n_2(\mathbf{q})|^2 \rangle &= \frac{VkT}{K_3 q_{\parallel}^2 + K_2 q_{\perp}^2}. \end{aligned} \quad (3.11)$$

Direct measurement of these fluctuations for various values of \mathbf{q} allows us to determine K_1, K_2 and K_3 . This is all very well for a light-scattering experiment that probes long-wavelength director fluctuations. However, in a typical simulation the accessible wavelengths are very short (typically 5-10 molecular diameters). On such short length scales the average director is an ill-defined quantity. In contrast, the tensor order parameter \mathbf{Q} is well defined. If we now employ equation (2.4) of section 2.1:

$$\mathbf{Q} = S \frac{3\mathbf{nn} - \mathbf{I}}{2},$$

we see that for small director fluctuations around the z -axis the following relation must hold:

$$Q_{z\alpha} = S \frac{3}{2} n_z \delta n_\alpha \quad (3.12)$$

or, using the fact that $n_z = 1$:

$$\delta n_\alpha = \frac{2}{3S} Q_{z\alpha}. \quad (3.13)$$

To go to a completely molecular description of the director fluctuations, it is convenient to define the tensor order-parameter density $\mathcal{Q}(\mathbf{r})$:

$$\mathcal{Q}_{\alpha\beta}(\mathbf{r}) = \sum_{i=1}^N \left(\frac{3u_\alpha^i u_\beta^i - \delta_{\alpha\beta}}{2} \right) \delta(\mathbf{r} - \mathbf{r}_i). \quad (3.14)$$

Clearly, the ensemble averaged value of \mathcal{Q} is equal to:

$$\langle \mathcal{Q} \rangle = \rho S \frac{3\mathbf{nn} - \mathbf{I}}{2}.$$

We can now express director fluctuations in terms of fluctuations of the completely microscopic quantity \mathcal{Q} :

$$Q_{z\alpha}(\mathbf{q}) = \frac{3\rho S}{2} \delta n_\alpha(\mathbf{q}). \quad (3.15)$$

Finally, we can insert eq. (3.11) in eq. (3.15) to obtain:

$$\frac{(9/4)\rho^2 S^2 V kT}{\langle |\mathcal{Q}_{z\alpha}(\mathbf{q})|^2 \rangle} = K_3 q_{\parallel}^2 + K_\alpha q_{\perp}^2. \quad (3.16)$$

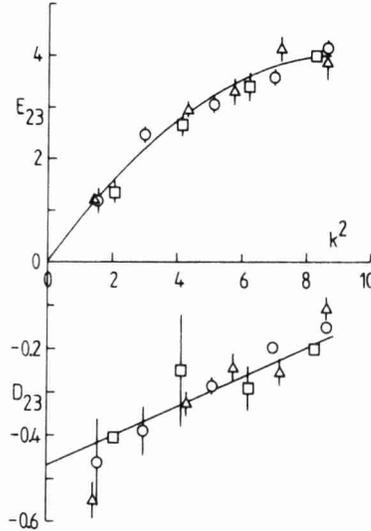


Fig. 14. Starting from eq. (3.16) we can compute the Frank constants K_3 and K_2 if we choose \mathbf{q} in the xz -plane and $\alpha = y$. Using the variables $k^2 \equiv k_z^2 + k_x^2$ and $\Delta \equiv k_x^2 - k_z^2$, we can plot the right-hand side of eq. (3.16) as a function of k^2 for $\Delta = 0$ (E_{23} in the figure) and the derivative of this function with respect to Δ (D_{23} in the figure). $K_2 + K_3$ is then obtained from the low- k slope of E_{23} and $K_2 - K_3$ is obtained from the zero- k intercept of D_{23} (see [46]).

Equation (3.16) provides the microscopic definition of the Frank elastic constants that we need. For more details, the reader is referred to the book by Forster [58] and the 1982 paper of Poniewierski and Stecki [47]. It should be noted that there are two serious drawbacks that limit the use of eq. (3.16) in numerical simulations. The first, and most obvious one is that the elastic continuum theory of nematics is only expected to hold for low q -values. In practice, the small wavevector cutoff in a simulation is at $q_{\min} = (2\pi/L)$ where L is the linear dimension of the simulation box. Figure 14 shows an example of a fit to the simulation results for the left-hand side of eq. (3.16). At very low q we would expect to observe a linear dependence on q^2 . However, for the small system-sizes studied in a simulation, higher order terms must be included in the fit. For more details, see [46] and [59]. A second (related) point is that eq. (3.16) implicitly implies that all fluctuations of \mathcal{Q} correspond to *director* fluctuations. However, at large q , we should also expect to see appreciable fluctuations in the magnitude of the order-parameter S . Such fluctuations correspond to the terms in ∇S that we have neglected in eq. (3.1). Finally, the statistical accuracy for the Frank constants that can be achieved at present using eq. (3.16) is

quite limited (10-20%). As a consequence, the comparison of the results of ref. [46] (including a correction factor (9/4) that is missing in ref. [46]) with existing density-functional theory predictions is only fair. However, in view of the small system-size that had to be used in the simulations, this might just as well be due to the simulations as to the theories. The simulation results could be improved by going to larger systems and longer simulations, i.e., by using (much) more computer power.

4. Two-dimensional nematics

Once we know the elastic constants of a nematic, it is possible to compute the free energy needed to create a topological defect in a uniform director pattern. The elementary defect in a nematic director pattern is a line-defect called a *disclination*. Tracing a path around the core of a disclination, the director orientation changes by a multiple of π . For the simplest disclination the alignment axis rotates over an angle of π . Using eq. (3.3) we can compute the elastic free energy of a disclination [very close to the core of a disclination we can no longer use eq. (3.3)]. It is natural to ask if the presence of topological defects in a three-dimensional liquid crystal has any consequences for its thermodynamic behaviour. For bulk nematics the answer is: no (apart from the somewhat unfortunate effect on the nomenclature).

However, there are situations where topological defects play a crucial role. The most spectacular example in 3D is the so-called blue phase that occurs in cholesterics close to the Ch-N transition (for a discussion that stresses the ‘defect’ interpretation of blue-phases; see [60]).

Here I shall discuss another situation where topological defects may be of crucial importance, namely the isotropic-nematic transition in two-dimensional systems. Of course, true two-dimensional nematics do not exist in nature. However, a 2D nematic may be a reasonable model for systems of non-spherical molecules adsorbed on structureless interfaces. Before proceeding with a discussion of defects in 2D nematics, let me briefly summarize what Landau theory tells us about the I-N transition in two dimensions. We start with the assumption that the orientational distribution function of a 2D nematic is of the form

$$f(\theta) = \frac{1}{2\pi} + \frac{1}{\pi} \sum_{m=1}^{\infty} S_m \cos m\theta . \quad (4.1)$$

This equation defines the nematic order-parameters S_m . As before, we expand the free energy in powers of the nematic order-parameters. If we

neglect all contributions of order-parameters other than the lowest, we obtain:

$$F = a(T - T^*)S^2 + cS^4 + eS^6 + \dots \quad (4.2)$$

This series only contains even powers of S , because a change of sign of $S \equiv \langle \cos 2\theta \rangle$ is equivalent to a rotation of the director over an angle $\pi/2$. Such a global rotation does not, of course, affect the free energy. If we assume that c in eq. (4.2) is positive, then this Landau-expansion predicts a second-order phase transition at temperature T^* . In fact, a second-order phase transition is also predicted by the 2D version of the Maier–Saupe theory [61] and even the two-dimensional equivalent of the Onsager theory for thin hard rods predicts a second-order I–N transition [19]. It should be stressed, however, that in two-dimensions the Onsager theory is *not* exact because the higher-order virial terms in the density expansion of the free energy are not negligible. The fact that three approximate models all yield a similar prediction for the nature of the 2D I–N transition might be taken as an indication that this transition is indeed second order. In fact, the situation is more subtle than that. First of all, there is always the possibility that the 2D I–N transition is simply first order (for instance, if c in eq. (4.2) is negative and e is positive, or if more order parameters are taken into account). But there is also the more interesting possibility that the transition is continuous, but not of finite order. Such transitions were first considered by Kosterlitz and Thouless (KT) in a slightly different context [62]. Here I shall only sketch the barest essentials of the Kosterlitz–Thouless scenario in the context of 2D-nematics.

Let us first consider the expression of the Frank free-energy density of a 2D-nematic. We choose the average director along the y -axis. We denote the angle between the average director and the instantaneous local director by θ . By analogy to the three-dimensional case, the expression for the deformation free energy is of the form:

$$\begin{aligned} F_D &= \frac{1}{2}K_1(\partial_x n_x)^2 + \frac{1}{2}K_3(\partial_y n_x)^2 \\ &= \frac{1}{2}K_1(\partial_x \theta)^2 + \frac{1}{2}K_3(\partial_y \theta)^2, \end{aligned} \quad (4.3)$$

where, in the last line of eq. (4.3) we have assumed that θ is small. We shall simply postulate that the deformation free energy of a 2D nematic is given by eq. (4.3). Moreover, we shall assume for the sake of convenience that $K_1 = K_3$. In that case we obtain a very simple expression for the deformation free-energy density:

$$F_D = \frac{1}{2}K(\nabla\theta)^2 \quad (4.4)$$

Using this expression, it is easy to compute the elastic contribution to the free energy of a single -disclination in a 2D-nematic. Consider a circular path (circumference $2\pi r$) around the dislocation core. Along this path, the director rotates over an angle π . Hence $(\nabla\theta)^2 = (1/2r)^2$. If we insert this expression in eq. (4.4) and integrate from the dislocation core (radius a_0 , say) to L (the linear dimension of the system) then we find that the elastic energy of an isolated disclination is:

$$F_{\text{el}} = \frac{1}{2}K \int_{a_0}^L \frac{2\pi r}{4r^2} dr = \frac{\pi K}{4} \log(L/a_0). \quad (4.5)$$

Clearly, $F_{\text{el}} \rightarrow \infty$ if $L \rightarrow \infty$. This would seem to suggest that no free disclinations are possible in a 2D nematic. However, we should also consider the ‘configurational entropy’ of a single disclination, i.e., the entropy $k \log \Omega$ associated with the number of distinct ways in which we can place a disclination in a two-dimensional area L^2 . If we use a_0 as our unit of length, then the configurational entropy is given by $k \log(L/a_0)^2$ (where we have neglected an additional constant, independent of system size). Combining this expression for the configurational entropy with our expression for the elastic free energy [eq. (4.5)] we obtain the following expression for the total free energy of a single disclination in a 2D nematic:

$$F_{\text{total}} = \left(\frac{\pi K}{4} - 2kT \right) \log(L/a_0). \quad (4.6)$$

Equation (4.6) suggests that if $kT < (\pi K/8)$ no free disclinations are possible, whereas for $kT > (\pi K/8)$ spontaneous generation of free disclinations may take place. However, if a nematic contains a finite concentration of free disclinations, orientational correlations are destroyed over distances longer than the characteristic separation of the free defects and the resulting phase is an isotropic fluid. This simple version of the Kosterlitz–Thouless scenario for defect mediated phase transitions predicts that the nematic phase cannot be stable above a critical temperature $kT^* = (\pi K/8)$. At that temperature there is a continuous phase transition (of ‘infinite’ order) from the nematic to the isotropic phase. However, there is an alternative possibility: namely that the I–N transition is simply first order. But if the I–N transition is first order then this transition must occur *before* the nematic phase has reached the point where it becomes unstable with respect to the formation of free disclinations: i.e., at a first-order I–N transition the following inequality *must* hold:

$$K > \frac{8kT}{\pi} .$$

This condition also follows from the more rigorous version of the K-T-theory.

Note that our discussion of the disclination-mediated I-N transition was based on the assumed form of the Frank free energy [eq. (4.3)]. It should be stressed that this form of the deformation free energy has quite drastic consequences for the nature of orientational order in 2D nematics. In particular, it implies that there exist no true long-ranged orientational order in such systems. To see this, consider the expression for the Frank free energy [eq. (4.4)]. If we expand the director angle $\theta(\mathbf{r})$ in Fourier components:

$$\theta(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} \theta(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}),$$

then the Frank free energy can be written as a sum of quadratic terms:

$$F_D = \frac{K}{2V} \sum_{\mathbf{k}} k^2 |\theta(\mathbf{k})|^2. \quad (4.7)$$

Using equipartition, we get:

$$\langle |\theta(\mathbf{k})|^2 \rangle = \frac{kTV}{Kk^2}. \quad (4.8)$$

Let us next consider long-range orientational correlations in 2D nematics. We define the ℓ -th orientational correlation function as:

$$g_\ell(r) \equiv \langle \cos 2\ell(\theta(0) - \theta(r)) \rangle = \text{Re} \langle \exp[-2i\ell(\theta(0) - \theta(r))] \rangle. \quad (4.9)$$

As the free energy [eq. (4.7)] is quadratic in $\theta(\mathbf{k})$, we may replace $\langle \exp(-2i\ell(\theta(0) - \theta(r))) \rangle$ in eq. (4.9) by the corresponding second-cumulant expression:

$$g_\ell(r) = \exp[-2\ell^2 \langle (\theta(0) - \theta(r))^2 \rangle]. \quad (4.10)$$

Next, we employ the fact that $\langle (\theta(0) - \theta(r))^2 \rangle = 2\langle (\theta(0))^2 \rangle - 2\langle \theta(0)\theta(r) \rangle$. Using the Fourier expansion of $\theta(\mathbf{k})$ we can write $\langle \theta(0)\theta(r) \rangle$ as:

$$\langle \theta(0)\theta(r) \rangle = \frac{1}{V^2} \sum_{\mathbf{k}} \langle |\theta(\mathbf{k})|^2 \rangle \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (4.11)$$

Inserting eq. (4.8) and replacing the Fourier sum by a Fourier transform from $k_{\min} = (2\pi/L)$ to $k_{\max} = (2\pi/a_0)$ we get:

$$\langle \theta(0)\theta(r) \rangle = \frac{kT}{(2\pi)^2} \int_{k_{\min}}^{k_{\max}} \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{Kk^2} d\mathbf{k}. \quad (4.12)$$

Hence,

$$\langle (\theta(0) - \theta(r))^2 \rangle = \frac{kT}{\pi K} \log(r/a_0)$$

and finally:

$$g_\ell(r) = \left(\frac{r}{a_0} \right)^{-(2\ell^2 kT/\pi K)} \equiv \left(\frac{r}{a_0} \right)^{-\eta_\ell}, \quad (4.13)$$

where the last term on the right-hand side of eq. (4.13) defines the exponent η_ℓ . Note that this equation implies that, provided that eq. (4.3) is valid, there is no true long-range orientational order in a 2D nematic, but algebraic or 'quasi long-range' order. Using the same approach we can show the average order parameter $\langle \cos 2\theta \rangle$ also vanishes algebraically with increasing system size:

$$\langle \cos 2\theta \rangle \propto \left(\frac{L}{a_0} \right)^{-(kT/\pi K)} \quad (4.14)$$

Now recall that we had derived that in order for a 2D nematic to be stable against the spontaneous generation of free disclinations, K could not be less than $\pi/(8kT)$. Hence, at the K-T transition the orientational correlation functions and the nematic order parameter must satisfy the following relations:

$$g_\ell(r) = \left(\frac{r}{a_0} \right)^{-(\ell^2/4)}, \quad (4.15)$$

$$\langle \cos 2\theta \rangle \propto \left(\frac{L}{a_0} \right)^{-(1/8)} \quad (4.16)$$

Two points should be stressed: [1] if the I-N transition is first order then, at the transition the exponents of g_ℓ and $\langle \cos 2\theta \rangle$ must be less than the critical values given by eq. (4.15). And [2]: the above arguments rest on the assumption that the deformation free energy is of the form given by eq. (4.4). If this expression is valid, 2D nematics can only have algebraic orientational order. However, it has thus far only been possible to prove the absence of true long-range orientational order for a certain class of short-ranged potentials called *separable* [63]. A pair-potential is called separable if the interaction energy of two molecules at fixed center-of-mass separation \mathbf{r}_{ij} depends only on the relative orientation of the two molecular

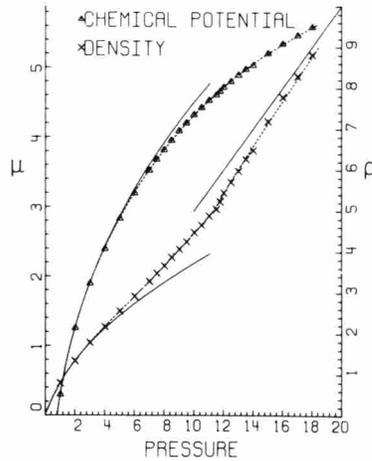


Fig. 15. Equation of state of two-dimensional fluid of infinitely thin hard needles of length 1, as obtained by Monte Carlo simulation [64]. Note that in this figure the reduced pressure is the independent variable. The reduced density (ρL^2) is indicated by crosses, the chemical potential μ by triangles. The drawn curves at low pressure were computed using a 5-term virial series. For more details, see ref. [64].

axes $\mathbf{u}_i \cdot \mathbf{u}_j$, but not on $\mathbf{r}_{ij} \cdot \mathbf{u}_i$ or $\mathbf{r}_{ij} \cdot \mathbf{u}_j$. Realistic pair-potentials are hardly ever separable.

There are therefore two obvious questions that one could ask about 2D nematics. [1]: If the pair potential is non-separable, do we find algebraic or true long-range order? And [2]: if we find algebraic order, do we observe a first order I–N transition or a continuous one of the Kosterlitz–Thouless type.

To start with the first question: a good starting point would be to choose a pair-potential that is as non-separable as possible. An obvious candidate is a two-dimensional model of infinitely thin hard needles [64]. This pair potential is very non-separable in the sense that, at fixed $|r_{ij}|$ and fixed $\mathbf{u}_i \cdot \mathbf{u}_j$ the pair potential is *not* constant, but may vary between 0 and ∞ . The equation of state of this system is shown in fig. 15. According to the bifurcation analysis of the corresponding Onsager limit [19] a second-order isotropic–nematic transition is expected at a density $\rho L^2 = (3\pi/2) = 4.712 \dots$ and a pressure $PL^2 = 11.78 \dots$. At first sight this seems to be quite a reasonable estimate of the I–N transition, because very close to this point the equation of state appears to exhibit a change of slope. However, analysis of the long-distance behaviour of the orientational correlation functions and of the system-size dependence of the order-parameter $\langle \cos 2\theta \rangle$ indicate

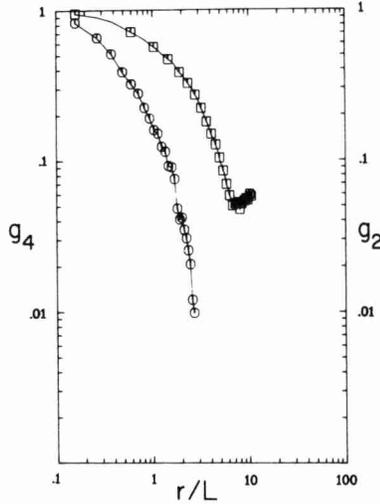


Fig. 16. Orientational correlation functions $g_2(r) \equiv \langle \cos 2(\phi(0) - \phi(r)) \rangle$ and $g_4(r) \equiv \langle \cos 4(\phi(0) - \phi(r)) \rangle$ for a two-dimensional system of hard needles of length $L = 1$. This figure shows that at a reduced density $\rho L^2 = 6.75$ the orientational order decays exponentially. In other words: the phase is isotropic.

that the higher density phase is not a stable nematic. The orientational correlation functions decay either exponentially (see fig. 16) or with an apparent algebraic decay that is larger than the critical value given in eq. (4.15). Only at a density that is almost twice the Onsager transition point does the observed behaviour conform to what is expected for a stable nematic with algebraic order (see figure. 17). However, at this density the equation of state is completely featureless. Such behaviour is to be expected if the I-N transition is in fact of the K-T type.

I am not aware of any 2D hard-core systems that show anything but quasi-long range nematic order. For continuous potentials the literature is a less clear [65,64], but I would be very surprised to see true long range orientational order in a 2D liquid crystal in the absence of positional order.

5. Smectics

5.1. Introduction

Thus far I have only discussed the simplest possible liquid-crystalline phase, i.e., the uniaxial nematic. We have found that simple excluded volume effects can give rise to nematic order, and that anisotropic van der Waals

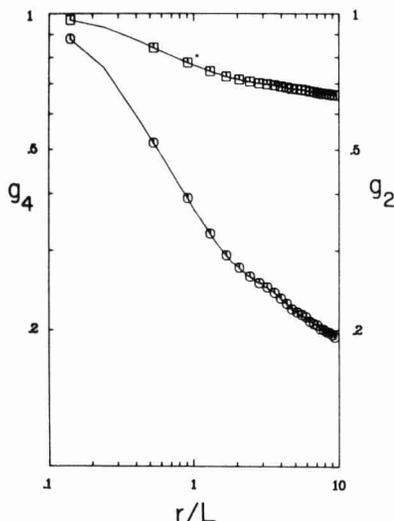


Fig. 17. Orientational correlation functions $g_2(r) \equiv \langle \cos 2(\phi(0) - \phi(r)) \rangle$ and $g_4(r) \equiv \langle \cos 4(\phi(0) - \phi(r)) \rangle$ for a two-dimensional system of hard needles of length $L = 1$. This figure shows that at a reduced density $\rho L^2 = 8.75$ the orientational order decays algebraically. From the values of the algebraic exponents η_2 and η_4 the effective Frank elastic constant can be computed. At $\rho = 8.75$ this Frank constant is large enough to make the 2D nematic stable with respect to disclination unbinding. The isotropic–nematic transition is estimated to occur somewhere around $\rho = 7.5$. Note that if we had only used fig. 15 to locate the isotropic–nematic transition, we might have concluded that this transition occurs at a density of approximately 5.0 in reduced units.

forces can do the same. It is legitimate to ask what new ingredients (if any) we must add to our molecular model, in order to account for the existence of other liquid crystalline phases? In the present section, we consider models for the smectic-A phase: as mentioned above, this phase has one-dimensional positional order in addition to the orientational order. It constitutes the next link in the series of phases between isotropic liquid and crystalline solid. As with the nematic phase there is a wide variety of phenomenological and molecular models that aim to explain smectic ordering. Unfortunately, there is no exactly solvable model that exhibits a transition to a smectic phase.

I shall first discuss the transition to the smectic-A phase phenomenologically. Next I shall discuss the N–S_A transition from a ‘molecular’ point of view. And finally I shall mention some numerical results obtained by computer simulation. The reader should not expect to find a mini-review of recent research on the N–S_A transition in this section. The majority of pub-

lications in this field deal with critical phenomena at the N-S_A transition. Yet, I shall not discuss this topic at all. Not because it is uninteresting: on the contrary, the critical behaviour at the N-S_A transition still remains to be explained and constitutes ‘one of the major unresolved theoretical questions in equilibrium statistical mechanics’ [3]. However, the ‘molecular’ picture of liquid-crystals becomes largely irrelevant on the length-scale of critical fluctuations. And it is this molecular description of liquid crystals that I intend to discuss.

5.2. Landau theory

The smectic-A phase is an orientationally ordered fluid with a one-dimensional density modulation along the direction of molecular alignment. If, for convenience, we assume that the molecules are cylindrically symmetric and that the director \mathbf{n} is aligned along the z -axis, the single-particle density ρ_1 is of the form:

$$\rho_1(x, y, z, \mathbf{u}) = \rho(z, \mathbf{n} \cdot \mathbf{u}) . \quad (5.1)$$

In general, ρ_1 may still be a very complicated function of z and $\mathbf{u} \cdot \mathbf{n} \equiv \cos \theta$. To simplify matters, let us first consider a perfectly aligned smectic. This is not a completely absurd model because in nature most smectics are strongly aligned: i.e., the orientational order-parameter $S = \langle P_2(\cos \theta) \rangle$ is close to 1. Next, we expand $\rho_1(z)$ in Fourier components:

$$\rho(z) \approx \langle \rho \rangle + \sum_{n=1}^{\infty} \rho_n \cos(2\pi n(z/d) + \phi_n) , \quad (5.2)$$

where d is the (as yet unknown) smectic layer spacing, ϕ_n is an arbitrary phase angle, and $\langle \rho \rangle$ is the average number density. In what follows we shall limit the discussion to the case $\phi_n = 0$. Experimentally, the Fourier components of the density can be measured using X-ray diffraction (see, e.g., ref. [3]). These experiments indicate that for most known smectics $\rho_1 \gg \rho_n$ ($n > 1$). Let us therefore start by considering a model where we ignore all ρ_n with $n > 1$. In that case the single-particle density has a simple sinusoidal modulation:

$$\rho(z) - \langle \rho \rangle = \rho_1 \cos(2\pi(z/d)) . \quad (5.3)$$

In the spirit of density-functional theory we assume that the free energy of the system is a functional of the single-particle density, and that therefore

the free energy difference between the smectic and the nematic state is a function of ρ_1 :

$$F_S - F_N = \frac{A}{2}\rho_1^2 + \frac{C}{4}\rho_1^4 + \dots \quad (5.4)$$

This equation contains only even powers of ρ_1 , because a change of sign of ρ_1 is equivalent to a translation of all layers over a distance $d/2$. Such a translation does not change the free energy of the system, and hence F is even in ρ_1 . Let us now assume that the coefficient A changes sign at a temperature T^* , while the higher order coefficients C, \dots are slowly varying. Then we have reduced the problem to the standard Landau scenario of second-order phase transitions. In particular, we find that for $T > T^*$ F has its minimum at $\rho_1 = 0$ (nematic phase), while for $T < T^*$ the most stable state corresponds to

$$\rho_1 = \sqrt{\frac{a}{C}(T^* - T)}.$$

The above phenomenological description of the nematic to smectic-A transition is too restricted for two reasons. First of all, the N-S_A transition may be first-order. And even when the N-S_A transition is not first-order, its critical behaviour is more complex than that of a simple 2nd-order transition [3].

It is quite simple to include the possibility of a first-order N-S_A transition in the Landau theory by including some additional terms. Actually, there is a wide choice of possible extensions to the Landau free energy density that will do the job. For example, we could extend eq. (5.4) by including terms containing powers of the second smectic order parameter (ρ_2) and mixed terms, such as $\rho_2\rho_1^2$. More interesting is the situation where we consider the coupling between density fluctuations and orientational order fluctuations. In this case the free energy is expanded around a nematic reference state with nematic order parameter S_0 . The change in free-energy density due to smectic fluctuations (ρ_1) and orientational order parameter fluctuations ($\Delta S \equiv S - S_0$) is:

$$F_S - F_N = \frac{A}{2}\rho_1^2 + \frac{C}{4}\rho_1^4 + \frac{A_S}{2}(\Delta S)^2 - B\rho_1^2\Delta S + \frac{D}{6}\rho_1^6 + \dots \quad (5.5)$$

If we first minimize this equation with respect to ΔS we find:

$$\Delta S = \frac{B}{A_S}\rho_1^2.$$

If we insert this expression in eq. (5.5) and we assume, as before, that A changes sign at a temperature T^* [$A = a(T - T^*)$], then eq. (5.5) can be written as:

$$F_S - F_N = \frac{a}{2}(T - T^*)\rho_1^2 + \frac{C - 2B^2/A_S}{4}\rho_1^4 + \frac{D}{6}\rho_1^6 + \dots \quad (5.6)$$

Equation (5.6) shows that the nature of the phase transition (first or second order) depends on the sign of $C - 2B^2/A_S$. If this term is positive the phase transition is second order. If it is negative the transition is first order. Clearly a strong coupling between fluctuations of the nematic order parameter S and the smectic order parameter ρ_1 (i.e., a large B) favours a first-order N-S_A transition. For more details the reader is referred to [9].

5.3. Mean-field theories

The early ‘molecular’ theories of the N-S_A transition [66–68] provide some more insight in the factors that determine the nature of the transition to the smectic phase. In the language of density-functional theory both the Kobayashi–McMillan model [66,67] and the Meyer–Lubensky model [68] can be considered as special cases of second-order density functional theory. In the Meyer–Lubensky model it is assumed that the molecules in the nematic phase are perfectly aligned. The change in free energy due to a smectic density modulation is given by:

$$\frac{\Delta F}{kT} = -\frac{1}{2} \int c_2(z_1 - z_2, r_{12}^\perp) \delta\rho(z_1) \delta\rho(z_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.7)$$

As before, all the physics of the problem is contained in the direct correlation function c_2 . In the Meyer–Lubensky molecular field theories it is assumed that c_2 is a short-ranged function, e.g., a Gaussian. The nature of the N-S_A transition is found to depend on the range of this Gaussian.

In the Kobayashi–McMillan model there is an additional degree of freedom in the theory, namely the orientational distribution of the molecules. If we retain the most general form for the direct correlation function c_2 in the nematic phase then even the mean-field theory would become totally intractable. In the Kobayashi–McMillan theory a judicious selection is made of the simplest ‘essential’ contributions to c_2 : one term that reflects the tendency of molecules to align [this contribution also appears in the Maier–Saupe theory, see eq. (2.16)] and one term that couples density modulations to fluctuations in the orientational order parameter. By varying the relative strength of these two terms it is possible to reproduce a rich phase

diagram. If the coupling between orientation and density modulation is strong, a first-order I- S_A transition is found. If the orientation-orientation coupling dominates we find a first order I-N transition and a second order N- S_A transition. And in between we also find a first-order I-N transition, but now the N- S_A transition is first-order too. Clearly, the Kobayashi-McMillan theory is quite successful in reproducing the phenomenology of the I- S_A , I-N and N- S_A phase transitions. However, it should be borne in mind that c_2 in this theory is postulated, not computed. So, although this theory may suggest what kind of microscopic interactions will favour the formation of a S_A phase, it is *not* a ‘microscopic’ theory. Below we shall encounter examples of recent density-functional theories for the smectic phase that aim to compute c_2 directly from knowledge of the intermolecular potential. However, first we shall discuss the results of computer simulation studies of the smectic state.

5.4. Hard-core models: beyond nematics

It would of course be nice if there existed something like the Onsager model for smectics: an exactly solvable model system that exhibits a transition to the smectic-A phase. Unfortunately, no such model is known. Hence the only way to test approximate ‘molecular’ theories of the smectic phase is to compare with computer simulations. In the spirit of the section 2.5 we look for the simplest possible model that will form a smectic phase. In the case of nematics convex hard-core models were the natural candidates because these constituted the natural generalization of the Onsager model. However, for smectics it is not obvious that hard-core models will work. In fact, in the existing textbooks on liquid-crystal physics the possibility of a hard-core smectic is not even discussed. To my knowledge the only pre-simulation article discussing the possibility of hard-core smectics is a paper by Hosino et al. [69]. The ‘traditional’ approach was to ascribe smectic ordering to attractive interactions between the molecular cores or, alternatively, to the change in packing entropy of the flexible tails of the mesogenic units [25].

5.4.1. Parallel molecules

Whereas essentially *any* fluid of sufficiently non-spherical convex hard bodies will form a nematic phase, non-sphericity alone is not enough to form a smectic phase. This is best demonstrated by the following simple example. We know from experiment that in many smectic phases the orientational order parameter $S \approx 1$. Let us therefore first consider the possibility to form a smectic phase in a fluid of *perfectly aligned* molecules ($S = 1$).

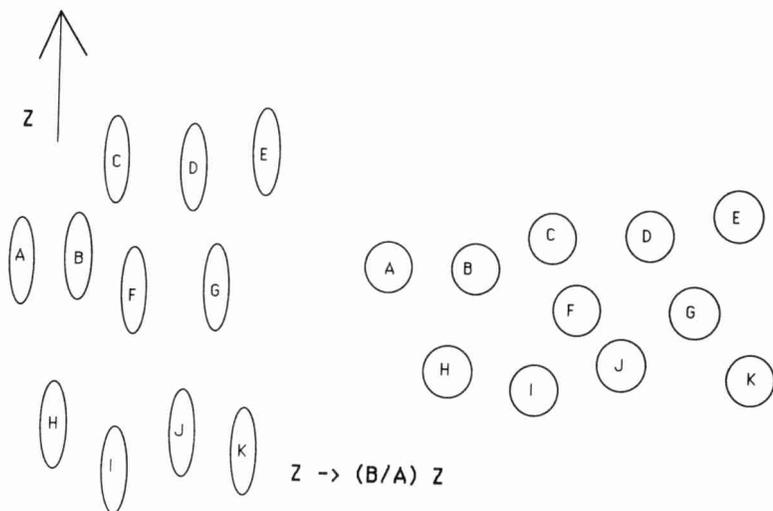


Fig. 18. Example of the affine transformation that maps a system of parallel ellipsoids with length-to-width ratio a/b onto a system of hard spheres. To facilitate the identification of particles before and after the transformation, all particles have been labelled with letters.

We know that sufficiently non-spherical hard ellipsoids can form a nematic phase (see section 2.5). It is natural to ask whether a perfectly aligned nematic of hard ellipsoids can transform into a smectic phase. The answer to this question is: no. The reason is quite simple. Consider a fluid of ellipsoids with length-to-width ratio a/b all aligned along the z -axis (say). Now we perform an affine transformation that transforms all z coordinates into coordinates z' , such that $z' = (b/a)z$. At the same time we transform to new momenta in the z -direction: $p'_z = (a/b)p_z$. Clearly, this transformation does not change the partition function of the system, and hence all thermodynamic properties of the system are unchanged. However, the effect of this affine transformation is to change a fluid of parallel ellipsoids into a system of hard spheres (see fig. 18). But, as far as we know, hard spheres can only exist in two phases: fluid and crystal. Hence parallel ellipsoids can only occur in the (nematic) fluid phase and in the crystalline solid phase. In particular: no smectic phase is possible. This makes it extremely improbable that a fluid of non-parallel ellipsoids will form a stable smectic. Such a phase is only expected in the unlikely case that the orientational fluctuations would *stabilize* smectic order.

This example demonstrates that we should be careful in selecting possible models for a hard-core smectic. Surprisingly (and luckily) it turned out that

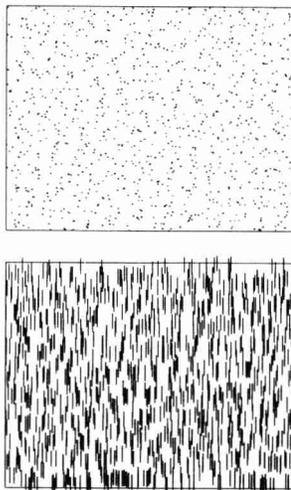


Fig. 19. Typical snapshot of a system of parallel spherocylinders with length-to-width ratio $L/D = 5$ in the nematic regime (density $\rho/\rho_{cp}=0.40$). The lower figure shows a side view of the system, the upper figure a top view. To enhance the clarity of the figure all spherocylinders are represented by line segments of length L

another very simple hard-core model system, namely a system of parallel hard spherocylinders, does form a smectic phase [70,71]. This is shown in figures 19,20 and 21 which show a nematic, smectic-A and crystalline phase of a system of hard parallel spherocylinders with length-to-width ratio $L/D = 5$. In fact, there is at least one more liquid crystalline phase of parallel hard spherocylinders, namely the columnar phase (see fig. 22). A stable smectic phase is possible for length-to-width ratios $L/D \geq 0.5$. The range of stability of the columnar phase is known less accurately: it is found for parallel spherocylinders with L/D ratios of 5 and larger. A tentative ‘phase-diagram’ of parallel hard spherocylinders is shown in fig. 23.

At first sight it may seem surprising that the columnar phase is found for large L/D values. In nature, columnar liquid crystals consist of flat, disk-like molecules. However, there is no contradiction between this observation and the simulation results. To see this, we apply once again an affine transformation of all z coordinates by a factor D/L . This transforms a spherocylinder with length-to-width ratio L/D into a cylinder of length 1, while the hemispherical caps are transformed into oblate ellipsoidal caps with axial ratio D/L . In the limit of large L/D these ellipsoidal caps become very flat. And in the limit $L/D \rightarrow \infty$ a system of parallel hard spherocylinders is equivalent to a system of hard ‘chequer stones’. This

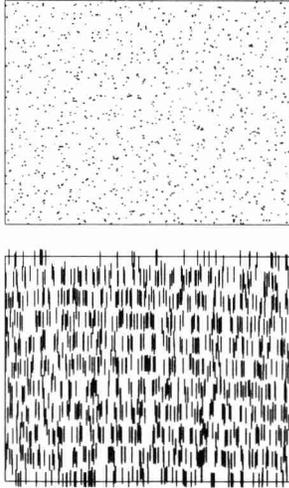


Fig. 20. Typical snapshot of a system of parallel spherocylinders with length-to-width ratio $L/D = 5$ in the smectic regime (density $\rho/\rho_{cp}=0.50$). Note that although the system is periodic in one direction (lower figure), there is no long-range positional ordering in the other directions (see upper figure).

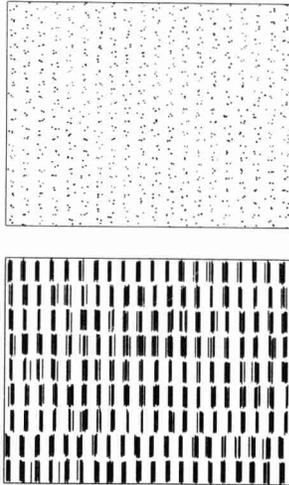


Fig. 21. Typical snapshot of a system of parallel spherocylinders with length-to-width ratio $L/D = 5$ at a density $\rho/\rho_{cp} = 0.82$ where the crystalline solid is stable. Note that the system is periodic in all three directions.

makes it plausible that a system of parallel spherocylinders with large L/D behaves like a system of flat, disk-like particles.

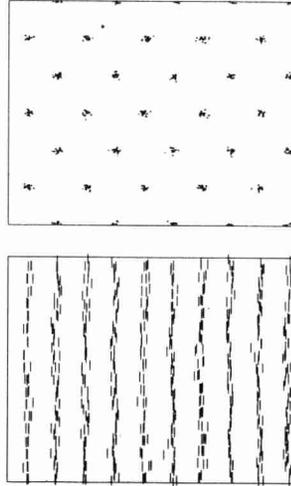


Fig. 22. Typical snapshot of a system of parallel spherocylinders with length-to-width ratio $L/D = 5$ at a density $\rho/\rho_{cp} = 0.80$ in the columnar phase. Note that the system is periodic in the direction perpendicular to the alignment axis (see top figure), but not along this axis.

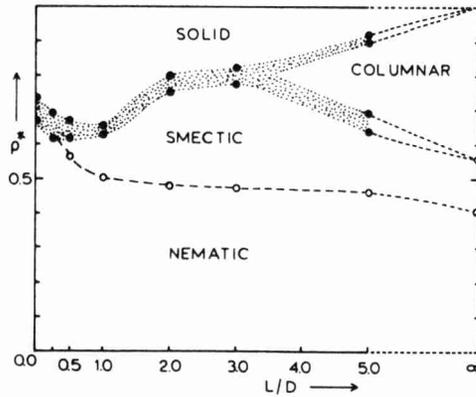


Fig. 23. Schematic 'phase diagram' of a system of parallel hard spherocylinders as obtained by computer simulation [71]. The abscissa indicates the length-to-width ratio L/D . The ordinate measures the density referred to the density at regular close packing. The grey area is the two-phase region associated with first-order phase transitions. The simulations of ref. [71] found evidence for a nematic, smectic-A, columnar and crystalline solid phase. However, more recent evidence suggests that the phase behaviour at large L/D -values is more complex than shown in the present figure.

5.4.2. Theories of parallel hard-core systems

At first sight it seems very surprising that pure excluded volume effects can give rise to smectic ordering. However, stimulated by the computer-simulation results a number of authors have reexamined the theoretical description of hard-core liquid crystals and have come up with quite simple models that do in fact predict smectic and, in some cases, columnar phases [72–78,80,81]. The earliest and most transparent density-functional theory of hard-core smectics is due to Mulder [72]. The basic results of the work of Mulder are in fact so surprisingly simple that they can literally be reproduced on the back of an envelope. Mulder considers the functional expansion of the free energy of a system of parallel hard ‘capless’ cylinders in powers of the single-particle density. In principle such an expansion is exact, and diagrammatic expressions for all the expansion coefficients are known (see ref. [20]). In practice, however, this diagrammatic expansion becomes increasingly cumbersome as higher powers of ρ_1 are included. What Mulder showed is that even a simple second-order density functional theory for hard right cylinders exhibits a second-order nematic–smectic transition. He thereupon showed that the inclusion of higher-order terms in the expansion does not change this qualitative picture. Here I shall only discuss the second order theory because it is both simple and illuminating.

The starting point for the present discussion is the Ornstein–Zernike expression for the structure factor of a fluid at particle density ρ :

$$S(\mathbf{q}) = \frac{1}{1 - \rho c(\mathbf{q})}, \quad (5.8)$$

where $c(\mathbf{q})$ is the direct correlation function. In the second-order density expansion that we are considering, $c(\mathbf{q})$ may be replaced by its low-density limit $c(\mathbf{q}) \rightarrow f(\mathbf{q})$, where $f(\mathbf{q})$ is the Fourier transform of the Mayer f -function. We are looking for the point where the system becomes unstable with respect to one-dimensional density modulations. In other words, we wish to find lowest value of ρ for which $S(\mathbf{q})$ diverges. At that density, we must have that $\rho c(\mathbf{q}) = 1$. Let us now consider what density modulations could give rise to such an instability. For the model consisting of aligned hard cylinders with length L and diameter D , this is very easy to compute, because the Mayer f -function itself can be simply written as a product of two θ -functions:

$$f(r) = -\theta(L - |z|)\theta(r_{\perp}^2 - D^2), \quad (5.9)$$

where we have chosen z as the alignment axis, while r_{\perp} denotes the distance in a plane perpendicular to z . It is now trivial to compute $f(\mathbf{q})$ and hence

$c(\mathbf{q})$:

$$f(\mathbf{q}) = -[2Lj_0(q_{\parallel}L)] \times [\pi D^2 \frac{J_1(q_{\perp}D)}{q_{\perp}D/2}], \quad (5.10)$$

where J_1 is the first-order Bessel function and j_0 is the zero-order spherical Bessel function. Defining reduced wavevectors $q_{\parallel}^* \equiv q_{\parallel}L$ and $q_{\perp}^* \equiv q_{\perp}D$, the condition $\rho c(\mathbf{q}) = 1$ is now equivalent to:

$$-8\eta j_0(q_{\parallel}^*) \frac{J_1(q_{\perp}^*)}{q_{\perp}^*/2} = 1. \quad (5.11)$$

We are looking for the lowest-density root of eq. (5.11). This will occur for that q -value that gives the largest positive value for eq. (5.10). This will happen either when $q_{\perp}^* = 0$ and $j_0(q_{\parallel}^*)$ is at its first (and lowest) minimum, or when $q_{\parallel}^* = 0$ and $J_1(q_{\perp}^*)/(q_{\perp}^*/2)$ is at its minimum. The corresponding solutions for η and \mathbf{q} are:

$$\begin{array}{lll} \eta_{\parallel} = 0.575 & q_{\parallel}^* = 4.493 & q_{\perp}^* = 0 \\ \eta_{\perp} = 0.945 & q_{\parallel}^* = 0 & q_{\perp}^* = 5.136 \end{array}$$

In this model, the transverse ('columnar') ordering is predicted to occur at unphysical packing fraction $\eta = 0.945$, but the longitudinal ('smectic') ordering is predicted to occur at a packing fraction $\eta = 0.575$. This value is higher than what is observed in the simulations of ref. [71]. However, the analysis of Mulder indicates that the addition of third and fourth-order terms in the density-functional expansion tends to lower the transition density to a value $\eta = 0.3694$ that is quite close to the one observed by Stroobants et al. ($\eta \approx 0.35$). Similarly, the higher-order density corrections increase q_{\parallel}^* to a value 4.85, which should be compared the simulation result: $q_{\parallel}^* \approx 4.95$.

Density-functional theories that predict a phase-diagram of hard parallel spherocylinders for *all* L/D -ratios were presented by Holyst and Poniewierski [75–77] and by Somoza and Tarazona [74]. These density-functional theories differ from the one used by Mulder in one important respect: they are *not* expansions around zero density. Physical arguments are used to construct an approximate density functional that can be used at all densities of interest. This advantage of the theories of [74–77] is at the same time their weakness: it is very difficult to improve systematically on a clever guess for c_2 . Both theories account quite well for the density-dependence of the smectic layer spacing observed in the Monte Carlo simulations. The

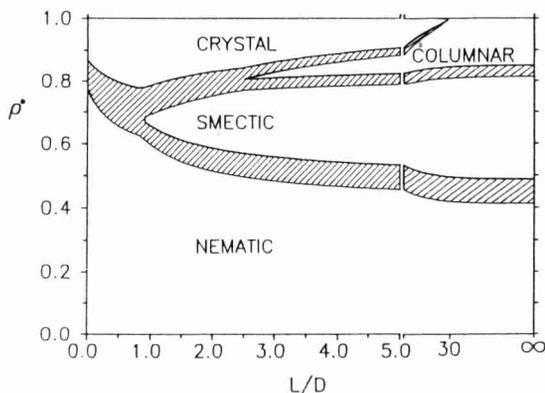


Fig. 24. Phase diagram of parallel hard spherocylinders as predicted by the free-volume/scaled-particle theory of [78].

Monte-Carlo results on the location of the nematic–smectic transition are best reproduced by the density-functional theory of ref. [74]. Columnar ordering in parallel hard (sphero)cylinders is also observed in the density-functional theories of refs. [74] and [77]. In addition, the latter paper also predicts the existence of a smectic-B phase for parallel hard cylinders.

A density-functional theory for hard-core smectics that also takes the effects of polydispersity into account was recently presented by Sluckin [81]. Kirkpatrick [82] has developed a kinetic theory that describes the pre-transitional dynamics of parallel hard spherocylinders in the vicinity of the nematic–smectic transition.

The theory formulated initially by Wen and Meyer [73] and subsequently expanded by Taylor, Hentschke and Herzfeld [78,79] is based on a quite different approach. Smectic (columnar) phases are considered as systems with liquid-like order in two (one) dimensions and solid-like order in the remaining one (two). In order to estimate the thermodynamic properties of a partially ordered phase with n solid-like dimensions and $d - n$ liquid-like dimensions, it is assumed that the liquid-like degrees of freedom can be described by scaled-particle theory, while the solid-like degrees of freedom are described by a free-volume theory. This approach results in a very simple picture for the formation of aligned hard-core liquid crystals. A drawback of the approach of [73,78,79] is that it forces all transitions to be first order. But apart from that the most recent results of Taylor et al. [79] are in good qualitative agreement with the computer simulations (see fig. 24).

Caillol and Weis [80] have investigated the parallel hard spherocylinder model using an integral-equation approach. They found that the Percus–

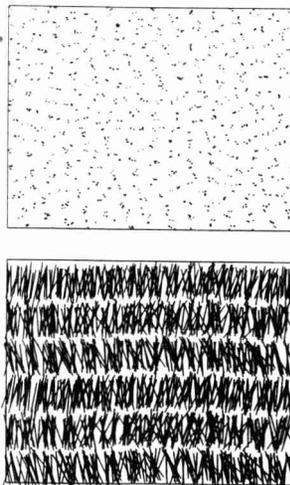


Fig. 25. Typical snapshot of a system of freely rotating spherocylinders with length-to-width ratio $L/D = 5$ in the smectic regime (density $\rho/\rho_{\text{cp}} = 0.625$). Note that there is appreciable short-range positional ordering in the smectic planes but apparently no long-range order.

Yevick equation does reproduce the MC equation-of-state data better than the HNC equation. However, the latter yields a better prediction of the nematic–smectic transition density.

5.4.3. The effect of rotation

Of course, a model system consisting of *parallel* spherocylinders is rather unphysical. It is therefore of considerable interest to know if a system of freely rotating hard-core molecules can form a smectic phase. This question is of some practical interest, in view of the recent experimental evidence that smectic [83] and columnar [84] ordering may take place in concentrated solutions of rod-like DNA molecules. We therefore carried out molecular dynamics and Monte Carlo simulations on a system of freely rotating spherocylinders with a length-to-width ratio $L/D = 5$ [85]. At low densities, the nematic order parameter S is always, within the statistical accuracy of the simulations, equal to zero. At 45% of close packing S fluctuates strongly: its average value is equal to 0.3. This is a typical value for a nematic order parameter at the transition to the isotropic phase. As the density is increased even more, the nematic order parameter S , grows from 0.3 at 45% of close packing to more than 0.9 at 60.4% of close packing. Although the fact that we observe spontaneous nematic ordering is gratifying, it is not really surprising. The more interesting question is whether the

smectic ordering that is observed in parallel spherocylinders, is preserved in a spherocylinder-fluid with full orientational freedom.

Upon further compression of a well equilibrated and annealed nematic phase, an increase was noted in the amplitude of one-dimensional density fluctuations along the nematic director. As the density increased the amplitude of these fluctuations grew as did their decay times. At 60% of close packing, the system developed a static one-dimensional density modulation. However, no translational ordering was observed in the directions perpendicular to the director. This is the hallmark of a smectic-A liquid crystalline phase. Although the fact that the latter phase formed spontaneously on compression indicates that it is stable with respect to both the isotropic and the nematic phases, its thermodynamic stability with respect to the crystalline state had to be established. This requires calculation of the free energy of both the solid and the liquid phase. Such calculations (reported in ref. [86]) show that the smectic phase of hard spherocylinders with $L/D = 5$ is indeed thermodynamically stable. Figure 25 shows a typical snapshot of the smectic-A phase of a system of hard spherocylinders with $L/D = 5$. A 'phase-diagram' of freely rotating spherocylinders has recently been worked out by Veerman and Frenkel [87].

Density-functional theories for hard spherocylinder systems have been proposed by Hołyst and Poniewierski [76,77] and by Somoza and Tarazona [57,88]. Both theories predict the presence of a stable smectic phase if the length-to-width ratio L/D exceeds a minimum value of ~ 3 . However, the two theories differ in their estimate of the point where the nematic-smectic transition has its tricritical point.

There are, of course, several qualitative differences between the phase diagrams of parallel and freely rotating spherocylinders. First of all, the freely rotating spherocylinders must always have an orientationally disordered low-density phase. In contrast, the parallel spherocylinder fluid remains (by construction) a nematic, even in the dilute gas phase. More interesting for the present discussion is the observation that, whereas parallel spherocylinders with $L/D = 5$ appear to form a columnar phase, freely rotating spherocylinders with the same L/D -ratio, apparently do not. There is, in fact, a good reason for this difference in behaviour. The reason is that, whereas aligned spherocylinders with large L/D ratios can be 'scaled' to capless platelets, the same transformation will *not* work for non-parallel rods. Any small rotation of a long axis of the spherocylinder away from the z -direction will destroy the mapping from spherocylinder to platelet. So, if we are interested in the effect of orientational freedom on a system of parallel spherocylinders with a given L/D ratio, it is not sufficient to study only freely rotating spherocylinders with the same L/D ratio. We

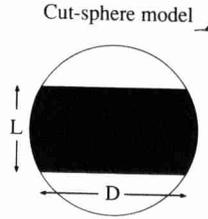


Fig. 26. Schematic drawing of the cut-sphere model. This model is used as an oblate counterpart of the hard spherocylinder model.

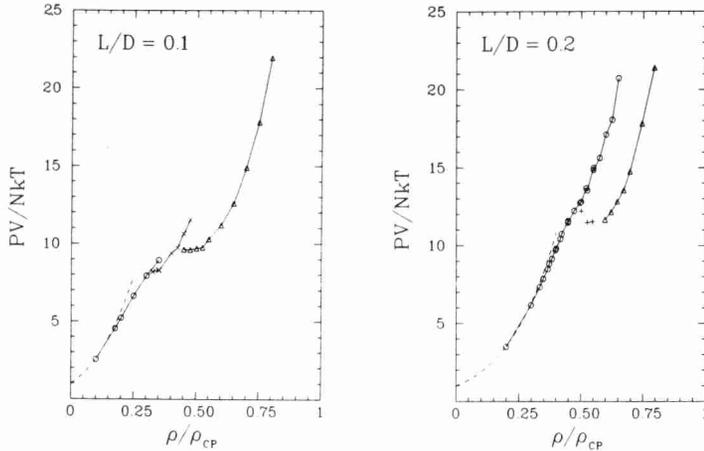


Fig. 27. Equation of state of cut spheres with length-to-width ratio $L/D = 0.1$ (left) and 0.2 (right). Simulation points obtained by compression of the low-density isotropic phase are indicated by circles. The triangles represent state points that were obtained by expansion of the crystalline solid and columnar phase. The crosses ($L/D = 0.1$ only) refer to points in the nematic phase. The pluses ($L/D = 0.2$ only) show how the columnar phase spontaneously melts at $\rho/\rho_{CP} = 0.55$. At that same density the thermodynamically stable phase appears to have cubic orientational order (see text).

should also consider the effect of free rotation on the flat, platelike particles that are equivalent to these spherocylinders, only when aligned.

For ellipsoids the transition from prolate to oblate shapes is controlled by a single parameter (the axial ratio a/b). In contrast, spherocylinders cannot be changed into oblate particles simply by changing L/D (unless we allow for the possibility of negative L/D). It turns out that a particularly convenient ‘oblate spherocylinder’ model is the so-called *cut sphere* [89] (see fig. 26).

The cut sphere is a hard convex body. Using the standard techniques

applicable to such objects (see, e.g., [90]), the second virial coefficient of cut spheres can be evaluated for arbitrary L/D -ratios:

$$B_2 = \frac{\pi D^3}{6} \left\{ \cos \theta_M \left(1 + \frac{\sin^2 \theta_M}{2} \right) + 3 \left(\cos \theta_M + \frac{\theta_M \sin \theta_M}{2} \right) \right. \\ \left. \times \left(\cos \theta_M + \frac{\sin^2 \theta_M}{2} \right) \right\}, \quad (5.12)$$

where $\theta_M \equiv \arccos(L/D)$.

At high densities, cut spheres can be stacked in a regular close-packed lattice. The volume fraction at regular close-packing is: $\eta_{\text{cp}} = (\pi/6)\sqrt{3 - (L/D)^2}$. Note that for $L/D = 1$ (hard spheres), this reduces to the well-known hard-sphere result $\eta_{\text{cp}} = \pi/\sqrt{18}$. For $L/D \rightarrow 0$ (flat, cylindrical platelets), we obtain the 2D hard-disk value $\eta_{\text{cp}} = \pi/\sqrt{12}$.

Monte Carlo simulations were carried out on a system of cut spheres with $L/D = 0.1$ and $L/D = 0.2$, over a range of densities between dilute gas and crystalline solid. The equation-of-state data for both model systems are shown in fig. 27. Surprisingly, it turned out that the systems with $L/D = 0.1$ and $L/D = 0.2$ behaved completely differently.

For the system with $L/D = 0.1$ it was observed that the system spontaneously ordered to form a nematic phase at a reduced density of 0.35 (i.e., at 35% of regular close packing). However, the director of this nematic phase was not aligned with any edge of the cubic simulation box. The system was thereupon *prepared* in a well-equilibrated, pre-aligned nematic state at the same density ($\rho = 0.35$). When the latter nematic was expanded to $\rho = 0.325$, the nematic order was found to disappear spontaneously. The subsequent compression runs were started from the pre-aligned nematic at $\rho = 0.35$. Finally, a series of runs was started from the crystalline state. In these simulations, subsequent state points were generated by expansion, followed by equilibration.

In the isotropic phase the orientational correlation functions $g_\ell(r) \equiv \langle P_\ell(\mathbf{u}(0) \cdot \mathbf{u}(r)) \rangle$ for $\ell = 2$ and 4, decay to zero essentially within one molecular diameter. In contrast, in the nematic phase these correlation functions do not decay to zero. Further compression of the nematic phase results in an increase of the overall orientational order and, in addition, increasing local ordering is observed in the fluid. As the system is compressed to a reduced density of $\rho = 0.45$, there is an increasingly clear tendency of the system towards local columnar ordering. The ‘nucleation’ of a columnar phase is greatly facilitated by allowing the shape of the periodic box to fluctuate. In fact, if the cubic box is allowed to become orthorhombic, the pressure of the system is found to drop rapidly, and ‘nucleation’ of

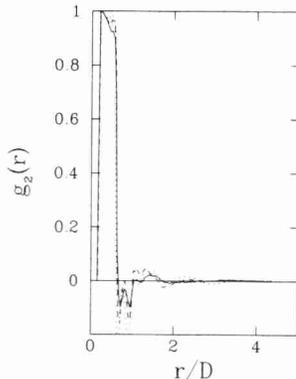


Fig. 28. Density dependence of the orientational correlation function $g_2(r) \equiv \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(r)) \rangle$ in a system of hard cut spheres with a length-to-width ratio $L/D = 0.2$. Drawn curve: $\rho/\rho_{\text{cp}} = 0.525$, dashed curve: $\rho/\rho_{\text{cp}} = 0.575$, dotted curve: $\rho/\rho_{\text{cp}} = 0.625$. Note that even at the highest densities studied $g_2(r)$ is short ranged.

a hexagonal columnar phase is observed. However, such a spontaneously formed columnar phase contains defects.

In order to prepare a defect free columnar phase the system was expanded starting from a crystalline configuration. As it turns out, true crystalline order already disappears at quite high densities ($\rho > 0.75$). Below that density the system is found to exhibit columnar ordering. In summary: for $L/D = 0.1$ we observe isotropic, nematic, columnar and crystalline phases.

At first sight, the equation-of-state for cut spheres with $L/D = 0.2$ looks similar to the one corresponding to $L/D = 0.1$ (see fig. 27).

At low densities the compressibility factor is well described by a 5-term virial series (dashed curve) and at higher densities the actual pressure is lower. In other hard-core systems this is usually an indication of a precursor to some kind of ordering transition (e.g., the I-N transition in the $L/D = 0.1$ case). And, indeed, at $\rho \approx 0.475$ we see a change of slope in the equation of state, as is to be expected in a simulation near weakly first-order (or, possibly, second-order) phase transition. The most natural assumption is that an isotropic–nematic transition takes place. After all, this is what happens in the $L/D = 0.1$ case, and we also know that oblate hard ellipsoids with a axial ratio less than 0.4 have a stable nematic phase. However, if we measure the orientational correlation function $g_2(r) \equiv \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(r)) \rangle$ we find that it decays to zero within one molecular diameter, even at the highest densities of the ‘fluid’ branch (see fig. 28). In a nematic phase, $g_2(r)$ should tend to a finite limit: $g_2(r) \rightarrow S^2$, as $r \rightarrow \infty$, where S is the

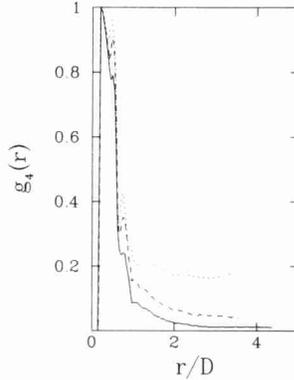


Fig. 29. Density dependence of the orientational correlation function $g_4(r) \equiv \langle P_4(\mathbf{u}(0) \cdot \mathbf{u}(r)) \rangle$ in a system of hard cut spheres with a length-to-width ratio $L/D = 0.2$. Drawn curve: $\rho/\rho_{\text{cp}} = 0.525$, dashed curve: $\rho/\rho_{\text{cp}} = 0.575$, dotted curve: $\rho/\rho_{\text{cp}} = 0.625$. Note that, unlike $g_2(r)$, $g_4(r)$ appears to be long-ranged at high densities.

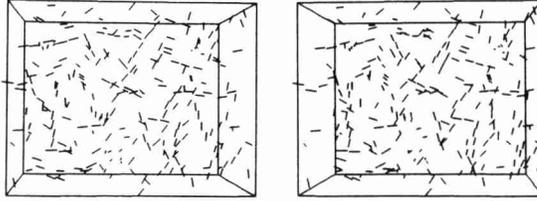


Fig. 30. Typical 'stereo'-snapshot of the molecular configuration in a system of cut spheres with $L/D = 0.2$ at a reduced density (with respect to regular close packing) of 0.55. In order to make the ordering (or lack thereof) in the system better visible, the molecules are represented by line-segments of length L along the molecular axis. Note that there is a strong tendency for the molecules to pack locally in short columns. This system has cubic orientational order.

nematic order parameter. It should be stressed that the absence of nematic order in the $L/D = 0.2$ system is not a consequence of the way in which the system was prepared. Even if we started with a configuration at a reduced density $\rho/\rho_{\text{cp}} = 0.50$ with all the molecules initially aligned, the nematic order would rapidly disappear. In other words, at that density the nematic phase is *mechanically* unstable.

The great surprise comes when we consider the higher-order orientational correlation function $g_4(r) \equiv \langle P_4(\mathbf{u}(0) \cdot \mathbf{u}(r)) \rangle$. Usually, when $g_2(r)$ is short ranged, the same holds *a fortiori* for $g_4(r)$. However, fig. 29 shows that for densities $\rho/\rho_{\text{cp}} > 0.5$, $g_4(r)$ is much longer ranged than $g_2(r)$. This suggests that the system has a strong tendency towards orientational order

with *cubic* symmetry ('cubatic', not to be confused with cubic, which refers to a system that also has *translational* order). In computer simulations one should always be very suspicious of any spontaneous ordering with cubic symmetry, because such ordering could be induced by the (cubic) periodic boundary conditions. In order to test if the boundary conditions were responsible for the cubatic order we did a number of long simulations with systems of up to 2048 particles. These simulations strongly suggest that the onset of cubatic orientational order is not an artifact of the boundary conditions. Another indication that the boundary conditions are not the cause of the observed ordering is that still higher order correlations (g_6 and g_8) that could also be induced by the periodic boundaries, are in fact rapidly decaying functions of r . If we make a log-log plot of $g_4(r)$ in the large system for several densities between $\rho = 0.525$ and $\rho = 0.625$, it appears that, at least at the lower densities, the cubatic order is not truly long-ranged but quasi-long-ranged, i.e., $g_4(r) \sim r^{-\eta}$, where η depends on the density ρ . In this respect the cubatic phase found in the computer simulations differs from the cubatic phase of hard 3D crosses (see section 2.4.1 and appendix B). A typical snapshot of the 'cubatic' phase is shown in fig. 30. The picture indicates that in this phase the molecules stack in short columns. And that these columns tend to pack approximately at right angles. At present, a microscopic theory of hard-core cubatics is still lacking, but fig. 30 strongly suggests what ingredients should go into such a theory.

At this stage there are more questions than answers about the possible nature of the cubatic phase that we observe in our simulations. For instance, we do not yet know whether the cubatic phase is thermodynamically stable or only metastable, nor do we know whether or not it is separated from the isotropic phase by a first order phase transition. Another open question concerns the relation between the present molecular 'cubatic' and the phase with cubatic bond order that has been predicted by Nelson and Toner [91]. In ref. [91] it is argued that cubatic bond order could occur in rapidly quenched atomic liquids. In the liquid-crystalline systems under study we observe cubatic order of the molecular orientations. However, this distinction need not be important because for a non-separable potential (see chapter 4) orientational order implies bond order.

These questions are clearly important and should be investigated. Even if it turns out that the cubatic phase is only metastable, this would not rule out the possibility of observing it in nature. Yet, I am not aware of any experimental observations of *cubatic* liquid crystals, although *cubic* liquid-crystalline phase of disk-like molecules have been observed experimentally [92].

6. Conclusion

In these lectures I have tried to approach the statistical mechanics of liquid crystals from the ‘simple liquids’ side. My main aim was to show that many properties of liquid crystals can be qualitatively understood using extremely simple molecular models. In this sense the present set of lectures is simply a tribute to the seminal work of Onsager.

I wish to stress that it was not my intention to present a quantitative molecular theory of thermotropic liquid crystals. Such a theory, if it could be constructed, would require accurate intermolecular potentials as an input. For most real mesogens such information is not yet available. And if it were, we still would lack a sufficiently powerful analytical theory to tackle the problem head-on. The situation looks distinctly better for lyotropic liquid crystals consisting of relatively rigid non-spherical particles, i.e., the class of systems originally considered by Onsager. Computer simulations have shown that the idea that excluded-volume effects are at the heart of the formation of lyotropic liquid crystals is even more powerful than Onsager indicated. We now know of hard-core smectics and columnar phases and possibly even more exotic liquid crystals that have not yet been recognized in nature.

In order to construct truly quantitative theories of lyotropic liquid crystals, such theories should take into account two factors that I have only hinted at: the presence of long-range attractive or repulsive forces and the effect of the flexibility of the colloidal particles. Much progress has already been made along these lines and I hope that the theory of colloidal liquid crystals may one day be considered the *Statistical Mechanics of Simple Liquid Crystals*.

Acknowledgments

The work of the FOM Institute is part of the research program of FOM and is made possible with financial help from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). I thank Drs. Hentschke and Taylor for giving me permission to use fig. 24. I am happy to acknowledge frequent discussions with Henk Lekkerkerker. Theo Odijk and Richard LeSar have helped me focus my ideas about what is simple about liquid crystals and what is not. I thank them both for their encouragement and patience.

Appendix A. Approximate solution of the Onsager model

The expression for the free energy of a gas of infinitely thin, hard spherocylinders at reduced density $c \equiv B_2\rho$ is:

$$F/(NkT) = \log c + \int d\Omega f(\Omega) \log(4\pi f(\Omega)) + \frac{4c}{\pi} \int d\Omega d\Omega' f(\Omega)f(\Omega') |\sin \gamma|. \quad (\text{A1})$$

We use the following trial function :

$$f(\Omega) = \frac{\alpha}{4\pi \sinh \alpha} \cosh(\alpha \cos \theta) \quad (\text{A2})$$

to minimize the free energy. Let us denote the part associated with the orientational entropy by $\sigma(\alpha)$:

$$\sigma(\alpha) \equiv \int d\Omega f(\Omega) \log(4\pi f(\Omega)), \quad (\text{A3})$$

$\sigma(\alpha)$ is lowest in the isotropic phase ($\alpha = 0$). On the other hand, the part associated with the translational entropy:

$$\rho(\alpha) \equiv \frac{4}{\pi} \int d\Omega d\Omega' f(\Omega)f(\Omega') |\sin \gamma| \quad (\text{A4})$$

is minimal in a perfectly aligned fluid. The competition between these two factors determines the value of α for which:

$$F/(NkT) = \log c + \sigma(\alpha) + c\rho(\alpha) \quad (\text{A5})$$

is lowest. Inserting the expression given in eq. (A2) for $f(\Omega)$ in equation (A3), we obtain by straightforward integration:

$$\sigma(\alpha) = \log \left(\frac{\alpha}{\tanh \alpha} \right) - 1 + \frac{\arctan \sinh \alpha}{\sinh \alpha}. \quad (\text{A6})$$

The expression for $\rho(\alpha)$ requires a bit more work (see ref. [2]). It can be obtained using a result derived by Onsager, namely that for any function $\mathcal{F}(\sin \gamma)$, the following identity holds:

$$J \equiv \int \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2) \mathcal{F}(\sin \gamma) d\Omega_1 d\Omega_2 = \frac{8\pi^2}{\alpha_1 \alpha_2} \{ 2 \sinh \alpha_1 \alpha_2 \mathcal{F}(0) + \int_{\gamma=0}^{\pi} \cosh(\sqrt{\alpha_1^2 + \alpha_2^2 + 2\alpha_1 \alpha_2 \cos \gamma}) d\mathcal{F}(\sin \gamma) \}. \quad (\text{A7})$$

Using eq. (A7) the final result for $\rho(\alpha)$ is:

$$\rho(\alpha) = \frac{4}{\pi} \left(\frac{\int_{\gamma=0}^{\pi} \cosh(2\alpha \cos(\gamma/2)) \cos \gamma \, d\gamma}{\sinh^2 \alpha} \right). \quad (\text{A8})$$

And finally we can express the nematic order parameter $\langle P_2 \rangle$ as a function of α :

$$\langle P_2 \rangle(\alpha) = 1 - \frac{3}{\alpha \tanh \alpha} + \frac{3}{\alpha^2}. \quad (\text{A9})$$

It is illuminating to look at the isotropic–nematic transition of the Onsager model in the ‘Gaussian’ limit. This case was studied extensively by Odijk [24]. In this simplified (and therefore approximate) solution of the Onsager model he exploits the fact that the nematic phase in a system of thin hard rods is always strongly ordered. Hence, to a good approximation we may replace the orientational distribution function $f(\cos \theta)$ by a Gaussian :

$$\begin{aligned} f(\cos \theta) &= \frac{\alpha}{4\pi} \exp\left(-\frac{\alpha\theta^2}{2}\right) \quad (0 \leq \theta < \pi/2) \\ &= \frac{\alpha}{4\pi} \exp\left(-\frac{\alpha(\theta - \pi)^2}{2}\right) \quad (\pi/2 \leq \theta < \pi). \end{aligned} \quad (\text{A10})$$

In this Gaussian limit, eqs. (A6), (A8) and (A9) become very simple:

$$\sigma(\alpha) \approx \log(\alpha) - 1, \quad (\text{A11})$$

$$\rho(\alpha) \approx \frac{4}{\sqrt{\pi\alpha}}, \quad (\text{A12})$$

$$\langle P_2 \rangle(\alpha) \approx 1 - \frac{3}{\alpha}. \quad (\text{A13})$$

It now becomes trivial to find the solution with the lowest free energy. We simply solve the equation:

$$\left(\frac{\partial F}{\partial \alpha} \right) = \frac{1}{\alpha} - \frac{2c}{\sqrt{\pi\alpha^3}} = 0. \quad (\text{A14})$$

This yields:

$$\alpha = \frac{4c^2}{\pi}.$$

Finally, to find the isotropic–nematic transition, we insert this value of α in the expression for the pressure P and the chemical potential μ . We use the pressure equation to relate the density of the nematic and isotropic phases at the same pressure:

$$3c_N = c_I + c_I^2. \quad (\text{A15})$$

The equality of the chemical potential of the coexisting phases then reads:

$$\log(c_I) + 2c_I + 1 = 3\log(c_N) + \log(4/\pi) + 4. \quad (\text{A16})$$

The solution is:

$$c_I = 3.4516$$

and

$$c_N = 5.1217$$

which should be compared with the exact values: $c_I = 3.29\dots$ and $c_N = 4.22\dots$.

Appendix B. Cubatic order and the Onsager model

Consider a molecule that consists of a rigid assembly of thin hard rods with length-to-width ratio L/D . We assume that the molecule contains no loops. Moreover, we assume for convenience that no two segments in the molecule are collinear. For such molecules it is clear that in the Onsager limit $L/D \rightarrow \infty$, the total pair-excluded volume is simply the sum of the excluded volumes of all the linear subunits. The leading correction to this expression for the pair-excluded volume is of order $\log(L/D)/(L/D)$.

Just as for the original Onsager model, the density-expansion of the free-energy of these composite molecules terminates at the second-order term. Given the geometry of the molecules, we can evaluate the free energy of the system exactly at any density.

Here I consider a very simple molecular shape, namely a particle made of three perpendicular rods (a ‘3D cross’). I will show that this ‘molecule’ undergoes an orientational ordering transition. However, the liquid-crystalline state that results is not a nematic. Rather, it has an orientational distribution with cubic symmetry, a ‘cubatic’ liquid crystal. Other (higher order)

liquid crystalline phases could be obtained by going to more highly symmetric molecules. However, to explain the phenomenon, the present example will suffice.

I shall treat the problem of the orientational ordering of 3D crosses in the Gaussian approximation. As a consequence my estimate for the isotropic-cubic coexistence point will be approximate. However, my conclusion about the *stability* of the orientationally ordered phase is not affected by the Gaussian approximation, because the latter distribution function necessarily yields a free energy that is *higher* than the true free energy of the system at that density. In contrast, the free energy of the *isotropic* phase is computed exactly.

Consider a molecule consisting of three perpendicular rods of length L and diameter D . The orientation of such a molecule is specified, for instance, by three Eulerian angles. The expression of the free energy F as a function of the orientational distribution function $f(\boldsymbol{\Omega})$ is given by:

$$F/(NkT) = \log c + \int d\boldsymbol{\Omega} f(\boldsymbol{\Omega}) \log(8\pi^2 f(\boldsymbol{\Omega})) + \frac{c}{2} \int d\boldsymbol{\Omega} d\boldsymbol{\Omega}' f(\boldsymbol{\Omega}) f(\boldsymbol{\Omega}') v_{\text{excl}}(\boldsymbol{\Omega}, \boldsymbol{\Omega}'). \quad (\text{B1})$$

In the isotropic phase, $f(\boldsymbol{\Omega}) = 1/(8\pi^2)$. In the orientationally ordered phase we assume that f is sharply peaked in the vicinity of the preferred orientations of the molecule. We choose our laboratory-frame such that these preferred directions coincide with the x, y and z axes. There are 24 distinct ways to align a 3D cross with the lab-axes (namely $(6 \times 4 \times 2)/2$). In the orientationally ordered phase we assume that the orientational distribution function is a sharply peaked Gaussian centered around the x, y and z axes. In fact, there are 24 such Gaussians corresponding to the 24 different, but equivalent alignments of the molecules. If we denote the Eulerian angles that describe the molecular rotation with respect to any one of such preferred direction by ϕ, θ, ψ then we can express the orientational distribution function $f(\boldsymbol{\Omega})$ in the vicinity of this orientation as:

$$f(\boldsymbol{\Omega}) = \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \frac{\exp(-\alpha(\phi^2 + \theta^2 + \psi^2))}{24}, \quad (\text{B2})$$

where α is a measure for the width of the Gaussian. It should be noted that, for convenience, I have used the so-called *xyz*-convention of Eulerian axis [93], because in this convention three infinitesimal Eulerian rotations are carried out around three perpendicular axes.

The ideal entropic contribution to the free energy of the ordered phase is:

$$\begin{aligned}\sigma(\alpha) &= \int f(\boldsymbol{\Omega}) \log(8\pi^2 f(\boldsymbol{\Omega})) \, d\boldsymbol{\Omega} \\ &= \log\left(\frac{8\pi^2}{24}\right) + \frac{3}{2} \log\left(\frac{\alpha}{2\pi}\right) - \frac{3}{2}.\end{aligned}\quad (\text{B3})$$

Similarly, the excluded volume contribution $c\rho(\alpha)$ equals:

$$c\rho(\alpha) = \frac{c}{3} \left(\frac{8}{\pi} + \frac{4}{\sqrt{\pi\alpha}} \right), \quad (\text{B4})$$

where we have defined the concentration c as B_2 times the number density. In the limit $L/D \rightarrow \infty$, the second virial coefficient of a 3D cross in the isotropic phase is equal to:

$$B_2 = \frac{9\pi}{4} L^2 D.$$

The next step is to minimize the free energy of the ordered phase, F_O :

$$F_O(\alpha) = \log c + \sigma(\alpha) + c\rho(\alpha),$$

with respect to α at constant c . This yields:

$$\alpha = \frac{16c^2}{81\pi}. \quad (\text{B5})$$

Substituting this value for α in the expression for the free energy of the ordered phase, we obtain:

$$F_O(c) = 4 \log c + \log \left[\frac{\pi^2}{3} \left(\frac{2\sqrt{2}}{9\pi} \right)^3 \right] + \frac{3}{2} + \frac{8c}{3\pi}. \quad (\text{B6})$$

In order to locate the coexistence point we must compute the pressure and the chemical potential of both the ordered and the disordered phases, using $P = c^2(\partial F/\partial c)$ and $\mu = F + P/c$. For the isotropic phase we find:

$$P_1 = c_1 + c_1^2,$$

while for the ordered phase the pressure is:

$$P_O = 4c_O + \frac{8c_O^2}{3\pi}.$$

Finally, we obtain the following two equations that specify the coexistence point:

$$c_I + c_I^2 = 4c_O + \frac{8c_O^2}{3\pi} \quad (\text{B7})$$

and:

$$\begin{aligned} \log c_I + 2c_I + 1 = 4 \log c_O + \log \left[\frac{\pi^2}{3} \left(\frac{2\sqrt{2}}{9\pi} \right)^3 \right] \\ + \frac{3}{2} + \frac{8c_O}{3\pi} + 4 + \frac{8c_O}{3\pi}. \end{aligned} \quad (\text{B8})$$

If we now solve these equations for c_I and c_O we find that there is coexistence between an isotropic and a 'cubic' phase at:

$$c_I = 48.83 \quad c_O = 50.80.$$

At this transition the value of α in the ordered phase is:

$$\alpha = 162.3.$$

which is quite large. This large value of α would seem to justify the use of the Gaussian approximation.

References

- [1] P.M. Knoll and H. Kelker: Otto Lehman. Eine Biographie, Frankfurt, 1988.
- [2] L. Onsager, Proc. NY. Acad. Sci. 51 (1949) 627.
- [3] P.S. Pershan, Structure of Liquid Crystal Phases, World Scientific, Singapore(1988).
- [4] D.C. Wright and N.D. Mermin, Rev. Mod. Phys. 61 (1989) 385.
- [5] P. G. de Gennes, Physics of Liquid Crystals, Oxford University Press, Oxford, England (1974).
- [6] S. Chandrasekhar, Liquid Crystals, Cambridge U.P., Cambridge, England (1977).

- [7] E.B. Priestley, P.J. Wojtowicz, Ping Sheng, Introduction to liquid crystals, Plenum, New York (1974).
- [8] The molecular physics of liquid crystals, G.R.Luckhurst and G.W.Gray, editors, Academic Press, London, 1979.
- [9] G. Vertogen and W.H. de Jeu, Thermotropic Liquid Crystals, Fundamentals. Springer, Berlin, 1988.
- [10] W. Maier and A. Saupe, Z.Naturforsch. A13 (1958) 564.
- [11] B.M. Mulder, preprint.
- [12] E.F. Gramsbergen, L. Longa and W.H. de Jeu, Physics Reports 135 (1986) 195.
- [13] L.D.Landau and E.M.Lifshitz, Statistical Physics, 3rd edition. Pergamon Press, London (1980).
- [14] E.Courtens and G.Koren, Phys. Rev. Lett. 35 (1975) 1711, 36 (1976) 281; E. Courtens, J. Chem. Phys. 66 (1977) 3995.
- [15] R. Eppenga and D. Frenkel, Mol. Phys. 52 (1984) 1303.
- [16] T.J. Sluckin and P. Shukla, J.Phys. A 16 (1983) 1539.
- [17] A.R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton University Press, Princeton, 1960.
- [18] G. Lasher, J.Chem. Phys. 53 (1970) 4141.
- [19] R.F. Kayser and H.J. Raveche, Phys. Rev. A17 (1978) 2067.
- [20] J.P.Hansen and I.R.McDonald: Theory of Simple Liquids, second edition, Academic Press, London, 1986.
- [21] D. Frenkel, J. Phys. Chem. 92 (1988) 5314; The corresponding results for ellipsoids are given in: D. Frenkel, Mol. Phys. 5 (1988) 493.
- [22] A. Stroobants, H.N.W. Lekkerkerker and T. Odijk, Macromolecules, 19 (1986) 2232.
- [23] H.N.W.Lekkerkerker in: Proceedings of NATO ASI on: Phase Transitions in Soft Condensed Matter, T.Riste ed. (preprint).
- [24] T. Odijk, Macromolecules 19 (1986) 2313.
- [25] F. Dowell and D.E. Martire, J. Chem. Phys. 68 (1978) 1088; *ibid.*: 68 (1978) 1094; *ibid.*: 69 (1978) 2322; F. Dowell, Phys. Rev. A28 (1983) 3526.
- [26] W.M. Gelbart and A. Gelbart, Mol. Phys. 33 (1977) 1387.
- [27] B.J. Alder and T.E. Wainwright, J. Chem. Phys. 27 (1957) 1208.
- [28] J.D. Weeks, D. Chandler and H.C. Andersen, J.Chem. Phys. 54 (1971) 5237.
- [29] See, for instance the paper of C. Zannoni in ref. [8]
- [30] P.A.Lebwohl and G.Lasher, Phys. Rev. A6 (1972) 426.
- [31] J. Vieillard-Baron, J. Chem. Phys. 56 (1972) 4729.
- [32] J. Vieillard-Baron, Mol. Phys. 28 (1974) 809.
- [33] D. Frenkel and B.M. Mulder, Mol. Phys. 55 (1985) 1171.
- [34] W.G. Hoover and F.H. Ree, J. Chem. Phys. 49 (1968) 3609.
- [35] D. Frenkel, Mol. Phys. 54 (1985) 145.

- [36] M.A. Cotter and D.E. Martire, *J. Chem. Phys.* 52 (1970) 1902; *J. Chem. Phys.* 53 (1970) 4500.
- [37] M.A. Cotter, *Phys. Rev. A*10 (1974) 625; *J. Chem. Phys.* 66 (1977) 1098.
- [38] B.M. Mulder and D.Frenkel, *Mol.Phys.* 55 (1985) 1193.
- [39] B. Barboy and W.M. Gelbart, *J. Chem. Phys.* 71 (1979) 3053; B. Barboy and W.M. Gelbart, *J. Stat. Phys.* 22 (1980) 685.
- [40] U.P.Singh and Y.Singh, *Phys. Rev. A*33 (1986) 2725.
- [41] M. Baus, J.-L. Colot, X.-G. Wu and H. Xu, *Phys. Rev. Lett.* 59 (1987) 2148.
- [42] J.F.Marko , *Phys. Rev. Lett.* 60 (1989) 325; J.F.Marko , *Phys. Rev. A*39 (1989) 2050.
- [43] J.L. Colot, X.G. Wu, H. Xu and M. Baus, *Phys. Rev. A*38 (1988) 2022.
- [44] A. Perera , P.G. Kusalik and G.N. Patey, *J. Chem. Phys.* 87 (1987) 1295, 89 (1988) 5969; A. Perera , G.N. Patey and J.J. Weis, *J. Chem. Phys.* 89 (1989) 6941; A. Perera and G.N. Patey, *J. Chem. Phys.* 89 (1989) 5861.
- [45] Ping Sheng in ref. [7], p.143.
- [46] M.P. Allen and D. Frenkel, *Phys. Rev. A*37 (1988) 1813. This paper reports data for the Frank elastic constants of a nematic phase of hard ellipsoids and a nematic of hard spherocylinders. It should be noted, however, that the quantities computed from equations 4 and 5 in Allen and Frenkel's paper are *not* the Frank constants themselves. To obtain the 'real' Frank constants, the numbers in table 1 and 2 of the paper should be multiplied by (9/4).
- [47] A. Poniewierski and J. Stecki, *Mol. Phys.* 38 (1979) 1931; J. Stecki and A. Poniewierski, *Mol. Phys.* 41 (1980) 1451; A. Poniewierski and J. Stecki, *Phys. Rev. A*25 (1982) 2368.
- [48] R.G. Priest, *Phys. Rev. A*7 (1973) 720.
- [49] J.P.Straley, *Phys. Rev. A*8 (1973) 2181.
- [50] Sin-Doo Lee and R.B. Meyer, *J. Chem. Phys.* 84 (1986) 3443.
- [51] T. Odijk, *Liquid Crystals*, 1 (1986) 553.
- [52] G.J. Vroege and T. Odijk, *Macromolecules* 21 (1988) 2848.
- [53] G.J. Vroege , thesis, Delft (1989).
- [54] J. Nehring and A. Saupe, *J. Chem. Phys.* 56 (1972) 5527.
- [55] Y. Singh and K. Singh, *Phys. Rev. A*33 (1986) 3481.
- [56] Sin-Doo Lee, *Phys. Rev. A*39 (1989) 3631.
- [57] A.M. Somoza and P. Tarazona, (preprint).
- [58] D. Forster, *Adv. Chem. Phys.* , 31 (1975) 231.
- [59] M.P. Allen, D. Frenkel and J. Talbot, *Computer Physics Reports* 9 (1989) 301.
- [60] S. Meiboom, M. Sammon and D.W. Berreman, *Phys. Rev. A*28 (1983) 3553; and references therein. See also ref. [4].
- [61] J.Y. Denham, G.R. Luckhurst and C. Zannoni, *Mol. Cryst. Liq. Cryst.* 60 (1980) 185.
- [62] J.M. Kosterlitz and D. Thouless, *J. Phys. C*6 (1973) 1181.

- [63] M. Romeiro, J. Math. Phys. 19 (1978) 802.
- [64] D. Frenkel and R. Eppenga, Phys. Rev. A31 (1985) 1776.
- [65] J. Tobochnik and G.V. Chester, Phys. Rev. B20 (1983) 1221.
- [66] K.K. Kobayashi, J. Phys. Soc. Japan 29 (1970) 101; K.K. Kobayashi, Mol. Cryst. Liq. Cryst. 13 (1971) 137.
- [67] W.L. McMillan, Phys. Rev. A4 (1971) 1238.
- [68] R.B. Meyer and T.G. Lubensky, Phys. Rev. A14 (1976) 2307.
- [69] M. Hosino, H. Nakano and H. Kimura, J. Phys. Soc. Japan 46 (1979) 1709.
- [70] A. Stroobants, H.N.W. Lekkerkerker and D. Frenkel, Phys. Rev. Lett. 57 (1986) 1452.
- [71] A. Stroobants, H.N.W. Lekkerkerker and D. Frenkel, Phys. Rev. A36 (1987) 2929.
- [72] B.M. Mulder, Phys. Rev. A35 (1987) 3095.
- [73] X. Wen and R.B. Meyer, Phys. Rev. Lett. 59 (1987) 1325.
- [74] A.M. Somoza and P. Tarazona, Phys. Rev. Lett. 61 (1988) 2566.
- [75] R. Hołyst and A. Poniewierski, Phys. Rev. 39 (1988) 2742.
- [76] A. Poniewierski and R. Hołyst, Phys. Rev. Lett. 61 (1988) 2461.
- [77] R. Hołyst and A. Poniewierski, preprint.
- [78] M.P. Taylor, R. Hentschke and J. Herzfeld, Phys. Rev. Lett. 62 (1989) 800; *ibid.* 62 (1989) 1577.
- [79] M.P. Taylor, R. Hentschke and J. Herzfeld, Phys. Rev. A40 (1989) 1678.
- [80] J.M. Caillol and J.J. Weis, J. Chem. Phys. 90 (1989) 7403.
- [81] T.J. Sluckin, Liquid Crystals 6 (1989) 111.
- [82] T.R. Kirkpatrick, J. Chem. Phys. 89 (1988) 5020.
- [83] T.E. Strzelecka, M.W. Davidson and R.L. Rill, Nature, 331 (1988) 457.
- [84] F. Livolant, A.M. Levelut, J. Doucet and J.P. Benoit, Nature 339 (1989) 724.
- [85] D. Frenkel, J. Phys. Chem. 92 (1988) 3280.
- [86] D. Frenkel, H.N.W. Lekkerkerker and A. Stroobants, Nature 332 (1988) 822.
- [87] J.A.C. Veerman and D. Frenkel, submitted for publication.
- [88] A.M. Somoza and P. Tarazona, J. Chem. Phys. 91 (1989) 517.
- [89] D. Frenkel, Liquid Crystals, 5 (1989) 929.
- [90] T. Boublik and I. Nezbeda, Coll. Czechoslovak. Chem. Commun. 51 (1986) 2301.
- [91] D.R. Nelson and J. Toner, Phys. Rev. B24 (1981) 363.
- [92] J. Billart, C. R. Acad. Sci. Paris, 305 (1987) 843.
- [93] H. Goldstein, Classical Mechanics, second edition, Addison-Wesley, Reading, 1980, Appendix B.

COURSE 10

COLLOIDAL SUSPENSIONS

P.N. PUSEY

Royal Signals and Radar Establishment
Malvern
WR14 3PS, UK

J. P. Hansen, D. Levesque and J. Zinn-Justin, eds.
Les Houches, Session LI, 1989
Liquides, Cristallisation et Transition Vitreuse/
Liquids, Freezing and Glass Transition
© Elsevier Science Publishers B.V., 1991