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Theories of phase behaviour and phase transitions in liquid crystals

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This paper reviews the microscopic statistical theories of liquid crystals for simple molecular systems. Starting from the early works of Onsager, Maier and Saupe to the recent advances and trends for the future. Particular attention is paid to the theories for systems of hard body molecules, which should play a central role in the development of the theories, as the hard spheres model was crucial in the theory of simple liquids.

1. Introduction

The aim of a molecular statistical theory of liquid crystals is the prediction of the phase behaviour and phase transitions from the molecular interactions. We are still far away from this goal, the beautiful variety of phases and behaviours observed in these systems and the complexity of their molecular interactions represent a double challenge to the theoretician. A first step is to extract from the molecular structure a simplified molecular model keeping only those aspects which are thought to be relevant for the macroscopic behaviour. The molecular model should then be analysed with the tools of the statistical physics which, for any non-trivial model, requires the development of workable approximations.

A useful perspective to the progress in the theory of liquid crystals is given by the theory of simple systems like argon, with a phase diagram composed of only three phases: solid, liquid and vapour. The relevant aspects of the atomic interaction were identified at the end of the last century by van der Waals as a short range core repulsion and the attraction, due to dispersion forces, at longer range. The qualitative aspects of the liquid–vapour coexistence were reproduced by van der Waals's approach with an excluded volume treatment of the hard cores and the mean field approximation for the attractive interactions. The development of theories capable of quantitatively predictions required a refined model for the interactions (as the Lennard–Jones potential) and the development, over the 60s and the 70s, of the theory of simple liquids, built around the simplified model of hard spheres as reference system. The critical region presented a separate and very interesting problem which was solved with the innovative concepts of scaling and the techniques of the renormalization group. The theoretical understanding of the liquid–solid coexistence came even later. The description of the crystal at low temperature, given by the theory of solid state physics, was difficult to fit in the framework of the liquid state theory. The solution of this problem came only in the last decade, with the application of the density functional formalism to describe the crystal as a self-structured fluid. In the last few years we have got density functional approximations

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capable of quantitative predictions for the freezing of hard spheres, and we are just now getting close to a good theoretical understanding of the full phase diagram of argon.

A glance to the molecular structure of any typical liquid crystal is enough to understand why the theory of liquid crystals is at least 30 years behind the theory of simple fluids. The first efforts by Onsager (1949) and Maier & Saupe (1958, 1960) were directed to the nematic, as the simplest liquid crystal phase. The relevant aspect of the interactions responsible of this phase was identified as the molecular anisotropy. Onsager explored the effects of anisotropy in the hard core repulsion, with an excluded volume approximation. He obtained qualitative agreement with the behaviour of lyotropic liquid crystals (those studied experimentally by changing the concentrations in a mixture), although the theory was far from quantitative accuracy. Maier & Saupe were involved in experiments with thermotropic liquid crystals (pure substances studied by changing the temperature) and they found their theory on the anisotropy of soft dispersion interactions, treated in a mean field approximation inspired in Weiss's theory of ferromagnetism. The quantitative accuracy of Maier–Saupe theory, although limited, was superior to that of Onsager, and the mean field treatment of soft interactions was much easier to extend to other liquid crystal phases, like smectics, than the packing effects of anisotropic hard cores. The theoretical development, from these pioneering works and during the past two decades, has been based on the achievements of the theory of simple fluids and on advent of computer simulations, as an intermediate step between theory and experiments. The theory of simple fluids made clear that the correlation structure in a liquid is mainly determined by the core repulsions. Any theory aiming for quantitative accuracy should include this effect, and that is why the hard spheres model became the basic reference system to describe simple fluids. The same should apply to the correlation structure, both of positions and molecular orientations, in molecular fluids and liquid crystals. Any attempt to include the effects of the soft dispersion interactions, beyond the pure mean field approximation, should include the anisotropy of the core repulsions. Thus, the study of systems with pure hard core interactions has become very important. These models should be the reference systems used to describe other, more realistic, with soft dispersion and electrostatic interactions. Even if the soft interactions are the dominating effect in the formation of the nematic, as postulated by Maier & Saupe, an accurate theory will only be possible with a good description of a hard core reference system.

Moreover, our increasing knowledge about the crystallization of simple liquids indicates that this transition is dominated by the packing effects of the hard cores, rather than by the soft attractive interactions. If the liquid crystals are regarded as 'mesophases' between the liquid and the solid, it will be surprising if the packing of the hard cores were not an important factor in the determination of the phase diagram. The phase diagram of a model with pure hard core interactions does not depend on the temperature, but this should not be taken as an indication of falling wide off the mark of a thermotropic liquid crystal. The use of temperature as the control parameter in experiments at constant pressure is much more convenient, for practical reasons, than the use of pressure as the control parameter, but it does not imply that the most relevant interaction is not the core repulsion. The liquid–solid coexistence in a Lennard–Jones system is mainly determined by the core packing, the attractive interactions produce only a weak dependence of the coexisting densities with the temperature. It is precisely this weak dependence what makes possible for the experimentalist to study the crystallization of a simple fluid or the fusion of a solid as temperature induced phenomena, but this should not be taken as a proof for the preeminence of the attractive interactions over the core repulsions in the problem.

It is hardly possible to overemphasize the role of the computer simulations in the development of the theory of liquid crystals. In the direct comparison of a theoretical result and the experimental data we are always uncertain about the source of the discrepancies. They may be the effect of the unavoidable approximations made in the statistical theory, or they may come from the difference between the real molecular interactions and the necessarily simplified model hamiltonian used in the theory. The computer simulations allow us to check the accuracy of the theoretical approaches without any incertitude about the interactions. On the other hand, they may be used to compare the behaviour of simplified models with that of real systems. Again from the perspective given by the theory of simple fluids, we see that theoretical progress will be next to impossible without the computer simulations.

The rest of this chapter gives a review of the main microscopic theories of liquid crystals, from the classical work of Onsager to the recent advances towards quantitative accuracy and the perspectives for the future. Section 2 is dedicated to the nematic phase and the transition from the isotropic liquid. Liquid crystals with spatial order, smectics and columnar phases, are reviewed in §3. The chapter ends with a general discussion over the present status and perspectives of the theory. The review is restricted to the microscopic statistical theories of bulk equilibrium phases, it is not an extensive account of the existing approaches but rather an introduction to the tendencies in a field of very active research. The subjects of dynamics, interfaces, defects and textures are leaved out entirely. The reader is directed towards the existing texts, in particular the book by de Gennes (1974), already a classic in the field, and the excellent and more recent one by Vertogen & de Jeu (1988). The review article by Frenkel (1991) is also recommended for the most recent advances.

2. Theories of nematics

The difference between a nematic liquid crystal and a molecular liquid is the long range order in the orientation of the molecular axes, described by a set of angles represented here as ω. In the simplest case, the order appears only in the orientation of one molecular axis, the 'main' axis, which is represented by the unit vector $\boldsymbol{a}$, with cartesian components a_α $(\alpha = x, y, z)$. In absence of polar order the configurations with orientations $\boldsymbol{a}$ and $-\boldsymbol{a}$ have the same probability and the statistical average of the vector $\boldsymbol{a}$ vanishes, $\langle \boldsymbol{a} \rangle = 0$. The order parameter is the symmetric traceless tensor, $S_{\alpha\beta} = \langle a_\alpha a_\beta \rangle - \frac{1}{3}\delta_{\alpha\beta}$, with the usual Kronecker tensor $\delta_{\alpha\beta}$ and α, $\beta = x, y, z$. In the isotropic liquid phase, without long range order in the molecular orientations, $S_{\alpha\beta} = 0$. In the usual uniaxial nematic liquid crystals the tensor $S_{\alpha\beta}$ may be expressed as $S_{\alpha\beta} = S(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta})$, in terms of the components of a unit vector $\boldsymbol{n}$, called the nematic director, which represents the direction of mean orientation for the main molecular axis. The scalar nematic order parameter S measures the degree of orientational order. Distortions of the nematic director correspond to changes of $\boldsymbol{n}$ over macroscopic scales and are responsible for some of the most characteristic properties of liquid crystals. However, in the development of a microscopic (molecular) theory of nematics the director $\boldsymbol{n}$ is fixed (say along the Z axis) and the system is uniaxial if the distribution function of molecular orientations, $f(\omega)$, depends only on the angle θ between the vectors $\boldsymbol{a}$ and $\boldsymbol{n}$. The nematic order parameter S is the mean value of the second order Legendre polynomial,

$$S = \langle P_2(\cos{(\theta)})\rangle = \int \mathrm{d}\omega f(\theta)\, P_2(\cos{(\theta)}) = 2\pi \int_0^{\pi} \mathrm{d}\theta \sin\theta f(\theta)\, \tfrac{1}{2}[3\cos^2{(\theta)} - 1]. \quad (1)$$

The isotropic liquid, without orientational order, corresponds to $S = 0$ and a system of parallel molecules, with perfect orientational order, has $S = 1$. A molecular theory of nematic liquid crystals and of the phase transition from the isotropic liquid to the nematic has to evaluate the statistical average over the molecular orientations in (1) from a microscopic model of molecular interactions and find spontaneous order, $S \neq 0$, in the nematic.

In his pioneering work on liquid crystals, Onsager (1949) studied a molecular model with pure hard core repulsions. This leaves out from the beginning the temperature as a relevant parameter, but it focuses the problem in the effects of packing which may be studied in terms of the molecular geometry. The obvious advantage is that the molecular model may be compared with the real molecules in a quantitative (although simplified) way. For elongated molecules Onsager proposed a hard-rod model, with length L and diameter D which should (roughly) reproduce the molecular shape. The statistical theory is then developed as a virial expansion of the free energy, F, which is written as a functional of the orientational distribution $f(\omega)$. The theory includes the exact free energy of a system with non-interactive molecules, the molecular ideal gas $F_{\mathrm{id}}[f(\omega)]$. The molecular interactions are included only through their first contribution, which is proportional to the excluded volume $V_{\mathrm{hb}}(\omega, \omega')$ between a pair of hard body molecules with orientations ω and ω':

$$\frac{F[f(\omega)]}{NkT} = \frac{F_{\mathrm{id}}[f(\omega)]}{NkT} + \tfrac{1}{2}\rho_0 \int \mathrm{d}\omega\, \mathrm{d}\omega' f(\omega) f(\omega')\, V_{\mathrm{hb}}(\omega, \omega'), \quad (2)$$

where ρ_0 is the density of molecules, assumed uniform over the system. The second term in (2) is the driving force for the formation of a nematic: the exclude volume between two hard rods or length L and diameter D, in the limit of $L \gg D$ (i.e. neglecting the end effects) is

$$V_{\mathrm{hr}}(\omega, \omega') = 2L^2 D\, |\sin\gamma|, \quad (3)$$

in terms of the angle γ between the two rod axes ($\cos\gamma = \boldsymbol{a}\cdot\boldsymbol{a}'$). This excluded volume is minimized for parallel orientations favouring the nematic order. The fully disordered distribution of molecular orientations, $f(\omega) = \frac{1}{4}\pi$, is favoured by the ideal gas free energy:

$$\frac{F_{\mathrm{id}}[f(w)]}{NkT} = \int \mathrm{d}\omega f(w) \ln{[4\pi f(\omega)\, \rho_0 \Lambda^3]} - 1, \quad (4)$$

where Λ is the usual thermal wavelength. At low density the ideal gas contribution is dominant and the system is an isotropic liquid. At higher density the packing efficiency is more important and the nematic phase becomes stable. The phase transition was searched with a parametrized distribution function and found, in terms of the packing fraction $\eta = \pi D^2 L \rho_0/4$, at $\eta_I = 3.3D/L$ of the isotropic liquid and $\eta_N = 4.5D/L$ for the nematic. The predicted phase transition has strong first order character; the density difference between the coexisting phases is large and the order parameter jumps from $S = 0$ in the isotropic liquid to $S = 0.84$ in the coexisting nematic. The nematic order observed in real liquid crystals at the transition point is much lower, $S \approx 0.3$, indicating a much weaker first order transition. An improved calculation by Lee & Meyer (1986), with the same free energy (2) and the full numerical minimization with respect to $f(\omega)$, gives $S = 0.79$ still far from the experimental data.

The approach of Maier & Saupe (1958, 1960) was directly inspired in Weiss's theory of ferromagnetism. The theory focuses on the role of temperature in a model of thermotropic liquid crystals, with a phase transition from the isotropic liquid (at $T > T_{IN}$) to the nematic (at $T < T_{IN}$) without change in the density, ρ_0. The nematic order is assumed to be induced by a soft anisotropic intermolecular potential, $\phi(\boldsymbol{r}-\boldsymbol{r}', \omega, \omega')$, which may be treated in a pure mean field approximation, integrating it over the relative positions of the molecular centres, $\boldsymbol{r}-\boldsymbol{r}'$, to given an effective potential $\Phi(\omega, \omega')$. The free energy per molecule is written as

$$\frac{F[f(\omega)]}{N} = \frac{F_{\mathrm{id}}[f(\omega)]}{N} + \tfrac{1}{2}\rho_0 \int \mathrm{d}\omega\, \mathrm{d}\omega'\, f(\omega) f(\omega')\, \Phi(\omega, \omega'). \qquad (5)$$

The phase transition comes from the balance between the molecular ideal gas entropy and the soft molecular interactions. The problem to get a truly microscopic theory was the lack of knowledge about these interactions in real molecules. The macroscopic symmetry of nematic liquid crystals impose symmetry requirements on $\Phi(\omega, \omega')$. Maier & Saupe suggested van der Waals like, induced dipoles interactions, with anisotropic molecular polarizability. Thus the angular dependence of the intermolecular potential was modelled by

$$\Phi(\omega, \omega') = -JP_2(\cos\gamma) \qquad (6)$$

in terms of the angle γ between the main axis of the two molecules and the Legendre polynomial of order 2. This is the smoothest function of the molecular orientations with the appropriate symmetry. The coefficient J of this anisotropic interaction should reflect the anisotropy of the molecular polarizability, but in practice it was taken as an empirical parameter to fit the experimental transition temperature, T_{IN}. The theory provided a prediction for the nematic order parameter below the transition temperature which was in remarkably good agreement with the experimental data. Other theoretical predictions, as the latent heat at the transition, were not so successful but altogether the theory of Maier & Saupe looked much closer to the real liquid crystals than Onsager's approach. This double start polarized somehow the development of microscopic theories of nematics in a 'hard-cores' versus 'soft-interactions' disjunctive. Sometimes the two approaches were regarded as separate theories of lyotropic and thermotropic liquid crystals respectively, although the separation seems to reflect more the 'experimental convenience' than a 'fundamental difference': most of the work is done at constant (atmospheric) pressure, so for pure systems the temperature is the practical control parameter and they are 'thermotropic' liquid crystals. For mixtures the relative concentration of each component may be used as the control parameter, at constant temperature, and they are considered 'lyotropic'. From the theoretical point of view the isotropic–nematic transition line in the concentration–temperature phase diagram may be crossed in different directions, and some of these directions may be easier to explore in experiments, but the essence of the transition is the same. Within the theoretical framework developed in the last decades the approaches of Onsager and of Maier & Saupe may be cast in the common form of a 'generalized mean-field' theory (Somoza & Tarazona 1992), with the free energy, as a functional of the distribution of molecular orientations, given by

$$\frac{F[f(\omega)]}{NkT}=\frac{F_{\mathrm{id}}[f(\omega)]}{NkT}+\zeta(\rho_0,T)+\lambda(\rho_0,T)\int \mathrm{d}\omega\,\mathrm{d}\omega'\,f(\omega)f(\omega')K(\omega,\omega'), \tag{7}$$

where ζ is the contribution from the molecular interactions independent of the molecular orientations. The phase transition from the isotropic liquid to the nematic liquid crystal results from the balance between the ideal molecular gas free energy, F_{id}, and the contribution from the molecular interactions through the integrals over ω and ω'. The kernel $K(\omega,\omega')$ reflects the nature of the interactions and may be normalized to unity, extracting all the dependence on temperature and density into the 'control parameter', $\lambda(\rho_0,T)$. In the theory of Maier & Saupe $\lambda\sim\rho_0/T$ and the kernel K represents the anisotropic intermolecular potential by (6). In Onsager's approach $\lambda\sim\rho_0$ and the kernel is the excluded volume between hard rods (3). If the phase transition between the isotropic liquid and the nematic is searched at constant value of the 'control parameter' λ (as in the original work of Maier & Saupe), the nematic order parameter at the transition depends only on the kernel $K(\omega,\omega')$. In this light, the good agreement with experimental data of Maier–Saupe prediction for S, compared to the apparent failure of Onsager's approach, is surprising. The later is based in a sensible (although simplified) microscopic model for the molecular interactions, while in the former the kernel is taken as the 'smoothest' function with the adequate symmetry, mainly to simplify the analysis of the model, with little physical justification.

Improvements over the original work of Maier & Saupe require the microscopic modelling of the molecular interactions. Any approach including, at least partially, the molecular correlations has to depend on the coupling between orientations and positions, this requires a model for the molecular interaction potential, $\phi(\boldsymbol{r}-\boldsymbol{r}',\omega,\omega')$, and not only for its integral over $\boldsymbol{r}-\boldsymbol{r}'$ as in (2.6). Plausible model for this potential should include a repulsive interactions produced by the overlap of the molecular cores. With the typical values of the density in liquid crystals, the packing effects of these cores should give an important contribution to the free energy, which cannot be described in a pure mean field approach like (2.5). Semi-empirical equations of state may include both the soft interactions, in mean field approximation, and the hard cores packing, as in the van der Waals equation of state for simple fluids. However, the empirical parameters used to fit the experimental data have a very poor correlation with the predictions from the molecular structure (Vertogen & de Jeu 1988; Flapper *et al.* 1981). The difficulties arise from both the very complex structure of the liquid crystal molecules (including flexible tails and other elements far from the simplified theoretical models) and from the crude approximations used in the statistical average of even the simplest hard rod model. The first difficulty may be bridged by computer simulations of systems with simple molecular interactions, like the potential proposed by Gay & Berne (1981), to provide the 'experimental' data for a theoretically treatable model. The second difficulty implies that, before we may construct theories with quantitative predicting power for a liquid crystal with soft interactions, we have to develop the theoretical treatment of the hard core models, much as the theoretical treatment of simple liquids followed the understanding of the hard sphere fluid (see Hansen & McDonald 1986).

Telo da Gama (1984) studied a microscopic model for the soft molecular interactions with isotropic hard cores (i.e. hard spheres) to represent the packing contribution to the free energy. The model, although still far from realistic, includes the dependence of the free energy on the density and the coexisting isotropic liquid and nematic liquid crystal at the same pressure, rather than at the same density. It also includes the coexistence between the isotropic liquid and a vapour, so that the usual experimental conditions for thermotropic liquid crystals may be mimicked by the phase diagram along the vapour–liquid coexistence line. The temperature for the transition from the isotropic liquid to the nematic corresponds to the triple point temperature. Within the general description (2.7), the control parameter λ is a nonlinear function of the density, and the effect is to increase the first order character of the phase transition. The nematic order parameter at coexistence depends on the parameters of the potential, but it raises well over the original predictions of Maier & Saupe and makes the comparison with experiments significantly worse. The model has been applied to study the properties associated to inhomogeneous spatial distributions, the structure of liquid crystal interfaces (Telo da Gama 1984*a*; Thurtell *et al.* 1985).

The theoretical approaches for hard body molecular models beyond Onsager's pioneering work, followed the advances in the understanding of the hard sphere system, in the theory of simple liquids. Onsager's approach is a virial expansion truncated after the second order term. The validity of such truncation is doubtful, even in the limit of very long rods ($L \gg D$), when the phase transition occurs at very low packing fractions (proportional to D/L), the effect of higher order coefficients may be important (Vertogen & de Jeu 1988). Higher order terms in the virial expansion for the isotropic liquid, were calculated for asymmetric hard bodies with simple geometry (sphero-cylinders and ellipsoids being the most popular shapes), but the virial expansion for the nematic phase requires the averages of the overlapping excluded volumes (in terms of the integrals of Mayer functions) with anisotropic distribution $f(\omega)$ of the molecular orientations, which are difficult to obtain for higher orders. The most successful approaches are based on approximated resumations which give the free energy as a functional of the orientational distribution $f(\omega)$ with a form similar to (3). The 'scaled particle approximation' of Cotter (1974, 1976), the 'y-expansion' of Barboy & Gelbart (1979, 1980) and the 'decoupling approximation', first proposed by Wulf (1977) and Parsons (1979) and later presented in equivalent forms by other authors (Lee 1987; Baus *et al.* 1987), are probably the most successful theory for nematic liquid crystals of hard body molecules. In the later, the free energy, as a functional of the molecular orientation distribution $f(\omega)$, is written in terms of the excluded volume between the hard body molecules, $V_{\mathrm{hb}}(\omega, \omega')$, and that of a 'reference' hard spheres system, V_{hs},

$$\frac{F[f(\omega)]}{NkT} = \frac{F_{\mathrm{id}}[f(\omega)]}{NkT} + \Delta\psi_{\mathrm{hs}}(\rho) \int \mathrm{d}^2\omega\, \mathrm{d}^2\omega' f(\omega) f(\omega') \frac{V_{\mathrm{hb}}(\omega, \omega')}{V_{\mathrm{hs}}}, \tag{8}$$

where $\Delta\psi_{\mathrm{hs}}(\rho)$ is the excess over the ideal gas for the free energy per molecule in the reference hard sphere system. This functional form reproduces Onsager's theory if this function is approximated by its first contribution in a density expansion,

$$\Delta\psi_{\mathrm{hs}}(\rho) = \tfrac{1}{2}\rho V_{\mathrm{hs}} + O(\rho^2).$$

Thus (2.8) may be interpreted (Somoza & Tarazona 1989) as an approximated resumation of the virial expansion at infinite order, with the virial coefficients for the hard body system, B_i^{hb}, assumed to scale with those of hard spheres, B_i^{hs}, as

$$B_i^{\mathrm{hb}} = (B_2^{\mathrm{hb}}/B_2^{\mathrm{hs}})\, B_i^{\mathrm{hs}} \quad i = 2, 3, \ldots. \tag{9}$$

In this way we may use the equation of state for a hard sphere fluid (known in very good approximations), to get the free energy of hard body systems. The volume of the reference hard spheres is chosen to optimize the accuracy of the scaling relation (2.9). In the isotropic liquid, $f(\omega) = \frac{1}{4}\pi$, the best empirical choice seems to be to take spheres with the same volume as the hard body molecules, so that the packing fraction in the real and reference systems is the same. However, in a nematic phase the results of this approximation may be improved by other judicious choice for the reference system, depending on the orientation distribution $f(\omega)$.

Recently, Tjipto-Margo & Evans (1990) have got the virial coefficient B_3 for hard ellipsoids. That allowed them to extend Onsager's approach exactly to the next order and to include this information in approximated resumations. The development of all these theoretical approaches with quantitative accuracy was made possible by the advent of computer simulations to provide the 'experimental' data for hard body systems, with different molecular shapes, to contrast the results of the theoretical approximations. One of the points clarified by computer simulations was that the high value of the nematic order parameter at the isotropic–nematic phase transition found in Onsager's approach, was only a slight overestimation of the real behaviour of simple hard body systems (Baus *et al*. 1987). The discrepancy with experimental data seems to be due mainly to the strong asymmetry of real molecules contrasted with simple geometrical forms assumed in the theoretical works. The study, within the decoupling approximation, of hard bodies with polar and biaxial asymmetry show that the first order character of the transition is strongly reduced (Barboy & Gelbart 1980; Hołyst & Poniewiersky 1989*b*; Somoza & Tarazona 1992). This offers a possible explanation for the surprising agreement of Maier–Saupe results with the experimental data commented above. The interaction potential between real molecules is a very complex function of the molecular orientations, but the effective kernel, as a function of main molecular axis orientations, after integration over all the other degrees of freedom in ω, will produce a relatively smooth function. Thus, that the kernel in (3) may be closer to the empirical choice of Maier–Saupe (2.6) than to the microscopic models of very symmetric hard bodies.

Somoza (1989) started the development of a perturbation theory for a system with the Gay–Berne potential. Following the ideas used in the theory of simple fluids, the interaction potential is split into a repulsive core and attractive interactions. The former is described by a hard body molecule with the adequate shape, and the free energy of this reference hard body system is obtained with the decoupling approximation. The attractive interactions are introduced at first order perturbation theory with, the pair distribution function of the reference fluid. The theory is still at a preliminary stage, involving severe approximations at different levels. The comparison with the computer simulations of de Miguel *et al*. (1991) show that, although there is still plenty of room for improvements, we are in the way towards a theory with good quantitative prediction power for these systems.

3. Smectics liquid crystals

Smectic liquid crystals present, besides the nematic order of the molecular orientations, a layer structure with long range spatial order along one direction. At least for the simpler cases, called smectics A and C, the structure within each layer remains fluid without long range spatial order. The difference between the smectic A and the smectic C phases is the relative orientations of the nematic director, $\boldsymbol{n}$, and the orientation of layers. In a smectic A liquid crystal the layers are perpendicular to the average orientation of the main molecular axis, given by $\boldsymbol{n}$, while in a smectic C phase these two directions form a 'tilt angle' φ. Other 'exotic' smectic phases present some kind of two-dimensional order within the layers. Liquid crystals made of oblate (disc-like) molecules may present a 'columnar phase', as a counterpart of the smectics formed by the prolate (rod-like) molecules. In the columnar phase the molecules organize themselves in a two-dimensional array of columns, so that the system presents long range positional order in the two dimensions perpendicular to the nematic director, but it is still fluid in the third direction, along the columns. All these liquid crystals phases, with nematic order plus partial crystalline order, are usually found between the isotropic liquid and the crystal phases, as intermediate steps in the development of the full crystalline order. The theoretical study of these phases is made in terms of the distribution function, $\rho(\boldsymbol{r},\omega)$, for a molecule centred at position $\boldsymbol{r}$ and with orientation ω. The approximate forms for free energy, as a functional of $\rho(\boldsymbol{r},\omega)$, are minimized with respect to this distribution function with the appropriate symmetry: $\rho(\boldsymbol{r},\omega)=\rho(\omega)=\rho_0 f(\theta)$ corresponds to the uniaxial nematic phase studied in the previous section, θ being the angle between the main molecular axis and the nematic director. Smectic A phases, with layers parallel to the XY plane and with uniaxial symmetry, are described by $\rho(z,\theta)=\rho(z+\lambda,\theta)$ with a period λ along the Z direction. The fully order crystal phase will be represented by a function $\rho(\boldsymbol{r},\omega)$ with the periodicity over $\boldsymbol{r}$ on a crystal lattice in three dimensions.

(*a*) *Theories of the smectic A phase*

A theory of smectic A liquid crystals was constructed 20 years ago independently by Kobayashi (1970) and McMillan (1971), as an extension of Maier–Saupe approach for nematics. The idea was to describe the nematic order as the result of soft anisotropic interactions which may be described within a pure mean field approximation. The difference with the theory of nematics is that the intermolecular potential has to be specified as a function of the molecular orientations and the relative position of the molecular centres, $\Phi(\boldsymbol{r}-\boldsymbol{r}',\omega,\omega')$. Following the same strategy as Maier & Saupe, this potential is included through an empirical function already integrated on the variables which do not appear in the distribution function:

$$\Phi(z-z',\theta,\theta')=-U(z-z')\,P_2(\cos\theta)\,P_2(\cos\theta'), \tag{10}$$

which keeps the simplest possible dependence in the molecular orientation (equivalent to (2.6)) to produce the nematic order. The function $U(z)$ represents the interaction between to parallel molecular layer at distance z. Thus, the mean field approximation for the free energy, as a functional of $\rho(z,\theta)$ is:

$$F[\rho(z,\theta)]=F_{\text{id}}[\rho(z,\theta)]+\frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\int \mathrm{d}\omega\,\mathrm{d}\omega'\,\Phi(z-z',\omega,\omega')\,\rho(z,\omega)\,\rho(z',\omega') \tag{11}$$

with the ideal molecular gas free energy given by the direct generalization of (4) to inhomogeneous systems. This free energy is minimized within a variational family of periodic functions, with period λ, in z:

$$\rho(z,\theta)=\rho_0 f(\theta)+2\rho_0\sum_n \rho_n(\theta)\cos(2\pi nz/\lambda). \tag{12}$$

The period λ is fixed to represent empirically the length of the hard core along the main molecular axis. This reduces the required knowledge of the function $U(z)$ in (3.1) to the Fourier components, U_n, with wave number $q = 2\pi n/\lambda$, $n = 0, 1, 2, \ldots$. In practice, only the terms with $n = 0$ and 1 were kept, so that the function interaction potential was fully specified by two parameters U_0, equivalent to J in (6), and U_1 as the driving force of the smectic order. It is clear that the function $U(z)$ represented in this way cannot pretend to be a truly microscopic model for the molecular interactions. The parameters λ, U_0 and U_1 are regarded as empirical coefficients to fit the experimental phase diagram and related to the molecular structure in a loose qualitative way.

The 'global phase diagram' in this approach represents the transition temperature for the isotropic liquid–nematic and the nematic–smectic A transitions, in reduced units kT/U_0, as functions of the ratio $\frac{1}{2}\alpha = U_1/U_0$. For values of $\alpha > 0.98$ there is a direct first order transition from the isotropic liquid to the smectic A liquid crystal, without stable nematic phase at any temperature. For $0.98 < \alpha < 0.7$ there are two first order phase transitions: from the isotropic liquid to the nematic and, at lower temperature, from the nematic to the smectic A. If the parameter α is reduced below 0.7, the second transitions becomes of second order, and the density modulation develops in a continuous way. This behaviour, including the existence of a tricritical point where the nematic–smectic A transition changes its character, is in qualitative agreement with the experimental data for homologous series of molecules, with the same central aromatic core and different chain lengths. However, those properties which may be compared directly with experimental data, like the ratio between the two transition temperatures at the tricritical point, are far from quantitative agreement. The real predictions of the theory are in fact little more than those of a macroscopic Landau–de Gennes theory, with two order parameters, nematic and smectic modulations, and the empirical free energy coupling them. It is not even necessary to keep the nematic order as one of the coupled order parameters, in the approach proposed by Meyer & Lubenski (1976), the molecules are assumed to be parallel to each other, with perfect nematic order $S = 1$, and the two order parameters are the amplitudes of density modulations with periods λ and $\frac{1}{2}\lambda$, so that the free energy depends on the Fourier components U_1 and U_2 of the function $U(z)$ in (3.1) and U_0 is irrelevant because the perfect nematic order. The phase diagram is qualitatively similar to that of Kobayashi–McMillan for the nematic to smectic A transition, with the ratio U_2/U_1 playing the role of the parameter α. Again there is a tricritical point which separates the regions of first and second order phase transitions. The perfect nematic order precludes the existence of the isotropic liquid phase but it is not an obstacle to the existence of the nematic–smectic A phase transition.

A perspective to the merits of these mean field theories for the smectic A phase is given by the theory of crystallization of a simple fluid. The theory of Meyer & Lubenski (1976) is very close to the theory of melting proposed by Kirkwood in 1951, with the solid phase described by density modulations in the three dimensions of space rather than only along the nematic director as in the smectic A. The major drawback in the approach is that the lattice parameter for the crystal order is fixed, in an empirical way, by the packing of the molecular repulsive cores, but only the attractive interactions contribute to the free energy (in the mean field approximation) and below the transition temperature stabilize the density modulations allowed by the core packing. Thus, the repulsive cores have a crucial role in the selection of the structural order but their contribution to the free energy is fully neglected. In a simple system, like argon described by a Lennard–Jones potential, the nature of the solid–liquid phase transition is qualitatively similar to that observed in computer simulations of the hard sphere model, in which driving force for the crystallization is the hard core packing contribution to the free energy. The core packing should also provide a very important contribution to the free energy. A truly microscopic theory for the crystallization of a simple fluid was only possible in the last decade, with the advent of good density functional approximations for the free energy, and the hard sphere model has played a central role (Tarazona 1985; Curtin & Ashcroft 1985; Baus 1991). Good theories for the crystallization of the Lennard–Jones system have appeared very recently (Curtin & Ashcroft 1986; Mederos *et al.* 1993), using a perturbation scheme from the hard spheres model similar to that used in liquid theory.

The main difference between the crystallization of simple fluids and the problem of liquid crystals was that the complexity of the molecular interactions for the later cover up for the semiempirical approaches. The arrival of computer simulations have changed this by providing ‘experimental’ data with relatively simple and perfectly specified intermolecular potentials. The comparison of the simulation with the predictions of the simple mean field theories makes clear that a truly microscopic theory for these models has to include the free energy associated to the packing of the repulsive cores. In this context, the models of hard body molecules are starting to play a crucial role in the development of a theory for smectic liquid crystals. They are very simplified models, in which the molecular interactions are described by the molecular shape, which is much easier to compare with the real molecules. Moreover, the computer simulations of Frenkel and coworkers (Stroobants *et al.* 1986, 1987; Frenkel 1988; Frenkel *et al.* 1988) have shown that the phase diagrams of these systems present a large variety of phases, depending in a subtle way on the molecular shape. These simulations provide the touchstone to develop theoretical approximations, using the experience gained with the density functional theory of hard spheres and the theory of nematics. This is a very active field, and it is still uncertain which approaches would become the most successful. What follows is a brief account of the theory proposed by Somoza & Tarazona (1988, 1989), which has been applied with relative success to several systems. Other related approaches (Hosino *et al.* 1979; Mulder 1987; Wen & Meyer 1987; Hołyst & Poniewierski 1989*a*; Poniewierski & Hołyst 1988) have been developed and applied to several systems.

The approach is an extension of the decoupling approximation for systems with inhomogeneous density distributions. The basic idea is to represent a system of hard body molecules with the help of a ‘reference system’ made of parallel hard ellipsoids. This reference system, with arbitrary length for the three main axis of the ellipsoids, may be obtained by the anisotropic scaling of a hard sphere system. The scaling cannot change the thermodynamic properties of the system, so that the equation of state and the phase diagram is the same as for hard spheres, which we know quite accurately. The only possible phases of the reference system are the hard sphere fluid, mapped into a system of ellipsoids with perfect nematic order, and the hard spheres crystal, mapped into the hard ellipsoid crystal. Smectic phases, with partial spatial order cannot appear in the reference fluid, but they may be obtained when the difference between the hard body molecules and the reference hard ellipsoid is taken into account in the following way:

$$F[\rho(z,\theta)] = F_{\mathrm{id}}[\rho(\boldsymbol{r},\theta)] + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\omega\, \rho(\boldsymbol{r},\theta)\, \Delta\psi_{\mathrm{phe}}(\bar{\rho}(\boldsymbol{r})) \times \frac{\int \mathrm{d}\boldsymbol{r}' \int \mathrm{d}\omega'\, \rho(\boldsymbol{r}',\omega')\, M_{\mathrm{hb}}(\boldsymbol{r}-\boldsymbol{r}',\omega,\omega')}{\int \mathrm{d}\boldsymbol{r}' \int \mathrm{d}\omega'\, \rho_0(\boldsymbol{r}')\, M_{\mathrm{phe}}(\boldsymbol{r}-\boldsymbol{r}')}, \qquad (13)$$

where M_{hb} and M_{phe} are the Meyer functions for the hard body and the parallel hard ellipsoids respectively. The integrals of these functions over the relative position of the molecular centres are the excluded volumes as functions of the molecular orientations. For the reference system of parallel hard ellipsoids the angular variables do not appear in the Meyer function and $\rho_0(\boldsymbol{r})$ is the integral of $\rho(\boldsymbol{r},\omega)$ over the angular variables, i.e. the local density of molecules. The function $\Delta\psi_{\mathrm{phe}}$ is the excess over the ideal gas free energy per molecule in the reference fluid, and it is evaluated in a 'weighted density', $\bar{\rho}(\boldsymbol{r})$, as in the weighted density approximation (WDA) for an inhomogeneous hard sphere system (Tarazona 1985; Curtin & Ashcroft 1985). In a system with homogeneous density, either the isotropic liquid or the nematic liquid crystal, the free energy (3.4) reduces to that of the decoupling approximation in (8). The formulation in terms of the Mayer function, instead of the excluded volume provides in fact the coupling between the molecular orientations and positions, required to construct a theory of smectics.

The choice of the reference parallel hard ellipsoids is made to include the main effects of the hard body packing in the reference system, the lengths of the ellipsoid principal axis should reflect both the shape and the degree of nematic order of the hard body molecules. In the isotropic liquid the reference system has to be made of spheres, to keep the macroscopic isotropy of the system, in a uniaxial nematic of prolate molecules the parallel ellipsoids should have a long axis parallel to the nematic director and shorter equal axis in the other two directions. For systems with homogeneous density the only relevant parameter of the reference system is the excluded volume, so that there is no difference between hard spheres and hard ellipsoids of the same volume as in the previous section. However, in systems with inhomogeneous density the anisotropy of the reference ellipsoids is very important; it should control the free energy of density modulations and select the smectic period λ to be similar to the length of the main molecular axis.

Somoza & Tarazona (1989, 1990) explored several empirical recipes to select the reference system in a system of parallel and free rotating hard molecules. In a system of parallel hard sphero-cylinders (cylinders of length L and diameter D with semi-spherical caps at the ends), the theory was compared with the computer simulations of Stroobants *et al.* (1988). The phase diagram shows a continuous phase transition from the nematic to the smectic. A phase at a critical packing fraction which depends on the aspect ratio L/D. The results, in relatively good agreement with the computer simulations, show that the approximation (3.4) includes the subtle effects of the molecular shape in the macroscopic behaviour: the system of parallel hard sphero-cylinders is not very different from the reference system of parallel hard ellipsoids, but the difference is enough to stabilize the smectic A phase for the sphero-cylinders and not for the ellipsoids.

The results for systems of free rotating hard sphero-cylinders are more sensitive to the map into the reference system. The theories of Somoza & Tarazona (1990) and of Poniewierski & Hołyst (1988) have been applied to the problem. In both cases there is a stable smectic A phase, formed from the nematic if the aspect ratio is larger than $L/D \sim 3$. The nature of the transition is sensitive to the details of the theory. For very long molecules the orientational degrees of freedom should be nearly frozen and the theories predict a second order phase transition, as in the case of parallel molecules. However, there is a strong discrepancy in the value of L/D at which the transition changes order. There are computer simulations of the model for $L/D = 5$, but the problem is still open.

The development of theoretical treatments for models with both soft attractions and hard core repulsions, beyond the empirical mean field theories, is a subject of very active interest. Mederos & Sullivan (1989) have developed a treatment with a reference system of parallel hard ellipsoids plus soft attractive interactions of the same type as in (10) and with some extra terms coupling the relative molecular position and their orientations. The phase diagrams are explored in the temperature–density plane and they may include isotropic liquid, nematic and smectic A phases. The later only appears as a consequence of the attractive interactions, as in the approach of Kobayaski & McMillan, but the reference system of parallels hard ellipsoids plays an active way in the determination of the smectic period λ, which is obtained in a consistent way within the approximation, taking into account the contributions to the free energy from both the repulsive cores and the attractive interactions. It was shown that the stability of the smectic A phase requires a sufficiently large elongation of the hard ellipsoids. However, the theory still retains a certain degree of empirical character in the determination of the reference ellipsoid. The ratio between the major and the minor axis diameters should reflect the shape of the molecular hard core and the distribution function of the molecular orientations, but Mederos & Sullivan (1989) take this ratio as a constant, independent of the nematic order. The attractive interactions included in the model have also an empirical form, lacking real correlation with a molecular model. The perturbation approach of Somoza (1989), for a system with the Gay–Berne interaction potential, is formulated as a density functional approximation for the free energy, so that it may be used to study also the smectic-A phase and it would provide a truly microscopic theory for a well-defined molecular model. The progress was hindered by the heavy computational requirements, but the approach seems to be in the right direction for future advances.

(*b*) *Theories of the smectic-C*

The smectic-C phase may appear in systems of molecules which broken axial symmetry. The description of the molecular orientation requires not only the direction of the main molecular axis $\boldsymbol{a}$, but also an angle, χ, to describe the orientation of a second molecular axis around the nematic director. Experimental data suggest that this secondary axis may be associated to the presence of permanent electric dipoles in a direction different from the main axis. The mean-field theories of smectic-C are based on the idea that without the broken axial symmetry the system would be a smectic-A phase and they figure out how the off-axis dipole (or any other element breaking the axial symmetry) may produce a tilt angle φ. These theories (Vertogen & de Jeu 1988), take the form of a Landau theory with φ or $\sin\varphi$ as order parameter and the molecular model is used to determine the sign of the coefficients in the expansion of the free energy in powers of the order parameter.

An important qualitative feature which may be discussed at this level of theoretical development is the coupling between the tilt angle φ and the presence of biaxiality in the molecular orientations, i.e. the breaking of the symmetry for the distribution function of the angle χ, producing the biaxiality with respect to the nematic director. This coupling is the simplest way to get a theoretical model for the smectic-C, but the experimental evidence indicates that in real smectic-C liquid crystals, the biaxiality of the molecular orientations is negligible. This favours models of molecular interactions, like the interaction between a permanent off-axis dipole and the induced dipole in a neighbouring molecule (Vertogen & de Jeu 1988), which may explain this behaviour. Other types of molecular interactions, like the interaction between permanent electric dipoles and quadrupoles, may also be responsible for the tilt angle without breaking the symmetry of the distribution function for χ.

Somoza & Tarazona (1988) have applied the density functional approximation (13) to a model of parallel hard oblique cylinders, showing that the smectic-C phase may be obtained in a system with hard body molecules. The approach is a truly microscopic theory, providing the link between the molecular model and the phase diagram, which has uniaxial and biaxial nematics, smectic-A and smectic-C phases, depending on the packing fraction and the molecular shape. However, the simplicity of the model forces some drawbacks: the main molecular axis are assumed perfectly oriented, so that the nematic order is frozen, and the presence of the tilt angle is only possible with the breaking of the axial symmetry. This and other related attempts should be considered as very preliminary steps in the development of microscopic theories for smectic-C liquid crystals. Other more exotic phases, like the smectic-B, the columnar or the cubatic phases are even further away from theoretical understanding.

4. Conclusions

The theory of liquid crystals is now getting beyond the empirical approaches towards a microscopic understanding of the phase behaviour and the phase transitions in terms of simplified molecular models. For the simplest case, the nematic liquid crystal phase, we have made a long way since the seminal works of Onsager, Maier & Saupe. The theory of hard body nematics is now capable of good quantitative predictions. This has been possible with the experience gained in the theory of the hard spheres fluid and with the guide of the computer simulation data for simple molecular shapes. The way to progress in the understanding of thermotropic nematics is now open, with the perturbations approaches, as in the theory of simple liquids. The main difficulty in this project is the need of a good description of the pair distribution function in the reference (hard bodies) system. The molecular correlation function in the isotropic liquid should give a very important correction over the mean field contribution of the attractive interactions to the free energy. Nearby molecules have a strong tendency to orientate their main axes parallel to each other, even in absence of long range orientational order. Any theory neglecting this fact overestimates the stability of the nematic with respect to the isotropic liquid, in a way similar to what happens with the contribution of the attractive interactions in the crystallization of a simple fluid.

The theory of smectic liquid crystals has also benefited from the experience with the hard spheres system. The map into a system of parallel hard ellipsoids, provides a starting point for the description of the packing effects and for the construction of microscopic theories for the smectic-A phase, in which the smectic period is obtained consistently within the density functional formalism, rather than being fixed as an empirical parameter as in the earlier theories of Kobayashi & McMillan.

It is now clear that most phases observed in the experimental phase diagrams of liquid crystals may be obtained in simple models with pure hard body interactions and also as the result of the coupling between the hard body packing and some kind of soft attractive interactions. However, different physical origins for the existence of these phases may produce important differences in their phase behaviour. Only a theory with quantitative accuracy for simple molecular models, will provide a better understanding of the relative importance of the hard cores, dispersion forces, electric dipoles, quadrupoles and flexible tails, in the phase diagram of real liquid crystals.

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