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Computer simulation of hard-core models for liquid crystals

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Liquid crystals are usually not thought of as 'simple' liquids. Nevertheless, a surprising number of features of liquid crystals can be reproduced in computer simulations of very simple model systems, viz. hard ellipsoids of revolution and parallel spherocylinders. In particular, depending on the density and the shape of the hard-core particles, stable isotropic, nematic, smectic and crystalline phases are found. The existence of hard-core models for liquid crystals is important for two reasons. First of all, they can be used to test molecular theories for the static and dynamic properties of liquid crystals. And secondly, they may provide a starting point for thermodynamic perturbation theories. These hard-core models exhibit large pre-transitional fluctuations in the vicinity of some of the phase transitions, similar to those observed in real mesogens. Examples are given of the 'experimental' consequences of nematic and smectic precursor effects.

1. INTRODUCTION

The structure of dense simple liquids is largely determined by short-range repulsive forces. In its original form, this concept is due to van der Waals [1]. The transformation of this idea from a bold assumption to an almost commonplace statement owes much to the fruitful combination of computer simulations and thermodynamic perturbation theory [2, 3, 4]. For example, the freezing of atomic liquids can be understood on the basis of the fluid-solid transition of hard spheres, first observed by Alder and Wainwright [5]. The liquid-vapour transition does not occur in a pure hard-core system, but can be explained in terms of a weak attractive perturbation added to the repulsive interactions.

It is much less clear to what extent excluded volume effects can help us to understand the thermodynamics and phase transitions of 'complex' liquids, in particular liquid crystal forming materials. Actually, the question to be addressed is twofold. Firstly: is it at all possible to explain a particular type of phase transition in a liquid crystal in terms of excluded volume effects alone, or is the presence of other interactions, such as attractive dispersion forces, essential? And secondly: even if we find that hard repulsive forces can cause a particular phase

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transition in a model system, do we have reasons to assume that excluded volume effects are also at the root of such phase transitions in *real* liquid crystals?

This paper focuses on the first question which I shall phrase here as: Can hard core models exhibit the phase transitions and pre-transitional behaviour found in liquid crystals? But I stress that a positive answer to this first question only implies that we now have to face the second, i.e. do hard core models contain the essential physics? At present the answer to this second question is still open.

Below I shall present the results of recent computer simulations on non-spherical hard core models. As we shall see, a surprising number of phenomena observed in real liquid crystal forming materials are reproduced by these simple models. The remainder of this paper is organized as follows: firstly I shall discuss the effect of molecular shape on the relative stability of crystalline and liquid crystalline phases. Next I shall present some preliminary results on pre-transitional fluctuations in nematogens, in particular collective orientational fluctuations. And finally I shall present some recent results on smectic ordering in hard-core model systems.

I wish to stress that this paper is not meant to be a general review of computer simulation of liquid crystals. As my emphasis is on hard-core models, I shall not discuss the extensive literature dealing with other model systems, such as for instance the 'Lebwohl-Lasher' model which has been studied in detail by Luckhurst and collaborators [6] or the simulation of a realistic model for an existing nematogen (see [7]). Liquid crystals are complex systems, and only by combining the results obtained by experiment, theory and different computer simulation techniques can we hope to increase our understanding of these fascinating materials.

2. SOLID OR NEMATIC?

Most isotropic molecular liquids freeze as the temperature is lowered. But only some form liquid crystals. The obvious question is: what factors determine whether a molecular liquid forms a liquid crystal before it freezes?

Let us first briefly summarize the essential characteristics of liquid crystals (for details the reader is referred to [8]). Liquid crystals are partially ordered fluids. The simplest is the *nematic* phase in which the molecules are translationally disordered but, unlike the isotropic fluid, the molecular orientations are not distributed randomly. Rather, the molecular axes tend to align parallel to some otherwise arbitrary direction. This alignment axis is usually referred to as the nematic director n . A quantitative measure for the degree of alignment is the nematic order parameter S . For axially symmetric molecules, S is defined as $\langle P_2(\cos \theta) \rangle$, where θ is the angle between the molecular symmetry axis and the nematic director. In the isotropic phase, $S = 0$. In a perfectly aligned nematic, $S = 1$. The phase transition from isotropic liquid to nematic liquid crystal is weakly first order. By 'weakly first order' I mean that the transition, although first order, is preceded by strong precursor effects as is usually the case in the vicinity of continuous phase transitions. The transition from both the nematic and the isotropic phases to the solid is a normal first order transition.

All molecules that form nematics are non-spherical, but the converse is not true. In other words, a certain degree of non-sphericity is a necessary, but not a sufficient, condition for liquid crystal formation. Several other factors also play a

role in determining the relative stability of the nematic phase. For instance, attractive inter-molecular interactions due to dispersion forces also tend to favour parallel alignment of the molecules. There are a number of models that attribute the orientational ordering in liquid crystals to the effect of dispersion forces [9, 10], including the original mean-field model due to Maier and Saupe. Although these models yield fair estimates for a number of properties of nematic liquid crystals, they cannot be used to explain the stability of the nematic phase with respect to the solid. It is quite conceivable that in some cases dispersion forces would stabilize the solid more than the nematic. Another factor that influences the stability of liquid crystals is the presence of flexible tails (often alkane or alkoxy chains) connected to the 'rigid' core of the nematogen. That flexible chains are indeed important for the stability of liquid crystals follows from the experimental observation that essentially all liquid crystal forming molecules ('mesogens') have them [11]. If the tail is shortened too much the liquid freezes without ever becoming nematic. Intuitively, the role of flexible tails in stabilizing the liquid crystal with respect to the solid is clear: if a flexible tail has to fit into a crystal lattice it will lose much of its conformation degrees of freedom with a concomitant loss in entropy. A model that takes into account the effect of the flexible tails on the relative stability of isotropic, nematic and smectic phases was developed by Dowell and Martire [12]. But, to my knowledge, a quantitative comparison with the solid has not been made.

The question which remains is: which of the factors mentioned above has the most important effect? For someone who is familiar with the theory of simple liquids it is natural to assume that the hard-core repulsions are most important. Of course, the 'natural' assumption is not necessarily the correct one, and the only way to find out is to try. Trying in this case means computer simulation. Still I would like to present some justification for my assumption that molecular shape effects are of primary importance while dispersion forces and flexibility effects can be considered as 'perturbations'. The point is that, since the work of Onsager [13], it is known that the isotropic-nematic transition can take place in a simple model that considers *only* the non-spherical excluded volume effects. In contrast, flexible tails *alone* cannot cause nematic order. Neither can anisotropic dispersion forces. To be more precise: a model which only includes dispersion forces but no hard-core repulsion will collapse. Of course, if one adds a spherical hard-core repulsion to stabilize the system, anisotropic dispersion forces can explain the transition to a nematic phase. However, in nature a molecule with a spherical hard core will most likely have isotropic van der Waals interactions. Hence, in the real world, anisotropy in the dispersion forces implies a non-spherical hard core anyway. Of course, the converse is also true, but at least for sufficiently non-spherical particles dispersion forces appear relatively unimportant. In summary, non-spherical hard-core repulsion is the most plausible mechanism to explain the formation of a nematic phase without the assistance of any of the other factors. It seems reasonable then, to treat hard-core repulsion as the 'primary' effect. One may hope some kind of thermodynamic perturbation theory can, at a later stage, take the effect of dispersion and flexibility into account. However, I should stress that at this stage we do not yet have any evidence that such a perturbation scheme will work.

Before we turn to the computer simulations let me briefly sketch what we know from experiment about the relation between molecular shape and the ten-

dency to form liquid crystals [14]. First of all, we know that liquid crystals can consist of both rod-like and plate-like molecules. Most rod-like mesogens have length-to-breadth ratios between 3 and 4 (it should be noted, however, that this ratio is a rather fuzzy concept for molecules with flexible tails). What we know at present about disc-like mesogens (see, for example, [15]) suggests that these molecules are even less spherical. It is not straightforward to tell from experiment how the isotropic-nematic and the nematic-solid transitions depend on the shape of the repulsive core of the molecules. The problem is that although a wealth of data on the phase transitions of molecules with different shapes are available, we do not know how to disentangle the effects of molecular shape, dispersion forces and flexible tails.

Next, let us consider what we know from theory and earlier computer simulations. Onsager [13] showed that thin spherocylinders with length L and diameter D (with $L \gg D$) exhibit a transition from the isotropic to the nematic phase at a density of order $1/(L^2 D)$. At this density the fraction of the volume occupied by the spherocylinders is still vanishingly small (of order D/L). The same holds for infinitely thin hard platelets [16]. For neither of these model systems do we know the melting point. For hard spheres we do know the melting point from the computer simulations of Hoover and Ree [17]. But these simulations do not tell us what will happen to the melting point as the molecular shape changes from spherical to rod-like or plate-like.

3. COMPUTER SIMULATIONS OF NEMATOGENS

3.1. General remarks

To fill this gap in our knowledge about the phase behaviour of non-spherical hard-core molecules, we performed Monte Carlo simulations on a simple model system, viz. hard ellipsoids of revolution. The shape of such a spheroid is characterized by a single parameter, x , the ratio of the length of the major axis ($2a$) to the minor axis ($2b$) being $x = a/b$. For the following special cases the phase transitions are already known. (1) Hard spheres ($x = 1$), which freeze at $2/3$ of close packing (see [17]), (2) Hard needles ($x \rightarrow \infty$), i.e. Onsager's model. This system has a transition to the nematic phase [13] at vanishing volume fraction. (3) Hard platelets ($x \rightarrow 0$), which also form a low-density nematic [16]. Technical details of the Monte Carlo simulations have been published elsewhere [18]. Here I shall concentrate on the results.

3.2. Virial coefficients and the Onsager limit

The reader may have been surprised that I referred to Onsager's theory to describe the behaviour of ellipsoids in the limit $x \rightarrow \infty$. After all, Onsager's result was derived for spherocylinders in the limit $L(\text{length})/D(\text{diameter}) \rightarrow \infty$. And, even though both ellipsoids and spherocylinders become 'needle-like' in this limit, they certainly do not become identical. For example, the volume fraction at regular close packing equals 0.74048 for ellipsoidal needles in contrast to 0.9069 for thin spherocylinders. The reason why Onsager's results apply to ellipsoidal needles is that the *angle dependence* of the pair excluded volume is the same for very thin ellipsoids and spherocylinders: $V_{\alpha\alpha}(\theta) = \text{constant} |\sin \theta|$. For spherocyl-

Figure 1. The reduced third (open circles), fourth (triangles) and fifth (closed circles) virial coefficients of prolate hard ellipsoids of revolution, as a function of the axial ratio a/b . The reduced n th virial coefficient is defined as B_n/B_2^n . In the case of the fourth virial coefficient, $-B_4/B_2^2$ is shown (see table 1).

linders, this angle dependence was of course well known from Onsager's work. However, for thin ellipsoids the corresponding expression is most easily obtained using the result [19] that the pair excluded volumes of prolate and oblate ellipsoids with inverse length-to-breadth ratios have the same angle dependence. Hence, $V_{ex}(\theta)$ for needle-like ellipsoids must be the same function of θ as for platelets. But for platelets we already know the answer (see, for example [8]), namely that $V_{ex}(\theta) \sim |\sin \theta|$. Therefore ellipsoidal needles behave as thin spherocylinders at the level of the second virial coefficient.

There is another condition which has to be met in order that the Onsager theory be applicable to needle-like ellipsoids, namely that all virial coefficients higher than the second are negligible, i.e. $B_n/B_2^{n-1} \rightarrow 0$. Onsager has shown that this condition is satisfied for B_3 in the case of spherocylinders, and has made the plausible assumption that it also holds for all higher virial coefficients [20]. Although it seems likely that the virial coefficients of needle-like ellipsoids exhibit a similar behaviour, a direct numerical test is useful. After all, there appears to be no simple relation between the higher-order virial coefficients of ellipsoids and spherocylinders. Hence, extending Onsager's (unproven) assumption [21] from spherocylinders to ellipsoids seems a bit dangerous. We therefore carried out Monte Carlo simulations of the third, fourth and fifth virial coefficients of prolate hard ellipsoids for a range of a/b ratios between 1 and 10^5 . The results of these calculations are shown in figures 1 and 2. The figures show clearly that the 'reduced' higher-order virial coefficients (i.e. B_n/B_2^{n-1}) do indeed vanish in the limit $a/b \rightarrow \infty$. In the asymptotic regime, the leading x -dependence of B_3/B_2^2 is

Figure 2. Asymptotic behaviour of the reduced virial coefficients of prolate ellipsoids. To emphasize the different asymptotic shape dependence of B_3 on the one hand, and B_4 and B_5 on the other, B_3 has been multiplied by $(a/b + 1)/\{\log(a/b + 1)\}$. B_4 and B_5 are both multiplied by $(a/b + 1)$. The meaning of the symbols is as in figure 1.

proportional to $\{\log(x + 1)\}/(x + 1)$ (cf. $\{\log(L/D)\}/(L/D)$ for spherocylinders). For B_4 and B_5 the leading x -dependence in the asymptotic regime is proportional to $1/(x + 1)$. Note that in order to observe this asymptotic behaviour, quite appreciable non-sphericity is required. The computation of virial coefficients at these rather extreme elongations requires special techniques (see [22]). The numerical results have been collected in table 1. These results strongly suggest that the assumptions underlying Onsager's excluded volume theory for the isotropic-nematic transition are indeed satisfied for hard ellipsoids in the limit $x \rightarrow \infty$.

3.3. Phase diagram

The construction of a 'phase diagram' by computer simulation is straightforward, though time consuming. First the equations of state of all phases must be

Table 1. Reduced third, fourth and fifth virial coefficients of hard ellipsoids of revolution, as a function of the axial ratio a/b . The estimated error in the last digit is indicated between brackets.

a/b	B_3/B_2^2	B_4/B_2^3	B_5/B_2^4
1	0.625	0.25	0.08594
10	$3.493(3)10^{-1}$	$4.9(5)10^{-3}$	$1.33(1)10^{-2}$
100	$8.41(2)10^{-2}$	$-3.06(2)10^{-2}$	$3.22(4)10^{-2}$
1000	$1.35(2)10^{-2}$	$-4.99(8)10^{-3}$	$5.7(2)10^{-3}$
10000	$1.89(3)10^{-3}$	$-5.6(3)10^{-4}$	$6.2(6)10^{-4}$
100000	$2.4(1)10^{-4}$	$-6.8(10)10^{-5}$	$6.4(20)10^{-5}$

Figure 3. 'Phase diagram' of hard ellipsoids of revolution. Vertical axis: density in units $(8ab^2)^{-1}$. Horizontal axis: Length-to-breadth ratio, x . The shaded areas correspond to two-phase regions. The dots are the computed coexistence points. The points for $x = 1$ were taken from [17]. The following phases can be distinguished: isotropic fluid (I), nematic liquid crystal (N), orientationally ordered solid (S) and plastic solid (PS).

determined at a large number of state points, and in addition the absolute free energies of all phases must be computed. For hard ellipsoids with axial ratios of 3, 2.75, 2, 1.25, 0.8, 0.5, $1/2.75$ and $1/3$, this was done employing the techniques described in [18]. The resulting 'phase diagram' is shown in figure 3. In this figure the molecular shape varies from left to right from extremely oblate ellipsoids ('platelets'), through spheres to extremely prolate ellipsoids ('needles'). The ordinate measures the density which, in the present units, varies between 0 and $\sqrt{2}$ (regular close packing). Four distinct phases can be identified, the isotropic fluid (I), nematic fluid (N), orientationally ordered solid (S) and orientationally disordered (plastic) solid (PS). The shaded areas represent two-phase coexistence regions. Several aspects of figure 3 are worth noting. First of all, the phase diagram provides us with an answer to the old question: what is the minimum non-sphericity needed to form a stable nematic phase? Clearly, for ellipsoids with axial ratios approximately between $1/2.5$ and 2.5 , no stable nematic phase is possible. As a bonus, we obtain an estimate of the range of stability of the orientationally disordered solid phase (approximately between $a/b = 1/1.5$ and $a/b = 1.5$) although in this case the boundaries are less well determined. Another conspicuous feature is the high (although not perfect) degree of symmetry of the phase diagram under the interchange of oblate and prolate ellipsoids. The physical reason for this near symmetry at these rather high densities is not understood at present. That there should be some symmetry between prolate and oblate ellipsoids at low densities is understandable because, in the present units, the second virial coefficients of spheroids with inverse length-to-breadth ratios are equal [22]. However, no such symmetry holds for the higher virial coefficients. In particular, in the limit $x \rightarrow \infty$, $B_3/B_2^2 \rightarrow 0$ [13], while in the limit $x \rightarrow 0$, this same ratio tends to a finite value of 0.4447 [16]. The approximate oblate-prolate symmetry at higher densities shown in the 'phase diagram' is therefore not exact, which makes it all the more surprising.

Now that we know the range of stability of the nematic phase in this model system, let us look in more detail at the physical consequences of the onset of orientational ordering. In the isotropic phase, the presence of a nematic is betrayed by an increase in the amplitude of collective orientational fluctuations. Below we shall illustrate what computer simulation can tell us about such pre-transitional phenomena. The static and dynamic properties of the nematic phase are even more strongly affected by the orientational ordering transition. However, for hard-core nematics there is a lack of numerical data because systematic computer simulations of such phases are at present only beginning. Therefore the discussion of the physical properties of the nematic phase is limited to a single example: a numerical study of the effect of nematic ordering on the refractive index of a molecular fluid.

3.4. *Orientational precursor effects*

At the transition to the nematic phase spontaneous ordering of the molecular orientations takes place. Although this macroscopic ordering occurs at a well-defined state point, strong pre-transitional fluctuations may be observed in the isotropic phase as the transition to the nematic phase is approached. Actually, the fact that such pre-transitional fluctuations can be observed at all is due to the peculiar nature of the isotropic-nematic transition. After all, usually there are no precursor effects near a first-order phase transition. The isotropic-nematic transition is different because it is a 'weak' first-order transition; it exhibits most of the 'critical' pre-transitional behaviour typical for a continuous phase transition, but before the 'critical' point is reached, a first-order transition intervenes. The most striking effect that is observed as the isotropic-nematic transition is approached from the isotropic side is the strong increase in the amplitude of order-parameter fluctuations, which results, among other things, in enhanced depolarized light scattering. To a first approximation, the intensity of depolarized light scattering, I_d , is proportional to the average trace of the square of the collective orientational tensor $\mathbf{Q}$ defined as

$$\mathbf{Q}_{\alpha\beta} = (1/N) \sum_i (3\mathbf{u}_\alpha^i \mathbf{u}_\beta^i - \delta_{\alpha\beta})/2, \quad (1)$$

where $\mathbf{u}^i$ is a unit vector specifying the orientation of molecule i . The expression for the scattering intensity I_d is

$$I_d \sim \langle \mathbf{Q}_{\alpha\beta} \mathbf{Q}_{\beta\alpha} \rangle = 3/2 \langle S^2 \rangle. \quad (2)$$

The Landau-de Gennes theory (see, for example, [8]) predicts that

$$\langle \mathbf{Q}_{\alpha\beta} \mathbf{Q}_{\beta\alpha} \rangle \sim (\rho^* - \rho)^{-1}, \quad (3)$$

where ρ^* is a density just beyond the I-N transition point. $\langle \mathbf{Q}_{\alpha\beta} \mathbf{Q}_{\beta\alpha} \rangle$ in equation (3) is a measure for the correlation of the orientation of different molecules. Combining equations (1) and (2), it is easy to show that $\langle \mathbf{Q}_{\alpha\beta} \mathbf{Q}_{\beta\alpha} \rangle = (1 + g_2)/N$, where g_2 is the static orientational correlation factor, defined as

$$g_2 = \sum_{j \neq i} P_2(\mathbf{u}_i \cdot \mathbf{u}_j). \quad (4)$$

The proximity of the isotropic-nematic transition influences not just the static orientational properties of the fluid but also the rotational dynamics. In particu-

lar, the relaxation time τ_2^c of the collective orientational fluctuations diverges as the I-N transition is approached. The relation between the divergence of g_2 and τ_2^c is of particular interest. Using Mori-theory, Keyes and Kivelson [23] derived the following expression relating g_2 to τ_2^c [24]:

$$\tau_2^c/\tau_2^s = (1 + j_2)/(1 + g_2). \quad (5)$$

Here τ_2^s is the single-particle correlation time and j_2 is the dynamic orientational correlation factor. The latter quantity can be expressed in terms of memory functions, but has no simple physical interpretation. A direct experimental determination of $(1 + g_2)$ and τ_2^c/τ_2^s is complicated by the fact that in real liquids part of the depolarized light scattering intensity is interaction-induced. It is not trivial to separate out the purely orientational contribution to the scattering intensity [25]. As a consequence, there is a scarcity of reliable data from which j_2 can be determined. The available information (see, for example, [26]) suggests that j_2 is small compared to 1, and it is common practice with light scattering to assume that $j_2 = 0$.

Numerical simulation offers a unique possibility to study the static and dynamic precursor effects to the I-N transition in simple model systems. As an example, we consider the pre-transitional behaviour in a system of prolate hard ellipsoids with $a/b = 3$ [27]. From the Monte Carlo simulations mentioned above, we know that this system has a transition from the isotropic to the nematic phase at 70 per cent of the density of regular close packing [18]. For comparison, we also studied the orientational dynamics of hard ellipsoids with $a/b = 2$. The latter system has no stable nematic phase and hence we should expect it to behave rather differently from the more anisometric $a/b = 3$ system. Figure 4 shows typical examples of $C_1(t) \equiv \langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$ and $C_2(t) \equiv \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$, the correlation functions of the first and second Legendre polynomials of the molecular orientation vectors. Both $C_1(t)$ and $C_2(t)$ are single-particle correlation functions [28]. In the rotational diffusion limit, the ratio of the relaxation times of $C_1(t)$ and $C_2(t)$, τ_1^s/τ_2^s , equals 3. We find that this behaviour obeyed well at densities that are not too low. Both single-particle relaxation times grow as the density is increased. This is simply a consequence of the rapid increase of the viscosity as the density of the fluid is raised, and the effect is observed for both shapes of ellipsoids. The density dependence of the collective orientational correlation function, $C_2^c(t) \equiv \sum \langle P_2(\mathbf{u}_i(0) \cdot \mathbf{u}_j(t)) \rangle$ is more interesting. At low densities, the decay of $C_2^c(t)$ closely follows that of $C_2(t)$, as can be seen from figure 4. However, as the density is increased, the decay of the collective orientational correlation function becomes much slower than the corresponding single-particle one. Hence, cooperative effects in the rotational dynamics become important at high densities, both for the $a/b = 2$ and for $a/b = 3$ case. Figure 5 shows the density dependence of the ratio τ_2^c/τ_2^s for both shapes of ellipsoids. In the same figure we have also plotted the corresponding values of $(1 + g_2)$. The difference in the behaviour of the $a/b = 3$ and $a/b = 2$ ellipsoids is immediately apparent. For $a/b = 2$ there is evidence for some cooperative behaviour, but even at the freezing density (at 84 per cent of close packing), there is no sign of diverging fluctuations or critical slowing down. In contrast, the results for $a/b = 3$ clearly show pre-transitional effects. Both τ_2^c/τ_2^s and $(1 + g_2)$ appear to diverge as the transition to the nematic phase is approached. If the dynamic orientational correlation factor j_2 vanishes, then the data points for τ_2^c/τ_2^s and $(1 + g_2)$ should superimpose. On this

Figure 4. Density and shape dependence of single-particle and collective orientational correlation function for hard ellipsoids of revolution. (a) $a/b = 2$, $\rho/\rho_0 = 0.5$; (b) $a/b = 2$, $\rho/\rho_0 = 0.8$; (c) $a/b = 3$, $\rho/\rho_0 = 0.3$; (d) $a/b = 3$, $\rho/\rho_0 = 0.7$. (---) Single-particle first-rank orientational correlation function, $C_1(t) = \langle P_1(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$; (.....) Single-particle second-rank orientational correlation function, $C_2(t) = \langle P_2(\mathbf{u}(0) \cdot \mathbf{u}(t)) \rangle$; (—) Collective second-rank orientational correlation function, $C_2^c(t) = \sum_j \langle P_2(\mathbf{u}_j(0) \cdot \mathbf{u}_j(t)) \rangle$. The single-particle orientational variable has been made orthogonal to the collective one by projection. Note that at high densities the decay of $C_2^c(t)$ becomes much slower than that of $C_2(t)$.

Figure 5. Density dependence of the ratio τ_2^c/τ_2^s (pluses), for hard ellipsoids of revolution with (a) $a/b = 2$ and (b) $a/b = 3$. Also shown is the behaviour of the static orientational correlation factor $(1 + g_2)$ (open circles). The best estimate for the dynamic orientational correlation factor $(1 + j_2)$ is shown as a horizontal line. In (b) the isotropic-nematic coexistence region is bordered by parallel vertical lines.

point the simulations appear inconclusive. The statistics on τ_2^e/τ_2^s and $(1 + g_2)$ are poor, even though these are fairly long runs ($O(10^6)$ collision for a 144-particle system). The reason for the large scatter in the data points is that the quantities shown are collective properties. The signal-to-noise ratio for such quantities is of order $\sqrt{(\tau/T)}$, where τ is a characteristic relaxation time, and T is the duration of the simulation [29]. Hence, as the correlation times of the collective orientational fluctuations grow larger, the statistics (for a fixed value of T) become worse. Clearly, it is not meaningful to extract estimates for j_2 from the individual data points. We therefore attempted to estimate j_2 in the following way. We assumed $(\tau_2^s/\tau_2^e)(1 + g_2) (= (1 + j_2))$ was independent of density, and carried out a linear least-squares fit to the data points. The results are indicated as drawn lines in figure 5. We see that for both shapes the estimate for $(1 + j_2)$ is less than 1. For the $a/b = 3$ case, where we have the largest number of data points, the fit suggests that j_2 is small and negative (typically $-0.08 + / - 0.05$).

For the $a/b = 2$ ellipsoids the estimated value of j_2 is slightly larger ($-0.26 + / - 0.16$), but the estimated error is also larger. It is amusing to note that a j_2 of the same sign and comparable magnitude followed from the light scattering experiments of Gierke and Flygare on a real nematogen ($j_2 = -0.3 + / - 0.3$ for MBBA) [30]. We do not wish to attach too much significance to the actual numbers that we have obtained for j_2 : clearly, much longer simulations are needed to carry out a direct comparison with the relevant theoretical predictions. In fact, such simulations are now in progress. The importance of the preliminary results presented here is that they provide the first numerical data on pre-transitional effects in the orientational dynamics of any model nematogen. In addition, our results indicate that the numerical determination of j_2 , although time-consuming, is certainly feasible.

3.5. Nematic order and bi-refringence

Bi-refringence is the property by which liquid crystals are usually recognized in nature. To a large extent, technological interest in nematic liquid crystals is related to the fact that they are optically anisotropic. However, the relation between the refractive indices of a nematic and its microscopic structure is not straightforward. The complexity of this problem is partly due to the fact that the optical properties of the constituent molecules are often known only approximately. Moreover, the local structure of the fluid has a pronounced effect on the effective polarizability of the molecules. Here we shall show how computer simulation on a simple model for a nematic can be used to gain insight into the latter factor. Such numerical information is important to test the validity of approximate theories for the optical properties of nematics [30-33].

The simplest description of the optical properties of liquid crystals starts from the assumption that the constituent molecules are point-polarizable particles, characterized by a polarizability tensor α , with components $\alpha_{\parallel}$ and $\alpha_{\perp}$ respectively along and perpendicular to the molecular axis. A systematic approach to compute the dielectric constant of fluids consisting of non-polar point-polarizable molecules has been described by Ladanyi and Keyes [34]. These authors show how the Clausius-Mosotti function $(\epsilon - I)/(\epsilon + 2I)$ may be expressed as an infinite series of integrals over molecular n -body distribution functions. For practical reasons, this series is usually truncated after the second term (i.e. three and more

body correlations are neglected):

$$(\epsilon - \mathbf{I})/(\epsilon + 2\mathbf{I}) = 4\pi\langle\mathbf{A}\rangle/3 + \int d\mathbf{r}' \langle\mathbf{A}(\mathbf{r}) \cdot \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{A}(\mathbf{r}')\rangle. \quad (6)$$

In equation (6), $\mathbf{A}(\mathbf{r})$ is the (tensor) polarizability density at a point $\mathbf{r}$ in the fluid and $\mathbf{T}(\mathbf{r})$ is the dipole tensor $(3\mathbf{r}\mathbf{r} - \mathbf{I}r^2)/r^5$. For a uniform fluid with density ρ , $\langle\mathbf{A}\rangle = \rho\alpha$. Note that for an atomic fluid the second term on the right hand side of equation (6) vanishes, and the usual Clausius-Mosotti equation results. However, for a molecular fluid this integral over the two-body distribution function is non-zero, even in the isotropic phase. The difference between equation (6) and the expression derived in [37] is that the present equation takes into account the correlation between orientational fluctuations of different molecules. It is useful to write equation (6) in a form that shows the explicit dependence of the Clausius-Mosotti function on the trace polarizability $\alpha_0 \equiv (\alpha_{\parallel} + 2\alpha_{\perp})/3$ and the anisotropy of the polarizability $\delta \equiv (\alpha_{\parallel} - \alpha_{\perp})/3\alpha_0$. This yields the following expression:

$$\begin{aligned} \{(\epsilon - \mathbf{I})/(\epsilon + 2\mathbf{I})\}/(4\pi\rho\alpha_0/3) &= \mathbf{I} + 2\delta\langle\mathbf{q}\rangle \\ &+ \rho\alpha_0\{\langle\mathbf{T}\rangle + 2\delta\langle\mathbf{q} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{q}\rangle + 4\delta^2\langle\mathbf{q} \cdot \mathbf{T} \cdot \mathbf{q}\rangle\}, \end{aligned} \quad (7)$$

where $\mathbf{q}$ is the traceless second rank tensor characterizing the molecular orientation ($\mathbf{q} = (3\mathbf{u}\mathbf{u} - \mathbf{I})/2$), and the angular brackets represent averages over the appropriate one- or two-body distribution function. The different contributions to equation (7) can easily be evaluated by computer simulation [35]. An example of the density dependence of $\{(\epsilon - \mathbf{I})/(\epsilon + 2\mathbf{I})\}/(4\pi\rho\alpha_0/3)$ for hard ellipsoids of revolution with $a/b = 3$ is shown in figure 6. For the parameters δ and $\rho\alpha_0$ we chose values typical of real nematogens (see, for example, [39]), namely $\alpha_0 = 0.113$ (resulting in a value of 0.08 for $\rho\alpha_0$ at close packing), and $\delta = 0.3$. The curves shown in figure 6 exhibit some of the features shown by real nematics. In particular, the trace of $\{(\epsilon - \mathbf{I})/(\epsilon + 2\mathbf{I})\}/(4\pi\rho\alpha_0/3)$ is continuous through the I-N transition. In addition, the actual values of the ordinary and extraordinary refractive indices are in the same range as those of real nematics (although this is not a very critical test). In one respect the optical properties of the model fluid appear to differ qualitatively from those of a real nematic [36]: we find that the anisotropy in the dielectric constant (i.e. $\epsilon_{\parallel} - \epsilon_{\perp}$) is not proportional to the order parameter S . Actually, the anisotropy in the individual terms in equation (7) is roughly proportional to S (see table 2), but due to the near cancellation of the different contributions, the sum appears to depend less strongly on S . Such a discrepancy between the optical properties of hard ellipsoids and real liquid crystals is hardly surprising. After all, real nematogens do not consist of hard, point-polarizable particles, and quantitative agreement with experiment should not be the primary aim of the simulations presented in this section. Rather, we wish to show how, given the molecular structure and polarizability distribution of a more realistic model, the refractive indices could be computed. Our reason for presenting the results of simulations on a very simple model system is that such data allow us to test theories for the refractive index of nematics based on the point-polarizability approximation.

Figure 6. Density dependence for the parallel (pluses), perpendicular (triangles) and trace (circles) components of the Clausius-Mosotti function $(\epsilon - 1)/(\epsilon + 2)$, divided by $(4\pi\rho_0\alpha_0/3)$. Within the approximation used, the resulting function would be equal to 1 for isotropic fluids consisting of spherical particles. Note that, due to the non-spherical character of the molecules (in this case, hard ellipsoids with $a/b = 3$), there are deviations from the simple Clausius-Mosotti relation, even in the isotropic phase. In this figure we used a value for the trace polarizability $\alpha_0 = 0.113$ (in units σ^3) and $\delta = 0.3$.

4. BEYOND NEMATICS

4.1. Introduction

In the previous sections we have shown that sufficiently anisometric hard ellipsoids of revolution can form thermodynamically stable nematic phases. And changes in the shape of the crystal unit cell, using an isotropic-stress Monte Carlo

Table 2. Expansion coefficients of the Clausius-Mosotti function $F(\epsilon) \equiv (\epsilon - 1)/(\epsilon + 2)$ $= (4\pi\rho_0\alpha_0/3)(\mathbf{I} + 2\delta\langle\mathbf{q}\rangle + \rho\alpha_0\{\langle\mathbf{T}\rangle + 2\delta\langle\mathbf{q} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{q}\rangle + 4\delta^2\langle\mathbf{q} \cdot \mathbf{T} \cdot \mathbf{q}\rangle\})$. The a and b coefficients are defined through: $Tr\{F(\epsilon)\} = (4\pi\rho_0\alpha_0/3)(1 + \rho\alpha_0\{\delta a_1 + \delta^2 a_2\})$, and $F(\epsilon_{\parallel}) - F(\epsilon_{\perp}) = (4\pi\rho_0\alpha_0/3)(3\delta S + \rho\alpha_0\{b_0 + \delta b_1 + \delta^2 b_2\})$, where S is the nematic order parameter and $\delta = (\alpha_{\parallel} - \alpha_{\perp})/3\alpha_0$.

ρ/ρ_0	S	a_1	a_2	b_0	b_1	b_2
0.550	0	-5.0	1.01	0	0	0
0.600	0	-5.2	0.94	0	0	0
0.625	0	-5.2	0.68	0	0	0
0.636	0	-5.2	0.82	0	0	0
0.675	0	-5.5	0.43	0	0	0
0.700	0	-5.7	0.53	0	0	0
0.707	0.571	-5.2	-0.64	-2.22	-4.3	-8.2
0.778	0.749	-5.4	-1.7	-3.05	-6.0	-11.2

that, moreover, these simple model systems exhibit many of the static and dynamic properties of real nematogens. Naturally, the question arises whether the nematic phase is the only type of liquid crystal that can be simulated with a hard-core model. For instance, one might wonder whether hard ellipsoids of revolution can also form a smectic phase, i.e. a fluid that has (at least) one-dimensional translational order, in addition to the orientational order already present in nematics (see, for example [8]). The answer to this question is almost certainly 'no'. The reason is the following: smectic phases tend to have a large degree of orientational order (i.e. the order parameter S is close to 1). Hence, to a first approximation, we can assume that a smectic consists of perfectly aligned, non-spherical molecules. However, a system consisting of hard ellipsoids of revolution with axial ratio a/b , all parallel to the z -axis (say), can be mapped onto the hard-sphere fluid by a simple scaling of all z -coordinates with a factor b/a . As hard spheres apparently do not form smectics, parallel hard ellipsoids cannot do so either. So, unless the orientational degrees of freedom stabilize the smectic phase (and this seems unlikely), hard ellipsoids of revolution cannot form smectics.

The question then arises whether smectic phases can be formed by other rigid hard-core models. This is not obvious *a priori*. In fact, to my knowledge, most textbooks on liquid crystals do not even seriously consider the possibility (see however [36]). Even more than in the case of nematics, dispersion forces [37] and the effects of flexible tails [12] are held responsible for the formation of smectic phases. Although we do not contest that these factors must have a pronounced effect on the stability of smectics, the question that must be answered is whether they are essential in the same way that attractive forces are essential to explain the liquid-vapour transition [38].

4.2. Computer simulations

In order to explore the possibility of smectic order in rigid hard-core systems, we carried out Monte Carlo and molecular dynamics simulations on model systems consisting of parallel spherocylinders with diameter D and length L (i.e. the hemispherical caps were separated by a straight cylindrical segment of length L) [39]. As the particles in this system are always perfectly aligned, the low-density phase is a 'nematic' fluid. The parallel spherocylinder fluid can be thought of as a model for a fluid of rod-like particles in a strong magnetic field. As mentioned above, we know that the corresponding hard-ellipsoid model will not exhibit smectic order. Simulations were carried out for systems of parallel spherocylinders with L/D ratios of 0.25, 0.5, 1, 2, 3 and 5. The well-known case $L/D = 0$ (i.e. hard spheres) was also studied, as a check. System sizes varying from 90 to 1080 particles were studied. Initially, the system was prepared in a regular close-packed lattice. We prepared this lattice by expanding a close-packed face-centred cubic hard-sphere crystal by a factor $(L/D + 1)$ along the [111]-axis. In order to avoid spurious translational order due to incomplete melting, the crystals were expanded to low densities (typically, 30 per cent of close packing), where the solid rapidly melted to form a translationally disordered fluid. Fluid configurations at higher densities were subsequently generated by slow compression. In contrast, solid configurations were generated by gradual expansion from the close-packed lattice. During the simulations of the solid phase we allowed for

Table 3. Densities and pressures of the solid-liquid coexistence points of parallel spherocylinders with length-to-width ratios L/D between 0.25 and 5.0.

L/D	$\rho/\rho_0(\text{fluid})$	$\rho/\rho_0(\text{solid})$	P_{FS}
0.25	0.610	0.685	4.75
0.50	0.612	0.665	4.58
1.00	0.624	0.650	4.50
2.00	0.751	0.802	9.99
3.00	0.771	0.818	11.22
5.00	0.693	0.759	7.83

method, as described in [18]. In addition, we computed the absolute free energies of both the fluid and the solid phases, employing the techniques described in [18], [39]. Combining the free energy and equation of state data, we can determine the dependence of the melting point of the spherocylinder crystal on L/D (see table 3). Having determined the limits of thermodynamic stability of the solid phase, the next step is to look for possible fluid-fluid phase transitions. No discontinuities or van der Waals loops are observed in the fluid branch of the equation of state [43], but for the larger L/D ratios we observe a rather sudden change in the compressibility at densities between 40 and 60 per cent of close packing. Snapshots of typical molecular configurations both below and above this 'cusp' in the equation of state (figure 7) show a dramatic change in the structure of the fluid. At low densities the fluid is translationally disordered. Then, at a higher density (but well before the freezing point), the fluid orders into parallel

Figure 7. Snapshots of typical molecular configurations of a system of 270 parallel hard spherocylinders with $L/D = 5$. Left, nematic phase ($\rho/\rho_0 = 0.24$); middle, smectic phase ($\rho/\rho_0 = 0.62$); right, solid phase ($\rho/\rho_0 = 0.89$). The upper figure (a) shows a projection in the plane perpendicular to the molecular axes; the lower figure (b) shows a projection in a plane parallel to the molecular axes. For the sake of clarity, the spherocylinders are indicated by a line segment of length L .

Figure 8. Density dependence of the first maximum in the longitudinal component of the structure factor of parallel hard spherocylinders with $L/D = 1.0$ (left) and $L/D = 0.25$ (right). The ordinate shows $1/S(k_{z\max})$. In the dilute gas, this quantity approaches 1. In a smectic phase it should vanish in the thermodynamic limit. The present results apply to a 270-particle system, hence $1/S(k_{z\max}) \geq 1/270$. From the behaviour of $S(k_{z\max})$ one may deduce the density dependence of the longitudinal correlation length of $\xi_{\parallel}$ of smectic precursor fluctuations.

layers but with no order within the layers. In other words, the parallel spherocylinder form a smectic A phase [40]. For comparison, the crystalline phase, at a still higher density, is also shown. In the latter case there is clearly translational order within the layers.

A more quantitative method for locating the transition to the smectic phase is to study the static and dynamic behaviour of the longitudinal component of the intermediate scattering function $F(k_z, t)$, defined as

$$F(k_z, t) = \langle \rho(k_z, 0) \rho(-k_z, t) \rangle, \quad (8)$$

where $\rho(k_z, t)$ is the instantaneous amplitude of a longitudinal density fluctuation with wavevector k_z . $F(k_z, t = 0)$ is the longitudinal part of the static structure factor, $S(k_z)$, which determines, for instance, the X-ray scattering intensity. As the smectic phase is approached from lower densities, there will be smectic precursor fluctuations. These will show up as peaks in $S(k_z)$, for values k_z equal to (multiples of) $2\pi/d$, where d is the spacing of the incipient smectic layers. If the transition to the smectic phase is continuous, the peaks in $S(k_z)$ will diverge at the transition. An example of this behaviour is shown in figure 8. If we define the smectic layer spacing, d , by $d = 2\pi/k_{z\max}$, where $k_{z\max}$ is the wavevector corresponding to the first (and largest) maximum in $S(k_z)$, then we can measure how many smectic layers fit into the simulation box. Figure 9 shows how the number of 'layers' depends on density for $L/D = 5$. The fact that the number of layers is not constant but changes on compression is gratifying. It indicates that the number of layers is an equilibrium property, and not the consequence of some residual, metastable solid order (the solid phase, in this case, consists of nine layers). The ordering of the fluid in layers has a pronounced effect on the diffusion of individual particles. At low densities, the longitudinal component of the self-diffusion constant, $D_{\parallel}$, is larger than the transverse component, $D_{\perp}$. This effect is strongest for the most elongated particles. But as smectic layers start to form at higher densities, the $D_{\parallel}$ decreases much more rapidly than $D_{\perp}$. So much so, that in the smectic phase $D_{\perp}$ becomes larger than $D_{\parallel}$ (see figure 10). Hence, in

Figure 9. Density dependence of the 'number of layers' in a system of 270 parallel spherocylinders with $L/D = 5$. The number of layers is defined as the number of oscillations of the largest longitudinal Fourier component in the periodic box $k_{\max} L_z/2\pi$. Note that the number of layers changes on compression. This shows that the observed layering is not a metastability effect associated with the insufficient equilibration of the initial configuration.

the smectic phase, intra-layer diffusion is more rapid than inter-layer diffusion. Incidentally, this effect is also observed in some real liquid crystals [41].

A particularly sensitive probe of incipient smectic ordering is the critical slowing down of the correlation function $\langle \rho(k_z, 0) \rho(-k_z, t) \rangle$ at $k_z = k_{z \max}$. As can be seen from figure 11, the decay rate of $F(k_{z \max}, t)$ first increases as the density is raised, because the fluid is less compressible at higher densities. But beyond a certain density the decay rate drops precipitously to zero. This provides us with an estimate for the nematic-smectic transition density. For comparison, figure 11 also shows an example of a fluid which does not become smectic ($L/D = 0.25$). In this case the decay rate of $F(k_{z \max}, t)$ depends only weakly on density.

Combining the information about the smectic order parameter fluctuations with the data in table 3 on the melting transition, we can construct a 'phase

Figure 10. Typical example of the density dependence of the longitudinal (circles) and transverse (pluses) components of the self-diffusion tensor in a system of parallel spherocylinders with $L/D = 1.0$ (left) and $L/D = 0.25$ (right). Note that the relative magnitudes of the parallel and perpendicular components of D change as the fluid goes from the nematic to the smectic phase.

Figure 11. Relaxation rate of the longitudinal density fluctuations with a wavevector corresponding to the first maximum in $S(k_z)$. Left: parallel spherocylinders with $L/D = 1$. This system forms a smectic phase. As the transition is approached, the decay rate of the smectic precursor fluctuations drops dramatically. Right: parallel spherocylinders with $L/D = 0.25$. This system does not form a stable smectic. The latter figure shows no evidence for critical slowing down.

diagram' of hard parallel spherocylinders (figure 12). This phase diagram shows the regions of stability of the nematic, smectic and solid phases as a function of L/D . For $L/D \geq 0.5$, a smectic phase is found between the crystalline solid and the 'nematic' fluid. As the non-sphericity of the particles is increased, the smectic range initially grows and then saturates [42]. It should be stressed that this phase diagram pertains to a system of parallel spherocylinders. The effect of the orientational degrees of freedom on the phase diagram is currently under investigation [43].

Figure 12. Schematic 'phase diagram' of hard parallel spherocylinders, as a function of length-to-width ratio L/D . The shaded area corresponds to the fluid-solid two-phase region. Black circles: densities of the coexisting fluid and solid phase. Open circles: densities at which smectic ordering sets in. The dashed line indicates the estimated nematic-smectic phase boundary.

5. CONCLUSIONS

In this paper I have tried to demonstrate that model systems consisting of non-spherical hard-core particles have a surprisingly rich phase diagram. In the case of hard ellipsoids, we found that the stability of the nematic phase is simply related to the degree of non-sphericity of the molecules. Moreover, even though parallel ellipsoidal particles cannot form stable smectics, parallel spherocylinders can. This result is quite unexpected because of the apparent similarity of long spherocylinders and needle-like ellipsoids.

In addition I have shown how many of the physically interesting static and dynamic properties of liquid crystal forming fluids can be studied by computer simulation. The interest of such calculations lies not in the possibility of reproducing the behaviour of real liquid crystals (although it is encouraging to find qualitative agreement). The use of these, and future, calculations is that they can be used to test approximate theoretical expressions for a wide variety of equilibrium and transport properties of molecular liquids and liquid crystals. Moreover, now that we have demonstrated the existence of stable hard-core nematics and (aligned) smectics for 'realistic' molecular shapes, we can prepare for the next step: thermodynamic perturbation theory.

There is more to liquid crystals than hard repulsive interactions. In the next few years we should be able to decide whether hard-core models are useful reference systems for real liquid crystals.

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