2.5 can be tolerated in a fcc lattice without either both components becoming localized or both fluid. We do not, however, know anything of the crystal structures formed in these runs, nor how they packed into the cells available to them. A full study of the problem of the crystallization of mixtures of hard spheres has yet to be made.

Acknowledgment. We thank Professor B. J. Alder for useful discussions. G.J. thanks the SERC for the award of a CASE studentship, and F.v.S. thanks the Ramsay Trustees for a Fellowship.

(11) Ermak, D. L.; Alder, B. J.; Pratt, L. R. *J. Phys. Chem.* **1981**, *85*, 3221.

Onsager's Spherocylinders Revisited

Daan Frenkel

FOM Institute for Atomic and Molecular Physics, 1009 DB Amsterdam, The Netherlands
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Since the work of Onsager, systems of hard spherocylinders have played a special role as the theoretician's "ideal" nematic liquid crystals. It is, however, well-known that the Onsager theory is only a good description for extremely nonspherical particles. A quantitative measure for the range of validity of this theory is obtained from direct numerical calculation of the third through fifth virial coefficients of hard spherocylinders with length-to-width ratios, L/D, between 1 and 10^6. The phase diagram of spherocylinders with "realistic" L/D ratios can only be obtained by computer simulation. We report molecular dynamics and Monte Carlo simulations for spherocylinders with $L/D = 5$. These calculations suggest that the oldest model for a hard-core nematic may, in fact, have a smectic liquid-crystalline phase as well.

Introduction

Liquid crystals are probably good candidates for the title "nonsimple liquids". They are complex both in the microscopic nature of their building blocks and in the diversity of partially ordered phases that may be found in nature. The implicit hope of theoreticians who propose models for liquid-crystalline mesophases is that only one or two aspects of the microscopic structure of mesogens (liquid-crystal-forming molecules) are essential for the understanding of the liquid-crystalline phases. Unfortunately, it appears that no single structural property can account for the wide diversity of known mesophases. What is worse, there is not even consensus about the choice of this "essential feature" for any given phase.

Onsager was the first to propose that orientational ordering in a molecular fluid may be explained as an excluded-volume effect.[1] The model considered by Onsager was an assembly of thin spherocylinders with length L and diameter D. Onsager showed that, in the limit $L/D \rightarrow \infty$, this model system undergoes a transition from the isotropic fluid phase to an orientationally ordered (nematic) liquid-crystalline phase. The physical reason for this phase transition is that, by forming a nematic, the system can gain translational entropy at the expense of some orientational entropy. The transition takes place at a density ρ^* of order $1/(L^2/D)$ ($\rho^* B_2 = 3.29$,[2] where the second virial coefficient $B_2 = \pi L^2 D/4$). At the transition, the volume fraction occupied by the spherocylinders is still vanishingly small (of order D/L).

Subsequently, alternative physical mechanisms have been invoked to describe the isotropic–nematic transition. For instance, the mean-field theory of Maier and Saupe[3] attributes the orientational ordering to anisotropic intermolecular dispersion forces. Among experimentalists, the Maier–Saupe theory enjoys much greater popularity than the Onsager description. The reason is simple: the Onsager theory yields rather poor predictions for the properties of real thermotropic nematics (such as the value of the nematic order parameter S and the density change $\Delta\rho$ at the isotropic–nematic transition.[4] Still, Onsager's model plays a unique role in the theory of liquid crystals, because it is the only exactly solvable model with full translational and orientational degrees of freedom which exhibits a transition to the nematic phase.

Virial Coefficients

Unfortunately, the Onsager theory is only valid in the limit $L/D \rightarrow \infty$, while most thermotropic liquid crystal have effective L/D ratios of 3–5.[5] The reason why the Onsager theory cannot be used to describe molecular systems with such "small" L/D values is the following: an essential assumption in its derivation is that, in the expansion of the free energy in powers of the density, all virial coefficients B_n with $n > 2$ may be neglected. This condition is satisfied if the reduced nth virial coefficient, defined as

$$B_n(\text{reduced}) \equiv B_n/B_2^{(n-1)} \qquad (1)$$

satisfies the condition $B_n(\text{reduced}) \ll 1$. Onsager gave a qualitative argument to show that for large L/D $B_3/B_2^2 \sim (D/L) \log (L/D)$. Hence, in the limit $L/D \rightarrow \infty$, the reduced third virial coefficient does indeed vanish.[6] Onsager made the plausible assumption that the higher virial coefficients can also be neglected in the same limit. Of course, the question arises whether this assumption about the higher virial coefficients is indeed correct and, if so, how large L/D must be to observe this asymptotic behavior. To find out, we computed the third through fifth virial coefficient of hard spherocylinders as a function of L/D, for L/D between 1 and 10^6. The Monte Carlo technique to compute the higher virial coefficients of hard-core particles was developed by Ree and Hoover[7] more than 20 years ago. However, for the

(1) Onsager, L. *Proc. N.Y. Acad. Sci.* **1949**, *51*, 627.
(2) Lasher, G. *J. Chem. Phys.* **1970**, *53*, 4141. Kayser, R. F.; Raveché, H. J. *Phys. Rev. A* **1978**, *17*, 2067.
(3) Maier, W.; Saupe, A. *Z. Naturforsch., A* **1958**, *13*, 564.
(4) For a discussion, see: Cotter, M. A. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic: London, 1979; p 169.
(5) The situation is different for lyotropic liquid crystals. In such systems L/D may be very large. However, for such systems the assumption that the particles are rigid may be incorrect. See: Odijk, T. *Polym. Commun.* **1985**, *26*, 197.
(6) This result applies to the isotropic phase. In a fluid with orientational order such that the molecular axes are restricted to a solid angle of order $(D/L)^2$ or less, the Onsager theory is no longer valid, even if $L/D \gg 1$.

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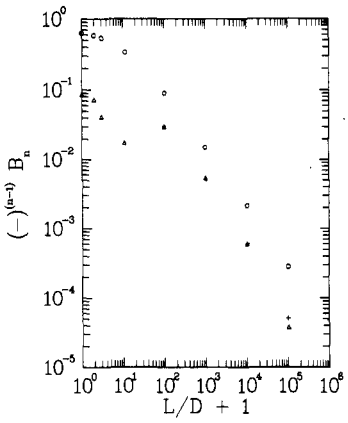

Figure 1. Reduced third (circles), fourth (pluses), and fifth (triangles) virial coefficients of prolate hard spherocylinders, as a function of the length-to-breadth ratio, L/D. The reduced nth virial coefficient is defined as B_n/B_2^n. In the case of the fourth virial coefficient, $-B_4/B_2^3$ is shown (see Table I).

TABLE I: Reduced Third, Fourth, and Fifth Virial Coefficients of Hard Spherocylinders, as a Function of the Length-to-Breadth Ratio L/D[a]

L/D	B_3/B_2^2	B_4/B_2^3	B_5/B_2^4
0	0.625	0.25	0.08594
10	$3.383\ (5) \times 10^{-1}$	$0.5\ (6) \times 10^{-3}$	$1.8\ (1) \times 10^{-2}$
100	$8.95\ (3) \times 10^{-2}$	$-3.01\ (3) \times 10^{-2}$	$2.98\ (7) \times 10^{-2}$
1000	$1.52\ (1) \times 10^{-2}$	$-5.2\ (1) \times 10^{-3}$	$5.4\ (3) \times 10^{-3}$
10000	$2.15\ (5) \times 10^{-3}$	$-6.0\ (4) \times 10^{-4}$	$6.0\ (9) \times 10^{-4}$
100000	$2.8\ (2) \times 10^{-4}$	$-0.5\ (1) \times 10^{-4}$	$0.4\ (2) \times 10^{-4}$
1000000	$2.7\ (6) \times 10^{-5}$	$-0.9\ (5) \times 10^{-5}$	$0.1\ (1) \times 10^{-4}$

[a] The estimated error in the last digit is indicated in parentheses.

extremely nonspherical shapes that concern us here, the Monte Carlo sampling requires special care. The reason is the following: when averaging over all possible configurations of n particles, the configurations that contribute to the nth virial coefficient are those for which all n particles belong to a single, irreducible cluster. Clearly, if the sampling of all particle coordinates is carried out independently, then the probability that the resulting configuration contributes to the virial coefficient becomes very small for large L/D. An alternative would be a sampling scheme in which the n particles are initially prepared in a configuration such that molecules i and $i + 1$ overlap. Subsequent configurations could then be generated by a Monte Carlo sampling of the particle coordinates, subject to the condition that the chain is never broken. This method suffers from the drawback that consecutive configurations are strongly correlated. A procedure that is efficient, even for very elongated molecules, is the following. To create a configuration, we first fix the orientation of molecule 1. Next, we pick a random orientation for molecule 2. We then construct the excluded volume of molecules 1 and 2. (For spherocylinders this is straightforward.) The center of mass of molecule 2 is then placed at a random position within this excluded volume. Similarly, molecule 3 is made to overlap with molecule 2, and so on. Thus, we ensure that every trial configuration is statistically independent. Of course, there is no guarantee that molecule n will overlap with molecule 1. In fact, this probability will become quite small for large L/D if the corresponding virial coefficient is small. But this cannot be avoided because it is a direct consequence of the effect that we are looking for.

Figure 1 shows the L/D dependence of B_3/B_2^2, B_4/B_2^3, and B_5/B_2^4 for hard spherocylinders with L/D between 1 and 10^5. The numbers, together with the error estimates, have been collected in Table I (including the results for $L/D = 10^6$, for which the statistics are very poor). As can be seen from Figure 1, the computed virial coefficients do indeed become small for large L/D. However, for B_4 and B_5 this decrease only sets in at rather large

(7) Ree, F. H.; Hoover, W. G. *J. Chem. Phys.* **1964**, *40*, 939.

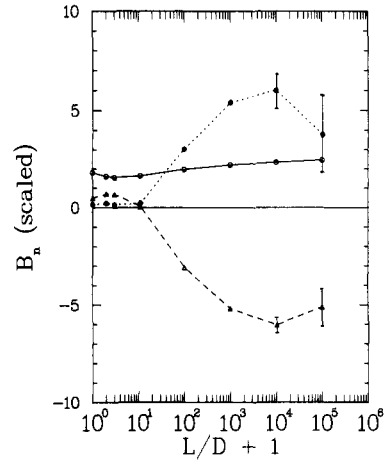

Figure 2. Asymptotic behavior of the reduced virial coefficients of hard spherocylinders. To emphasize the different asymptotic shape dependence of B_3, on the one hand, and B_4 and B_5, on the other, B_3 has been multiplied by $(L/D + 2)/\{\log (L/D + 2)\}$. B_4 and B_5 are both multiplied by $(L/D + 2)$. Symbols: B_3, open circles; B_4, open triangles; B_5, closed circles. Estimated error bars are indicated whenever they are larger than the symbols.

L/D values. This effect can be visualized by dividing the reduced virial coefficients by a factor proportional to the value that one should expect if the asymptotic L/D dependence was valid for all L/D:

$$B_3(\text{scaled}) = (B_3/B_2^2)/\{(D/L) \log (L/D)\} \quad (2a)$$

$$B_4(\text{scaled}) = (B_4/B_2^3)/(D/L) \quad (2b)$$

$$B_5(\text{scaled}) = (B_5/B_2^4)/(D/L) \quad (2c)$$

The resulting "scaled" virial coefficients are shown in Figure 2. Apparently, for B_3 the asymptotic behavior already sets in for small L/D. Not so for B_4 and B_5. As can be seen from Figure 2, the approach to the asymptotic behavior is only observed beyond $L/D = O(10^2)$. The reason is that, whereas only one (positive) cluster integral contributes to B_3, B_4 and B_5 contain several contributions from diagrams of different sign and different asymptotic L/D dependence. The partial cancellation of these contributions is responsible for the behavior of B_4 and B_5 for small L/D. In the limit $L/D \rightarrow \infty$, only the leading diagram (i.e., the one involving the product $f_{12}f_{23}f_{34}\cdots f_{n1}$) survives. This diagram is positive for odd n and negative for even n. Incidentally, it is worth noting that almost identical behavior is observed for the virial coefficients of hard ellipsoids.[8]

The foregoing discussion confirms the generally accepted notion that systems of hard spherocylinders with shapes resembling real liquid-crystal-forming molecules cannot be described by the Onsager theory.[9] The fact that real nematics do not obey the predictions of this theory is not surprising. However, this does not imply that excluded-volume effects cannot be responsible for phase transitions involving liquid crystals. It just means that we have run out of exactly solvable models. For this reason, a number of approximate theories have been proposed to describe the phase behavior of nonspherical hard-core molecules with finite length-to-breath ratios.[10] But the problem with such approximate theories is that one cannot tell in advance whether the answers they give are reliable. This is where computer simulation comes into the picture.

Computer Simulations

Not surprisingly, hard spherocylinders were among the first nonspherical hard-core systems to be studied by computer sim-

(8) Frenkel, D. *Mol. Phys.* **1987**, *60*, 1.
(9) Straley, J. P. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 7.
(10) See: Cotter, M. A. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic: London, 1979 and references therein. More recent references can be found in: Mulder, B. M.; Frenkel, D. *Mol. Phys.* **1985**, *55*, 1171.

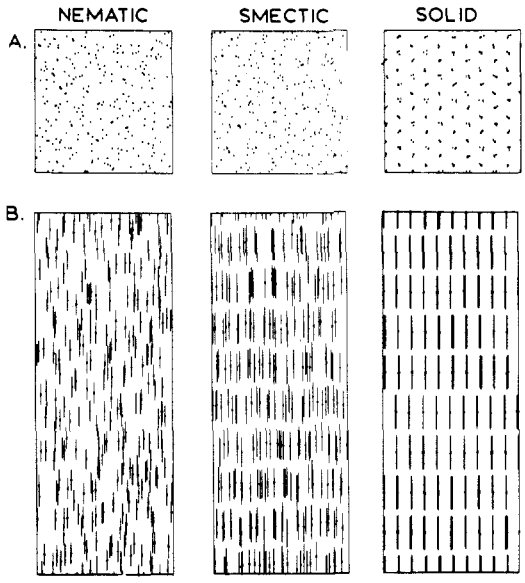

Figure 3. Snapshots of typical molecular configurations of a system of 270 parallel hard spherocylinders with $L/D = 5$: left, nematic phase ($\rho/\rho_0 = 0.24$, where ρ_0 is the density of closest packing); middle, smectic phase ($\rho/\rho_0 = 0.62$); right, solid phase ($\rho/\rho_0 = 0.89$). The upper figures (A) show a projection in the plane perpendicular to the molecular axes, and the lower figures (B) show 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.

ulation. But neither in the early simulations of Vieillard-Baron[11] nor in those of subsequent authors[12] could a transition to the nematic phase be observed. The reason for this disappointing result was that it proved very difficult to equilibrate the spherocylinder fluid in the density regime where the nematic phase is expected.[11] Below, we discuss a possible reason for this behavior. But first, let us briefly review the results of computer simulations on a closely related system of nonspherical hard-core molecules, namely, hard ellipsoids of revolution. Such spheroids are characterized by a single shape parmeter, $x \equiv a/b$, where $2a$ is the length of the symmetry axis of the ellipsoid and $2b$ is the length of an axis perpendicular to the symmetry axis. The phase diagram of hard ellipsoids of revolution with axial ratios between $^1/_3$ and 3 was studied by Frenkel et al. using Monte Carlo simulations.[13] These calculations showed that, for ellipsoids with $x > 2.5$ and $x < 0.4$, a thermodynamically stable nematic phase exists between the isotropic fluid and the crystalline solid. In the limits $x \rightarrow \infty$ and $x \rightarrow 0$, the location of the isotropic–nematic transition is also known, because in the former limit the Onsager theory is valid, while the case $x = 0$ was studied numerically by Eppenga and Frenkel.[14]

At first sight one might be inclined to think that the phase behavior of hard spherocylinders as a function of molecular anisometry should be qualitatively similar to that of hard ellipsoids. However, at high densities the seemingly subtle difference between the shapes of these two hard-core molecules can lead to completely different behavior. This effect can be demonstrated quite clearly by comparing the properties of two simplified model systems, viz., aligned ellipsoids and aligned spherocylinders. Let us first consider parallel ellipsoids. As was already discussed by Lebowitz and Perram,[15] the partition function of ellipsoids aligned parallel to the z axis can be mapped into that of hard spheres simply by scaling all z coordinates with a factor b/a. Hence, the phase diagram of aligned ellipsoids follows directly from hard spheres.

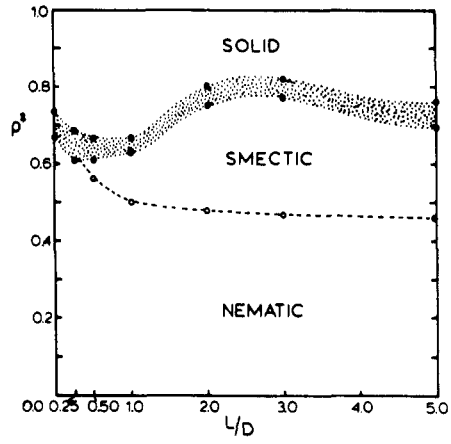

Figure 4. Schematic "phase diagram" of hard parallel spherocylinders, as a function of length-to-width ratio, L/D. The shaded area corresponds to the fluid–solid two-phase region. Black circles represent densities of the coexisting fluid and solid phase, and open circles represent densities at which smectic ordering sets in. The dashed line indicates the estimated nematic–smectic phase boundary.

In particular, one should expect a melting transition at approximately $^2/_3$ of the close packing density.[16] Clearly, as hard spheres have only one fluid phase, the same must hold for aligned ellipsoids.

For aligned spherocylinders the situation is drastically different. Monte Carlo and molecular dynamics simulations on this model system were reported by Stroobants et al.[17] These simulations showed that parallel spherocylinders with an L/D ratio of at least 0.5 form *smectic* phases between the low-density fluid and the crystalline solid. As an illustration, Figure 3 shows snapshots of typical molecular configurations of a system of parallel spherocylinders with $L/D = 5$ in the low-density nematic phase (A), the intermediate-density smectic phase (B), and the high-density solid phase (C). The smectic ordering observed in these systems was not due to incomplete melting, as the smectic phase was generated by compressing the translationally disordered fluid.[18] Moreover, absolute free energy calculations[19] indicate that the smectic phase is thermodynamically stable with respect to both the solid and the translationally disordered fluid. A schematic drawing of the phase diagram of aligned spherocylinders as a function of L/D is shown in Figure 4.[20]

Let us now return to spherocylinders with both translational and orientational freedom. What phase diagram should we expect? Clearly, the orientational degrees of freedom will affect the phase diagram in an important way. For instance, at low densities we should now expect an isotropic fluid phase. The question is, what happens at higher densities? Will the orientational freedom destroy the smectic order found in the aligned system, or will the nematic phase disappear at the expense of the smectic phase? Once again, to find out we resort to numerical simulation.

To this end, we carried out Monte Carlo and molecular dynamics simulations on a system of hard spherocylinders with an L/D ratio of 5. The simulations proceeded in two stages: first, we prepared an equilibrated system of aligned spherocylinders at a given density. Next, we removed the constraint on the molecular orientations. In this way the effect of the rotational degrees of freedom on the stability of the different phases could be studied directly. In order to exclude collisions between particles that are not nearest images, the linear dimensions of the simulation box must be at least twice the length of a molecule. This condition puts a practical limitation on the maximum value of L/D that

(11) Vieillard-Baron, J. *Mol. Phys.* **1974**, *28*, 809.
(12) Rebertus, D. W.; Sando, K. M. *J. Chem. Phys.* **1977**, *67*, 2585. Monson, P. A.; Rigby, M. *Chem. Phys. Lett.* **1978**, *58*, 122. Nezbeda, I.; Boublik, T. *Czech. J. Phys.* **1978**, *B28*, 353. Nezbeda, I.; Pavlicek, J.; Labik, S. *Collect. Czech. Chem. Commun.* **1979**, *44*, 3555.
(13) Frenkel, D.; Mulder, B. M.; McTague, J. P. *Phys. Rev. Lett.* **1984**, *52*, 287. Frenkel, D.; Mulder, B. M. *Mol. Phys.* **1985**, *55*, 1171.
(14) Eppenga, R.; Frenkel, D. *Mol. Phys.* **1984**, *52*, 1303.
(15) Lebowitz, J. L.; Perram, J. W. *Mol. Phys.* **1983**, *50*, 1207.
(16) Hoover, W. G.; Ree, F. H. *J. Chem. Phys.* **1968**, *49*, 3609.
(17) Stroobants, A.; Lekkerkerker, H. N. W.; Frenkel, D. *Phys. Rev. Lett.* **1986**, *57*, 1452.
(18) For a more detailed discussion, see: Frenkel, D. *Mol. Phys.* **1987**, *60*, 1.
(19) Stroobants, A.; Lekkerkerker, H. N. W.; Frenkel, D., submitted for publication.
(20) Actually, recent simulations have revealed that the phase diagram is even richer than shown in this figure. See ref 19.

can be simulated, because the volume of the periodic box scales as L^3 while the molecular volume goes as LD^2. Hence, the minimum number of particles in the periodic box goes as $(L/D)^2$. The simulations reported here were carried out for a system of 576 spherocylinders in an almost cubic box. Initially, the spherocylinders were prepared in a regular close-packed lattice. This lattice was generated from a face-centered-cubic hard-sphere crystal, by expansion along the [111] direction with a factor $1 + L/D$. This lattice was thereupon expanded to a low density (20% of close packing), but the molecular orientation was kept fixed. The translationally disordered fluid was thereupon compressed to 50% of close packing, and equilibrated configurations were generated at a number of intermediate densities. For an aligned spherocylinder with $L/D = 5$, the transition from the "nematic" low-density phase to the smectic phase takes at a reduced density of 0.47 (see Figure 4), where the reduced density ρ(reduced) is defined as

$$\rho(\text{reduced}) = \rho/\rho_0 \tag{3}$$

where ρ_0 is the density at regular close packing.

Next, the molecular orientations were released. This had a drastic effect: at densities below $\rho/\rho_0 = 0.45$ all orientational order disappeared. However, for higher densities orientational order persisted. This suggests that spherocylinders with $L/D = 5$ have an isotropic–nematic transition around $\rho/\rho_0 = 0.45$. A sensitive method to locate the transition to the nematic phase is to study the pretransitional dynamics of collective orientational fluctuations in the isotropic phase. To this end, we studied the autocorrelation function $C_2^c(t)$, of the second-rank orientational tensor $\mathbf{Q}_{\alpha\beta}(t)$, defined as

$$C_2^c(t) \equiv \langle \mathbf{Q}_{\alpha\beta}(0)\, \mathbf{Q}_{\beta\alpha}(t)\rangle \tag{4}$$

with

$$\mathbf{Q} = (1/N)\sum_i (3\mathbf{u}_i\mathbf{u}_i - \mathbf{I})/2 \tag{5}$$

In eq 5 $\mathbf{u}_i$ is a unit vector in the direction of the symmetry axis of molecule i. In the isotropic phase, the correlation function $C_2^c(t)$ decays to zero with a characteristic decay time τ_2^c. In the nematic phase, $C_2^c(t)$ goes to a finite value as $t \to \infty$: $C_2^c(t \to \infty) = 1.5S^2$, where S is the nematic order parameter. The correlation time τ_2^c is expected to diverge as the transition to the nematic phase is approached.[21] Figure 5 shows the density dependence of the rate of decay of collective orientational fluctuations, as measured by the inverse of the correlation time τ_2^c. The figure clearly shows that, for spherocylinders with $L/D = 5$, the isotropic–nematic transition takes place at 45% of the close-packed density. This, incidentally, is the first numerical demonstration of the existence of a nematic phase in a system of spherocylinders with a "realistic" L/D ratio.

The next question is whether this system has a transition to a smectic phase. Once again, the most sensitive way to probe the onset of smectic ordering is to study the dynamics of smectic order parameter fluctuations in the nematic phase. The order in a smectic A liquid crystal is characterized by a one-dimensional density modulation in the direction of the molecular axes. It is therefore natural to look for pretransitional fluctuations of the Fourier components of the one-particle density. An efficient method to detect incipient smectic ordering is to look at the decay of the longitudinal component of the intermediate scattering function $F(k_z,t)$, defined as

$$F(k_z,t) = \langle \rho(k_z,0)\, \rho(-k_z,t)\rangle \tag{6}$$

where $\rho(k_z,t)$ is the instantaneous amplitude of a longitudinal density fluctuation with wavevector k_z. (For convenience, we have chosen the nematic director parallel to the z axis). $F(k_z,t=0)$ is

(21) As the isotropic–nematic transition is first-order, the correlation time τ_2^c saturates at a finite value at the coexistence point. For a recent molecular dynamics study of rotational dynamics near the isotropic–nematic transition of hard ellipsoids of revolution, see: Allen, M. P.; Frenkel, D. *Phys. Rev. Lett.*, in press.

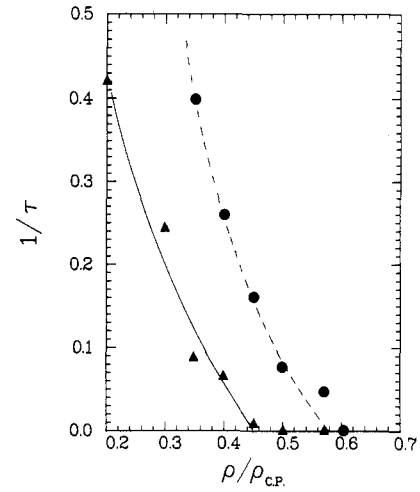

Figure 5. Density dependence of the collective orientational relaxation rate $1/\tau_2^c$ (triangles), for hard spherocylinders with $L/D = 5$. Also shown in the same figure is the behavior of the relaxation rate of the longitudinal density fluctuations with a wavevector corresponding to the first maximum in $S(k_z)$ (circles). The curves through the data points have been drawn as guides to the eye. The figure shows that the isotropic–nematic transition takes place around $\rho/\rho_0 = 0.45$, while the nematic has a transition to a smectic A phase at $\rho/\rho_0 = 0.58$. Due to slow pretransitional fluctuations, the statistical errors in the relaxation rates become large in the vicinity of the phase transitions.

the longitudinal part of the static structure factor, $S(k_z)$, which determines, for instance, the X-ray scattering intensity. If a transition to a smectic phase is approached from lower densities, there should 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. In the vicinity of the nematic–smectic A transition, we expect critical slowing down of the correlation function $\langle \rho(k_x,0)\, \rho(-k_z,t)\rangle$ at $k_z = k_z(\max)$, where $k_z(\max)$ is the wavevector that correponds to the first maximum at $S(k_z)$. In Figure 5, the rate of decay of $F(k_z(\max),t)$ is plotted as a function of density. As can be seen from the figure, there is a dramatic increase with density of the lifetime of smectic order parameter fluctuations. The figure suggests a transition from the nematic to the smectic A phase[22] at a density of ~55% of close packing. As we compress the system to still higher densities, we find that the smectic order parameter, which is initially very small (3% at $\rho/\rho_0 = 0.57$), starts to grow rapidly. Our simulations indicate that the nematic to smectic transition in this system is either continuous or weakly first order. In real liquid crystals the nematic–smectic A transition can be either first-order or continuous. A continuous transition is usually observed if the nematic order parameter at the transition is large. In the present simulations, the nematic order parameter at the transition is quite large ($S \approx 0.92$; perfect orientational order would correspond to $S = 1$). It therefore seems likely that the nematic–smectic A phase transition for hard spherocylinders with $L/D = 5$ is continuous.

Discussion

Systems of hard spherocylinders have long been considered the "typical" model for a nematic liquid crystal. The computer simulations presented above indicate that the phase diagram of this very simple model system is richer than expected. Not only do we find a nematic phase, but in addition we find that spherocylinders with an L/D ratio of 5 also form a smectic A phase. In other words, pure excluded-volume effects are enough to cause smectic ordering. That this should be so was far from obvious. In fact, the most popular models to describe the formation of smectics[23,24] do not even consider excluded-volume effects.

(22) We checked for other forms of ordering, in particular smectic C, smectic B, and hexatic B, but found no evidence for such ordering.

(23) McMillan, W. L. *Phys. Rev. A* **1971**, *4*, 1238.

The fact that hard spherocylinders can have both a nematic and a smectic phase may explain the problems that Vieillard-Baron[11] experienced in his search for the isotropic–nematic transition in a system of 616 hard spherocylinders with $L/D = 2$. Vieillard-Baron found in his Monte Carlo simulations that extremely long preparatory runs were required to generate an equilibrated (isotropic) fluid configuration, starting from the crystalline solid. In retrospect, it seems likely that Vieillard-Baron's simulations were plagued by critical slowing-down effects due to the vicinity of both the isotropic–nematic and the nematic–smectic phase transitions. Whether the system studied by Vieillard-Baron does in fact have thermodynamically stable nematic and smectic phases is still an open question. Simulations on spherocylinders with L/D ratios other than 5 are currently under way.

To conclude, let us return to Onsager's model system consisting of long, thin spherocylinders. As mentioned earlier, this model plays a special role in the statistical mechanical theory of liquid-crystal formation because it is the only exactly solvable model that predicts a transition to the nematic phase. However, in the strongly aligned nematic phase the "second virial" theory is no longer valid (see footnote 6). Actually, a breakdown of the Onsager approximation at high densities is to be expected, because at sufficiently high packing fraction thin spherocylinders should form a crystal, rather than a liquid crystal. However, the present simulations on spherocylinders with a finite L/D ratio (both aligned and nonaligned) suggest that, before they freeze, Onsager's spherocylinders may well form a smectic liquid crystal.

From the work of Rahman, I learned that the "complex" behavior of many-body systems can often be explained in terms of very simple intermolecular interactions. It is gratifying to see that this approach is fruitful, even for systems as complex as liquid crystals.

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(24) Dowell, F. *Phys. Rev. A* **1983**, *28*, 3526.

Frequency-Dependent Specific Heat in a Simulation of the Glass Transition

Gary S. Grest*

Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801

and Sidney R. Nagel*

The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637
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Recent experiments have shown that there is a frequency dependence to the specific heat of liquid glycerol as it is cooled through the glass transition. We show that in a simulation of a simple Lennard-Jones fluid the same phenomenon can be observed. There is a large difference between the behavior of the constant pressure and constant volume specific heats. The former shows a pronounced drop as the temperature is lowered while the latter shows very little signature of the transition at all.

Introduction

The glass transition occurs when a liquid is cooled sufficiently far below its equilibrium freezing temperature so as to become an amorphous solid. To reach this glass state the liquid must be supercooled rapidly in order to prevent the nucleation of the crystalline phase. The nature of the glass transition is still open to debate. For example, there is ongoing controversy over whether all classical liquids can form a glass if cooled rapidly enough or whether only liquids which have certain properties can be glass formers. It is also unsettled whether the glass transition is a true phase transition or whether it is simply a kinetic freezing of the liquid.

Experimental attempts at studying this phenomenon have been hampered by one of the essential characteristics of the glass transition itself. The liquid becomes so viscous as the transition temperature, T_g, is approached that it becomes progressively more difficult to keep the sample in equilibrium. Thus the time scale determined by the experiment depends either on the cooling rate or on the frequency of the probe being used and static susceptibility cannot be measured near T_g. On the other hand, theoretical investigations of the glass transition have not been able to agree on the microscopic mechanism which is responsible for the phenomenon. Should the same mechanism be responsible for the glass formation in polymers as well as in metals or does one need different theories for different types of systems?

It may seem paradoxical that a computer simulation of the glass transition could provide much help at sorting out these various issues. After all, glass transitions are inextricably bound up with long relaxation times whereas computer simulations can only be run for relatively short times. The slowest cooling rate used in a computer simulation is much faster than can be achieved in even the most rapid experimental quench. The simulation is thus forced to study glass formation very far away in temperature from what would occur in an ideal, infinitely slow, cooling rate experiment. Another problem with simulations is that they usually are on systems with very simple interparticle interactions. It is much more difficult to simulate a liquid of complicated molecules interacting via long-range forces.

Despite these drawbacks computer simulations have provided a number of insights about the glass state and about the transition itself. Rahman and co-workers[1] studied the properties of a frozen Lennard-Jones fluid and showed that it behaved much like a solid. They also investigated the nucleation rates for various potentials and showed that in some cases the sample could remain amorphous during very long simulations.[2,3] It was also found[4] that the

(1) Rahman, A.; Mandell, M. J.; McTague, J. P. *J. Chem. Phys.* **1976**, *64*, 1564.

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