Simulation of Structure and Dynamics near the Isotropic-Nematic Transition

Michael P. Allen and Mark A. Warren
H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom

(Received 24 June 1996)

We present a computer simulation study of orientational correlations in a molecular liquid approaching the isotropic-nematic transition, including the first calculation of the direct correlation function $c(1,2)$ in this regime. While the second-rank orientational correlation length diverges, the associated component of $c(1,2)$ remains short ranged, and its spatial integral approaches the mechanical instability limit for the isotropic phase as predicted by density-functional theory. Orientational correlation lengths and times are quite well described by Landau–de Gennes theory. [S0031-9007(97)02459-9]

PACS numbers: 64.70.Md, 61.20.Ja, 61.25.Em

The nematic liquid crystal phase is characterized by long-ranged correlations of molecular orientation, while the positional degrees of freedom remain disordered. The appropriate orientational order parameter is a second-rank quantity [1]; it is conveniently expressed as

$$S = \langle P_2(\mathbf{u} \cdot \mathbf{n}) \rangle , \tag{1}$$

where P_2 is the second Legendre polynomial, $\mathbf{u}$ is a typical molecular orientation vector, $\mathbf{n}$ is the bulk preferred orientation or director, and $\langle \cdots \rangle$ represents an ensemble average. The transition between the isotropic liquid and the nematic phase is known, experimentally, to be weakly first order. This means that, for example, if one approaches the transition by lowering the temperature T from the isotropic side, the second-rank orientational correlation length ξ_2 becomes large, and it is possible to extrapolate $\xi_2^{-1} \to 0$ at a divergence temperature T^*. This limit, however, is preempted by the occurrence of the transition at a slightly higher temperature T_{NI}, where $(T_{\mathrm{NI}} - T^*)/T_{\mathrm{NI}} \approx 10^{-3}$. Both the statics and the dynamics of orientational correlations are of interest in the vicinity of this transition.

Computer simulations to fully characterize the isotropic-nematic (I-N) transition present great challenges. Studies of simplified lattice spin models [2,3] using finite-size scaling approaches [4–6] required system sizes of the order of $N = 30^3$ spins, and run-lengths of order 10^6 Monte Carlo moves per spin, to convincingly demonstrate weak first-order character. However, such lattice models relate to real liquid crystals only in the most coarse-grained sense; no connection to molecular properties is possible.

Molecular simulations are more expensive than those using spins, and a study analogous to the ones described above is out of reach at present. Nonetheless, there is great interest in locating the I-N transition, and in studying pretransitional phenomena, using molecular models. An early study on systems of a few hundred molecules [7] presented some evidence of the slowing down of collective reorientation, and the growth of static orientational correlations, for the hard ellipsoid fluid. However, these results were limited to ranges of a few molecular diameters. One aim of the present Letter is to study the growth of a rather longer ranged structure in the appropriate components of the pair correlation function $h(1,2)$ on approaching the transition. It is of particular interest to show whether or not the corresponding components of the direct correlation function $c(1,2)$ (defined below) remain short-ranged in this limit. A second aim of this work is to examine the way in which correlation times for collective reorientation scale with the range of the relevant correlations, on the approach to the transition; in other words, how orientational domain size affects collective reorientation.

We describe pair structure in the isotropic phase through the function

$$h(1,2) \equiv g(1,2) - 1 = g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) - 1 ;$$

$g(1,2)$ is the usual pair distribution function [8], $\mathbf{r}_1, \mathbf{r}_2$ are the center-of-mass coordinates of particles 1 and 2, and $\mathbf{u}_1, \mathbf{u}_2$ are unit vectors defining the orientations (we focus throughout on the case of axially symmetric molecules).

The direct correlation function $c(1,2)$ is defined through the Ornstein-Zernike equation [9]

$$h(1,2) = c(1,2) + \frac{\rho}{4\pi} \int \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{u}_3 \, h(1,3) c(3,2) , \tag{2}$$

where ρ is the number density. In applying this equation we restrict ourselves to the isotropic, homogeneous fluid phase. Equation (2) expresses the transmission of direct effects between particles via neighboring molecules; $c(1,2)$ is hopefully a shorter-ranged function than $h(1,2)$. Although experiments and simulations do not provide a direct route to this function, $c(1,2)$ is of equal importance to $h(1,2)$ in the statistical mechanics of liquids, playing a central role in density functional theories [10,11]. Among other applications, it is possible to express the condition of mechanical stability of the isotropic phase relative to the nematic liquid crystal in terms of expansion coefficients of $c(1,2)$ [12–14]; this gives an estimate of T^*. This is part of the motivation for the work described here.

It is convenient to expand $h(1,2)$ in a complete set of angular functions which depend on the separation

0031-9007/97/78(7)/1291(4)$10.00

$r = |\mathbf{r}_1 - \mathbf{r}_2|$ [8,9,15–17]:

$$h(1,2) = \sum_{mnl} h^{mnl}(r)\Phi^{mnl}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = 4\pi \sum_{mn\chi} h_{mn\chi}(r) Y_{\chi}^{m}(\mathbf{u}_1) Y_{-\chi}^{n}(\mathbf{u}_2), \quad (3)$$

with a similar expansion for $c(1,2)$. The coefficients $h^{mnl}(r)$ are based on a laboratory frame of reference, and the $\Phi^{mnl}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}})$ are rotational invariants [18]; the alternative coefficients $h_{mn\chi}(r)$ are calculated in an intermolecular frame of reference, and the $Y_{\chi}^{m}(\mathbf{u})$ are spherical harmonics. $\hat{\mathbf{r}}$ is the unit vector along $\mathbf{r}_1 - \mathbf{r}_2$. For molecules having a center of inversion, m, n, l are all even and there is $m \leftrightarrow n$ symmetry. The expansion coefficients are easily calculated in computer simulations [19,20], and some of them may be determined experimentally. Then Eq. (2) takes a matrix form involving the coefficients $h_{mn\chi}$ and $c_{mn\chi}$, which is suitable for inversion in real space or reciprocal space. This means that from simulation-determined coefficients $h_{mn\chi}(r)$ it is possible to calculate the $c_{mn\chi}(r)$ subject only to truncating the system of equations at an upper limit $n, m \leq n_{\max}$; the functions $c^{mnl}(r)$ are obtained from these by a simple transformation. We have applied the method successfully with $n_{\max} = 4, 6, 8$, as described elsewhere [21].

Defining suitably normalized integrals

$$h^{(m)} \equiv \rho(2m + 1)^{-1/2} 4\pi \int_0^{\infty} \mathrm{d}r\, r^2 h^{mm0}(r), \quad (4a)$$

$$c^{(m)} \equiv \rho(2m + 1)^{-1/2} 4\pi \int_0^{\infty} \mathrm{d}r\, r^2 c^{mm0}(r), \quad (4b)$$

the instability criterion for the isotropic phase [12–14] may be expressed as $c^{(m)} \to 1, m = 2, 4, 6 \ldots$. This turns out to be related to an *exact* factorization of the Ornstein-Zernike equation at zero wave vector [8] which may be expressed $h^{(m)} = c^{(m)}/(1 - c^{(m)})$. Thus, $c^{(m)} \to 1$ coincides with the divergence of the integral in Eq. (4a), and hence divergence of the range of $h^{mm0}(r)$, always assuming that $c^{(m)}$ remains well behaved.

In this study we simulate molecules interacting through a variant of the Gay-Berne potential [22] with parameters proposed by Berardi *et al.* [23]. This is an anisotropic Lennard-Jones style of pair potential, with the depths and locations of the potential minima dependent on relative molecular orientations. The molecules are roughly ellipsoidal, with diameter σ_0 (which we take to define the unit of length, of the order of 1 nm) and length-to-breadth ratio $\kappa = 3$. The attractive interactions are scaled by a strength parameter ε_0 (which defines a unit of energy, and by implication a unit of temperature ε_0/k_B, where k_B is Boltzmann's constant). An anisotropy parameter $\kappa' = 5$ determines the variation of potential well depth with orientation, the maximum attraction being for side-by-side arrangements of molecules. We follow Berardi *et al.* [23] in choosing the version of the potential with exponents $\mu = 1$, $\nu = 3$. For the reduced density $\tilde{\rho} = N\sigma_0^3/V = 0.3$, they find $\tilde{T}_{\rm NI} = k_B T_{\rm NI}/\varepsilon_0 \approx 3.57$, for system sizes $N = 512$ and $N = 1000$. Henceforth, we drop the tilde denoting reduced variables. We study the same density, and concentrate our effort in the temperature range $3.45 \leq T \leq 4.00$, using a larger system size, $N = 8000$, to enable us to study long-range correlations. Periodic boundary conditions are used; at this density the side of the cubic box is nearly $30\sigma_0$. We employ a molecular dynamics program which parallelizes efficiently on the Cray T3D supercomputer using a domain-decomposition approach [24]. Typical runs on 64 nodes take 0.25 s per timestep. We set the molecular mass M and moment of inertia to unity; this in turn defines the reduced unit of time $\tau_0 = \sqrt{M\sigma_0^2/\epsilon_0}$ (of order 10 ps for reasonable molecular parameters). Each timestep represents $0.004\tau_0$, and runs of up to 450 000 steps were judged necessary to ensure orientational equilibrium very close to the I-N transition, as monitored through the variation of the order parameter S.

A complete account of the simulation results will be the subject of a future publication. Here we summarize our observations. From lengthy heating and cooling runs, we established that $T = 3.50$ lies in the isotropic phase (an ordered system at this temperature spontaneously disorders) and that $T = 3.45$ lies in the nematic phase (spontaneous ordering occurs at this temperature). Thus we can definitely bracket $T_{\rm NI}$ between these limits, a significantly lower estimate than that of Ref. [23], but not inconsistent, bearing in mind that the transition occurs when the correlation length approaches the box dimension, which is larger here.

The laboratory-based, second-rank component $h^{220}(r)$ is shown in Fig. 1 at various temperatures. This measures

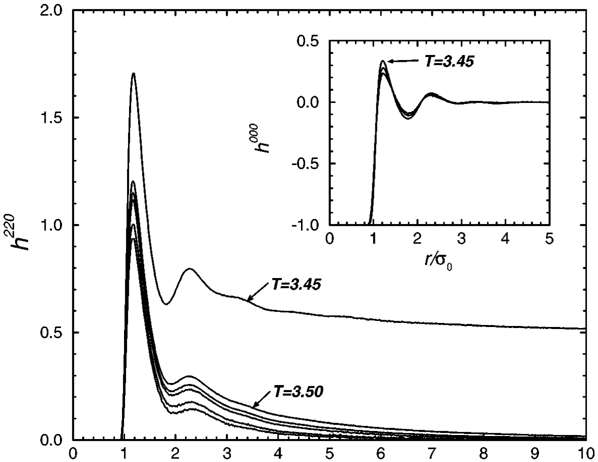

FIG. 1. The $h^{220}(r)$ orientational correlation function at temperatures $T = 3.45$, 3.50, 3.55, 3.60, 3.80, and 4.00. Inset: the $h^{000}(r)$ center-center correlation function at temperatures $T = 3.45$, 3.50, and 4.00. r is scaled by the molecular diameter σ_0.

correlations of the $P_2(\mathbf{u}_1 \cdot \mathbf{u}_2)$ type [see Eq. (1)] as a function of distance. The range of this function increases dramatically, very close to the transition, and becomes infinite in the nematic phase. On the isotropic side, the long-range decay fits very well an Ornstein-Zernike form $h^{220}(r) \propto \exp(-r/\xi_2)/r$ and fitting to this enables the correlation length ξ_2 to be extracted; this is reported in Table I. At the lowest isotropic temperature studied, ξ_2 is comparable with half of the simulation box length. We find that the data fit $\xi_2^{-2} \propto (T - T^*)$ quite well, as expected from Landau–de Gennes theory [1], with $T^* = 3.47 \pm 0.02$. The fourth-rank function $h^{440}(r)$ (not shown) exhibits greater short-range structure, and the amplitude of the long-range decay is smaller. In the vicinity of the transition, there are only small changes in the orientation-independent center-center pair correlation function $h^{000}(r)$, shown in the inset of Fig. 1, and these changes result from a slight increase in local neighbor alignment as the temperature is lowered.

The components of $c(1,2)$ were determined as described in Ref. [21]; convergence of the procedure was checked using $n_{\max} = 4, \ldots, 8$. The second-rank component $c^{220}(r)$ is shown in Fig. 2 for temperatures on the isotropic side of the transition. Two striking points are apparent. Firstly, the function remains very short-ranged throughout, decaying to essentially zero within the molecular length of $3\sigma_0$. Secondly, no substantial change in the form of the function occurs as the transition is approached; the negative region in the inner core of the molecule, $r < \sigma_0$, becomes a little stronger as the temperature is lowered, as does the peak at $r \approx 1.2\sigma_0$. These changes alone are associated with the dramatic increase in range of $h^{220}(r)$. The zero-k transforms, $c^{(m)}$, should reach the well-defined mechanical stability limits $c^{(m)} \to 1$ at the divergence temperature; $c^{(2)}$, $c^{(4)}$ are illustrated in the inset of Fig. 2, as well as being reported in the table. Note that while $c^{(2)}$ varies almost linearly with temperature close to the transition, the $c^{(4)}$ plot is more strongly curved, and $c^{(4)}$ is not particularly close to unity at $T = 3.50$. Although we cannot hope to extrapolate these functions to the divergence temperature T^* with sufficient accuracy to distinguish it from T_{NI}, we can see that they do behave in a manner consistent with the occurrence of the transition between $T = 3.45$ and $T = 3.50$. More detailed study would require the use of simulation boxes of large dimension compared with the correlation length ξ_2 at T_{NI}.

TABLE I. Static correlations in the vicinity of the isotropic-nematic transition. For each temperature T we report values of ξ_2, the second-rank correlation length in units of the molecular diameter σ_0, and the integrals defined in Eqs. (4a) and (4b) for rank-2 and rank-4 correlation functions.

T	ξ_2/σ_0	$h^{(2)}$	$h^{(4)}$	$c^{(2)}$	$c^{(4)}$
3.50	16.1	27.9	1.75	0.965	0.637
3.55	9.43	18.5	1.21	0.949	0.548
3.60	6.94	13.9	1.03	0.933	0.507
3.65	6.85	12.7	0.924	0.927	0.480
3.80	4.48	7.74	0.669	0.886	0.401
4.00	3.65	5.76	0.572	0.852	0.364

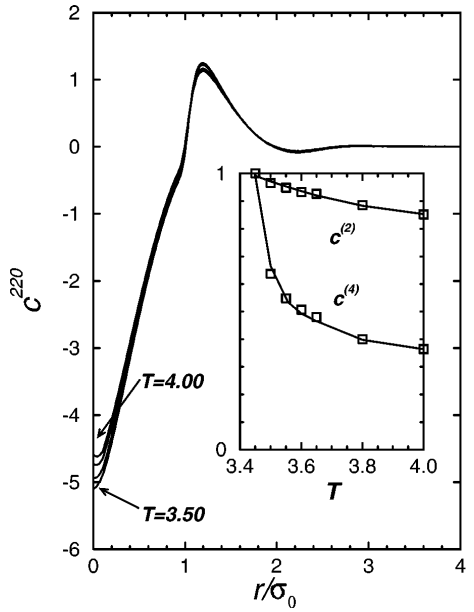

FIG. 2. The $c^{220}(r)$ orientational direct correlation function at temperatures $T = 3.50$, 3.60, 3.80, and 4.00. r is scaled by the molecular diameter σ_0. The inset shows the approach of the quantities $c^{(2)}$ and $c^{(4)}$ toward the stability limit (unity) as the temperature is varied; the lines are to guide the eye.

It is of great interest to examine the collective orientational dynamics in the vicinity of the transition, and we do this by calculating the time correlation function of the dynamical variable $Q_{\alpha\beta}(\mathbf{k},t) = \sum_i (\frac{3}{2} u_{i\alpha} u_{i\beta} - \frac{1}{2}\delta_{\alpha\beta}) \exp\{i\mathbf{k} \cdot \mathbf{r}_i\}$, where $\alpha, \beta = x, y, z$ and $\delta_{\alpha\beta}$ is the Kronecker delta. In other words, we calculate, for a given wave number $k = 2\pi/\lambda$,

$$C(k,t) = \sum_\alpha \sum_\beta \langle Q_{\alpha\beta}(-\mathbf{k},0) Q_{\alpha\beta}(\mathbf{k},t)\rangle \propto \sum_{ij} P_2(\mathbf{u}_i(0) \cdot \mathbf{u}_j(t)) \exp\{i\mathbf{k} \cdot [\mathbf{r}_i(0) - \mathbf{r}_j(t)]\}. \tag{5}$$

We find that this function decays exponentially, for k not too large: $C(k,t) = A(k) \exp\{-t/\tau(k)\}$. Moreover, both the amplitude $A(k)$ and the decay time $\tau(k)$ are roughly proportional to k^{-2} (see Fig. 3) for all but the lowest few values of k, and in fact the proportionality constants are quite insensitive to temperature. Notwithstanding this, values of $\tau(k)$ as $k \to 0$ become very large, and significant differences are seen here as the transition is approached (see Fig. 3). At $k = 0$ we find $\tau^{-1} \propto \xi_2^{-2} \propto (T - T^*)$, again in agreement with the Landau–de Gennes theory [1]. These results indicate that all but the longest wavelength dynamical properties remain unaffected by the approach of the I-N transition.

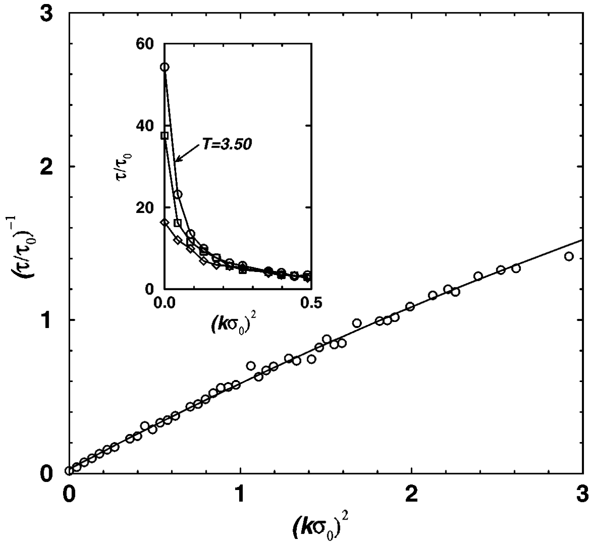

FIG. 3. The inverse orientational correlation time $\tau(k)^{-1}$ as a function of k^2 at $T = 3.50$; results for $T = 3.55, 3.60$ are almost indistinguishable when plotted in this way. Inset: Values of $\tau(k)$ vs k^2 at the lowest few k values studied. Here the effect of temperature can be seen: $T = 3.50$ (circles), $T = 3.55$ (squares), and $T = 3.60$ (diamonds); the lines are to guide the eye. τ and $k = 2\pi/\lambda$ are expressed in dimensionless form using the simulation units of time (τ_0) and distance (σ_0).

This study has shown that the direct correlation function $c(1,2)$ can be calculated from simulation data in the vicinity of the isotropic-nematic transition, that it is not strongly affected by the approach to this transition, and that it remains short-ranged. This suggests that successful theories of $c(1,2)$ in the isotropic phase may be equally successful in the nematic phase, where they will be useful in predicting, for example, liquid crystal elastic constants. The study has also shown that molecular-scale simulations can systematically investigate the wavelength-dependent timescales of orientational fluctuations close to the transition, reaching the length scale for which measurable pretransitional slowing-down effects can be observed. Our results support the view that simulation box dimensions determine the transition temperature by setting an upper limit on the wavelength of orientational fluctuations, but are otherwise not significant.

Financial support from the Engineering and Physical Sciences Research Council, through a CASE studentship to MAW, is gratefully acknowledged. The simulations were conducted on Cray T3D computers at Edinburgh (supported by the High Performance Computing Initiative of EPSRC) and CINECA, Bologna (supported by an Icarus project grant). Conversations with Claudio Zannoni, Roberto Berardi, and Andrew Masters are gratefully acknowledged.

[1] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974).
[2] P. A. Lebwohl and G. Lasher, Phys. Rev. A **6**, 426 (1972).
[3] P. A. Lebwohl and G. Lasher, Phys. Rev. A **7**, 2222 (1973), erratum.
[4] U. Fabbri and C. Zannoni, Mol. Phys. **58**, 763 (1986).
[5] Z. Zhang, O. G. Mouritsen, and M. J. Zuckermann, Phys. Rev. Lett. **69**, 2803 (1992).
[6] Z. Zhang, M. J. Zuckermann, and O. G. Mouritsen, Mol. Phys. **80**, 1195 (1993).
[7] M. P. Allen and D. Frenkel, Phys. Rev. Lett. **58**, 1748 (1987).
[8] C. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon Press, Oxford, 1984).
[9] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, London, 1986).
[10] R. Evans, in *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier Science Publishers B.V., Amsterdam, 1989), Chap. 1, pp. 1–98, les Houches, Session XLVIII 1988.
[11] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), Chap. 3, pp. 85–175.
[12] J. Stecki and A. Kloczkowski, J. Phys., Paris **C3**, 40 (1979).
[13] J. Stecki and A. Kloczkowski, Mol. Phys. **51**, 42 (1981).
[14] A. Perera, G. N. Patey, and J. J. Weis, J. Chem. Phys. **89**, 6941 (1988).
[15] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).
[16] L. Blum, J. Chem. Phys. **57**, 1862 (1972).
[17] L. Blum, J. Chem. Phys. **58**, 3295 (1973).
[18] P. H. Fries and G. N. Patey, J. Chem. Phys. **82**, 429 (1985).
[19] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987), 385pp., ISBN 0-19-855375-7.
[20] J. Talbot, A. Perera, and G. N. Patey, Mol. Phys. **70**, 285 (1990).
[21] S. Tang, G. T. Evans, C. P. Mason, and M. P. Allen, J. Chem. Phys. **102**, 3794 (1995).
[22] J. G. Gay and B. J. Berne, J. Chem. Phys. **74**, 3316 (1981).
[23] R. Berardi, A. P. J. Emerson, and C. Zannoni, J. Chem. Soc. Faraday Trans. **89**, 4069 (1993).
[24] M. R. Wilson, M. P. Allen, M. A. Warren, A. Sauron, and W. Smith, J. Comput. Chem. (to be published).