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1996 J. Phys.: Condens. Matter 8 9433

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Computer simulation of liquid crystals

Michael P Allen, Julian T Brown and Mark A Warren

H H Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, UK

Received 15 July 1996

Abstract. Computer simulations, using the molecular dynamics and Monte Carlo techniques, and employing simple molecular models, yield insight into general features of phase equilibria, structure, and dynamics of liquid crystals. Here, results are reported from extensive simulations of the Gay–Berne family of molecular models, in which potential parameters are adjusted to vary the molecular length-to-width ratio in a systematic way. Attention is paid to the characterization of nematic, smectic-A and smectic-B phases as functions of these parameters.

A simulation study of the approach to the isotropic–nematic phase transition, using a large system size and lengthy runs on the T3D parallel supercomputer, is described. Spatially long-ranged collective orientational correlations develop in the isotropic phase, close to the transition. The direct correlation function has been calculated for these systems, and remains short-ranged, as expected, as the transition is approached. The simulation results are compared with the density functional analysis of isotropic instability relative to the nematic phase.

1. Introduction

Computer simulation can contribute to our understanding of liquid crystals by relating detailed molecular structure to observed phase behaviour and properties; and by testing, in a microscopic way, the basis of theories of phase transitions, structure and dynamics. This paper reports briefly on two pieces of work carried out in our group with these aims in mind.

We are examining the Gay–Berne family of models [1], which represent nematogenic molecules as rigid, axially symmetric units interacting through a pair potential of the general form

$$U^{\text{GB}} = 4\varepsilon(\hat{r}, \mathbf{u}, \mathbf{v}) \left[\left(\frac{1}{r - \sigma(\hat{r}, \mathbf{u}, \mathbf{v}) + 1} \right)^{12} - \left(\frac{1}{r - \sigma(\hat{r}, \mathbf{u}, \mathbf{v}) + 1} \right)^6 \right].$$

Here r is the centre–centre vector, r its magnitude, and \hat{r} is a unit vector in the same direction; \mathbf{u} , \mathbf{v} are unit vectors along the molecular axes. The potential depends upon an orientation-dependent diameter $\sigma(\hat{r}, \mathbf{u}, \mathbf{v}|\kappa, \kappa', \mu, \nu)$ and an orientation-dependent energy parameter $\varepsilon(\hat{r}, \mathbf{u}, \mathbf{v}|\kappa, \kappa', \mu, \nu)$, each of which in turn depends parametrically on shape and energy anisotropies, κ, κ' respectively, plus two exponents μ, ν . The quantities σ and ε define the length scale and attractive well depth of a Lennard-Jones-like potential form for any given pair orientation.

2. Molecular shape and phase behaviour

The most thoroughly studied member of the Gay–Berne family [2, 3, 4] is defined by $\kappa = 3, \kappa' = 5, \mu = 2, \nu = 1$: this system exhibits phases identified as isotropic liquid

(I), vapour (V), nematic (N) and smectic-B (S_B); the nematic phase occurs at temperatures higher than the I–V critical point. It is of great interest to examine systematically the effects of varying the parameters around these values. Martín del R  o, de Miguel *et al* [5, 6] have studied $\kappa = 3, \kappa' = 1, \dots, 25$, showing that a reduction in the well-depth anisotropy, κ' , increases the liquid–vapour coexistence range until it intersects with the nematic phase: thus nematic–vapour coexistence may be simulated. In this study, we report our preliminary results on increasing the molecular length-to-width ratio $\kappa = 3, \dots, 4$ while keeping $\kappa' = 5$.

We have studied $\kappa = 3.0, 3.2, 3.4, 3.6, 3.8$ and 4.0 using molecular dynamics and Monte Carlo techniques. The liquid–vapour coexistence curve in the temperature–density, T – ρ , plane was investigated by Gibbs ensemble Monte Carlo [7] and Gibbs–Duhem integration [8, 9] but in fact we could only locate this curve for $\kappa \leq 3.2$ and it is possible that it disappears altogether for higher elongations. This means that at low T and medium ρ , the phase diagram is dominated by the S_B –V coexistence region. At higher temperature and density, we find a narrow region of stability for the smectic-A (S_A) phase for $\kappa \geq 3.4$, whereas this is absent or at best metastable for $\kappa < 3.4$. The S_A appears to be squeezed out between N and S_B as the temperature is increased further. Full details of these simulations will be given in future publications.

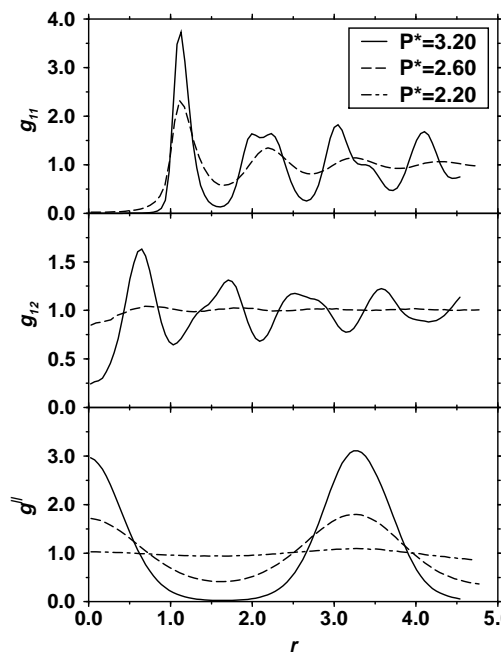


Figure 1. The transverse correlation functions g_{11} and g_{12} , and the longitudinal correlation function g^{\parallel} , for S_B (solid line), S_A (dashed line) and N (chain line) phases.

In studying these smectic phases we found it essential to use extremely long simulation runs (of order 5×10^5 MD timesteps or MC attempted moves per particle) to allow metastable states to properly equilibrate. System sizes of order $N = 600$ permitted typically six layers to form in a cuboidal periodic box with independently varying dimensions, but the study of larger systems would be highly desirable. In characterizing these phases, we found it useful to calculate three kinds of pair distribution function. The first, $g^{\parallel}(z)$, measures correlations

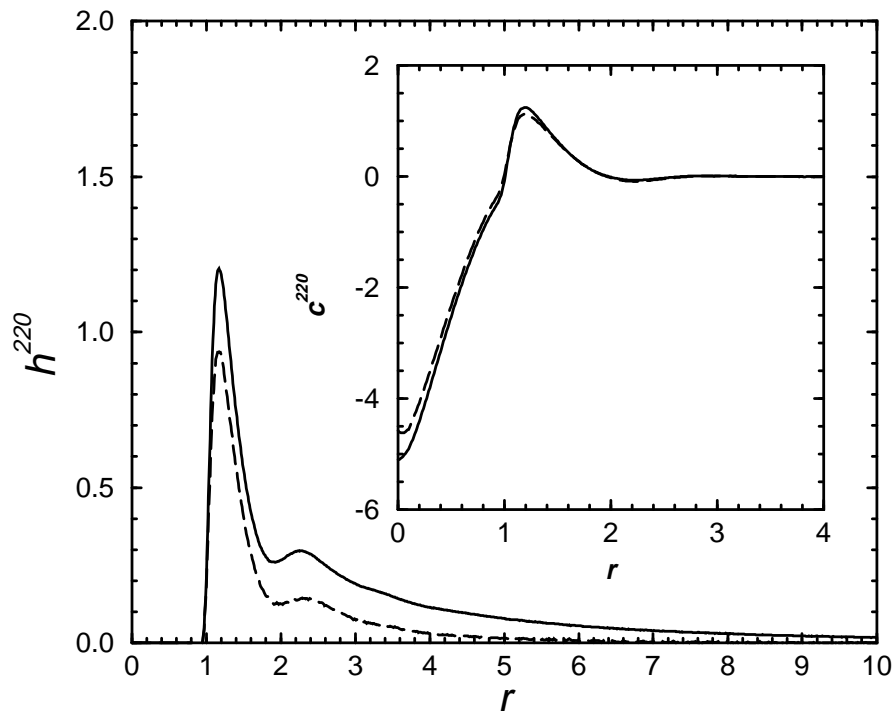


Figure 2. The orientational correlation function $h^{220}(r)$ and (inset) direct correlation function $c^{220}(r)$, at temperatures $T = 3.50$ (solid line) and 4.00 (dashed line). The N-I transition temperature is estimated to lie just below $T = 3.50$.

along the director, and reveals the formation of smectic layers. The second, $g_{11}(s)$, is a two-dimensional pair correlation function between molecules in *the same layer*, where s measures the distance between molecules in the xy -plane. The third, $g_{12}(s)$, is similarly defined, but for pairs in *adjacent layers*. All three are illustrated in figure 1 for $\kappa = 3.8$. In the nematic phase, $g^{\parallel}(z)$ shows no long-ranged structure and $g_{11}(s)$, $g_{12}(s)$ cannot be properly defined. In a smectic-A phase, $g^{\parallel}(z)$ reveals well-defined layers, $g_{11}(s)$ shows two-dimensional liquid-like correlations decaying with distance, and $g_{12}(s)$ indicates almost no registry at all between layers. Finally, in a smectic-B phase, all three functions show well-defined correlations characteristic of crystal-like packing (our systems are too small to distinguish hexatic-B phases). We note that, on cooling these smectic-B phases to very low T at zero pressure, we see no phase transitions; indeed, they already exhibit well-defined solid-like structure, and a preliminary calculation of their shear moduli suggests that it may be more appropriate to refer to them as solids rather than S_B phases.

3. The direct correlation function and the I-N transition

The pair correlation function $h(1, 2)$ is defined in terms of the usual pair distribution function $g(1, 2)$: $h(1, 2) \equiv g(1, 2) - 1 = g(\mathbf{u}, \mathbf{v}, \mathbf{r}) - 1$. The *direct* correlation function $c(1, 2)$ is

obtained from the Ornstein–Zernike (OZ) equation:

$$h(1, 2) = c(1, 2) + \frac{\rho}{4\pi} \int d3 h(1, 3)c(3, 2)$$

where we integrate over position and orientation of a third, intermediate, molecule. $c(1, 2)$ is expected to be a shorter-ranged function than $h(1, 2)$ for the molecules of interest to us. These functions are conveniently expanded in rotational invariants [10]; for example, in the isotropic phase,

$$h(\mathbf{u}, \mathbf{v}, \mathbf{r}) = \sum_{mnl} h^{mnl}(r) \Phi^{mnl}(\mathbf{u}, \mathbf{v}, \hat{\mathbf{r}})$$

where for the molecules of interest to us, m, n, l are all even integers. The set of functions $h^{mnl}(r)$ describe angular correlations as functions of distance. The component $h^{220}(r)$ measures the second-rank orientational correlations that grow in range as one approaches the I–N transition, and eventually diverge on entering the nematic phase. It is of interest to discover whether or not the direct correlation function remains short-ranged in this limit.

We have recently presented a method for inverting the OZ equation and obtaining $c(1, 2)$ in the isotropic phase, from simulation $h(1, 2)$ -data, for molecular systems [11]. We have studied the version of the Gay–Berne model with $\mu = 1, \nu = 3, \kappa = 3, \kappa' = 5$ originally proposed by Berardi *et al* [12], very close to the I–N transition. We used a system size $N = 8000$ in a cubic box, employing an efficient parallel MD code, and using up to 450 000 timesteps ($\delta t = 0.004$) to ensure relaxation of orientational modes.

Typical results are shown in figure 2. We see that $c^{220}(r)$ indeed remains short-ranged even when $h^{220}(r)$ indicates very close proximity to the phase transition. The amplitude of $c^{220}(r)$ within the molecular core increases slightly, as T is lowered. The instability criterion for the isotropic phase relative to nematic phase, discussed in terms of density functional theory [13, 14, 15] may be expressed in terms of the integral

$$c^{(m)} \equiv \rho(2m + 1)^{-1/2} 4\pi \int_0^\infty dr r^2 c^{mm0}(r) \rightarrow 1.$$

We find that $c^{(2)}$ does indeed approach this limit as the transition is approached. Further details of this work will be published elsewhere [16].

Acknowledgments

Financial support from the Engineering and Physical Sciences Research Council and Bristol University, and computing support from the High Performance Computing Initiative, and the European Union (through CINECA, Italy), are gratefully acknowledged, as are helpful conversations with Claudio Zannoni, Roberto Berardi, Jeroen van Duijneveldt and Andrew Masters.

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