Computer Simulation of Nematic Reentrance in a Simple Molecular Model

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We report a computer simulation study of a system of parallel hard ellipsoids with attractive interactions represented by a spherically symmetric square well of range λ. For suitable values of λ the results are consistent with the sequence of phases nematic (N), smectic-A (SmA), reentrant nematic (N_{re}), and crystal (Cr) under pressure. Both the N-SmA and the SmA-N_{re} transitions are found to be first order or continuous depending on temperature. Moreover, we show that a generalized van der Waals–type theory provides a qualitative description of the observed phase behavior.

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One of the most intriguing phenomena occurring in liquid crystals is the observation of reentrant behavior, that is, transitions to phases of increasing disorder and fluidity with decreasing temperature [1,2]. The sequence of phases nematic (N), smectic-A (SmA), reentrant nematic (N_{re}) was first reported by Cladis [3] in mixtures of cyano compounds at atmospheric pressure. It was shortly after demonstrated that reentrance can also be driven by increasing pressure in pure compounds and their mixtures [4,5]. Typically, the structure of molecules exhibiting reentrance includes a fairly rigid central core (aromatic rings) and two end groups, one of which has a strong dipole. A possible explanation of nematic reentrance has been given in terms of the formation of antiparallel associated pairs (dimers) [5]. In this way, the dipolar interactions stabilizing the layered smectic phase would be weakened, this making the smectic phase unstable relative to a low-temperature (reentrant) nematic liquid. However, reentrant behavior has been reported in nonpolar compounds [6], for which the above mechanism clearly does not apply.

A molecular theory, appropriate for nonpolar liquid crystals, has been given by Longa and de Jeu [7], where the system is treated as a mixture of monomers and dimers interacting through hard-core repulsions and attractive induced soft interactions. In their approach, nematic reentrance is brought about by the repulsive steric forces due to the unfavorable packing of the dimers in the smectic layers. A related mechanism has been suggested by Sear and Jackson [8], who have reported reentrant behavior in a mixture of associating parallel hard cylinders. A different interpretation has been given by Dowell [9], who has formulated a molecular lattice theory where nematic reentrance is explained in terms of steric packing of both the rigid molecular cores and the partially flexible tails. Reentrant behavior has also been reported [10] within the context of the McMillan theory of the smectic phase [11].

Here we consider a molecular model that, in spite of its simplicity, exhibits a nontrivial phase behavior and shows nematic reentrance. The model is a generalized version of the square-well model appropriate for molecular fluids. Molecules consist of a hard ellipsoidal core defined by their long (L) and minor (D) axis. It is assumed that molecules are parallel to each other, thereby disallowing orientational fluctuations. The repulsive interactions arise from the impenetrability of the hard cores, and the longer-ranged attractive interactions are represented by a spherically symmetric square well of range λ and strength ϵ. We have recently analyzed this model in light of a generalized van der Waals theory [12] and have shown that smectic ordering is promoted by coupling the anisotropic short-range repulsions with the isotropic contribution of the attractive interactions. The theory predicts an increase of the range of stability of the SmA phase with increasing λ. The calculations, however, did show that smectic ordering is no longer stable if the attractions are made too long ranged. This was found to occur for values above $\lambda/D \approx 4.1$.

In this Letter, we present simulation results of the phase behavior of the generalized square-well model with parameters $L/D = 5$ and $\lambda/D = 3.4$. We explore different regions of the phase diagram, and find reentrant behavior under pressure. Moreover, the simulation results indicate the existence of two tricritical points on the N-SmA transition line. We compare these unexpected results to the predictions of the theory formulated in Ref. [12].

Most of the simulations reported here were carried out for systems of $N = 1008$ parallel molecules using the Monte Carlo technique under constant-pressure (NPT) conditions. The molecules were enclosed in a cuboidal box and usual periodic boundary conditions were applied to the x, y, and z directions. The common direction defined by the long molecular axes (director) was taken as the z axis. At low densities, we found it more efficient to simulate the nematic phase by sampling the constant-volume (NVT) ensemble. Translational order along z was probed by calculating the ensemble average of the leading Fourier component of the particle density along the director,

$$\tau(q) = \frac{1}{N}\left|\sum_{j=1}^{N}\exp(iqz_j)\right|, \tag{1}$$

where $q = 2\pi/d$, with d being the spacing between smectic layers, and z_j is the z coordinate of the center of mass of particle j. The above expression was evaluated for a discrete set of values of q, and the smectic order parameter was defined as $\tau = \max\{\tau(q)\}$. Hereafter, the pressure P is reported in units of ϵ/v_0, and the temperature in units of ϵ/k, where k is the Boltzmann constant, $v_0 = (\pi/6)LD^2$ is the molecular volume, and ϵ is the strength of the attractive interactions.

We show in Fig. 1 the variation of the pressure P with packing fraction η upon compression of a low-density nematic liquid along a number of isotherms. From the simulation data, the N phase was seen to undergo a phase transition at temperatures $T \leq 3.0$. Following the behavior of τ along these isotherms, it was concluded that the N phase gives way to a layered structure; the layers were found to be perpendicular to the director with no in-layer positional order, so that the phase was identified as Sm*A*. The onset of smectic ordering appears to occur in a continuous way at $T = 3.0$ with no measurable density or enthalpy change within the accuracy of the simulation data. At lower temperatures, however, the N-Sm*A* transition was found to be clearly first order, this being confirmed by the observation of an incipient van der Waals–like loop in the nematic side at the lower temperatures. As can be inferred from Fig. 1, the transition pressure increases with temperature, and so the slope of the N-Sm*A* transition line is positive. These results point to the presence of a tricritical point at $T_t = 2.9 \pm 0.1$ and $P_t = 0.15 \pm 0.05$. The existence of a tricritical point on the N-Sm*A* line was predicted by McMillan [11] and first observed by McKee and McColl [13] with varying pressure in p-cyanobenzylidene-p-nonylanine. At higher temperatures ($T = 3.5$), the nematic fluid could be compressed up to high pressures without developing smectic ordering. This indicates that the Sm*A* phase does not extend to arbitrarily high temperature (or pressure) but remains stable in a bounded region.

The variation of the smectic order parameter τ with packing fraction along several isotherms is shown in Fig. 2. In all cases, τ increases, then reaches a maximum, and afterwards drops to an essentially zero value. No sign of positional order was found in the high-density phase: this rules out the possibility of a transition from the Sm*A* to a columnar or a smectic-*C* phase. According to our results, the destabilization of the smectic layers is accompanied by the reappearance of the nematic phase (N_{re}), in spite of the increase of the average density resulting from compressing the smectic fluid at constant temperature. As shown in Fig. 2, the smectic order parameter seems to fall continuously to zero at the higher temperatures ($T = 3.0$ and 2.8). The reentrant transition is therefore continuous at these temperatures. For the lowest temperatures, τ is seen to drop discontinuously at the transition, this indicating a first-order Sm*A*-N_{re} transition. These results suggest the existence of a second tricritical point, the latter located on the Sm*A*-N_{re} phase boundary at $T_t = 2.7 \pm 0.1$ and $P_t = 1.8 \pm 0.1$. The period of the density wave of the intermediate Sm*A* phase was found to decrease from $1.7L$ to $1.1L$ with increasing density.

We next investigated the stability of the high-density N_{re} phase relative to the crystal (Cr) phase. For this purpose, we carried out a series of runs where an equilibrated high-density crystalline structure was slowly expanded at constant temperature. In all cases, the crystal structure was found to melt into a high-density nematic liquid. Upon

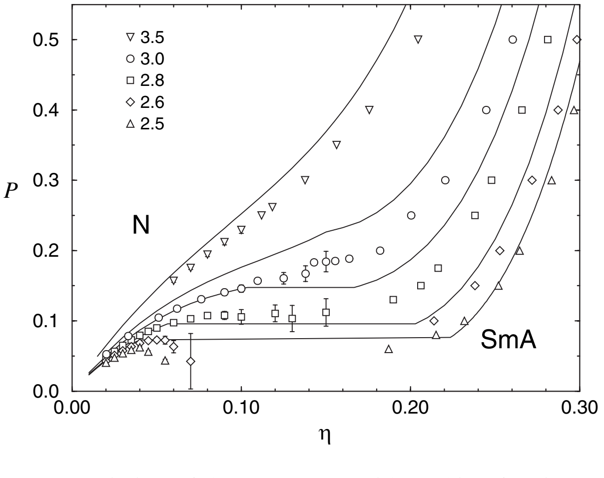

FIG. 1. Variation of the pressure P with packing fraction η in the N-Sm*A* transition region for the generalized square-well model with $L/D = 5$ and $\lambda/D = 3.4$. Symbols correspond to simulation data along different isotherms (temperatures are labeled on the plot). The curves are the predictions from density functional theory.

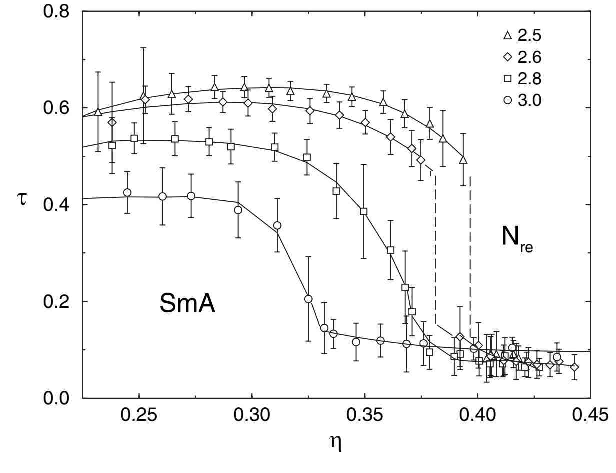

FIG. 2. Variation of the smectic order parameter τ at the Sm*A*-N_{re} transition at high densities for the generalized square-well model with $L/D = 5$ and $\lambda/D = 3.4$ as obtained from simulation along several isotherms. Lines are included as a guide to the eye.

further expansion, this phase was seen to transform into a SmA phase at essentially the same pressures at which the SmA-N_{re} transition takes place in the compression series. This transition occurs with a finite density jump at $T = 2.5$ and 2.6 and with no clear density discontinuity at higher temperatures. Moreover, the SmA-N_{re} transition pressure *decreases* with increasing temperature. According to this, the slope of the corresponding transition line turns out to be negative. Although no free energies were computed, the presence of the N_{re} phase in both compression and expansion series of simulations gives strong support to the conclusion that this phase is thermodynamically stable and appears in the fluid region of the phase diagram.

The P-T phase diagram of the model is depicted in Fig. 3. In order to have a more complete picture of the phase behavior, additional runs were performed. These included NPT heating series along isobars ($P = 1.5$, 1.0, and 0.5) to estimate the location of the Cr-SmA transition line, as well as simulations at $P = 1.5$, 1.0, and 0.8 in the neighborhood of the SmA-N_{re} transition. It is to be noted that the pressures (temperatures) associated with the melting transition correspond to the limits of mechanical stability of the Cr phase under expansion (heating) along paths at constant temperature (pressure). As melting proceeds irreversibly with significant hysteresis, the actual transition lines involving the Cr phase will be shifted to lower temperatures or higher pressures. The extent of this shift is unknown as no free-energy calculations were undertaken. No significant shifts are anticipated for the rest of transitions as they essentially take place in a reversible way. This would obviously affect our estimate of the Cr-SmA-N_{re} triple point ($T_{\mathrm{tp}} \approx 2.45$, $P_{\mathrm{tp}} \approx 2.0$) but not our estimate of the tricritical points.

The most relevant features of the phase behavior of the model can be understood within the framework of a recently proposed density functional theory [12]. The theory is formulated in terms of a free-energy functional where the hard-core contributions are treated within a (nonlocal) weighted-density approximation [14], and the attractive contributions are treated at a mean-field (MF) level. A detailed account of the theory can be found in Ref. [12]. A bifurcation analysis was used to locate the points where the N phase becomes unstable with respect to a smecticlike density modulation. A similar analysis was reported in Ref. [12], where it was shown that increasing the range of the attractions leads to an increasingly larger region of stability of smectic ordering. This scenario, however, was seen to reverse at intermediate values of λ: making the attractions too long ranged destabilizes smectic layering, and the bifurcation equation is found to have no physical solution for values above $\lambda/D \approx 4.1$. In this case, the interactions are not anisotropic enough to stabilize smectic ordering and the N phase dominates the fluid region. According to the theory, the destabilization of the SmA phase with increasing λ is accompanied by the reappearance of the nematic phase at high pressure: the slope of the bifurcation line changes from positive to negative with increasing pressure for values $3.2 \leq \lambda/D \leq 4.0$. For smaller values of λ, this slope is positive at all pressures. As found in the simulations, the theory predicts two tricritical points located on the N-SmA and SmA-N_{re} transition lines, respectively.

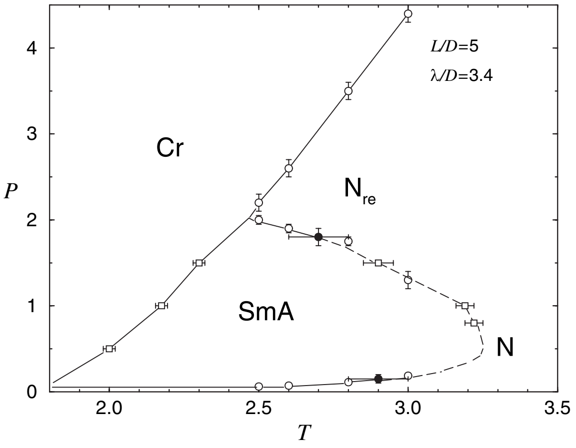

FIG. 3. Approximate phase diagram of the generalized square-well model with $L/D = 5$, $\lambda/D = 3.4$ as obtained from simulation showing crystal (Cr), smectic A (SmA), nematic (N), and reentrant nematic (N_{re}) phases. Solid lines indicate first-order transitions, and discontinuous lines indicate continuous transitions. Solid symbols represent tricritical points.

In summary, our simulation study gives strong evidence of the onset of the N_{re} phase in a simple molecular model consisting of parallel hard ellipsoids with superimposed square-well attractions. For appropriate choices of the model parameters, the sequence of phase transitions N-SmA-N_{re} is observed with increasing pressure. The N-SmA transition as well as the reentrant transition that takes place at higher pressure are seen to be either first order or continuous depending on temperature, these two regimes being separated by a tricritical point. A density functional theory has been shown to account for the most relevant features of the phase behavior resulting from our simulation study. Although the theory describes the SmA phase reasonably well (Fig. 1) and predicts reentrant behavior, it largely overestimates the pressure at which the SmA phase gives way to the reentrant nematic. This can be ascribed to the failure of a simple MF approach to give a quantitative account of a highly dense *uniform* phase. That a MF approach appears to perform better for the SmA phase seems to be due to the fact that the structure in the two-body distribution function $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is dominated by the highly structured one-particle density that, even under the assumption of the absence of two-particle correlations, gives $\rho^{(2)}$ the translational order characteristic of the SmA phase [15].

The relation between molecular shape and reentrant behavior is far from trivial. One could argue that reentrance in the present model (ellipsoidal shape) must be a consequence of the expected destabilization of smectic ordering

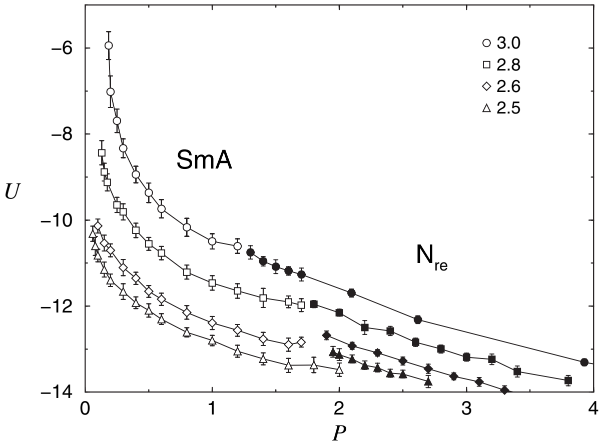

FIG. 4. Variation of the internal energy per particle U (in units of ϵ) with pressure P at the SmA-N_{re} transition as obtained from simulation along different isotherms (temperatures are labeled on the plot). Open symbols are for the SmA phase and solid symbols are for the N_{re} phase. Lines are a guide to the eye.

at high T (hard ellipsoids do not form the SmA phase). The existence of a bounded region of smectic stability is not, however, a sufficient condition for reentrance. It should be added that a related system of hard spherocylinders with square-well interactions (which must exhibit the SmA phase at high T) is less likely to show nematic reentrance. The reappearance of the nematic phase in the present model is to be understood in the following way. Compressing the nematic liquid leads to the SmA phase: the decrease in energy associated with the formation of the layers overcomes the lost in entropy and the layered structure becomes stable. The N-SmA transition is therefore driven by energy. Compressing the SmA phase is accompanied by a strong decrease in energy, as shown in Fig. 4. For suitable values of λ, the energy of the SmA phase becomes saturated *at fluid densities*: no further decrease in energy could take place if the system remained in the layered structure. However, the free energy of the system can be minimized at the expense of an increase in entropy with the subsequent collapse of the smectic layering. As nematic reentrance takes place at high densities (with expected nearly saturated orientational order), one might anticipate that relaxing the constraint of perfect molecular alignment should not change substantially the above scenario. Investigation on the effect of orientational fluctuations is currently under way.

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[1] P.E. Cladis, Mol. Cryst. Liq. Cryst. **165**, 85 (1988).
[2] P.E. Cladis, in *Handbook of Liquid Crystals*, edited by D. Demus, J.W. Goodby, C.W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), p. 391.
[3] P.E. Cladis, Phys. Rev. Lett. **35**, 48 (1975).
[4] P.E. Cladis, R.K. Bogardus, W.B. Daniels, and G.N. Taylor, Phys. Rev. Lett. **39**, 720 (1977).
[5] P.E. Cladis, R.K. Bogardus, and D. Aadsen, Phys. Rev. A **18**, 2292 (1978).
[6] G. Pelzl, S. Diele, I. Latif, W. Weissflog, and D. Demus, Cryst. Res. Technol. **17**, K78 (1982); S. Diele, G. Pelzl, I. Latif, and D. Demus, Mol. Cryst. Liq. Cryst. **92**, 27 (1983).
[7] L. Longa and W.H. de Jeu, Phys. Rev. A **26**, 1632 (1982).
[8] R.P. Sear and G. Jackson, Phys. Rev. Lett. **74**, 4261 (1995).
[9] F. Dowell, Phys. Rev. A **28**, 3526 (1983); **36**, 5046 (1987).
[10] G.R. Luckhurst and B.A. Timimi, Mol. Cryst. Liq. Cryst. **64**, 253 (1981); A. Ferrarini, G.R. Luckhurst, P.L. Nordio, and E. Spolaore, Mol. Phys. **89**, 1087 (1996).
[11] W.L. McMillan, Phys. Rev. A **4**, 1238 (1971).
[12] E. Martín del Río and E. de Miguel, Phys. Rev. E **71**, 051710 (2005).
[13] T.J. McKee and J.R. McColl, Phys. Rev. Lett. **34**, 1076 (1975).
[14] P. Tarazona, Phys. Rev. A **31**, 2672 (1985).
[15] W.A. Curtin and N.W. Ashcroft, Phys. Rev. A **32**, 2909 (1985).