Orientational Order in Simple Dipolar Liquid-Crystal Models

J. J. Weis, D. Levesque, and G. J. Zarragoicoechea
Laboratoire de Physique Théorique et Hautes Energies, Université de Paris XI, Bâtiment 211, 91405 Orsay CEDEX, France
(Received 28 May 1992)

The orientational order in simple systems of dipolar hard-core molecules is determined by Monte Carlo simulations. Dipolar hard spherocylinders are shown to form a monolayer smectic-A phase with unpolarized layers. In the columnar phase of dipolar cut spheres, evidence is given for a transition, with increasing dipole moment, from a phase with unpolarized columns to a phase with completely polarized columns arranged with antiferroelectric order. Ferroelectric orientational order is demonstrated for strong dipolar hard spheres.

PACS numbers: 61.30.Gd, 61.20.Ja, 61.25.Em, 64.70.Md

Although the precise role of the dipole-dipole interaction on the onset and stabilization of mesophases is not fully understood there is a vast amount [1] of experimental evidence that compounds with strongly polar head groups exhibit unusual properties which distinguish them from the more conventional liquid crystals, such as, for example, bilayer or partially bilayer smectic-A (S_A) phases [2], reentrant phenomena [3], and S_A-S_A transitions [4]. The most straightforward way to investigate the importance of the dipolar interaction on the structures of mesophases would be to compare the properties of these phases with and without molecular permanent dipole moments. Obviously, such experiments are not possible with real molecules but are easily realized by computer simulations. It is the purpose of this Letter to report the variations of the structural arrangement of mesophases of hard-core elongated or oblate molecules due to the presence of a dipolar interaction. The phase diagrams of two species of such hard-core molecules, spherocylinders and disklike particles (the so-called cut spheres), have been determined by Frenkel and coworkers [5–7] and the results of these studies can be used as a starting point for our simulations. Specifically, we have made simulations of the smectic phase of spherocylinders with a decentralized longitudinal dipole moment and of the columnar phase of cut-sphere molecules with dipole moment along the symmetry axis or perpendicular to it. Also we have realized calculations for hard spheres with a very large dipole moment.

Most calculations were performed for a system of N molecules with periodic boundary conditions in a noncubic orthorhombic simulation cell with side lengths L_x, L_y, L_z and volume $V = L_x L_y L_z$ to accommodate easily an appropriate number of smectic layers or columnar rows. The dipolar interactions superimposed on the hard-core interactions were taken into account by the Ewald summation procedure as described in the work of de Leeuw, Perram, and Smith [8]. For the discussion of our results it is essential to remark that the total internal Ewald energy is composed of the sum of periodic pair potentials between the molecules and a term proportional to $\mathbf{M}^2$, the square of the total electric dipole moment of the system. Generally this last term is phenomenologically combined with the reaction field of a continuous dielectric medium of dielectric constant ϵ' supposed to surround the (infinitely) large sphere filled with the periodic replica of the basic simulation cell. The resulting contribution to the total Ewald energy is $2\pi\mathbf{M}^2/(2\epsilon'+1)V$. For unpolarized phases [$\mathbf{M}^2 \sim O(N)$] this contribution to the energy, although essential for a faithful estimate of the dielectric constant of the system [8], is marginal. However, for polarized phases [$\mathbf{M}^2 \sim O(N^2)$] it may contribute in a significant manner to the internal energy and thus to the structural and orientational arrangements of the molecules.

In our simulations the orientational order and the possible polarization of the mesophases were characterized by two order parameters S and P; the former is the average value of the largest eigenvalue of the second-order rank tensor

$$\overleftrightarrow{Q} = \frac{1}{N}\sum_{i=1}^{N} \left(\tfrac{3}{2}\hat{\mathbf{u}}_i\hat{\mathbf{u}}_i - \tfrac{1}{2}\overleftrightarrow{I}\right) \tag{1}$$

($\hat{\mathbf{u}}_i$ is the unit vector along the symmetry axis of the molecule), and the latter, P, the average value of

$$P = \frac{1}{N}\left|\sum_{i=1}^{N} \hat{\mathbf{u}}_i \cdot \hat{\mathbf{e}}\right|, \tag{2}$$

where $\hat{\mathbf{e}}$ is the instantaneous eigenvector (normalized to unity) corresponding to the largest eigenvalue of $\overleftrightarrow{Q}$.

Spherocylinders.—We consider a system of spherocylinders of total length $l = L/D + 1 = 6$ (L is the length of the cylindrical part of the molecule, and D its diameter) with longitudinal dipole moment located at a distance $2.5D$ off the molecular center. The initial configuration of the system was generated from a close-packed structure with hexagonal symmetry within the layers parallel to the x-y plane and $ACAC\ldots$ stacking sequence of the planes along the z direction. The number of layers in the x, y, and z directions was $N_x = 8$, $N_y = 8$, and $N_z = 6$. Initially all dipole moments were aligned in the same direction parallel to the z axis. In the sampling of configuration space, allowance was made, besides

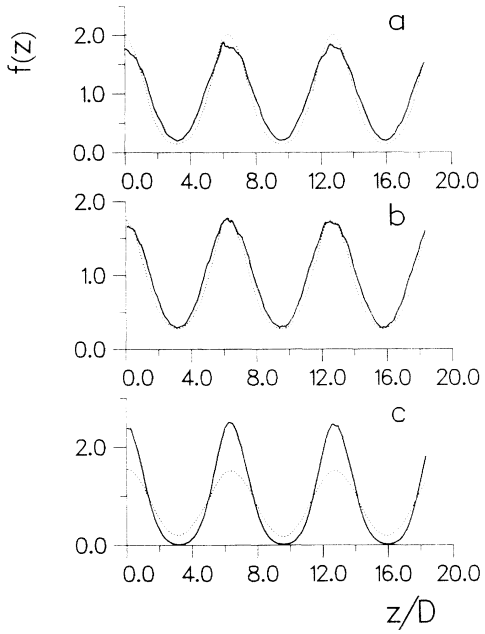

FIG. 1. Density modulation of the smectic-A phase of dipolar spherocylinders as given by the correlation function (3). Full line: density of the centers of mass; dotted line: density of the polar heads. (a) $\mu^*=2$, (b) $\mu^*=\sqrt{2}$, (c) $\mu^*=0$.

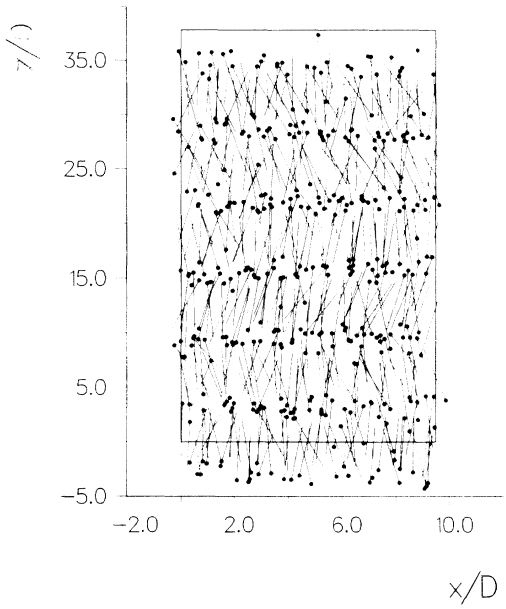

FIG. 2. Snapshot of a configuration of 384 dipolar spherocylinders with $\mu^*=\sqrt{6}$ in the smectic-A phase (projection of all the molecules on the x-z plane of the periodic box). The spherocylinders are represented by a thin line of length L and the solid dot indicates the location of the dipole moment.

translation and rotation, for flips of the molecular long axis in order to generate polarized as well as unpolarized configurations.

The Monte Carlo (MC) calculations were performed in the isothermal-isobaric ensemble at pressure $P^*=PD^3/kT=3.8$ and the reduced dipole moment $\mu^*=(\mu^2/D^3kT)^{1/2}$ was varied from 0 to $\sqrt{6}$. The density of the system was $\rho^*=\rho D^3\sim 0.13$ for all values of μ^*.

Smectic and polar ordering along the direction perpendicular to the smectic planes (here the z axis) can be conveniently analyzed by the following correlation functions:

$$f(i\Delta z)=\frac{\langle\sum_{j=0}^{m}n(j\Delta z)n((i+j)\Delta z)\rangle}{m\bar{\rho}^{*2}S_{xy}^2\Delta z^2}\quad(i\neq 0),\qquad(3)$$

where $n(z)$ is the number of particles having the z coordinate of their center of mass or polar head in the interval $(z,z+\Delta z)$, $m=L_z/\Delta z$, $S_{xy}=L_xL_y$, $\bar{\rho}^*$ is the average density of the system, and $\Delta z=0.02D$.

Figure 1 shows how the density waves of the centers of mass and polar heads evolve with increasing dipole moment. Both functions oscillate with the same period indicating monolayer structure with interlayer spacing slightly larger than the molecular length. However, whereas for $\mu^*=0$ the density modulation of the centers of mass is much sharper than that of the polar heads, the situation reverses with increasing dipole moment due to the sharper localization of the polar heads as a result of the strong interaction between them.

Figure 2 provides a snapshot of the smectic layering for the dipole moment $\mu^*=\sqrt{6}$ and $\rho^*=0.125$. It clearly shows an unpolarized monolayer arrangement. Some interpenetration of the polar heads is observed which allows the system to lower its internal energy. For example, the energy (per particle) of a configuration of spherocylinders with centers fixed in ideal smectic planes separated by a distance $d\sim 1.05l$ is 5.3 whereas the average energy per particle of the thermodynamic state considered in Fig. 2 is -2.04.

Cut spheres.—The second system investigated is the columnar phase of disklike molecules modeled by cut spheres of thickness $L/D=0.1$ (a cut sphere is obtained by chopping off from a sphere of diameter D two caps symmetrically disposed with respect to an equatorial plane) with dipole moment either along the symmetry axis of the disk or perpendicular to it. The simulations were started off from a typical perfect close-packed configuration of a columnar phase with hexagonal symmetry within the layers parallel to the x-y plane and cut spheres sitting on top of each other along the z direction (columnar axis). There were 32 columns each comprising 18 cut spheres. The system was then expanded to a density well inside the columnar phase region identified by Frenkel at $\mu^*=0$ [6,7]. The initial orientation of the dipoles was as follows: All dipole moments within a column had the same orientation; columns having their axes in planes parallel to the x-z plane had identical polarization but columns within successive planes were given opposite polarization. Configuration space was sampled by implementing the following types of MC moves: (i) translation and rotation of the disk; (ii) flip of

the dipole moment of an individual disk; and, when columns had a net polarization, (iii) flips of all the dipoles inside a column chosen at random; (iv) simultaneous flips of all the dipoles inside two columns chosen at random.

The MC calculations (isothermal-isobaric ensemble, 50000 moves/particle after equilibrium) at pressure $Pv_0/kT=7.4$ (v_0 is the volume of a cut sphere) give evidence for a transition, at $\mu^*\simeq 0.125$, from a phase with unpolarized columns at low dipole moments to a state in which each column is completely polarized, the total polarization of the system being zero (note that the total number of columns is even). This result contrasts with the conclusions of Ref. [9]. Each column is surrounded by approximately the same number of "up" and "down" columns but no well-defined pattern could be detected. The effect of the phase transition on the longitudinal dielectric constant $\epsilon_\parallel$ is shown in Fig. 3. $\epsilon_\parallel$ passes through a maximum near $\mu^*\simeq 0.125$, then drops rapidly to 1 with increasing dipole moment.

For cut spheres with dipole perpendicular to the symmetry axis orientational order was characterized along columns by the average value of the scalar product $\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j$ of the dipole moments as a function of separation of two molecules in the same column. Well-defined orientational order is found over distances $\sim 0.5D$ corresponding to a succession of domains of size $(2-3)L$ in which the dipoles alternatively point roughly in opposite directions.

Hard spheres.—Recent molecular-dynamics simulations [10] have shown that for sufficiently high dipole moments, dipolar soft spheres ($1/r^{12}$ short-range potential) exhibit an orientationally ordered phase having ferroelectric character. The present MC calculations extend these results to dipolar hard spheres and, in essence, confirm the results. For instance, at density $\rho^*=\rho D^3=0.84$ (D is the hard-sphere diameter) and dipole moment $\mu^*=(\mu^2/D^3kT)^{1/2}=3$ we find, for a 500-particle system, an orientationally ordered phase with order parameters $S=0.65$ and $P\sim 0.85$. However, dipolar ordering occurs already at the smaller dipole moment $\mu^*=2.5$. For this dipole moment we studied the density range $\rho^*=0.8$–1.2 covering the liquid to solid regions. Starting from a completely disoriented fcc-crystal configuration we generally equilibrated the system for more than 100000 moves/particle. Orientational order then took about 100000 moves/particle to build up. Nematic ferroelectric phases are obtained at $\rho^*=0.8$ with order parameters $S=0.4$ and $P\sim 0.7$ and at $\rho^*=0.86$ where the order parameters are 0.5 and 0.8, respectively. At higher density, $\rho^*=1.0$, we observe formation of a columnar phase with columnar axis parallel to the y axis and square lattice in the plane perpendicular to the columnar axis (cf. Fig. 4). The preferential orientation of the dipoles is parallel to the x-y plane along a direction making an angle of 40° with the x axis. At $\rho^*=1.2$ the fcc crystal remained stable over a period of more than 200000 moves/particle and developed ferroelectric orientational order with order parameters $S=0.5$ and $P\sim 0.7$.

All the results presented up to here pertain to a periodic system with conducting boundary which suppresses the depolarization field (case $\epsilon'=\infty$, cf. introductory re-

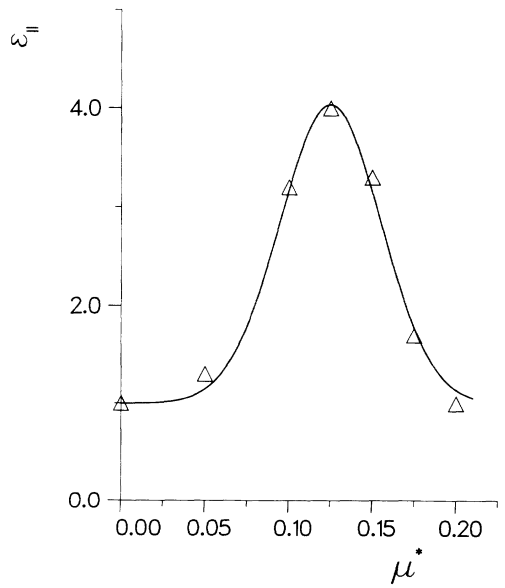

FIG. 3. Variation with dipole moment strength of the longitudinal dielectric constant $\epsilon_\parallel$ of dipolar cut spheres in the columnar phase. The solid line is drawn as a guide to the eye.

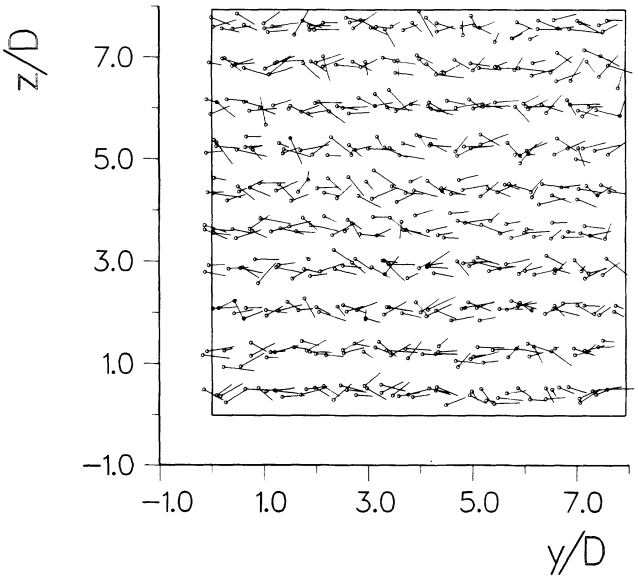

FIG. 4. Snapshot of a configuration of dipolar hard spheres with dipole moment $\mu^*=2.5$ and density $\rho^*=1.0$ in the columnar phase (projection of all the dipolar spheres on the y-z plane of the periodic box). The dipoles are represented by the projections on the y-z plane of thin lines of length $0.6D$ having their middles on the centers of the spheres. The open circle indicates the direction of the dipole moment.

marks). If, instead, a large spherical part of the periodic replica of the basic simulation cell is surrounded by vacuum (case $\epsilon' = 1$), the large depolarization field is expected to discourage any polarization effect. In fact, with this boundary condition, the net polarization of the system was found to be zero for all cases considered. At $\rho^* = 0.8$ the system breaks up into two polarized domains with antiparallel directions in complete similarity with the dipolar-soft-sphere behavior [10]. At $\rho^* = 1.0$ the columnar phase melts and the system breaks up into polarized subdomains similar to the previous case. At $\rho^* = 1.2$, the solid phase remains stable but the parallel orientational order of the dipoles breaks up into a rather complex arrangement which for the present system of 500 particles is formed of four subdomains. A detailed description of this arrangement and a full account of the work described in this Letter will be given in a forthcoming paper.

We thank Dan Frenkel for communicating his work on cut spheres prior to publication and Gren Patey for detailed information on his published and unpublished dipolar-soft-sphere calculations. G.J.Z. is a member of Carrera del Investigador Científico, Comisión de Investigaciones Científicas de la Prov. de Buenos Aires (CICPBA). He acknowledges financial support from Fundación Antorchas (Argentina), CICPBA, and the ICSC-World Laboratory. Laboratoire de Physique Théorique et Hautes Energies is a laboratoire associé au Centre National de la Recherche Scientifique.

[1] F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, J. Chim. Phys. **80**, 53 (1983).

[2] A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray, and A. Mosley, J. Phys. (Paris) **40**, 375 (1979).

[3] P. E. Cladis, Phys. Rev. Lett. **35**, 48 (1975).

[4] G. Sigaud, F. Hardouin, M. F. Achard, and A. M. Levelut, J. Phys. (Paris) **42**, 107 (1981); K. K. Chan, P. S. Pershan, L. B. Sorensen, and F. Hardouin, Phys. Rev. A **34**, 1420 (1986); F. Hardouin, Physica (Amsterdam) **140A**, 359 (1986).

[5] D. Frenkel, J. Phys. Chem. **92**, 3280 (1988); D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants, Nature (London) **332**, 822 (1988); J. A. C. Veerman and D. Frenkel, Phys. Rev. A **41**, 3237 (1990).

[6] D. Frenkel, Liq. Cryst. **5**, 929 (1989); in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 691.

[7] J. A. C. Veerman and D. Frenkel, Phys. Rev. A **45**, 5632 (1992).

[8] S. W. de Leeuw, J. W. Perram, and E. R. Smith, Proc. R. Soc. London A **373**, 27 (1980).

[9] P. Palffy-Muhoray, M. A. Lee, and R. G. Petschek, Phys. Rev. Lett. **60**, 2303 (1988).

[10] D. Wei and G. N. Patey, Phys. Rev. Lett. **68**, 2043 (1992); (to be published).