Nematic-Smectic-*A*-Smectic-*C* Transitions in Systems of Parallel Hard Molecules

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The phase diagram for liquid-crystal models of hard molecules is studied by use of a nonlocal density functional for the free energy. Nematic, smectic-*A*, and smectic-*C* phases can be obtained from purely packing effects without any attractive interaction. A system of parallel hard spherocylinders shows a continuous phase transition from the nematic to a smectic-*A* phase, in good agreement with existing computer simulations. In a system of parallel oblique cylinders we predict first- or second-order phase transitions between the smectic-*A* and the smectic-*C* phases.

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The orientational order of the molecules in a nematic liquid crystal may be predicted from the anisotropy of the hard cores or from the soft attractive forces. The first route, pioneered by Onsager,[1] leads to well developed theories[2,3] in good agreement with computer simulations for systems of hard bodies (HB).[4] The second route follows the work of Maier and Saupe,[5] using a mean-field treatment for the attractions, and may give good qualitative agreement with experimental data.[6] However, it is now clear that the accurate description of real nematics has to include the joint effects of hard cores and attractions, as is well established in the case of simple fluids, for which the correlation structure is mainly determined by the hard cores.[7]

In a smectic liquid crystal, the molecules are oriented along a preferential axis and distributed in layers, which may be perpendicular (smectic *A*) or not (smectic *C*) to the orientational director. In most theoretical studies of these phases, following the work of McMillan,[8] the smectic order is given by the attractive interactions. This is somehow surprising if the smectic phase is regarded as a preliminary to the full crystallization, which results mainly from hard-core packing. Some insight is given by models of fully oriented molecules, as in a perfect nematic, so that the smectic may be studied without the troubles of partial orientational order. The simplest case to consider is a system of hard ellipsoids with parallel principal axes for all the molecules. This model maps, by appropriate scaling, into a hard-sphere (HS) system[9] which cannot show any kind of smectic phase. It was conjectured, from this result, that no smectic order could appear in purely HB systems,[10] but the computer simulations of Stroobants, Lekkerkerker, and Frenkel,[11] for parallel hard spherocylinders (PHSC) proved this to be wrong: The PHSC have a second-order nematic-smectic-*A* transition, well before the crystallization of the system. This made clear the interest in understanding the full role of the hard cores in real liquid crystals.

There are already some theoretical studies of smectic-*A* order in HB.[12-14] Here we present a theory which can be used to analyze the full phase diagram of these systems, including nematic, smectic-*A*, and smectic-*C* phases. We start with the model of a hard-rod nematic described by Lee,[2] who takes advantage of the quasiexact Carnahan-Starling equation of state for HS,[7] to get the thermodynamics of other HB systems, with uniform density but arbitrary angular distribution, $\rho(\boldsymbol{\omega})$, $\boldsymbol{\omega}$ being the set of angles describing the molecular orientation. The integral of $\rho(\boldsymbol{\omega})$ gives the total density ρ_0. The free energy per molecule (in $k_BT=1$ units) has the ideal-gas term

$$\Psi_{\rm id}[\rho(\boldsymbol{\omega})]=\int d\boldsymbol{\omega}\,\rho(\boldsymbol{\omega})\{\ln[\Lambda^3\rho(\boldsymbol{\omega})]-1\}\,,$$

independent of the molecular shape (Λ is the usual thermal wavelength which contains the kinetic energy contributions), and the interaction part which is approximated by

$$\Delta\Psi_{\rm HB}[\rho(\boldsymbol{\omega})]=\Delta\Psi_{\rm HS}(\rho_0)B_2^{\rm HB}[\rho(\boldsymbol{\omega})]/B_2^{\rm HS}\,, \qquad (1)$$

where $\Delta\Psi_{\rm HS}(\rho_0)$ corresponds to a HS system with the same packing fraction $\eta=\rho_0 v_0$ (v_0 being the molecular volume) as the real HB system, and $B_2^{\rm HS}$ and $B_2^{\rm HB}$ are the second virial coefficients, which are half the excluded volume around a molecule, $B_2^{\rm HS}=2\pi\sigma^3/3$ (σ being the HS diameter) and

$$B_2^{\rm HB}[\rho(\boldsymbol{\omega})]=\tfrac{1}{2}\int d\boldsymbol{\omega}\,d\boldsymbol{\omega}'\,\rho(\boldsymbol{\omega})\rho(\boldsymbol{\omega}')V_{\rm exc}^{\rm HB}(\boldsymbol{\omega},\boldsymbol{\omega}')\,,$$

with the excluded volume for fixed orientations, $V_{\rm exc}^{\rm HB}(\boldsymbol{\omega},\boldsymbol{\omega}')$, averaged over molecular orientations. $\Delta\Psi_{\rm HB}$ may be interpreted as the entropy lost to create the hole to add a new molecule in the system. The minimum hole volume is $B_2^{\rm HB}$, which depends on the molecular shape and orientational distribution. In (1) the entropy lost per unit volume is approximated by that of HS with the same packing fraction. This gives the exact second virial coefficient and shows good agreement with computer simulations for both isotropic and nematic phases of hard spherocylinders.[2,15]

To construct a theory of smectic phases, with nonuniform density distributions, we first realize that an approximation in terms of HS should be much poorer for the correlation structure than for the thermodynamics, especially in systems with orientational order, because the average contact distance is different along different directions.[3] To include this effect we use the exact mapping from HS to the parallel hard ellipsoids (PHE) and use the latter as the reference system for the real HB. In systems with uniform density, the thermodynamic properties are exactly the same in the PHE and in the HS systems, but now we can generalize the theory of Lee to describe inhomogeneous density distributions and correlation structures from a free-energy functional of the position and angle distribution function, $\rho(\mathbf{r},\boldsymbol{\omega})$. The integral of $\rho(\mathbf{r},\boldsymbol{\omega})$ with respect to the angles gives the density distribution, $\rho(\mathbf{r})$, which was constant in (1). The interaction free energy per particle in HS is accurately given by $\Delta\Psi_{\text{HS}}[\bar{\rho}(\mathbf{r})]$, where the averaged density, $\bar{\rho}(\mathbf{r})$, is the convolution of $\rho(\mathbf{r})$ with a weight function taking into account the nonlocal structure.[16] The modification to PHE is straightforward, by simple scaling of the weight function.[17] The interaction part of our free-energy-functional model is written as

$$\Delta F[\rho(\mathbf{r},\boldsymbol{\omega})]=\int d\mathbf{r}\,d\boldsymbol{\omega}\,\rho(\mathbf{r},\boldsymbol{\omega})\,\Delta\Psi_{\text{PHE}}[\bar{\rho}(\mathbf{r})]\frac{\int d\mathbf{r}'d\boldsymbol{\omega}'\rho(\mathbf{r}',\boldsymbol{\omega}')f_{\text{HB}}(\mathbf{r}-\mathbf{r}',\boldsymbol{\omega},\boldsymbol{\omega}')}{\int d\mathbf{r}'\rho(\mathbf{r}')f_{\text{PHE}}(\mathbf{r}-\mathbf{r}')} \tag{2}$$

where $f_{\text{HB}}(\mathbf{r}-\mathbf{r}',\boldsymbol{\omega},\boldsymbol{\omega}')$ and $f_{\text{PHE}}(\mathbf{r}-\mathbf{r}')$ are the Mayer functions, which give the second virial coefficients by integration over all the variables. We have to specify how to choose the reference ellipsoid in (2). It has to resemble as much as possible the real HB and reduce, by symmetry, to HS in systems without orientational order. We have tested several ways and finally propose to do it on the basis of the tensor of inertia of the HB, $\langle I^{\text{HB}}(\boldsymbol{\omega})\rangle$, averaged over the orientations with the function $\rho(\mathbf{r},\boldsymbol{\omega})$.[18] The length of the PHE along the principal axes are taken so that the eigenvalues of its inertia tensor, I_i^{PHE} (with $i=1,2,3$ for the three principal axes) are proportional to the corresponding eigenvalues of the hard-body tensor of inertia:

$$\frac{I_1^{\text{PHE}}}{\langle I_1^{\text{HB}}(\boldsymbol{\omega})\rangle}=\frac{I_2^{\text{PHE}}}{\langle I_2^{\text{HB}}(\boldsymbol{\omega})\rangle}=\frac{I_3^{\text{PHE}}}{\langle I_3^{\text{HB}}(\boldsymbol{\omega})\rangle}\,. \tag{3}$$

This, together with the equal packing fraction, gives a full specification for the choice of the reference system. Equation (2) may be regarded as a way to study the general HB system as a perturbation from the PHE system, for which we can use the direct mapping onto HS. A good prescription for the reference system may improve the results of the approximation but, as long as the process is done consistently, the choice of the PHE is not crucial. We believe that (3) is just a convenient way to take into account the molecular shape and orientational distribution; other methods like minimization of the Mayer function difference may be used, but they are much more cumbersome to use, without improvement in the results.

For any system with uniform density, $\rho(\mathbf{r},\boldsymbol{\omega})=\rho(\boldsymbol{\omega})$, our functional (2) reduces to the Lee approximation (1), the use of PHE instead of HS being irrelevant for thermodynamics. Thus, the existing results for the isotropic and nematic phases given by (1) will be recovered in our theory. Here we start studying the system of parallel hard spherocylinders for which the nematic-smectic-*A* transition was first observed in a computer simulation.[11]

The reference PHE has a long axis parallel to the cylinder axis. The prescription (3) gives results very close to other possible choices in this case, like keeping equal length-to-width ratios. By a numerical solution of the Euler-Lagrange equation for the functional minimum of the free energy, we got the density profiles and the free energy of the smectic phase, to be compared with the homogeneous nematic. The results give a second-order phase transition (in agreement with the computer simulations[11]) at the critical density ρ_c and with the smectic period $\lambda=2\pi/q_c$, which are shown in Fig. 1 as functions of the length-to-width ratio of the PHSC. The quantitative agreement with the simulations[11] is quite good for ρ_c and excellent for λ, in the en-

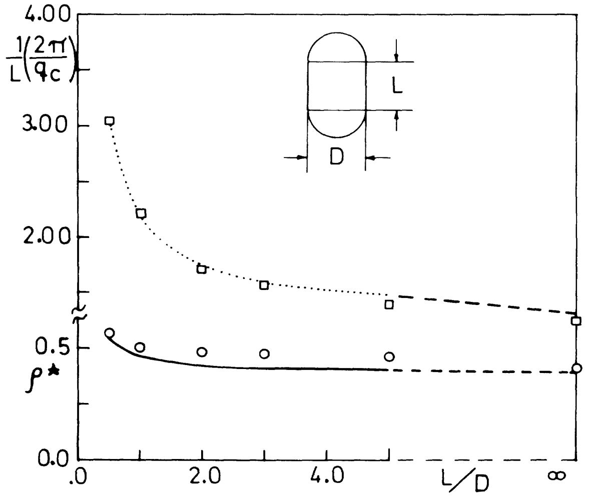

FIG. 1. Critical density in units of the complete packing, $\rho^*=\rho/\rho_{\text{cp}}$, with $\rho_{\text{cp}}=2^{1/2}/[D^3+(\frac{3}{2})^{1/2}LD^2]$, and critical wavelength (in units of the cylinder length L), for the nematic-smectic-*A* transition in a system of parallel hard spherocylinders (the inset gives a sketch of the molecule). The circles and squares give the computer simulation results of Ref. 11. The dashed lines are the extrapolations to the parallel-cylinder system corresponding to $L/D\rightarrow\infty$.

tire range from nearly spherical molecules to the limit of very elongated spherocylinders, for which the difference from the ellipsoids becomes more important.

The transition being continuous, it is easier and more instructive to look for it as the instability of the nematic against a density modulation. The second functional derivative of the free energy with respect to $\rho(\mathbf{r})$ (keeping all the molecules aligned, so that we may omit the variable $\boldsymbol{\omega}$) has a trivial ideal-gas part plus the interaction contribution which is usually expressed in terms of the direct correlation function. From (2) we get

$$-\beta\frac{\delta^2\Delta F}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\equiv C_{\mathrm{PHSC}}(\mathbf{r}-\mathbf{r}')$$
$$=C_{\mathrm{PHE}}(\mathbf{r}-\mathbf{r}')+\Delta C(\mathbf{r}-\mathbf{r}')\,, \qquad (4)$$

where the direct correlation function of the reference PHE, $C_{\mathrm{PHE}}(\mathbf{r})$, is given by an anisotropic scaling of that of hard spheres, $C_{\mathrm{HS}}(|\mathbf{r}|)$. The second term in (4) gives the difference between the PHSC and the reference of PHE.

The instability of the nematic is given by a divergence of the structure factor $S(\mathbf{q})$, which may be easily obtained from the Fourier transform of $C_{\mathrm{PHSC}}(\mathbf{r})$. Contrary to the case of simple liquids, in a nematic phase $S(\mathbf{q})$ depends on the direction of $\mathbf{q}$. For the PHE term the dependence is only through a simple scaling of $|\mathbf{q}|$ and $S_{\mathrm{PHE}}(\mathbf{q})$ will have no divergence before the full crystallization of the system, as for HS. The term $\Delta C(\mathbf{r})$ gives a correction which is small but very important because it produces $S(\mathbf{q})$ diverging at a lower density along the direction of the cylinder axis, so that the system goes into a smectic-*A* phase.

We turn now to the question of a smectic-*C* phase, with density modulation in a direction different from the orientational director. We will show that this phase can also be obtained from the packing effects of purely hard molecules. Hosino, Nakano, and Kimura[12] considered a system of oblique cylinders, with the axes and the bases of all molecules parallel to each other. The system may be mapped into parallel right cylinders which have a smectic-*A* phase (this corresponds to the $L/D\rightarrow\infty$ in Fig. 1). The mapping takes the smectic-*A* phase for the right cylinders into a density modulation oblique to the cylinder axis which was interpreted as a smectic-*C* phase. However, this is not a real description of nematic–smectic-*C* ordering, which is qualitatively different from the smectic-*A* case and needs a complex order parameter to represent the amplitude and direction of the density modulation.[6] This difference is destroyed in Ref. 12 by the direct ordering of the oblique cylinders which corresponds to a biaxial phase rather than a nematic phase. Instead we propose a model of oblique cylinders with parallel axes but free rotation around them. In the nematic phase there is perfect disorder in the orientation of the bases, and the reference PHE will have the same symmetry as in the PHSC system. The smectic-*A* order may be studied as before. When the orientational symmetry is broken we get a biaxial nematic or, if coupled with a density modulation, a true smectic-*C* phase. We have simplified the calculation by doing the integral of the Mayer function in (2) in an approximate way, with only two particular orientations for the bases: parallel and antiparallel. This will produce no qualitative changes and we have no computer simulations of this model with which to do qualitative comparisons. The resulting phase diagram in Fig. 2 gives the transition density as function of Δ/L, which is the relevant shape parameter (see inset in Fig. 2). We get continuous nematic–smectic-*A* transition for small Δ/L (nearly right cylinders) and first-order nematic–smectic-*C* transitions at larger Δ/L. The smectic-*A*–smectic-*C* transition has a tricritical point, in qualitative agreement with Landau theory and experimental results.[19] For large Δ/L the nematic phase goes to a biaxial phase before any smectic ordering. This kind of phase has been predicted before,[20] but in our model it may be artificial because of the imposed perfect orientation of the cylinder axis.

To conclude, we have shown that nematic–smectic-*A*–smectic-*C* phase transitions can appear in systems of purely hard molecules, as the result of end-to-end packing effects. This strongly supports the idea that an important part of the liquid-crystal structure and phase diagrams comes from the hard-core repulsions, which has been neglected in many theoretical models, where the smectic ordering was considered a result of the soft attractive interactions. We have developed a free-energy-

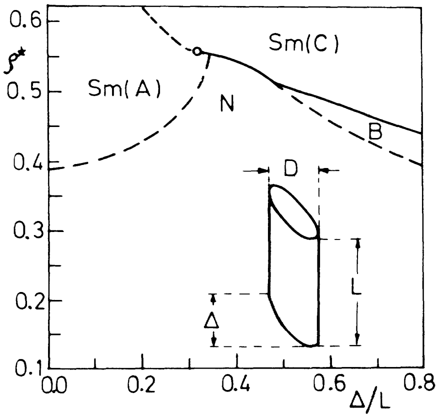

FIG. 2. Phase diagram for a system of parallel oblique cylinders (see the inset for the definition of the shape parameters). Nematic (N), smectic (Sm) *A* and *C*, and biaxial nematic (B) phases may appear. The transition densities are in units of the complete packing, $\rho_{\mathrm{cp}}=2/3^{1/2}D^2L$. The dashed lines represent continuous transitions and the full lines are first-order transitions. The circle separates first- and second-order smectic-*A*–smectic-*C* transitions.

density functional which can be used to study the full phase diagram of any hard-body system, and yields good agreement with the existing computer simulations; we present here applications to systems of parallel molecules, but the theory is not restricted to that case. Work is in progress to obtain the phase diagram of systems of free hard molecules. Our treatment may also be used as a reference system in the description of a real liquid crystal, with the attractive interactions included as perturbation, following a scheme which has proved to be very useful for simple liquids.[7]

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[1] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).

[2] Sin-Doo Lee, J. Chem. Phys. **87**, 4972 (1987).

[3] M. Baus, J. L. Colot, X. G. Wu, and H. Xu, Phys. Rev. Lett. **59**, 2184 (1987).

[4] D. Frenkel, B. M. Mulder, and J. P. McTague, Phys. Rev. Lett. **52**, 287 (1984); D. Frenkel and B. M. Mulder, Mol. Phys. **55**, 1171 (1985); D. Frenkel, Mol. Phys. **60**, 1 (1987); M. P. Allen and D. Frenkel, Phys. Rev. Lett. **58**, 1748 (1987).

[5] W. Maier and A. Saupe, Z. Naturforsch. **13a**, 564 (1958).

[6] For detailed references and discussion on the classical theories of nematics, see P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[7] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).

[8] W. L. McMillan, Phys. Rev. A **4**, 1238 (1971).

[9] M. D. Lipkin and D. W. Oxtoby, J. Chem. Phys. **79**, 1939 (1983).

[10] A. Kloczkowski and J. Stecki, Mol. Phys. **55**, 689 (1985).

[11] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, Phys. Rev. A **36**, 2929 (1987).

[12] M. Hosino, H. Nakano, and H. Kimura, J. Phys. Soc. Jpn. **46**, 1709 (1979).

[13] B. M. Mulder, Phys. Rev. A **35**, 3095 (1987).

[14] X. Wen and R. B. Meyer, Phys. Rev. Lett. **59**, 1325 (1987).

[15] D. Frenkel, J. Phys. Chem. **92**, 3280 (1988).

[16] We have used the model described by P. Tarazona, Phys. Rev. A **31**, 2672 (1985), with corrections given by P. Tarazona, U. Marini Bettolo Marconi, and R. Evans, Mol. Phys. **60**, 573 (1987).

[17] A similar scheme has been used to describe the hard cores of molecules with attractive interactions by D. E. Sullivan and L. Mederos, private communication, and to be published.

[18] By the tensor of inertia of the hard molecule we refer to that of a homogeneous density distribution extended over the molecular volume, without any reference to the tensor of inertial of a real molecule.

[19] D. Johnson, D. Allender, R. de Hoff, C. Maze, E. Oppenhein, and R. Reynolds, Phys. Rev. B **16**, 470 (1977); C. C. Huang and S. C. Lien, Phys. Rev. Lett. **47**, 1917 (1981); S. Witanachchi, J. Huang, and J. T. Ho, Phys. Rev. Lett. **50**, 594 (1983).

[20] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).