

Columnar versus Smectic Order in Binary Mixtures of Hard Parallel Spherocylinders

A. Stroobants

*Van 't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht, Padualaan 8,
3584 CH Utrecht, The Netherlands*

(Received 23 July 1992)

We present Monte Carlo simulations of binary mixtures of hard parallel spherocylinders with length-to-width ratios $L_1/D=1.0$ and L_2/D ranging from 1.3 to 2.1. The composition is such that the partial volume fractions are equal. For $L_2/D > 1.6$, we observe a thermodynamically stable columnar phase which is not formed by the monodisperse components separately. The nematic-smectic transition, which is postponed by increasing the L_2/D ratio, is eventually preempted by a nematic-columnar transition for $L_2/D > 1.9$, showing that in these mixtures bidispersity favors columnar order over smectic order.

PACS numbers: 64.70.Md, 61.20.Ja, 61.30.Cz

Solutions of monodisperse, rodlike tobacco mosaic virus prepared at sufficiently high concentrations exhibit a smectic liquid crystal phase [1] which is essentially a periodic stack of two-dimensional liquid layers with the particles perpendicular to the layers. The properties of the observed smectic phase are in close analogy to the smectic phase found in a computer simulation study of a simple model system of hard parallel spherocylinders [2-4] (i.e., cylinders capped at each end by a hemisphere of the same radius). The smectic phase also occurs in a less artificial model system of freely rotating, hard spherocylinders [5,6]. This strongly suggests that under the experimental conditions for which the smectic phase has been observed, the virus system is a good analog of the system of hard rods of uniform length.

Many rodlike particles, however, are not monodisperse but show a finite length dispersity. Very little is known about the influence of length dispersity on the formation of liquid crystalline phases with partial translational order. The onset of smectic order is expected to be postponed [7] as rods having different lengths do not fit into layers as easily as do rods of the same length. Furthermore, some highly concentrated biopolymer solutions [8-10] do not form a smectic phase, but rather a columnar phase. In the latter phase, the particles are confined to liquidlike columns which, in turn, are organized in a hexagonal array. In order to assess the effect of deviations from monodispersity, we have carried out Monte Carlo (MC) simulations of binary mixtures of hard parallel spherocylinders with different lengths but the same diameter.

The length-to-width ratio L_1/D of the shorter spherocylinders (L_1 is the length of the cylindrical segment) is fixed at 1.0. The second component has the following L_2/D ratios: 1.3, 1.6, 1.9, 2.1. The fraction X_1 of the shorter rods is adjusted so as to keep the mixtures at their equivalence point, where the partial volume fractions of both components are equal. The size of the systems studied was 144 particles.

In order to obtain the equation of state, we carried out constant-pressure MC simulations. In phases with (par-

tial) translational order, the box edges were allowed to fluctuate independently to let the system relax to its equilibrium volume and shape, at a given pressure. Initially, the system was prepared in a close-packed fcc lattice distorted along the (111) axis by a factor $1+L_2/D$. Subsequently, a fraction X_1 of randomly chosen particles had its L/D ratio reduced to L_1/D . To study the fluid phase, the initial configuration was expanded to low densities where it rapidly melted to form a translationally disordered nematic fluid. Subsequent runs to generate the fluid branch were always started from previously equilibrated configurations at lower pressure. A suitable starting configuration to study the solid phase was obtained by expanding the initial configuration to a volume fraction of

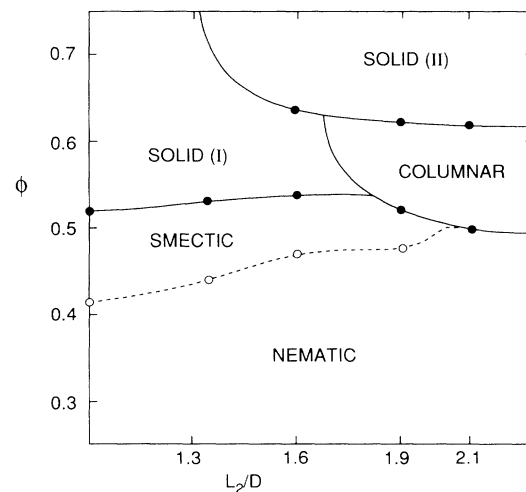


FIG. 1. Phase behavior of binary mixtures of hard parallel spherocylinders at the equivalence point, as a function of the L_2/D ratio of the longer rods. The volume fractions at which monodisperse systems of the shorter rods with $L_1/D=1.0$ undergo phase transitions are shown on the ϕ axis. Solid (I): substitutionally disordered binary crystal. Solid (II): phase separated pure component crystals. Open circles: volume fraction corresponding to a continuous transition. Solid circles: location of a first-order transition. Two-phase regions are not shown.

about 0.70, typically corresponding to the highest pressure under study, and letting the system equilibrate. Evidently, a substitutionally disordered binary crystal is not necessarily the most likely structure at such a high density, especially for large L_2/D values. By allowing particles with different L/D ratios to swap positions, the system was given the possibility to transform efficiently and spontaneously into a more convenient arrangement. It turned out that the two-component crystal phase separated into essentially pure component solids for $L_2/D \geq 1.6$. The solid branch was then generated by gradually lowering the pressure.

As hysteresis between the different branches of the equation of state appeared to be absent or marginal (unless mentioned explicitly otherwise), reasonable estimates of the location of first-order transitions could be obtained without having to carry out free energy calculations. Approximating the actual location of the transition by its lower limit, does not, in any case, underestimate the volume fraction at the transition by more than 0.025, which amounts to a maximum of 5% in relative terms. Density jumps at first-order transitions do not exceed 5%.

Using the techniques and the approximations described above, we present in Fig. 1 a tentative phase diagram of bidisperse, parallel hard spherocylinders at the equivalence point. It is observed that the continuous nematic-smectic transition is postponed from $\phi_{N-S} = 0.416$ in the case of monodisperse spherocylinders with $L_1/D = 1.0$ to $\phi_{N-S} = 0.474$ in a bidisperse system with $L_2/D = 1.9$, to be preempted by a direct nematic-columnar transition for $L_2/D = 2.1$.

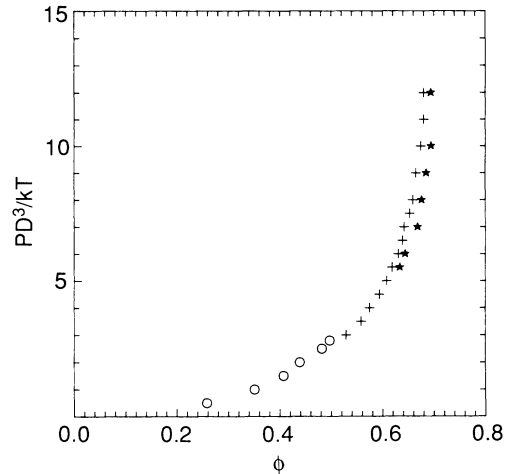


FIG. 2. Equation of state of a bidisperse system with $L_1/D = 1.0$ and $L_2/D = 2.1$. Open circles: nematic branch. Crosses: columnar branch. Stars: solid branch.

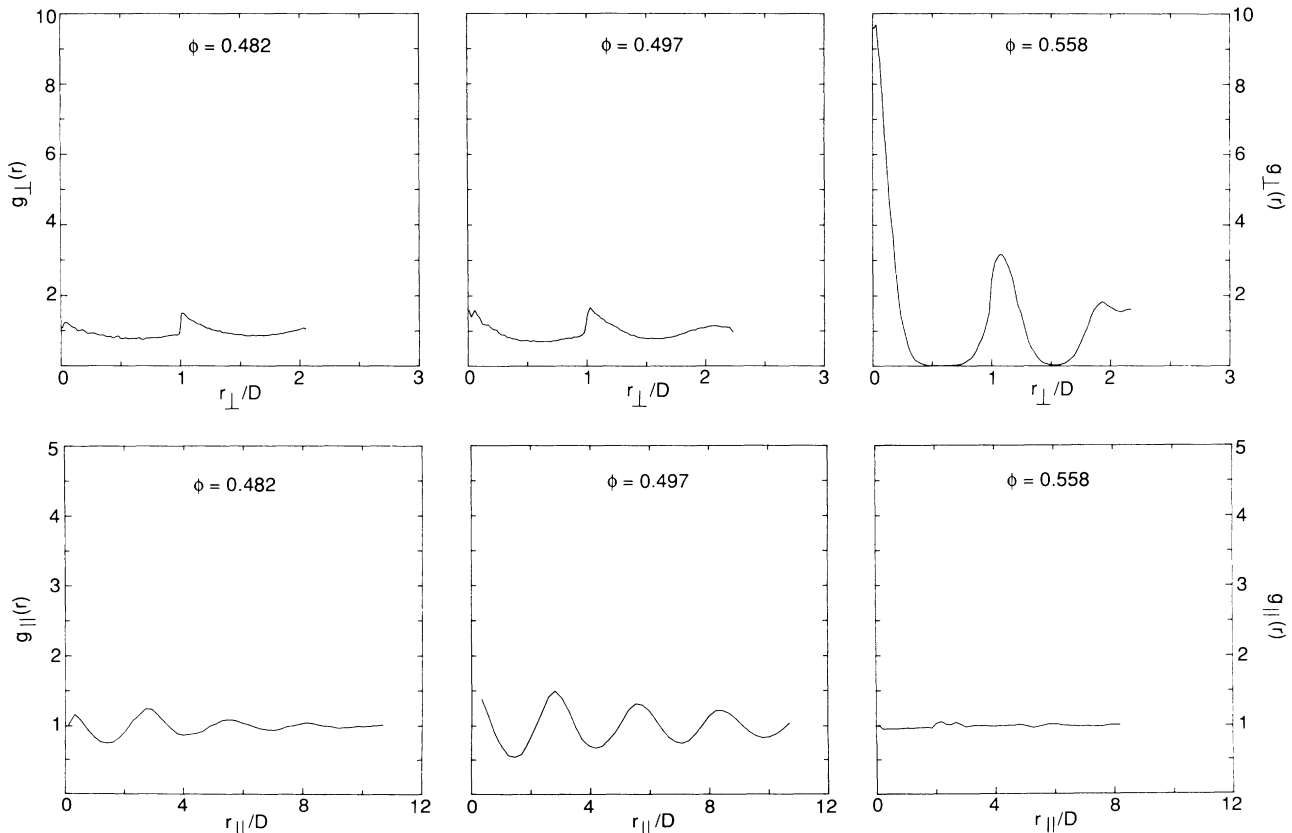


FIG. 3. Transverse correlation function $g_{\perp}(r)$ and longitudinal correlation function $g_{\parallel}(r)$ in the vicinity of the nematic-columnar transition in a binary mixture with $L_1/D = 1.0$ and $L_2/D = 2.1$.

Closer inspection of Fig. 2 reveals that there is a cusp in the equation of state of the latter system at $\phi_{N-S} = 0.497$. The longitudinal pair correlation function $g_{\parallel}(r)$ and the transverse pair correlation function $g_{\perp}(r)$, presented in Fig. 3, are sensitive probes [3] of translational ordering parallel and perpendicular, respectively, to the direction of molecular alignment. It appears that, upon compressing the nematic phase, both smectic and columnar fluctuations start developing simultaneously. Once the volume fraction exceeds $\phi_{N-C} = 0.497$, the smectic fluctuations collapse instantaneously while a columnar phase is established. The partial longitudinal correlation functions do not provide any evidence for correlations between neighboring columns. Although we do not observe any hysteresis effects when traversing the transition point in both directions, we expect the nematic-columnar transition to be (weakly) first order. As a result of strong hysteresis between the columnar branch and the solid branch, equation-of-state data are, in principal, insufficient to determine the range of stability of the columnar phase. However, as the solid melts towards the columnar phase, the nematic and solid branches do not overlap. Consequently, the columnar phase is both mechanically and thermodynamically stable in a finite density interval.

The phase diagram in Fig. 1 has been constructed by considering this interval as a lower-limit approximation to the actual range of stability, which, of course, might extend to higher densities.

Using the same criterion, we still find a thermodynamically stable columnar phase when L_2/D is lowered from 2.1 to 1.9, although the smectic phase persists in a narrow density interval as well. This is actually quite remarkable as the elongation ($L_2 + D$) of the longer spherocylinders exceeds the wavelength of the smectic modulation with nearly 10%. Absence of bond orientational order indicates that the smectic layers remain liquidlike. Compressing the smectic phase does not reduce the wavelength of the modulation; neither does it enhance significantly its amplitude, as is commonly observed in monodisperse systems. Instead, columnar fluctuations develop (Fig. 4). Eventually, the smectic phase transforms through a weakly first-order transition (no hysteresis) into a columnar phase for $\phi > \phi_{S-C} = 0.521$.

The equation of state of a bidisperse system with $L_2/D = 1.6$ (Fig. 5) does not have a columnar branch. The smectic phase, upon compression, crystallizes directly into a substitutionally disordered binary crystal which finally phase separates. In fact, "prepared" columnar

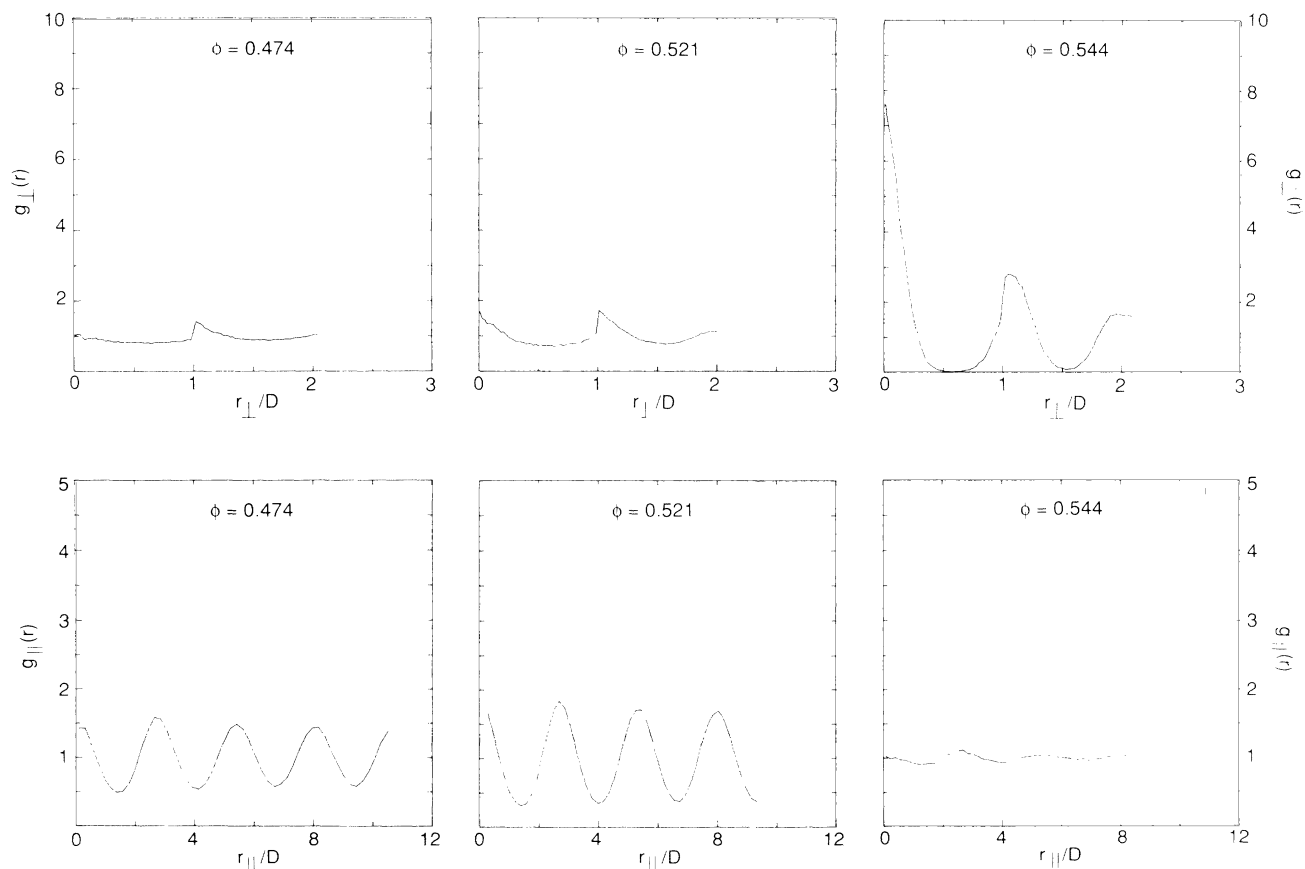


FIG. 4. Transverse correlation function $g_{\perp}(r)$ and longitudinal correlation function $g_{\parallel}(r)$ in the vicinity of the smectic-columnar transition in a binary mixture with $L_1/D = 1.0$ and $L_2/D = 1.9$.

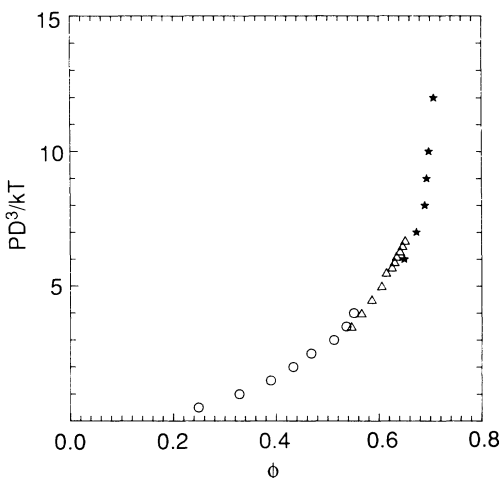


FIG. 5. Equation of state of a bidisperse system with $L_1/D=1.0$ and $L_2/D=1.6$. Open circles: nematic+smectic branch. Triangles: substitutionally disordered binary crystal. Stars: pure component crystals.

configurations, depending on the pressure, crystallize or phase separate, demonstrating they are mechanically and consequently thermodynamically unstable in this system. All transitions occur spontaneously. Only weak hysteresis effects are observed.

Summarizing, we conclude that the phase behavior of binary mixtures of hard parallel spherocylinders differs markedly, quantitatively as well as qualitatively, from the behavior of the monodisperse components separately. In particular, it is found that bidispersity favors columnar order at the expense of smectic order. Neither the smectic-columnar transition nor the nematic-columnar

transition occurs in monodisperse hard spherocylinder systems. Both transitions appear to be weakly first order. The range of stability of the columnar phase as a function of the composition remains to be determined. We have evidence that the columnar phase does not persist in nearly pure component binary mixtures containing 10% of impurities.

These simulations indicate that finite length dispersity might contribute to columnar phase formation in real systems, although in many cases [8-10] the effects of polydispersity and chain flexibility are intertwined.

The author would like to thank H. N. W. Lekkerkerker and D. Frenkel for stimulating discussions.

-
- [1] X. Wen, R. B. Meyer, and D. L. D. Caspar, *Phys. Rev. Lett.* **63**, 2760 (1989).
 - [2] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, *Phys. Rev. Lett.* **57**, 1452 (1986).
 - [3] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, *Phys. Rev. A* **36**, 2929 (1987).
 - [4] J. Veerman and D. Frenkel, *Phys. Rev. A* **43**, 4334 (1991).
 - [5] D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants, *Nature (London)* **332**, 822 (1988).
 - [6] J. Veerman and D. Frenkel, *Phys. Rev. A* **41**, 3237 (1990).
 - [7] T. J. Sluckin, *Liq. Cryst.* **6**, 111 (1989).
 - [8] F. Livolant and Y. Bouligand, *J. Phys. (Paris)* **47**, 1813 (1986).
 - [9] F. Livolant, A. M. Levelut, J. Doucet, and J. P. Benoit, *Nature (London)* **339**, 724 (1989).
 - [10] S.-D. Lee and R. B. Meyer, *Liq. Cryst.* **7**, 451 (1990).