

Influence of polydispersity on the phase behavior of colloidal liquid crystals: A Monte Carlo simulation study

Martin A. Bates and Daan Frenkel

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam. The Netherlands

(Received 30 April 1998; accepted 7 July 1998)

Using isobaric semigrand Monte Carlo simulations, we have investigated the phase behavior of a model for polydisperse rodlike colloids. The system consists of hard spherocylinders in the limit of infinite aspect ratio, with polydispersity in the length of the particles. If the polydispersity is small (standard deviation $s < 0.08$), the phase behavior is essentially unchanged from that observed in monodisperse systems; thus nematic, smectic, and crystal phases are exhibited. For an intermediate range of polydispersities ($0.08 < s < 0.18$), the smectic phase is found to become increasingly destabilized with respect to the nematic phase at low densities and a columnar phase at high densities. This eventually leads to a terminal polydispersity ($s \approx 0.18$) above which the smectic phase is no longer stable. Beyond this value, only nematic and columnar phases are observed.

© 1998 American Institute of Physics. [S0021-9606(98)51038-0]

I. INTRODUCTION

Computer simulation has played an important role in understanding the liquid crystalline behavior of systems composed of monodisperse hard rodlike colloids. Following Onsager's theoretical demonstration that a system of infinitely long hard particles can exhibit an orientationally ordered phase if the density is sufficiently high,¹ computer simulation studies gave the first indication that smectic phases can also be formed by systems of particles which interact through excluded volume interactions alone.² Prior to this observation, it was thought that smectic phases could only be exhibited by models which included attractive interactions. This prompted many further theoretical and simulation studies of simple hard-body liquid crystal models. Recently, the entire phase diagram of monodisperse hard spherocylinders has been determined by computer simulation, from the hard-sphere limit at one extreme to the limit of infinite aspect ratio at the other.³ This encompasses nematic and smectic phases for sufficiently high aspect ratios^{3,4} and a plastic crystal phase for nearly spherical particles,³ in addition to isotropic fluid and crystal phases. However, many real systems are not monodisperse but have a distribution of particle sizes. Indeed, the best experimental realizations of hard-body liquid crystalline systems, suspensions of nonspherical colloidal particles, are hardly ever truly monodisperse.⁵

Size polydispersity can have a significant effect on the location of the phase boundaries. Sluckin⁶ has generalized the Maier-Saupe and Onsager theories to include polydispersity and has explained the broadening of the nematic-isotropic transition for a system composed of parallel rodlike particles with a distribution of lengths. He has also shown that the onset of smectic order is postponed in such polydisperse systems; thus the density at which the nematic-smectic transition occurs increases with increasing polydispersity.⁶ The simple explanation for this is that rods of differing lengths do not pack into layers as effectively as rods of the same length. Size polydispersity can also be responsible for

the modification of the phase behavior. For example, simulations of binary mixtures of parallel spherocylinders have shown that, if the species differ in length by a sufficient amount, columnar rather than smectic order is favored.⁷ Density-functional theory also suggests that the columnar phase occurs not only in bidisperse systems, but also in a truly polydisperse system of parallel cylinders.⁸ The smectic phase present in the monodisperse system is found to be increasingly destabilized as the polydispersity in the lengths of the cylinders is increased until, after a terminal polydispersity, only the nematic and columnar phases are observed. However, although the general features of the phase behavior are consistent with intuition, there appear to be both quantitative and qualitative disagreements between the results of the density-functional study⁸ in the monodisperse limit and the most recent simulation^{3,4,9} and theoretical^{10,11} work for similar monodisperse systems. For example, the nematic-smectic transition is predicted to occur at a reduced density, $\rho^* = \rho/\rho_{CP}$, of 0.31, where ρ_{CP} is the close packed density. However, this transition is found to occur at much higher densities in simulations of freely rotating spherocylinders. The exact location depends on the aspect ratio, L/D , but the nematic phase is found to be stable at reduced densities greater than 0.50 for $L/D = 3-5$ (Refs. 3,4) and up to $\rho^* = 0.46$ for infinite aspect ratios.⁹ Thus the density-functional theory of Bohle *et al.*⁸ significantly underestimates the density at which the nematic-smectic transition occurs. In addition, the nature of the nematic-smectic transition is predicted to be continuous, whereas simulations of spherocylinders of finite^{3,4} and infinite aspect ratios⁹ and recent theoretical works¹⁰⁻¹² indicate that this is not the case and that the transition is actually first order.

In this paper, we aim to investigate the influence of polydispersity on the phase behavior of colloidal liquid crystals using computer simulation techniques. Given the success of simulation in determining the phase behavior and the nature of the transitions of monodisperse systems, we have used

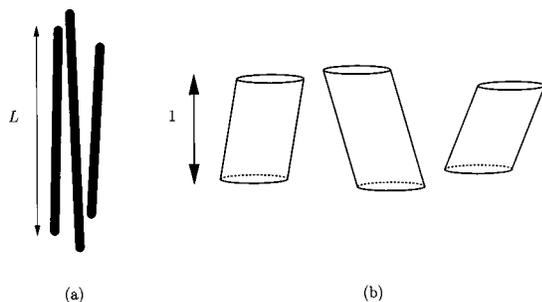


FIG. 1. Scaling of polydisperse spherocylinders in the limit $\langle l \rangle / D \rightarrow \infty$. (a) Polydisperse spherocylinders with finite l/D . (b) The system scaled along the director by a factor $1/L$. The diameters of the spherocylinders and the cross sections of the shifted cylinders are all equal to D .

isobaric semigrand simulations^{13,14} to gain an insight into how polydispersity affects the behavior of colloidal liquid crystals. Just as the results of hard spherocylinder simulations are now used as a reference system for both theoretical predictions and experimental results, these simulations should provide a useful test bed for theories and experiments on polydisperse systems.

II. THE MODEL SYSTEM AND SIMULATION DETAILS

A. The model polydisperse system

The colloidal suspension is modeled as a system of freely rotating polydisperse spherocylinders of average length $\langle l \rangle$ and diameter D in the limit of infinite aspect ratio, $\langle l \rangle / D \rightarrow \infty$. Simulations in this limit are possible by applying an appropriate scaling so that the particles have finite volume but variable shape. This scaling exploits the fact that at reasonably high densities the particles are almost completely aligned;³ the average angle between a particle and the director scales inversely with its length. For a monodisperse system of spherocylinders of length L and diameter D , scaling by a factor $1/L$ along the director results in a system of shifted cylinders with constant unit height and a circular cross section of diameter D perpendicular to the director.³ For a polydisperse system of spherocylinders with a distribution of lengths but fixed diameter, this scaling produces a system of shifted cylinders with equal diameters but differing heights (see Fig. 1). The polydisperse colloidal system can, therefore, be viewed as a continuous mixture in which the species are shifted cylinders with heights distributed according to a composition distribution function, $P(h)$. As the scaling argument is only valid for high densities, this excludes the possibility of investigating the isotropic phase. However, the use of this scaling is ideal to study the nematic (N), smectic (Sm), crystal (Cr), and columnar (Col) phases and, in particular, the nematic-smectic transition.

B. Simulation of the polydisperse system

Various simulation methods have been used to study systems composed of a continuous distribution of species. Standard techniques based on the canonical or grand canonical ensembles are found not to be well suited for such continuous mixtures.¹³ The former has the disadvantage that a finite random sample taken from a known composition dis-

tribution does not truly represent a polydisperse system and so many simulations with different random realisations of the same system must be performed to average out these discrepancies. In addition, guaranteeing the equality of the chemical potential of each species in two different phases is clearly difficult for a small number of components and impossible for a large number and so this seems to rule out the possibility of studying phase equilibria. The latter is not practical because the random particle insertions performed during a grand canonical simulation at high density are nearly always rejected. An alternative ensemble—the semi-grand canonical ensemble—has been shown to be more practical and the advantages of this ensemble over the canonical and grand canonical ensembles are discussed in detail for continuous mixtures by Kofke and Glandt.¹³

We have used the isobaric semigrand ensemble to investigate the phase behavior of our polydisperse system. This ensemble has the number of particles N , the pressure P , and the temperature T constant. However, it differs from the more usual isothermal-isobaric (constant NPT) ensemble¹⁵ in that the identities of the particles are not fixed but are allowed to change during the simulation, subject to an underlying chemical potential function, so that a truly polydisperse system can be simulated. Isobaric semigrand Monte Carlo simulations are performed in a similar way to those in the isothermal-isobaric ensemble. Thus particle translations and rotations and box volume changes are used to construct trial configurations which are accepted or rejected in the usual way.¹⁵ However, the composition of the system is also sampled by using additional identity change trials. In the scaled model colloid system, the identity of each shifted cylinder is its height and so it is also necessary to construct trials in which the height of particle i is changed from h_i to $h_i + \delta h$, where δh is chosen from the range $(-\Delta h, \Delta h)$, in which Δh is a variable parameter which governs the maximum allowed change. Assuming no overlap results from such a trial (in which case the trial is rejected), it is accepted with probability¹³

$$P_{\text{Acc}}(h_i^{\text{old}} \rightarrow h_i^{\text{new}}) = \text{minimum}[1, \exp([\mu(h_i^{\text{new}}) - \mu(h_i^{\text{old}})]/k_B T)], \quad (1)$$

where $\mu(h)$ is the imposed chemical potential as a function of the particle height h . For large Δh , this scheme is essentially equivalent to choosing a trial height with a probability governed by the underlying chemical potential distribution and then accepting the trial if no overlaps occur.¹⁶ However, at high densities, this second route is not found to be efficient and a better choice is the former scheme with small Δh . In practice, Δh is varied to achieve between 30% and 50% acceptance. This is reminiscent of the way particle translations are made in Monte Carlo simulations. Thus, just as a trial is much more likely to be accepted at liquid densities if the particle is moved a small random distance from its original position than if it is randomly inserted in a new position, small random changes in particle height have a higher acceptance probability than a new height selected with a weight

according to the underlying activity distribution, especially at the high densities characteristic of the nematic and smectic phases.

One clear disadvantage of the semigrand ensemble is that it is the chemical potential function, $\mu(h)$, which is imposed and not the composition distribution, $P(h)$. Thus the composition must be determined during the simulation and cannot be chosen *a priori*. However, its form is found to be similar to the imposed activity distribution, $\exp([\mu(h) - \mu(h_0)]/k_B T)$.^{13,14} Therefore, following other simulations of continuous mixtures,^{13,14} we choose the chemical potential function to be

$$[\mu(h) - \mu(h_0)]/k_B T = -(h - h_0)^2/2\nu, \quad (2)$$

which gives a Gaussian activity distribution with a maximum at h_0 and so should also lead to a Gaussian composition distribution. The width of the activity distribution, $\nu^* = \nu/h_0^2$, can be varied to simulate different composition distributions and, therefore, systems with different polydispersities.

To determine the influence of polydispersity on the phase behavior, six series of simulations were performed for different activity distributions characterized by different widths, ν^* . For each series, the equation of state was determined for a system of 720 particles using isobaric semigrand simulations. Three types of sequences were used in the simulations; compression from the nematic phase, expansion from a perfectly aligned AAA crystal³ with the usual periodic boundary conditions and expansion from an AAA crystal with shifted boundary conditions. In the simulations with shifted boundary conditions, the periodic boundaries in the z direction were shifted by one column spacing in the xy plane; thus a particle leaving the simulation box at the top will reappear at the bottom in a neighboring column shifted by $(\Delta x, \Delta y) = (\frac{1}{2}\sigma_c, (\sqrt{3}/2)\sigma_c)$, where σ_c is the column spacing. We note that these shifted columnar boundary conditions are similar to those used for the study of the smectic A phase in a similar system,³ in which, on exiting one side of the box, a particle reappears one layer higher at the opposite side. Thus the system is effectively transformed into one layer, which allows diffusion through the system without a particle physically jumping between layers. The use of such boundary conditions are necessary to ensure that the structure can relax without being influenced by the relatively small box size. For example, in a simulation of a columnar phase at high density with normal periodic boundary conditions, the heights of neighboring columns must be equal and we may expect that this will impose an inappropriate constraint on the particle heights, since the sum of all particle heights in each (close packed) column must be equal. This constraint is clearly removed by using the shifted boundary conditions.

To ensure that our scaling argument remains valid, the director must remain aligned along the z axis. Monte Carlo trials were performed by selecting a pair of random particles, i and j , and giving each a random displacement. In addition, a random tilt was applied to particle i and an equal but opposite tilt was applied to particle j to maintain the director alignment.³ The identities of the particles were sampled in

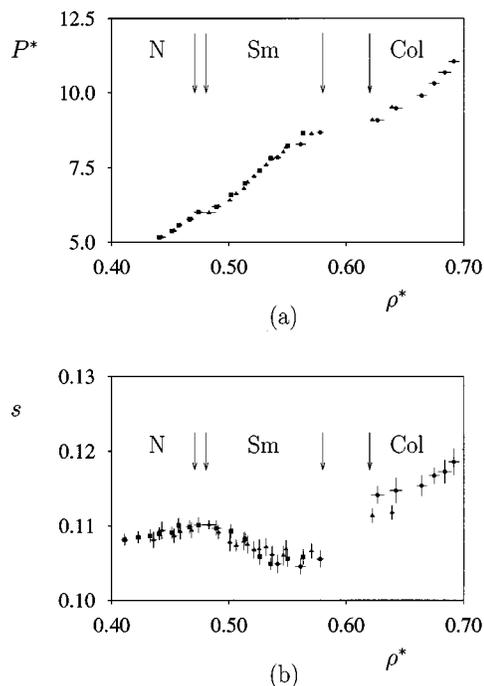


FIG. 2. (a) Equation of state for hard spherocylinders in the limit of infinite aspect ratio and (b) the polydispersity as a function of density for an activity distribution with width $\nu^*=0.010$. The arrows indicate the approximate locations of the first order N–Sm and Sm–Col phase transitions. The following sequences were used: (■) compression from nematic, (▲) expansion from the AAA crystal, (●) expansion from the AAA crystal with shifted boundary conditions. The reduced density is defined as $\rho^* = \rho/\rho_{CP}$ and the reduced pressure as $P^* = PD^2\langle h \rangle/k_B T$, where $\langle h \rangle$ is the average height of the shifted cylinders, D is their diameter, and ρ_{CP} is the close packed density for a system of aligned cylinders of height $\langle h \rangle$.

independent trials by selecting a particle at random and randomly changing its height, as previously discussed. During a typical Monte Carlo cycle, each particle had on average one trial displacement and one trial identity change. Volume changes were attempted once per cycle. Simulation lengths were typically between 50 000 and 75 000 cycles for both equilibration and production stages. However, the evolution of the system is found to be slow in the vicinity of the transitions. Therefore, to ensure full equilibration near the transitions we follow Ref. 9 and increase the number of trial volume changes per cycle by a factor of 10. After the initial equilibration stage, extra equilibration runs consisting of 50 000 cycles (500 000 volume trials) were found to be necessary, during which time the maximum volume change was continually adjusted so that between 20% and 30% of the trials were accepted.

III. SIMULATION RESULTS AND PHASE DIAGRAM

A. Equation of state ($\nu^*=0.010$)

The equation of state for the system with an activity distribution with width $\nu^*=0.010$ is shown in Fig. 2(a). Since hysteresis between the different branches of the equation of state is marginal, we can use this to obtain reasonable estimates for the locations of the transitions. The offset in density between the nematic and smectic branches indicates that the N–Sm transition is first order rather than continuous,

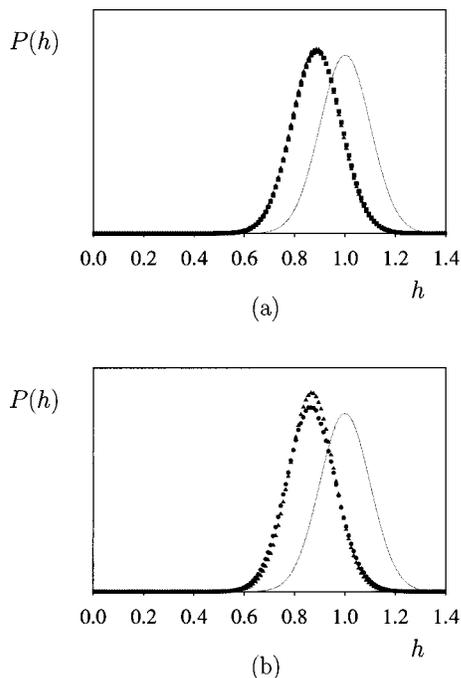


FIG. 3. The composition distribution, $P(h)$, at the (a) N–Sm and (b) Sm–Col coexistence points for the system with an activity distribution with width $\nu^*=0.010$. (■) Nematic, (▲) smectic, (●) crystal. The dotted line is the imposed activity distribution.

as predicted by density-functional theory.⁸ We estimate the nematic and smectic coexistence densities $[\rho_N^*, \rho_{Sm}^*]$ to be $[0.470(4), 0.480(4)]$. For polydisperse systems, we define the reduced density, $\rho^* = \rho/\rho_{CP}$, in terms of the close packed density, ρ_{CP} , of a system of parallel monodisperse cylinders of height $\langle h \rangle$. We have not used a thermodynamic integration scheme to obtain the coexistence densities more accurately since it would be computationally expensive to do so for each series of simulations nor have we attempted to compute the chemical potential of the reference component¹³ (cylinders of height h_0) because techniques such as the Widom insertion method¹⁷ will undoubtedly fail at such high densities. Moreover, as we shall see, this is not necessary since a clear picture of the influence of polydispersity can be obtained using just these estimates. Polson and Frenkel⁹ have recently shown that the N–Sm transition for a monodisperse system of hard spherocylinders in the limit of infinite aspect ratio is first order. It is, therefore, apparent that the introduction of polydispersity has not changed the nature of the transition. However, the reduced coexistence densities at the transition have shifted from $[0.46, 0.47]$ (Ref. 9) to the slightly higher values of $[0.47, 0.48]$. At higher densities, the system is found to exhibit a columnar phase. The large offset between the branches in the equation of state indicate that the transition between the smectic and columnar phases is strongly first order.

The composition distribution, $P(h)$, was determined during the simulations and this is shown in Fig. 3 for systems at state points corresponding to N–Sm and Sm–Col coexistence. These and all other composition distributions are found to be essentially Gaussian. We note that the composition distributions are shifted to lower values of h with respect to

the activity distribution. This occurs since large particles are entropically less favored than small ones,¹³ especially at high density. The similarity of the two distributions in Fig. 3(a) indicates that the composition of the nematic and smectic phases at their coexistence point is the same. However, we do not find this to be the case for coexisting smectic and columnar phases [see Fig. 3(b)]. Thus the composition distribution in the smectic phase [$s=0.105(2)$] is slightly narrower than that in the columnar phase [$s=0.114(2)$]; see also Fig. 2(b). We note that as a measure of the polydispersity, we have taken the normalised standard deviation of the distribution, s ,

$$s^2 = \frac{\langle h^2 \rangle}{\langle h \rangle^2} - 1. \quad (3)$$

B. Phase diagram and discussion

Series of simulations were performed for other activity distribution widths to investigate the influence of polydispersity on the phase behavior; full details are given in Table I. In each case, the locations of the transitions were determined from the equation of state as described above. Figure 4 shows the phase behavior as a function of the polydispersity, s . We can clearly identify three different regimes of phase behavior, corresponding to small ($s < 0.08$), intermediate ($0.08 < s < 0.18$), and large ($s > 0.18$) polydispersity. In the monodisperse limit, the system exhibits nematic, smectic, and crystal phases.^{3,9} This phase sequence and the location of the transitions are essentially unchanged for systems in which the polydispersity is small $s < 0.08$.¹⁸ We do not expect the location of the N–Sm transition to change if the polydispersity is small since, for a monodisperse system, the translational distribution along the director is not sharp but reasonably broad in the smectic phase in the vicinity of the transition (see Fig. 5). Thus small deviations in the heights of the particles will not destroy the smectic phase, since the different lengths can be accommodated in the layer structure. This feature is not taken into account in the bifurcation analysis of Sluckin.⁶ He assumes that the translational distribution function is sharp and so the smectic phase is found to be destabilized with respect to the nematic phase, even for very small values of the polydispersity. In contrast, at higher densities near the transition to the crystal phase, the translational distribution function is expected to be sharper and more similar to that of the crystal. It seems reasonable, therefore, that small deviations in the particle heights will neither stabilize nor destabilize the smectic phase with respect to the crystal. However, the columnar phase will become increasingly stabilized with respect to both of these phases. Thus as the polydispersity is increased in the intermediate regime ($0.08 < s < 0.18$), the maximum density at which the smectic phase is stable is decreased. Within this regime, we also observe that, at lower densities, the nematic phase becomes stabilized with respect to the smectic phase. Presumably this arises because the layered structure can no longer cope with the increasingly wider distribution of cylinder heights and so the transition to the smectic phase is shifted to higher densities, as predicted by Sluckin.⁶ For higher polydispersities still ($s > 0.18$), the smectic phase is

TABLE I. Simulation results for the coexistence densities and polydispersities. The reduced density is defined as $\rho^* = \rho/\rho_{CP}$ and the polydispersity as the normalized standard deviation $s = \sqrt{(\langle h^2 \rangle / \langle h \rangle^2 - 1)}$, where $\langle h \rangle$ is the average height of the shifted cylinders and ρ_{CP} is the close packed density for a system of aligned cylinders of height $\langle h \rangle$.

| Activity distribution width (ν^*) | Coexistence densities, ρ^* | | | | | | | |
|---|---------------------------------|-----------------------|-----------------------------------|-----------|-----------|-----------|-----------|-----------|
| | N | Sm | N | Col | Sm | Cr | Sm | Col |
| 0.0000 | 0.460(4) | 0.472(4) ^a | | | 0.620(10) | 0.650(15) | | |
| 0.0050 | 0.462(4) | 0.472(4) | | | 0.610(10) | 0.640(15) | | |
| 0.0100 | 0.470(4) | 0.480(4) | | | | | 0.585(10) | 0.615(15) |
| 0.0150 | 0.485(8) | 0.495(8) | | | | | 0.575(10) | 0.605(15) |
| 0.0175 | 0.502(8) | 0.520(8) | | | | | 0.570(10) | 0.600(15) |
| 0.0200 | | | 0.580(15) | 0.620(15) | | | | |
| 0.0210 | | | 0.585(15) | 0.625(15) | | | | |
| | | | Coexistence polydispersities, s | | | | | |
| 0.0000 | 0.000(0) | 0.000(0) | | | 0.000(0) | 0.000(0) | | |
| 0.0050 | 0.074(1) | 0.074(1) | | | 0.068(1) | 0.072(1) | | |
| 0.0100 | 0.110(1) | 0.110(1) | | | | | 0.105(2) | 0.114(2) |
| 0.0150 | 0.142(2) | 0.142(2) | | | | | 0.150(2) | 0.157(2) |
| 0.0175 | 0.165(2) | 0.165(2) | | | | | 0.172(2) | 0.179(2) |
| 0.0200 | | | 0.212(4) | 0.213(4) | | | | |
| 0.0210 | | | 0.235(4) | 0.235(4) | | | | |

^aData taken from Ref. 9.

not observed. Above this terminal value, there is a first order transition from the nematic to the columnar phase.

Fractionation is not observed at either the N–Sm or N–Col transitions, at least away from the terminal polydispersity (or N–Sm–Col triple point). Thus as a nematic phase is compressed, it undergoes a transition to either a smectic phase or a columnar phase, depending on the extent of polydispersity, in which the composition is unchanged (see Fig. 4). However, this is not the case for the Sm–Col transition. Here, the composition distribution is always narrower in the smectic phase than in the columnar phase (see Figs. 3 and 4 and Table I). We note that, although the predicted coexistence densities are relatively low, this feature of the phase behavior is correctly predicted by the density-functional theory of Bohle *et al.*⁸ We have not studied the detailed phase behavior or the composition distributions in the vicinity

of the N–Sm–Col triple point; rather, we are interested in the general behavior over a range of polydispersities and an estimate for the terminal polydispersity above which a smectic phase will not be observed. The behavior of the system very close to the terminal polydispersity is not clear. On the low polydispersity side of the terminal polydispersity, we would expect the nematic phase to coexist with a smectic phase with the same composition distribution (i.e., $s_N = s_{Sm}$). This smectic phase would coexist with a columnar phase in which the polydispersity was slightly larger (i.e., $s_{Col} > s_{Sm}$). However, just above the triple point, we would expect a nematic phase to coexist with a columnar phase with the same polydispersity (i.e., $s_N = s_{Col}$). Presumably, at the triple point we would observe that the smectic phase coexists with a columnar phase of equal polydispersity. An investigation to locate this point would be computationally demanding and so we shall not dwell on this point.

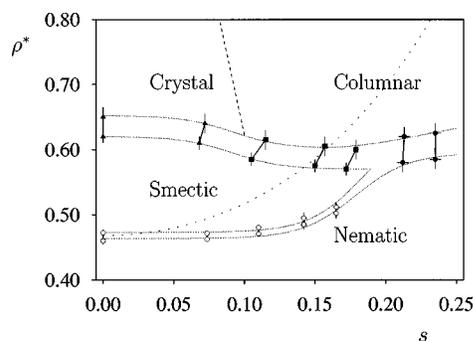


FIG. 4. The phase behaviour of polydisperse spherocylinders in the limit of infinite aspect ratio. The coexistence densities are determined from isobaric semigrand ensemble Monte Carlo simulations. The symbols indicate the (○) N–Sm, (▲) Sm–Cr, (■) Sm–Col, and (●) N–Col transitions and the coexisting phases are joined by heavy solid lines. The dotted lines indicate the approximate phase boundaries and are intended as a guide to the eye only. The dashed line (---) is an intuitive estimate of the Cr–Col transition and (· · ·) gives the position of the N–Sm transition from the bifurcation analysis of Sluckin (see text).

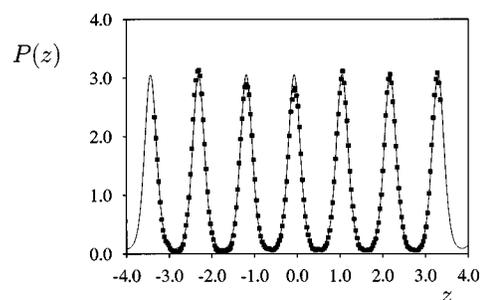


FIG. 5. The translational distribution, $P(z)$, for the smectic phase of a monodisperse system of shifted cylinders at a density just above the N–Sm transition ($\rho^* = 0.48$). Here, $P(z)$ is defined as the average of the number of particles located in a slab between $z - \frac{1}{2}\delta z$ and $z + \frac{1}{2}\delta z$, divided by the number expected in this slab in the absence of any translational ordering. Note that, as the distribution is not sharp but broadened, the layer structure can accommodate a narrow range of particle lengths. Thus for a weakly polydisperse system, we do not expect the location of the N–Sm transition to change.

The transition between the crystal and columnar phases is difficult to study using simulation techniques. At such high densities, single particle moves of more than a percent or so of the particle dimensions are nearly always rejected and so the particles cannot diffuse away from their initial sites. Multiple particle moves, such as shifting entire columns in one trial, are also ineffective, since these almost certainly result in an overlap. However, we have attempted to obtain an estimate for the location of the transition between these phases. To do so, we have performed semigrand canonical simulations at state points just above the transition densities from either the nematic or smectic phase, depending on the polydispersity. In each case, two initial perfectly aligned structures were used, a crystal and a columnar, constructed by randomly shifting columns in the crystal up and down to destroy the layer structure. These were allowed to equilibrate and the structures of the resulting phases compared. For systems with high polydispersity ($s > 0.15$), the columnar phase was found to be mechanically stable. In contrast, for low polydispersity ($s = 0.00, 0.08$) the crystal was found to be the preferred state. For the intermediate region ($s \approx 0.10$), neither the crystal nor the columnar could unambiguously be determined as the stable phase. However, given the relatively large change in the standard deviation of the composition distribution at transition with the smectic (see Fig. 4 and Table I), it seems intuitively reasonable that the columnar phase is more stable than the crystal, since the crystal would not favor a wider composition distribution whereas the columnar phase would. Clearly, we cannot hope to accurately determine the position of the transition line between the columnar and the crystal using computer simulation as the density is further increased. However, we can make some intuitive suggestions about the slope of this line. In the monodisperse limit, the crystal phase is more favorable than the columnar because small fluctuations in the positions and orientations of the particles will tend to stabilize the layered structure of the crystal. Indeed, this is corroborated by our observation that a columnar phase is not stable with respect to the crystal for a monodisperse system. In contrast, in the limit of high density, any polydispersity in the heights of the shifted cylinders will disrupt the crystal and so it seems reasonable that the columnar phase will be stable for densities near to the close packed density. We also expect that the destabilization of the crystal would become more prevalent as the polydispersity is increased. This intuitively implies that the transition boundary between these phases should be such that the location of the Cr-Col transition decreases with increasing polydispersity; this is indicated in Fig. 4. We note that this intuitive view is opposite to the behavior proposed by Bohle *et al.*⁸ In their phase diagram, for large polydispersities ($0.27 > s > 0.15$), the crystal is present above the columnar. However, for such high polydispersities, the smectic phase is destabilized with respect to the columnar. It therefore seems reasonable that the crystal should also be destabilized with respect to the columnar, since the distribution of lengths which do not fit into the 1D smectic structure cannot fit into the 3D crystal structure, since this involves ordering along the same direction as in the smectic.

Finally, we note that the terminal polydispersity above

which the smectic phase is not stable is lowered from the value of $s = 0.30$ predicted by Sluckin⁶ to a value of $s = 0.18$. Sluckin's estimate was obtained by determining the density range over which the smectic is stable as a function of polydispersity. This region was taken to have the nematic as a lower bound and, as an upper bound, the close packing density for a 2D fluid. As noted by Sluckin, we observe from the simulation results that this upper bound is a clear overestimation, since we find that the transition to the columnar phase is reduced from $\rho^* = 1.0$ to $\rho^* \approx 0.60$ – 0.65 . Indeed, if this revised value for the upper bound is used together with the average value of the density at the N-Sm transition for a monodisperse system determined by Polson and Frenkel,⁹ then Sluckin's analysis leads to a much more reasonable terminal polydispersity of $s \approx 0.15$ – 0.17 . It appears, therefore, that the effect of the polydispersity on the N-Sm transition was actually overestimated by Sluckin, but is in fair qualitative agreement with our simulation results (see also Fig. 4). The major difference appears to be that, in the phase diagram determined by the simulations, the N-Sm transition starts to be shifted to higher densities only after the polydispersity is increased past a value of $s \approx 0.08$, whereas in the theory, the transition density increases as soon as polydispersity is introduced. As discussed earlier, this feature arises because of the reasonably broad translational distribution function in the smectic phase of the monodisperse system, which is able to accommodate a weakly polydisperse distribution of particles (see Fig. 5).

IV. CONCLUSIONS

We have shown that computer simulation techniques can be used to study the phase behavior of polydisperse colloidal liquid crystals. The rodlike colloids are approximated by a hard spherocylinder in the Onsager limit of infinite aspect ratio. The use of such a model is feasible by applying a scaling argument which changes the shape of the particle but gives it finite volume. The phase behavior observed as a function of polydispersity is in semiquantitative agreement with density-functional theory. Thus the smectic phase is observed to be gradually squeezed out of the phase diagram with increasing polydispersity. However, the transition densities predicted by density-functional theory seem to be rather low compared to those observed in the simulations. We qualitatively explain the destruction of the smectic phase by considering the translational distribution function in the monodisperse smectic system. As this is reasonably broad rather than sharp, the N-Sm transition is not affected until the polydispersity is fairly large ($s \approx 0.08$). Below this value the phase behavior and the locations of the transitions are essentially unchanged from those observed for the monodisperse system. We find that the maximum polydispersity above which the smectic phase is no longer stable is $s \approx 0.18$.

ACKNOWLEDGMENTS

The work of the FOM Institute is part of the research program of FOM (Stichting Fundamenteel Onderzoek der Materie) and is supported by the NWO (Nederlandse Organi-

satie voor Wetenschappelijk Onderzoek). M.A.B. acknowledges the financial support of the EU through the Marie Curie TMR Fellowship programme. We are grateful to R. Blaak and E. Trizac for careful readings of the manuscript.

- ¹L. Onsager, Ann. (N.Y.) Acad. Sci. **51**, 627 (1949).
- ²D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants, Nature (London) **332**, 822 (1988).
- ³P. G. Bolhuis and D. Frenkel, J. Chem. Phys. **106**, 666 (1997).
- ⁴S. C. McGrother, D. C. Williamson, and G. Jackson, J. Chem. Phys. **104**, 6755 (1996).
- ⁵G. J. Vroege and H. N. W. Lekkerkerker, Rep. Prog. Phys. **55**, 1241 (1992).
- ⁶T. J. Sluckin, Liq. Cryst. **6**, 111 (1989).
- ⁷A. Stroobants, Phys. Rev. Lett. **69**, 2388 (1992).
- ⁸A. M. Bohle, R. Holyst, and T. Vilgis, Phys. Rev. Lett. **76**, 1396 (1996).
- ⁹J. M. Polson and D. Frenkel, Phys. Rev. E **56**, 6260 (1997).
- ¹⁰A. Poniewierski, Phys. Rev. A **45**, 5605 (1992).
- ¹¹Y. Martinez-Raton, R. van Roij, J. A. Cuesta, and B. M. Mulder (in preparation).
- ¹²A. Poniewierski and R. Holyst, Phys. Rev. A **41**, 6871 (1990).
- ¹³D. A. Kofke and E. D. Glandt, J. Chem. Phys. **87**, 4881 (1987).
- ¹⁴P. G. Bolhuis and D. A. Kofke, Phys. Rev. E **54**, 634 (1996).
- ¹⁵M. P. Allen and D. J. Tildesley, *The Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ¹⁶M. R. Stapleton, D. J. Tildesley, T. J. Sluckin, and N. Quirke, J. Phys. Chem. **92**, 4788 (1988).
- ¹⁷B. Widom, J. Chem. Phys. **39**, 2808 (1963).
- ¹⁸We note that we performed additional simulations for a monodisperse system in the vicinity of the N–Sm and Sm–Cr transitions. We find that the crystal is stable at $\rho^*=0.65$, below the Sm–Cr transition determined in Ref. 3; however, the equation of state in Ref. 3 indicates that the crystal may be stable as low as $\rho^*=0.62$. We therefore take $\rho^*=0.65$ to be a coexistence density for the crystal in the monodisperse system and obtain a reasonable estimate for the corresponding value in the smectic phase from the equation of state (see Table I).