Entropy-driven demixing in binary hard-core mixtures:
From hard spherocylinders towards hard spheres

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We present a computer simulation study of a binary mixture of hard spherocylinders with different diameters ($D_1 < D_2$) and the same lengths ($L_1 = L_2 = L$). We first study a mixture of spherocylinders with lengths $L = 15D_2$ and $D_1 = 0$, which can be regarded as a mixture of rodlike colloids and ideal needles. We find clearly an entropy-driven isotropic-isotropic (I-I) demixing transition in this mixture. In addition, we study a mixture of spherocylinders with diameter ratio $D_1/D_2 = 0.1$ and we investigated the I-I demixing transition as a function of the length L of the particles. We observe a stable I-I demixing for all values of L in the range of $3 \leq L/D_2 \leq 15$, but we could not reach the limit $L = 0$, i.e., the hard-sphere mixture with diameter ratio of 0.1. Striking agreement is found for $L/D_2 = 15$ with the results that follow from the second virial theory for infinitely elongated rods. For $L/D_2 = 2$, we did not find a demixing transition till a total packing fraction of $\eta = 0.581$, which is higher than the packing fraction at which freezing occurs for a pure system of thick rods. Thus this result and the extrapolation of our finite-L data to $L = 0$ gives us a fingerprint that the fluid-fluid demixing transition in the binary hard-sphere mixture with a diameter ratio of 0.1 is metastable with respect to freezing or does not exist at all at densities below close packing. [S1063-651X(97)07310-8]

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I. INTRODUCTION

One of the most intriguing aspects of mixtures is the possibility of a spontaneous transition from a mixed to a demixed state. Such demixing transitions have been observed in binary alloys and also in complex fluids, as, e.g., in oil-water mixtures. Traditionally, such transitions have been explained on the basis of relatively unfavorable interaction energies between unlike particles, as, e.g., described by the Bragg-Williams theory for solutions and the Flory-Huggins theory for polymers. However, an interesting and longstanding question is whether a demixing transition can also be observed in a mixture in which potential energy does not play a role. In a hard-core mixture, for instance, the total potential energy of the system vanishes, as only nonoverlapping configurations contribute to the configurational integral. In that case only entropic contributions are left to the free energy, and phase separation can only occur in such an athermal fluid if demixing results in an increase of the entropy. The main contribution to the entropy of mixing of a binary mixture comes from the entropy of mixing of an ideal mixture, given by $S_{id}(x) = -Nk_B[x \ln x + (1-x)\ln(1-x)]$, where x denotes the number fraction of one component and N the number of particles. It follows from the convexity of this function that phase separation always results in a decrease of $S_{id}(x)$. This would imply that one would never observe a demixing transition in a hard-core mixture. Also the intuitive notion that entropy is related to the disorder of the system suggests that a mixed system should have a higher entropy than a demixed one at the same density and energy.

The simplest example of a well-studied mixture is the binary hard-sphere mixture. The Ornstein-Zernike (OZ)

equations of this system were theoretically analyzed in 1964 by Lebowitz and Rowlinson, who concluded that the homogeneous fluid phase is stable with respect to demixing, regardless of the diameter ratio, composition, or pressure [1]. These conclusions, which are based on the Percus-Yevick (PY) closure of the OZ equations, were supported by other theoretical studies [2] and by computer simulations [3–7], and do agree with our intuitive notion of entropy. However, in the early 1990s Biben and Hansen provided evidence for a spinodal instability if the diameter ratio is more extreme than 1:5 [8]. Their conclusion is based on the Rogers-Young closure of the OZ equations, which is supposed to be more accurate than the PY closure. They identified the *depletion effect*—known from colloid-polymer mixtures [10,11]—as the demixing mechanism. Essentially the same instability was also reported by Lekkerkerker and Stroobants [9]. The depletion mechanism in a binary hard-sphere fluid is based on the gain of free volume for the small spheres due to clustering of the larger spheres. To be more precise, in the case that two large spheres are far apart from each other the small spheres are excluded from a depletion layer with thickness $\sigma_1/2$ around the large spheres, where σ_1 is the diameter of the small spheres. When the two large spheres are brought into contact, the depletion zones overlap and the volume accessible to the small particles increases. The resulting gain in entropy of the small particles is the driving force that makes the large particles cluster. Apart from this entropic picture of depletion effect, there is also the kinetic picture in which the ''sea'' of small particles generates an effective attractive interaction between two large spheres, if the latter are so close together that no small particle fits in between. This unbalanced osmotic attraction is then responsible for the liquid-vapor like demixing into a phase rich in large spheres and

one rich in small spheres [9]. For completeness, we mention that the effective potential or depletion force between two large spheres due to a solvent of small spheres has been calculated theoretically by Mao *et al.* [12], and computed in a simulation by Biben *et al.* [13]. Using this effective pair potential in a Monte Carlo study a tendency for phase separation is found. However, this phase separation is different from that found in simple liquids, since it results in a rapid growth of huge clusters and subsequently a very slow relaxation of the clusters. We finally also note that the demixing transition in the binary hard-sphere fluid has also been found by Rosenfeld, within a self-consistent density functional theory [14].

Experiments, however, suggest that the demixing transition in sufficiently asymmetric binary hard-sphere mixtures is strongly coupled to the freezing transition, and that the actual coexistence is that between a crystalline phase of primarily big spheres and a fluid phase with primarily small spheres [17,18]. These results are supported by recent density functional calculations, which show a fluid-solid phase separation in binary hard-sphere mixtures [15,16]. Whether or not there is a (metastable) fluid-fluid spinodal in binary hard-sphere mixtures remains an open question.

Computer simulation of phase separation in a mixture of very dissimilar spheres is difficult because of slow equilibration. The numerical difficulties are less severe for lattice models. Indeed, a purely entropic demixing transition has been shown by computer simulation of a lattice model of a binary mixture of hard parallel cubes, if the diameter ratio of the cubes is sufficiently large [19,20]. Recent density functional calculations on this system have shown similar results [21]. Thus these results show that a demixing transition can be driven by entropic effects alone. It is, however, unclear to what extent this demixing transition is enhanced by the lattice and by the discrete orientations of the cubes. It is thus desirable and interesting to consider an off-lattice system of hard-core particles.

An example of such an off-lattice mixture that has been studied by computer simulation is the mixture of spherical colloids and rodlike polymers [22]. The colloids are represented by hard spheres with a diameter σ, and the rodlike particles by infinitesimally thin needles of length L. A demixing transition was found for $L/\sigma > 0.3$. Also, in computer simulations of a colloid-polymer mixture, where the colloids are modeled as hard spheres and the polymers as ideal lattice chains, a demixing transition was found [23]. However, in both cases the polymers are ideal and do not interact with each other.

In this paper we present a computer simulation study of binary mixtures of hard spherocylinders with different diameters ($D_1 < D_2$) and the same lengths ($L_1 = L_2 = L$). Within the Onsager theory for hard rods, Sear and Jackson showed for $D_1 = 0$ and $L/D_2 \rightarrow \infty$ that isotropic-isotropic (I-I) demixing can preempt the isotropic-nematic (I-N) transition [24]. Our simulations of a system of $L/D_2 = 15$ and $D_1 = 0$ clearly show an I-I demixing transition and thus confirm the results of Sear and Jackson. For a finite diameter D_1, van Roij and Mulder estimated recently that this I-I demixing in thick-thin mixtures of hard rods is stable with respect to the I-N transition, as long as $D_1/D_2 > 0.2$ [25]. Again in these cases, the depletion effect is identified as the demixing

mechanism. It is important to realize that these theoretical results only apply to hard rods in the limit of extreme elongation. In the present simulation study we consider the I-I demixing transition as a function of the length L of the particles, for a diameter ratio $D_1/D_2 = 0.1$. Since the theoretical results are supposed to be exact for $L/D_2 \rightarrow \infty$, we expect to reproduce the theoretical results closely for sufficiently large—but finite—values of L/D_2. For $L = 0$ the system reduces to the binary hard-sphere mixture with diameter ratio $D_1/D_2 = 0.1$. Although we could not reach the limit $L = 0$ (with $D_1/D_2 = 0.1$), we did find stable I-I demixing for all values of L considered, ranging from $3 \leqslant L/D_2 \leqslant 15$. To our knowledge, this is the first evidence of a fluid-fluid demixing transition driven by entropy alone in an off-lattice system of nonideal hard-core particles. Moreover, extrapolating our finite-L data to $L = 0$ gives us a fingerprint that the fluid-fluid demixing spinodal in the binary hard-sphere system is metastable with respect to freezing.

II. COMPUTER SIMULATIONS

In order to determine the coexistence curve of the two demixed phases directly, we carried out Gibbs ensemble Monte Carlo simulations. In this method, the two coexisting phases are simulated in separate simulation boxes which may exchange volume and particles at a given temperature in order to fulfill the phase equilibrium requirements of equal pressures and chemical potentials. During the simulation ordinary Monte Carlo steps are performed in both phases in order to equilibrate both systems internally. However, the acceptance ratio for exchanging a large particle is small in a dense system of small particles, as a large particle will almost always overlap with one of the small particles. In order to speed up equilibration, we used collective particle moves that employed a generalization of the configurational-bias Monte Carlo scheme of Refs. [26, 27]. In this approach, we first choose randomly a large spherocylinder in one box and try to insert this particle at a random position in the other box. When the particle overlaps with another large spherocylinder the trial move is immediately rejected. If no such an overlap is found, the small spherocylinders overlapping with the large spherocylinder in its new position are removed and are then moved to the volume vacated by the large spherocylinder in the first box using a generalization of the Rosenbluth sampling. The trial move is then accepted with a probability determined by the ratio of the Rosenbluth weights of the new and old configurations. For more technical details, we refer the reader to the Appendix. In our simulations, we performed four types of trial moves.

(1) Random displacement and rotation of a particle in one of the boxes.

(2) Small particle exchange between the boxes.

(3) Large particle exchange between the boxes using configurational bias Monte Carlo method.

(4) Volume exchange between the boxes.

In each simulation, we measure the number fraction x of the thick spherocylinders in both boxes, given by $x = N/(N + M)$, where N and M are, respectively, the number of the thick and thin particles in that box. In addition, the numerical value of the pressure was determined by virtual volume changes. This method is based on the fact that the pressure is
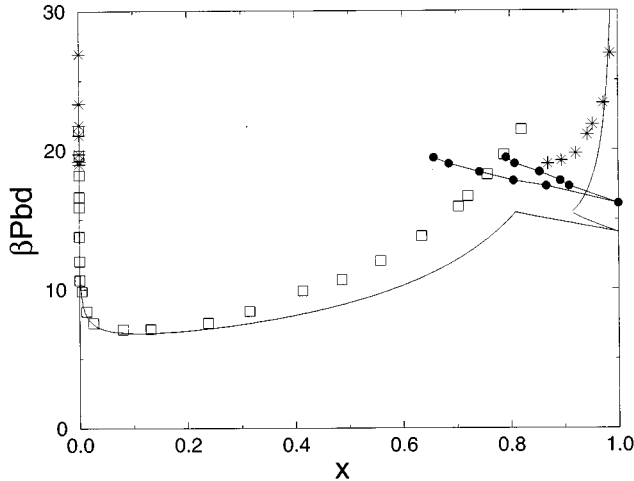
FIG. 1. The reduced pressure βPbd versus the number fraction x for a mixture of hard spherocylinders with lengths $L_1 = L_2 = 15D_2$ and diameter $D_1 = 0$. The open squares denote the I-I demixing, the full circles and the stars the I-N demixing. The full lines are the theoretical binodals taken from Ref. [29].

TABLE I. The reduced pressure βPbd and the number fraction of the thick particles x of the critical points predicted by theory (Ref. [25]) and estimated from the simulations for different diameter ratios $d = D_2/D_1$ and length $L = 15D_2$.

	Theory		Simulation	
d	βPbd	x	βPbd	x
∞	6.75	0.1111	7.1	0.11
10	14.6854	0.1873	15.96	0.1953

minus the volume derivative of the Helmholtz free energy, which can be related to the acceptance ratio of virtual volume changes as described in Ref. [28].

Most runs consisted of $10^4 - 10^5$ cycles per particle per thermodynamic state point. In each cycle, we attempt a displacement and rotation of a particle in one of the boxes, and we try to exchange volume and a particle between the boxes. For the particle exchange we select with equal probability the box where a particle is removed and the species of the particle that will be transferred. The system size varies from about 100 to 200 thick spherocylinders with 400–800 thin spherocylinders.

III. RESULTS

A. $L = 15D_2$, $D_1/D_2 = 0$ and 0.1

The first set of Gibbs ensemble Monte Carlo simulations was performed on a binary mixture of hard spherocylinders of lengths $L_1 = L_2 = L = 15D_2$ with $D_1 = 0$. Here, and in the sequel of this paper, we use D_2 as unit length. In Fig. 1, we show the resulting dimensionless pressure βPbd of the coexisting phases as a function of the number fraction x. Here $b = \pi L_1^2 D_1/4$, $d = D_2/D_1$, and $\beta = 1/k_B T$ with k_B Boltzmann's constant and T the temperature. We observe clearly a demixing transition in the isotropic phase for pressures $\beta Pbd > 7$. Phase coexistence is found between an isotropic phase of primarily thin spherocylinders ($x \simeq 0$) and an isotropic phase with a mixture of thick and thin spherocylinders ($0.1 \leq x \leq 0.8$). From Table I, we see that the critical point as estimated from the simulation agrees very well with the one that followed from the second virial theory for infinitely elongated rods of Ref. [25]. This good agreement is mainly due to the fact that $x \approx 0.11$ corresponds to only a small fraction of particles with a finite aspect ratio, while most of the particles have diameter $D_1 = 0$ and hence satisfy $L/D_1 \rightarrow \infty$. Another reason for this good agreement is that this transition occurs at low densities, so that the higher-

order virial coefficients of the thicker rods are not that important. In the same figure we also plotted the theoretical binodals obtained from Ref. [29], which is based on previous work. The deviation of the theoretical binodal and the simulated coexistence data at higher pressures at $x > 0.2$ can be attributed to the third- and higher-order virial coefficients of the thicker rods, which are neglected in the theory.

In order to investigate if this I-I demixing transition is stable with respect to the isotropic-nematic transition, we also performed Gibbs ensemble simulations starting from a box in which the particles are aligned and a box with an isotropic configuration. We traced the I-N coexistence curve starting from the pure thick system ($x = 1$) and gradually adding more and more thin rods. For a pure system of thick spherocylinders, the I-N coexistence is found to be at a pressure of $\beta Pbd = 16.15$, which is slightly lower than the value of $\beta Pbd = 17.141$ in Ref. [22] obtained by integration of the Gibbs-Duhem equation that describes the L/D dependence (instead of the temperature dependence) of the pressure at which the two phases coexist. The addition of small particles to this pure system of thick spherocylinders leads to an I-N phase separation at higher pressures. Phase coexistence is found between an isotropic phase and a nematic phase with a slight tendency of the large particles to be in the nematic phase and a slight tendency of the small particles to be in the isotropic phase. However, the phase coexistence region is narrow. At higher pressures, we find that this I-N transition intervenes in the I-I demixing transition, giving rise to an I-I-N triple point, at which two isotropic phases (one with primarily thin rods and the other with a mixture of thick and thin) coexist with a nematic phase of primarily thick rods. At even higher pressures, we find a wide phase coexistence region between an isotropic and a nematic phase.

The simulation results of Ref. [22] show that a first-order phase transition occurs from a nematic to a smectic phase for a pure system of thick rods ($x = 1$) with $L/D = 15$ at a density of about $\rho^* = 0.5$, where $\rho^* = \rho/\rho_{CP}$ and $\rho_{CP} = 2/(\sqrt{2} + \sqrt{3}L/D)$. We only performed simulations up to a density of $\rho^* = 0.4484$ for a system consisting of thick rods ($x = 1$), which corresponds with a pressure $\beta Pbd = 30.16$, so we did not consider the smectic phase in any detail.

Next we performed simulations of a spherocylinder mixture with both diameters finite. We set $D_1/D_2 = 0.1$ and kept $L/D_2 = 15$. In Fig. 2, we plot again the resulting coexistence pressure versus the number fraction. From Table I, we see that we find again good agreement between the critical point estimated in the simulations and calculated in the theory of Ref. [25]. We again investigated if this I-I demixing transition is stable with respect to the I-N transition. Starting from a pure system of thick spherocylinders, we find a broader
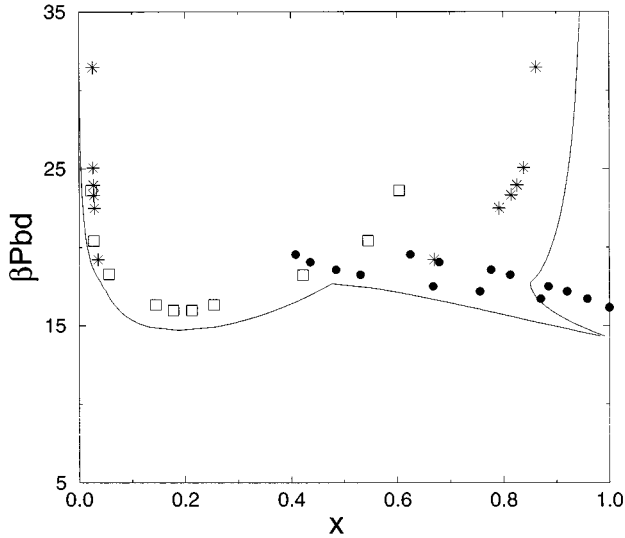
FIG. 2. The reduced pressure βPbd versus the number fraction x for a mixture of hard spherocylinders with lengths $L_1=L_2=15D_2$ and diameter $D_1=0.1D_2$. The open squares denote the I-I demixing, the full circles and the stars the I-N demixing. The full lines are the theoretical binodals taken from Ref. [29].

FIG. 3. The reduced pressure βPbd versus the number fraction x for a mixture of hard spherocylinders with varying lengths $L_1=L_2$ and diameter $D_1=0.1D_2$.

I-N demixing region at higher pressures, when we add thin spherocylinders. Again, we found a triple point at which two isotropic phases coexist with a nematic phase, and a wide I-N coexistence region for even higher pressures.

B. Towards hard spheres . . .

We showed above that we have been able to find a purely entropy-driven fluid-fluid (I-I) demixing transition that preempts the I-N transition. The question immediately arises why this transition is found in simulations of hard-spherocylinder mixtures, while it is still not found in computer simulations of hard-sphere mixtures. One of the reasons is that the fluid-fluid demixing transition for spherocylinder mixtures occurs at much lower packing fractions than for hard-sphere mixtures. To illustrate this, we compare three different theoretical estimates for the total packing fraction η at the critical point of the fluid-fluid demixing transition of a hard-sphere mixture with a diameter ratio of $D_1/D_2=0.1$ with the corresponding simulated value in the hard-spherocylinder mixture of $L/D_2=15$. The total packing fraction $\eta=\eta_1+\eta_2$ is the sum of the packing fractions of the thinner and thicker species. For the hard spheres we have $\eta\simeq0.47$ [8], 0.53 [9], and 0.37 [14], which is to be contrasted with $\eta=0.0736$ for the spherocylinders. Another reason why simulations of hard-sphere mixtures are difficult is the low number fraction x at which the demixing transition takes place. The same three hard-sphere theories give for the critical x the values $x\simeq0.02$ [8], 0.0056 [9], and 0.002 [14], while the spherocylinders show $x=0.2$. A low number fraction means that a huge amount of small particles is needed for each large particle. Computer simulations of very asymmetric mixtures are difficult as all the computer time will be spent on moving the small particles around, while displacement of a large particle is hardly accepted in a dense system of small particles.
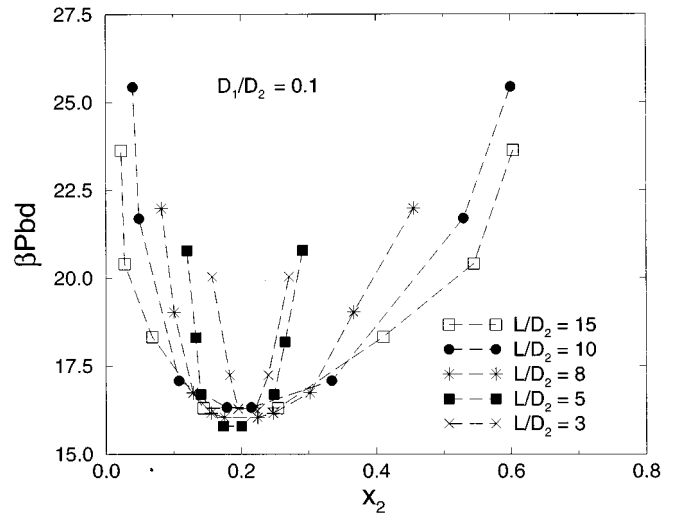
In order to make a connection with the hard-sphere mixtures, we considered for fixed $D_1/D_2=0.1$ a number of decreasing lengths $L/D_2=10,8,5,3$. In Fig. 3, we show the results for the I-I demixing for the different values of L/D_2. We see that the phase coexistence region becomes smaller with decreasing L. A second and third virial theory of a hard-rod mixture with discrete orientations (Zwanzig model [30]) does not reproduce this narrowing of the I-I coexistence region, which remains therefore unexplained. The number fraction of the thick spherocylinders x and the reduced pressure of the critical point remain more or less the same for all lengths considered. In Fig. 4, we plot the packing fractions η_2 of the thick spherocylinders versus the packing fractions η_1 of the thin spherocylinders for the estimated critical

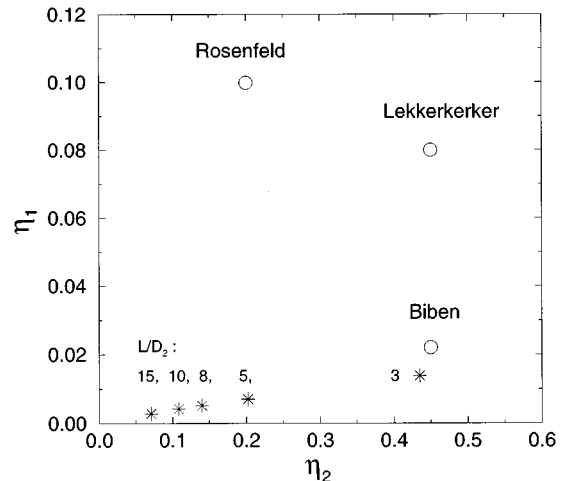FIG. 4. The packing fraction η_1 of the thin spherocylinders versus the packing fraction η_2 of the thick spherocylinders for the estimated critical points of the I-I demixing transition in a mixture of hard spherocylinders with varying lengths $L_1=L_2=L$ and $D_1=0.1D_2$ (stars) and the theoretical predicted critical points for the hard-sphere mixtures with $D_1=0.1D_2$ taken from Refs. [8, 9, 14].

TABLE II. The packing fractions of the thin particles η_1, the thick particles η_2, and the total packing fraction $\eta = \eta_1 + \eta_2$, at which the critical point of the I-I demixing transition is estimated from the simulations for a mixture of hard spherocylinders with lengths $L_1 = L_2 = L$ and diameter ratio of $D_1/D_2 = 0.1$. We also tabulated for comparison the packing fractions at which a certain type of phase transition occurs from the isotropic phase for a pure fluid of thick spherocylinders ($x = 1$) for different values of L/D_2.

	Critical point			Pure fluid	
L/D_2	η_1	η_2	$\eta_1 + \eta_2$	η	Type of transition
15	0.0028	0.0708	0.0736	0.1777	isotropic-nematic
10	0.0042	0.1084	0.1126		isotropic-nematic
8	0.0052	0.1398	0.1450		isotropic-nematic
5	0.0079	0.2131	0.2210	0.4532	isotropic-nematic
3	0.0138	0.4349	0.4487	0.5115	isotropic-solid
2				0.532366	isotropic-solid
0				0.47	isotropic-solid

points of the I-I demixing transition for the various lengths. We also plot the three above mentioned theoretically predicted critical densities for the hard-sphere mixtures with $D_1/D_2 = 0.1$ [8,9,14]. We see that the packing fraction at which the critical point is estimated increases enormously when we decrease the length of the spherocylinders. In Table II, we compare the critical packing fractions of the spherocylinders with those at which a *pure* fluid of thick spherocylinders will undergo a phase transition. The latter data are taken from Ref. [22]. For $L/D_2 = 2$, we found no phase separation below a total packing fraction of $\eta = \eta_1 + \eta_2 = 0.581$. From Table II, we can see that the isotropic-solid transition for a pure system of thick spherocylinders with $L/D = 2$ occurs already at a lower packing fraction. This might be a fingerprint that the isotropic-isotropic demixing transition becomes metastable with respect to the freezing transition, or does not exist at all at densities below close packing. A possible reason for the apparent absence of a spinodal instability might be the narrowing of the I-I coexistence region with decreasing length of the spherocylinders as discussed above. Unfortunately, equilibration problems prevented us from increasing the packing fraction even more, so that we could not investigate whether a metastable isotropic-isotropic demixing transition exists above the freezing transition. Also, slow equilibration prevented us from decreasing the length-to-diameter ratio even more, so that the hard-sphere mixture ($L = 0$) could not be studied directly—as expected.

In summary, we present the results of a computer simulation study of binary mixtures of hard spherocylinders with different diameters ($D_1 < D_2$) and the same lengths ($L_1 = L_2 = L$). We find clearly an I-I demixing transition in a mixture of spherocylinders with lengths $L_1 = L_2 = 15D_2$, and $D_1 = 0$ or $D_1 = 0.1D_2$. Good agreement is found with the results obtained from a second virial theory for infinitely long rods. To our knowledge, this is the first evidence of a fluid-fluid demixing transition driven by entropy alone in an off-lattice system of nonideal hard-core particles. In addition, we investigated the I-I demixing transition as a function of the length L and diameter ratio $D_1/D_2 = 0.1$. We find a stable I-I demixing for all values of L in the range of $3 \leq L/D_2 \leq 15$, but we could not reach the limit $L = 0$, i.e., the hard-sphere mixture with diameter ratio of 0.1. For $L/D_2 = 2$, we could not observe a demixing transition below a total

packing fraction of $\eta = 0.581$, which is above the packing fraction of the freezing transition of a pure mixture of thick rods. Slow equilibration prevented us from increasing the packing fraction even more and from decreasing the length-to-diameter ratio. A similar slowing down of the dynamics has been found in simulations of the hard-sphere mixture by Biben *et al.* [13]. Thus extrapolating our finite-L data to $L = 0$ gives us a fingerprint that the fluid-fluid demixing transition in the binary hard-sphere mixture with a diameter ratio of 0.1 is metastable with respect to freezing, or does not exist at all at densities below close packing.

APPENDIX

In Gibbs ensemble Monte Carlo simulations, the two coexisting phases are simulated in separate simulation boxes and exchange of particles in the boxes are essential for obtaining equal chemical potentials. However, in a dense system of thin spherocylinders, random insertion of a thick spherocylinder is difficult. To overcome this problem, we remove the thin particles that hinder the insertion of the thick particle and reinsert them into the space vacated by the thick particle. The algorithm for exchanging a thick spherocylinder goes as follows.

(1) Choose first one of the boxes with equal probability.

(2) Choose randomly one of the thick spherocylinders and insert this in the other box at a random position and with a random orientation.

(3) Check if the thick particle at its new position overlaps with another thick particle. If there is such an overlap this move will immediately be rejected.

(4) If there is no such overlap, check which of the thin particles have an overlap with the thick particle at its new position.

(5) The thin particles that have an overlap with the thick particle at its new position, say m particles, will be inserted in the volume that will become free in the old box of the thick spherocylinder, where we have removed the thick particle.

The insertion of the m thin particles into the free volume is not simple since the probability of random insertion of m particles in a restricted volume is small. We therefore used a method similar to the one proposed by Biben for hard-sphere mixtures [27]. We will describe the method below. When we have already inserted $i-1$ small particles, we will attempt to insert the ith particle.

(1) Choose first k random orientations for the ith particle, say $\hat{\omega}_i(j)$ and $(j=1,\ldots,k)$.

(2) Define for each orientation $\hat{\omega}_i(j)$ a rectangular box, centered around the center of the removed thick particle. The diameter of each box is given by the absolute value of the components of the vector $\vec{R}=L_2\hat{\Omega}_2+L_1\hat{\omega}_i(j)+(D_1+D_2)(1,1,1)$, where $\hat{\Omega}_2$ is the old orientation of the removed thick particle, and where the axes of the simulation box were chosen as basis vectors. We then choose for each orientation $\hat{\omega}_i(j)$ a random position $\vec{r}_i(j)$ for the thin particle in the corresponding box. We then check if this thin particle has indeed overlap with the removed thick particle. If not, we try a new $\vec{r}_i(j)$ until the overlap condition is satisfied.

(3) We now compute the Boltzmann factor $\exp[-\beta u(\vec{r}_i(j),\hat{\omega}_i(j))]$ for all these trial insertions by checking if there is an overlap with any of the other thick and thin particles and the $i-1$ particles that are already inserted. For hard-core particles, this Boltzmann factor is either zero in the case of overlap, or one when there is no overlap with other particles.

(4) One of the trial insertions, say position $\vec{r}_i$ with orientation $\hat{\omega}_i$, is now selected with a probability

$$P_{\vec{r}_i,\hat{\omega}_i}=\frac{\exp[-\beta u(\vec{r}_i,\hat{\omega}_i)]}{Z_{\{\vec{r}_i,\hat{\omega}_i\}}}, \quad (A1)$$

with

$$Z_{\{\vec{r}_i,\hat{\omega}_i\}}=\sum_{j=1}^{k}\exp[-\beta u(\vec{r}_j,\hat{\omega}_j)]. \quad (A2)$$

The subscript $\{\vec{r}_i,\hat{\omega}_i\}$ means that the selected position $\vec{r}_i$ and orientation $\hat{\omega}_i$ are one of the k trial insertions. The ith thin particle will be inserted at this position and the corresponding partial ''Rosenbluth weight'' w_i will be stored, where

$$w_i=\frac{Z_{\{\vec{r}_i,\hat{\omega}_i\}}}{k}. \quad (A3)$$

(5) These steps will be repeated until we have inserted all m particles.

(6) For the old configuration, a similar procedure is used in order to calculate the old Rosenbluth factor. We again try to add the m overlapping particles in the space that is vacated by moving the thick particle from its new position to its old position. When we have already inserted $i-1$ thin particles, we will attempt to insert the ith particle. In order to do that, we select $k-1$ trial directions for the thin particle. The kth trial direction will be the original configuration of the thin particle. We store the corresponding partial ''Rosenbluth weight'' and we se-

lect the original configuration of the thin particle. We repeat this until we have added all m particles.

In order to use this method to transfer a thick particle from one box to the other box in a Gibbs ensemble simulation, we impose detailed balance on the Monte Carlo scheme. This implies that in equilibrium, the rate at which thick particles are transferred from one box to the other equals the reverse rate.

Let us first consider the partition function of a system of N_I thick particles in a box with a fixed configuration of M_I thin particles and a volume V_I.

$$Q(N_I,V_I,T)=\frac{V_I^{N_I}}{\mathcal{V}^{N_I}N_I!}\int ds_I^{N_I}\exp[-\beta U(\Gamma_I)], \quad (A4)$$

where $\mathcal{V}$ is the thermal volume [31], and $U(\Gamma_I)$ is the external potential of N_I thick particles and the M_I thin particles in box I interacting with each other by a hard-core potential. Note that we used scaled coordinates s^{N_I} and that the configurational integral of the thin particles is neglected as the configuration of the thin particles is fixed. However, the thick particles do interact with the thin particles and thus the external potential $U(\Gamma_I)$ depends on the configuration of the thin particles. If we now consider $N_{II}=N-N_I$ particles in another box with a fixed configuration of M_{II} thin particles and a volume $V_{II}=V-V_I$, the partition function of the two boxes becomes

$$Q(N_I,N_{II},V_I,V_{II},T)=\frac{V_I^{N_I}(V-V_I)^{N-N_I}}{\mathcal{V}^N N_I!(N-N_I)!}\int ds_I^{N_I}$$
$$\times\exp[-\beta U(\Gamma_I)]\int ds_{II}^{N_{II}}$$
$$\times\exp[-\beta U(\Gamma_{II})]. \quad (A5)$$

Now we consider the case that the two systems can exchange particles in such a way that the total number of particles distributed over the two boxes remains constant, and that the volumes V_I and V_{II} can change in such a way that the total volume $V=V_I+V_{II}$ remains constant. In this case, we have to consider all possible distributions of the N particles over the two boxes and we have to integrate over the volume V_I, which gives for the partition function

$$Q(N,V,T)=\sum_{N_I=0}^{N}\int_0^V dV_I\frac{V_I^{N_I}(V-V_I)^{N-N_I}}{\mathcal{V}^N N_I!(N-N_I)!}\int ds_I^{N_I}$$
$$\times\exp[-\beta U(\Gamma_I)]\int ds_{II}^{N-N_I}$$
$$\times\exp[-\beta U(\Gamma_{II})]. \quad (A6)$$

It follows now that the probability to find a configuration with N_I particles in box I with a volume of V_I and position $s_I^{N_I}$ and $N-N_I$ particles in box II with a volume $V-V_I$ with positions $s_{II}^{N-N_I}$ is given by

$$\mathcal{N}(N_{\mathrm{I}},V_{\mathrm{I}},T,s_{\mathrm{I}}^{N_{\mathrm{I}}},s_{\mathrm{II}}^{N-N_{\mathrm{I}}})\sim\frac{V_{\mathrm{I}}^{N_{\mathrm{I}}}(V-V_{\mathrm{I}})^{N-N_{\mathrm{I}}}}{N_{\mathrm{I}}!(N-N_{\mathrm{I}})!}$$
$$\times\exp[-\beta U(\Gamma_{\mathrm{I}})]\exp[-\beta U(\Gamma_{\mathrm{II}})].$$
$$(\mathrm{A7})$$

For the configurational-bias method, we used the detailed balance condition [26] to determine the probability of acceptance

$$\mathcal{N}(o)\pi(o\rightarrow n)=\mathcal{N}(n)\pi(n\rightarrow o),\qquad(\mathrm{A8})$$

where $\mathcal{N}(o)$ and $\mathcal{N}(n)$ are, respectively, the probabilities that the system is in the original conformation o and in the new conformation n. The transition matrix $\pi(o\rightarrow n)$ is equal to the probability to generate a trial move from o to n times the probability to accept this trial move, i.e., $\pi(o\rightarrow n) = \alpha(o\rightarrow n)\times\mathrm{acc}(o\rightarrow n)$. In order to satisfy the detailed balance condition one can use the Metropolis scheme with the acceptance rule:

$$\mathrm{acc}(o\rightarrow n)=\min\left(1,\frac{\mathcal{N}(n)\alpha(n\rightarrow o)}{\mathcal{N}(o)\alpha(o\rightarrow n)}\right).\qquad(\mathrm{A9})$$

Let us now assume that we want to move a thick spherocylinder from box I to box II. The overlapping m thin spherocylinders in box II are now moved to box I. In order to compute the acceptance rule, it is convenient to split the particles in box I in particles that will keep their position and orientation going from the old to the new configuration, say N_{I} thick particles and M_{I} thin particles, and in particles that will be moved, so one thick particle and m thin particles. In box II, we find N_{II} thick particles and M_{II} thin particles that will keep their position and orientation and again one thick particle and m thin particles that will be moved. We illustrate this in Fig. 5 for clarity. Note that the number of thick and thin particles in the old configuration of box I is equal to $N_{\mathrm{I}}+1$ and M_{I} and that the number of thick and thin particles in the old configuration of box II is N_{II} and $M_{\mathrm{II}}+m$. Using Eq. (A7), we find for the probability of the new configuration
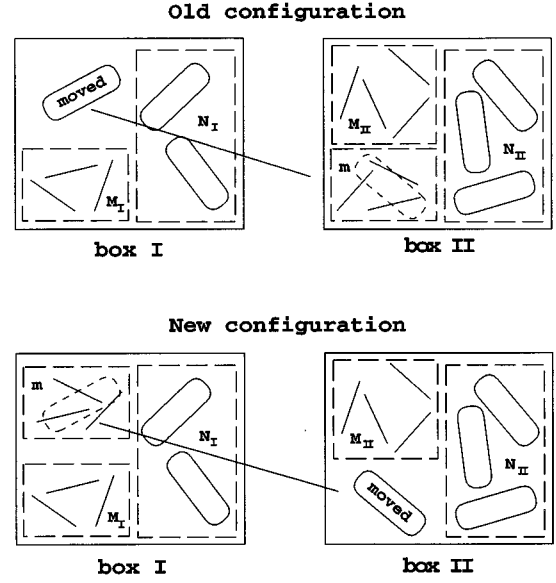

FIG. 5. Schematic picture of the configurational-bias Monte Carlo method for moving a thick spherocylinder from box I to box II in a Gibbs ensemble simulation.

$$\mathcal{N}(n)=\frac{V_{\mathrm{I}}^{N_{\mathrm{I}}}(V-V_{\mathrm{I}})^{N-N_{\mathrm{I}}}}{(N_{\mathrm{I}})!(N-N_{\mathrm{I}})!}\exp[-\beta U(\Gamma_{\mathrm{I}}(n))]$$
$$\times\exp[-\beta U(\Gamma_{\mathrm{II}}(n))]\qquad(\mathrm{A10})$$

while the old configuration has a probability of

$$\mathcal{N}(o)=\frac{V_{\mathrm{I}}^{N_{\mathrm{I}}+1}(V-V_{\mathrm{I}})^{N-N_{\mathrm{I}}-1}}{(N_{\mathrm{I}}+1)!(N-N_{\mathrm{I}}-1)!}\exp[-\beta U(\Gamma_{\mathrm{I}}(o))]$$
$$\times\exp[-\beta U(\Gamma_{\mathrm{II}}(o))].\qquad(\mathrm{A11})$$

For the ratio of the two probabilities, we find

$$\frac{\mathcal{N}(n)}{\mathcal{N}(o)}=\frac{(V-V_{\mathrm{I}})(N_{\mathrm{I}}+1)}{V\mathrm{I}(N-N_{\mathrm{I}})}$$
$$\times\frac{\exp[-\beta U(\Gamma_{\mathrm{I}}(n))]\exp[-\beta U(\Gamma_{\mathrm{II}}(n))]}{\exp[-\beta U(\Gamma_{\mathrm{I}}(o))]\exp[-\beta U(\Gamma_{\mathrm{II}}(o))]}.$$
$$(\mathrm{A12})$$

The Boltzmann factor for the new configuration can now be written as follows:

$$\exp[-\beta U(\Gamma_{\mathrm{I}}(n))]\exp[-\beta U(\Gamma_{\mathrm{II}}(n))]=\exp\{-\beta[U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})]\}$$
$$\times\exp\{-\beta[U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})$$
$$+U(\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})]\},\qquad(\mathrm{A13})$$

where $U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})$ and $U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})$ are, respectively, the external potential of a cluster of N_{I} thick particles and a cluster of M_{I} thin particles interacting with each other by a hard-core potential. The external potential of a cluster of N_{I} thick particles with a cluster of M_{I} thin particles is denoted by $U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})$, while $U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})$ is the external potential of the moved thickparticle in box II with a cluster of N_{II} thick particles. The superscript denotes in which box the particles are. The Boltzmann factor for the old configuration is given by

$$\exp[-\beta U(\Gamma_{\mathrm{I}}(o))]\exp[-\beta U(\Gamma_{\mathrm{II}}(o))]=\exp\{-\beta[U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})]\}$$

$$\times\exp\{-\beta[U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})$$

$$+U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})]\}. \tag{A14}$$

We now find for the ratio of the two probabilities

$$\frac{\mathcal{N}(n)}{\mathcal{N}(o)}=\frac{(V-V_{\mathrm{I}})(N_{\mathrm{I}}+1)}{V_{\mathrm{I}}(N-N_{\mathrm{I}})}\frac{\exp\{-\beta[U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})]\}}{\exp\{-\beta[U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})]\}}$$

$$\times\frac{\exp\{-\beta[U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})]\}}{\exp\{-\beta[U(\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})]\}}. \tag{A15}$$

The probability to generate the new configuration starting from the old configuration is given by the probability to insert the m thin particles in box I in the space vacated by moving the thick particle.

$$\alpha(o\rightarrow n)=\prod_{i=1}^{m}\frac{\exp[-\beta u(\vec{r}_i,\hat{\omega}_i)]}{Z_{\{\vec{r}_i,\hat{\omega}_i\}}}$$

$$=\frac{\Pi_{i=1}^{m}\exp\left\{-\beta\left[U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m_i}^{\mathrm{I}})+U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m_i}^{\mathrm{I}})+\sum_{j=1}^{i-1}U(\Gamma_{m_j}^{\mathrm{I}},\Gamma_{m_i}^{\mathrm{I}})\right]\right\}}{k^m\mathcal{W}}$$

$$=\frac{\exp\{-\beta[U(\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}},\Gamma_{m}^{\mathrm{I}})+U(\Gamma_{m}^{\mathrm{I}})]\}}{k^m\mathcal{W}_n}, \tag{A16}$$

where $\mathcal{W}_n=\Pi_{i=1}^{m}w_i^n$, i.e., the total Rosenbluth weight of the m particles in the new configuration.

The probability to generate the old configuration starting from the new configuration is given by the probability to insert the m thin particles in box II in the space vacated by the thick particle.

$$\alpha(n\rightarrow o)=\frac{\exp\{-\beta[U(\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}},\Gamma_{m}^{\mathrm{II}})+U(\Gamma_{m}^{\mathrm{II}})]\}}{k^m\mathcal{W}_o} \tag{A17}$$

and we find for the acceptance rule

$$\mathrm{acc}(o\rightarrow n)=\min\left(1,\frac{(V-V_{\mathrm{I}})(N_{\mathrm{I}}+1)\mathcal{W}_n}{V_{\mathrm{I}}(N-N_{\mathrm{I}})\mathcal{W}_o}\frac{\exp\{-\beta[U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{N_{\mathrm{II}}}^{\mathrm{II}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{II}},\Gamma_{M_{\mathrm{II}}}^{\mathrm{II}})]\}}{\exp\{-\beta[U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{N_{\mathrm{I}}}^{\mathrm{I}})+U(\Gamma_{\mathrm{moved}}^{\mathrm{I}},\Gamma_{M_{\mathrm{I}}}^{\mathrm{I}})]\}}\right). \tag{A18}$$

Note that the number of thin particles does not occur in the acceptance rule, as the thin particles cannot be chosen freely once a thick particle, that will be moved, is selected. The acceptance rule depends only on the potential energy of the thick particle with all the particles that will keep their positions and orientations in boxes I and II.

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