Evidence for Entropy-Driven Demixing in Hard-Core Fluids

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We report the first observation, by computer simulation, of a purely entropic demixing transition in a three-dimensional binary hard-core mixture. This transition is observed in a mixture of large and small cubes. We also find evidence for demixing in other hard-core fluids and, in the case of an athermal polymer solution, we observe a purely entropy-driven polymer collapse. For the study of both the hard-core demixing and polymer collapse, it was essential to use novel collective Monte Carlo moves.

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The theoretical study of the causes of phase separation in binary mixtures is one of the oldest in statistical thermodynamics. In fact, for simple liquid mixtures [1] the first microscopic theories date back to van der Waals, while for polymer solutions the Flory-Huggins theory plays a similar role. In view of the almost overwhelming amount of experimental and theoretical work that has since been spent on the study of liquid mixtures, one might think that the factors that are responsible for demixing are, by now, well understood. Surprisingly, this is not the case. In particular, it is still an unresolved question if demixing can be driven by entropic effects alone.

Of course, from thermodynamics we know that phase separation will take place in a system at constant volume and temperature T, if this results in lowering the Helmholtz free energy $A = E - TS$. There are two ways to lower the free energy of a system: One is to lower the energy E; the other is to increase the entropy S. Most theories of fluid mixtures are based on the assumption that demixing results in a lowering of E and, at the same time, an *increase* of $-TS$. However, if we consider *athermal* mixtures, i.e., mixtures of particles that have only excluded volume interactions, then phase separation can only occur if demixing results in an *increase* of the entropy. One trivial way in which this can happen is if the hard-core interactions in the mixture are "nonadditive," i.e., $\sigma_{AB} > (\sigma_{AA} + \sigma_{BB})/2$, where σ_{ij} denotes the distance of closest approach of particles of type i and j. In fact, the demixing transition in nonadditive hard-sphere mixtures is well established and has been studied extensively [2–4].

More interesting is the case of *additive* hard-core mixtures, i.e., $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$, and here the situation is more confused. For additive hard-sphere mixtures, we have two conflicting predictions. In 1964 Lebowitz and Rowlinson [5] showed that the (approximate) Percus-Yevick integral equation for hard-sphere mixtures predicts no fluid-fluid phase separation for any size ratio or density. Indeed, simulations of hard-sphere mixtures have thus far not provided any evidence for fluid-fluid demixing [6–10]. However, more recently Biben and Hansen [11], using the so-called Rogers-Young integral equation for hard-sphere mixtures, found evidence for a spinodal instability in a fluid mixture of spheres of sufficiently dissimilar sizes. Similar predictions have subsequently been made with other approximations [12]. Clearly, it would be interesting if the existence of a demixing transition could be unambiguously demonstrated in a computer simulation of an additive, hard-core mixture.

In this Letter we present the results of such a simulation study. The model that we consider is a mixture of large and small cubes on a lattice. This model is clearly additive: It differs from hard-core lattice models studied previously [13] in that it can fill space at close packing both in the mixed and in the pure phases. Hence there is no trivial volume-driven demixing. In our simulation we considered mixtures of cubes with diameter ratios (i.e., ratios of the edge lengths) of 2 or 3. The diameter of each cube corresponds to an even number of lattice spacings. We performed grand canonical Monte Carlo (GCMC) simulations [14] where the independent variables were the fugacities of the large and the small cubes. In order to speed up equilibration, we used collective particle moves that employed a generalization of the configurational-bias Monte Carlo scheme of Ref. [15]. In this approach, the large particle was moved to a random trial position. Typically several small particles would occupy this region in space. These particles were then moved to the volume vacated by the large particle, and inserted using Rosenbluth sampling [16]. The trial move was then accepted with a probability determined by the ratio of the Rosenbluth weights of the new and the old configuration. Of course, a trial move would be rejected immediately if it resulted in overlap of two or more large particles. In addition to the moves in which we displace particles, we also perform trial moves in which we add or remove a large or small particle and trial moves that attempt to change the identity of a particle (large to small, or vice versa).

In Fig. 1, the fugacity of the large cubes is plotted versus the volume fraction of the large cubes for a mix-

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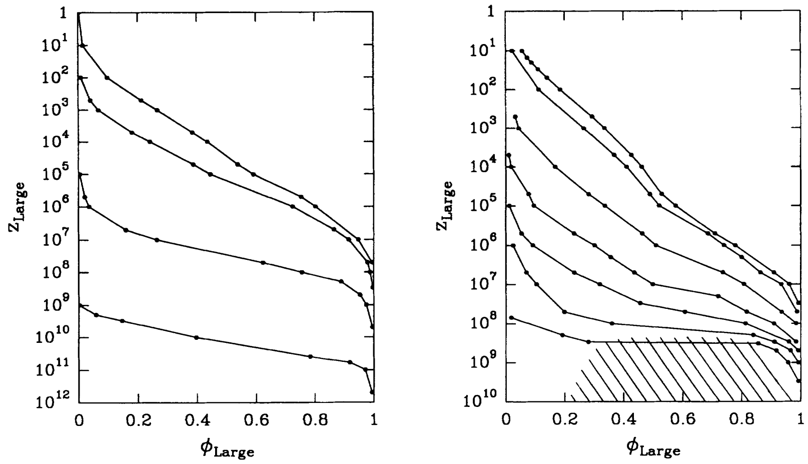

FIG. 1. Equation of state of a binary mixture of large and small cubes on a lattice. The figure shows the dependence of the fugacity z on volume fraction ϕ for the large cubes at different values of the fugacity of the small particles. The left half of the figure shows the results for a binary mixture of cubes with diameter ratio 2 ($z_{\rm small} = 100, 10^3, 10^4$, and 10^5, from top to bottom) and the right half shows the results for diameter ratio 3 ($z_{\rm small} = 0$, 100, 500, 10^3, 1.5×10^3, 2×10^3, and 5×10^3, from top to bottom). The shaded area indicates the approximate location of the two-phase region.

ture of cubes with diameter ratio 2 or 3. For a diameter ratio of 3, we observe that, as we increase the fugacity of the solvent (i.e., of the small particles), the slope of the curves of constant solvent fugacity tends to zero at the inflection point. For still higher solvent fugacity, we find *two* different volume fractions for the large cubes for the *same* fugacity for the large particles. This is exactly what we expect for a demixing transition. When we take this into account we can sketch the demixing region, as shown in Fig. 1. In both phases, the cubes are equally likely to be found on all lattice sites (i.e., there is no sublattice ordering). Hence, the present phase transition corresponds most closely to liquid-liquid coexistence in an off-lattice system. As simulations in the demixing region are very time consuming, we have not attempted to locate the binodal curve more accurately. For a diameter ratio of 2, we find no evidence for a similar flattening of the isofugacity curves. Thus we find no evidence for a demixing transition in the latter system. However, if instead of cubes we consider platelets, with a comparable volume ($6 \times 6 \times 2$, instead of $4 \times 4 \times 4$ in units of the lattice spacings), we again observe demixing. This is plausible for the following reason: When two large particles are brought into contact, the volume accessible to the small particles increases by an amount that is proportional to the diameter of the small particles and the area of contact of the large particles. The resulting gain in entropy of the solvent is the driving force that makes the large particles cluster. The larger the surface-to-volume ratio of the large particles, the stronger is the tendency to demix. The above argument should apply not only to rigid particles, such as rods and disks, but also to flexible particles such as linear polymers.

We therefore also looked for entropic demixing in an athermal polymer solution. In fact, in this case we did not study the demixing directly. Rather, we looked for a closely related phenomenon, namely, the solvent-induced collapse of an isolated polymer. This collapse signals the transition from the good-solvent to the poor-solvent regime. There are compelling theoretical arguments to assume that a polymer collapse must occur in an athermal polymer solution, when the polymer-solvent interaction is *nonadditive* [13]. In order to investigate if such a collapse can occur in an "additive" athermal polymer solution, we performed simulations of a single hard-core polymer in a solvent of cubes, where the size of the cubic monomers of the polymer was the same as the size of the solvent molecules, namely, $2 \times 2 \times 2$ in units of the lattice spacings. For the equilibration of

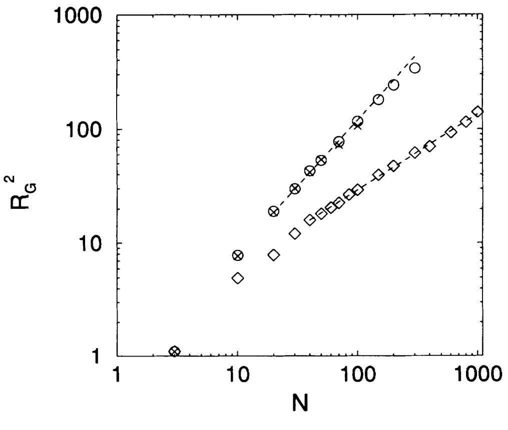

FIG. 2. The mean square of the radius of gyration $\langle R_g^2 \rangle$ of a polymer with cubic monomers with and without solvent versus the number of segments. Average solvent volume fraction: 0.0 (open circles), 0.3 (crosses), and 0.7 (open diamonds). The dashed lines are a guide to the eye and have a slope of 0.58 (polymer in a good solvent) and 1/3 ("Euclidean" scaling).

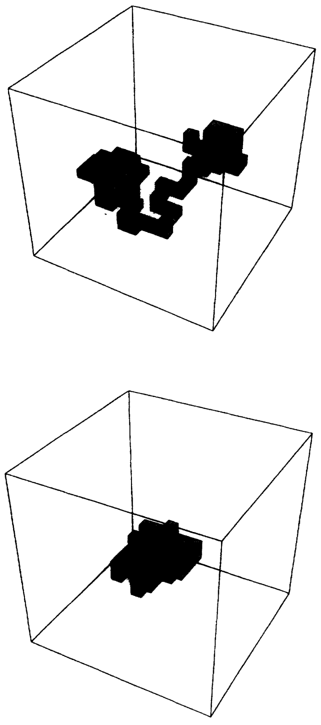

FIG. 3. Snapshot of conformation of a hard-core lattice polymer ($N = 100$) *without* hard-core solvent (top) and in a solution of hard-core monomers with a volume fraction of 0.7 (bottom). Note the solvent-induced collapse.

the polymer it was essential to use a novel Monte Carlo scheme. In this scheme, we included collective Monte Carlo moves that allowed us to carry out conformational changes on any subsection (interior or terminal) of the polymer chain [17].

We performed simulations of a single polymer at different values of the chemical potential of the solvent. We find that the square of the radius of gyration R_g^2 scales as $N^{2\nu}$, where N denotes the number of monomeric units in the polymer (see Fig. 2). For low solvent fugacities that correspond with solvent volume fractions of 0 and about 0.3, we find $\nu = 0.56 \pm 0.02$, which corresponds to the case of a polymer in a good solvent ($\nu \approx 0.58$). In contrast, for a higher value of the solvent fugacity (corresponding to an average solvent volume fraction of 0.7), we find $\nu = 0.34 \pm 0.02$. For a collapsed polymer we expect "Euclidean" scaling: $\nu = 1/3$. Hence, by increasing the solvent fugacity in this athermal polymer solution, we can make the polymer collapse. Figure 3 illustrates the very drastic change in the polymer shape with increasing solvent fugacity. It is important to note that the collapse of the polymer chain in a solvent is, in a sense, counterintuitive. If one considers the polymer chain, there is a large amount of entropy lost by the polymer. However, the increase in entropy of the solvent molecules overrides this apparent loss. The observation of such a solvent-induced polymer collapse immediately implies the existence of a demixing transition in this athermal polymer solution. The present simulations support existing theoretical predictions of the existence of entropy-driven demixing in polymer blends and solutions [18,19]. Although simulations of athermal polymer solutions have been reported before [20], the present result is to our knowledge the first unambiguous demonstration of a purely entropic polymer collapse.

In summary, we have presented the first observation of a demixing transition in an additive hard-core lattice mixture and we have found a purely entropy-driven collapse in a lattice model of an athermal polymer in a hard-core solvent.

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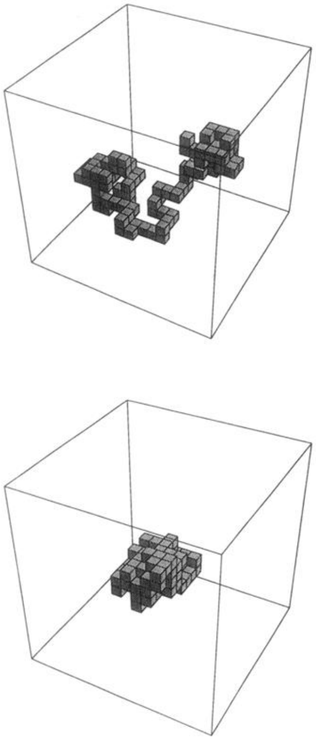

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