Phase separation in two-dimensional additive mixtures

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We study two-dimensional binary mixtures of parallel hard squares as well as of disks. A recent cluster algorithm allows us to establish an entropic demixing transition between a homogeneously packed fluid phase and a demixed phase of a practically close-packed aggregate of large squares surrounded by a fluid of small squares. [S1063-651X(99)00803-X]

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Binary mixtures of impenetrable objects pose one of the important, and lively, problems of statistical physics [1]. For many years it has been discussed whether objects of different types l (large) and s (small) would remain homogeneously mixed as the number of these objects per unit volume increases. Particularly interesting cases concern so-called additive mixtures [2], such as hard spheres with radii r_l and r_s or cubes with length d_l and d_s. The problem of phase separation in binary mixtures is of importance as the simplest model for colloids. It has been a meeting ground for many different theoretical, computational, and experimental approaches. As an example, the well-known closure approximations, as well as virial expansions, both of very great importance for the theory of simple liquids [3], have been brought to bear on this problem, often with contradictory results [1].

In this paper we discuss additive systems in two dimensions, parallel hard squares and also hard disks. Previous work on the lattice version of the present system was done in [4], where no transition was found. Cuesta [5] has studied the fluid-fluid phase separation transition within the Rosenfeld fundamental measure approximation [7]. For hard squares, such a transition is predicted not to occur [5]. We present in this paper full-scale off lattice simulations of such systems. For hard squares, we show that instead of the fluid-fluid transition, a fluid-solid phase separation transition appears for sufficiently dissimilar sizes. For hard *disks*, we expect an analogous transition for extremely dissimilar sizes that must satisfy $r_s/r_l<1/100$ for packing fractions $\eta_l=\eta_s<0.3$.

Monte Carlo simulations have long been performed on these systems [4]. They were recently boosted by a new cluster algorithm [8,9], which allows thermalization of systems orders of magnitude larger than previously possible. The algorithm sidesteps a problem readily apparent in Fig. 1, which shows a typical configuration in the homogeneous phase. There, each large square is surrounded by many small objects. Trial moves of large squares will, therefore, be rejected in the overwhelming majority of cases, and the algorithm will get stuck quickly. Our algorithm rather swaps large patches of the configuration in a way that preserves detailed balance [8–10]. The algorithm is applicable for arbitrary shapes and in any dimension, and in continuous space as well as on the lattice. Most importantly, the method works even for objects very dissimilar in size as long as the total density is not too high.

We are able to converge our simulations of two-dimensional parallel squares for total packing fractions $\eta=\eta_s+\eta_l$, which do not sensibly exceed the percolating threshold η_{perc}. As in three dimensions [9], we notice that η_{perc} depends very little on the ratio $R=d_s/d_l\leqslant 1$. We find $\eta_{perc}\simeq 0.5$. Figures 1 and 2 show snapshots of the simulations for 200 large squares and 20 000 small squares at equal composition ($\eta_s=\eta_l$) and total packing fractions $\eta=0.44$ and $\eta=0.60$, respectively. Evidently, Fig. 1 represents a homogeneous mixture. Following the classic method of Monte Carlo simulation [6], we monitor the phase of the system as we slowly increase the total packing fraction at constant composition $x=\eta_l/\eta$. At a certain η, the system becomes unstable. A compact solid of large particles appears, which is surrounded by a fluid of primarily small ones. The system shown in Fig. 2 consists of such a ''solid'' block of large

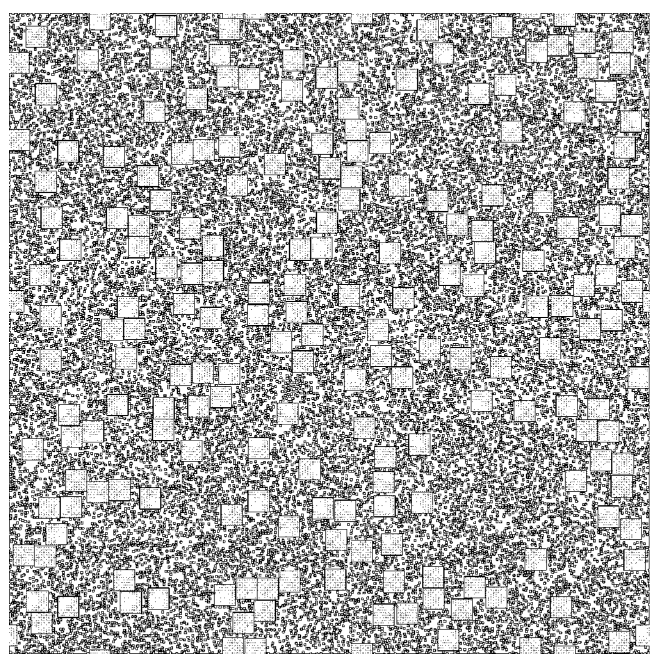

FIG. 1. Snapshot of 200 big squares ($d_l=1$) and 20 000 small squares ($d_s=0.1$) in a periodically continued box of size 30×30 (packing fractions $\eta_l=\eta_s=0.22$).

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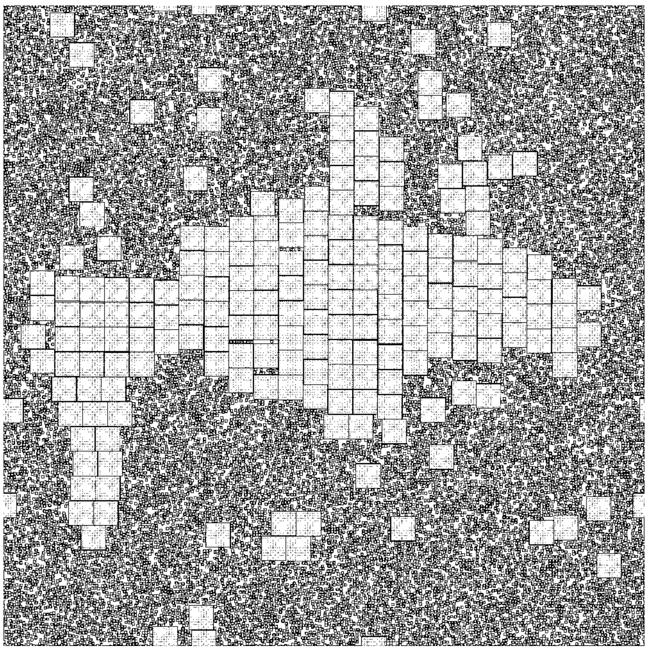

FIG. 2. Snapshot of 200 big squares ($d_l=1$) and 20 000 small squares ($d_2=0.1$) in a periodically continued box of size 26×26 (packing fractions $\eta_l=\eta_s=0.30$).

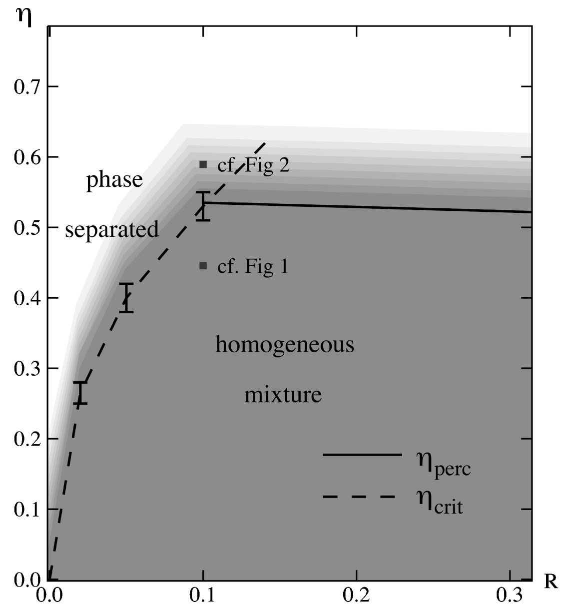

FIG. 3. Phases of the two-dimensional hard square system at equal composition $\eta_s=\eta_l$ (total packing fraction $\eta=\eta_s+\eta_l$ vs. $R=d_s/d_l$). The squares locate the parameters of the snapshots in Figs. 1 and 2. The region in which our algorithm performs excellently is shaded in gray.

squares surrounded by a fluid of small squares. In our opinion, these runs present direct evidence for a transition of the homogeneously mixed fluid into a (solid-fluid) phase.

In the simulations at $\eta=0.60$, we have slightly exceeded the percolation threshold η_{perc}. Therefore, the algorithm will swap patches, which usually comprise almost the whole system. This generates problems for large systems, and we have, e.g., been unable to converge (at $\eta=0.60$) a sample with $N_l=800$, $N_s=80\,000$. In contrast, the simulations at lower packing fractions converge extremely rapidly for arbitrary system size. We can summarize the situation for equal composition ($\eta_s=\eta_l$) by the diagram of Fig. 3: The gray area corresponds to the region of the diagram in which our algorithm performs extremely well. As mentioned, this region is delimited for the homogeneous system by the percolation threshold and by the appearance of high-density areas as a consequence of phase separation. We also studied the instability line as a function of the composition where we find that the critical packing fraction increases with the composition [$\eta_{\text{crit}}=0.49\pm 0.02$ $(x=0.3)$, 0.53 ± 0.02 $(x=0.5)$ and 0.60 ± 0.05 $(x=0.7)$ for $R=0.1$].

In our three-dimensional simulation [9], it was impossible to interpret the data by direct inspection, as in Fig. 1 and Fig. 2. We analyzed the transition, therefore, with the help of the integrated pair correlation function $G_{ll}(r)=4\pi\rho_l\int r'dr'g_{ll}(r')$ with $\rho_l=N_l/V$ the density of large particles [3]. We repeat the analysis in the two-dimensional case in order to stress the soundness of our procedure, which considers G_{ll} rather than the much noisier g_{ll}. $G_{ll}(r)$ determines the average number of large particles around a given large particle within a distance r. For the special case of parallel hard squares, we define $r=\max(\Delta x,\Delta y)$, where Δx and Δy are the two (periodically continued) lateral distances. With this definition, the distance of two large squares in contact is $r=d_l$ and $G_{ll}=\rho_l\int_{\max(|x|,|y|)<r}g_{ll}(x,y)dxdy$ with g_{ll} the usual pair correlation function [3]. In Fig. 4, one can see that the mixed system's G_{ll} has pulled away from the pure system's correlation function on all scales, showing that the large scale structure of the fluid has changed. The staircase pattern is a very clear indication of solid order. Finally, the rather large finite-size effects at large separation are easily explained since $G_{ll}(r)$ has to meet the curve of the corresponding monodisperse system with $\eta=\eta_l$ for half the box length. A similar analysis was used to establish the instability line in Fig. 3.

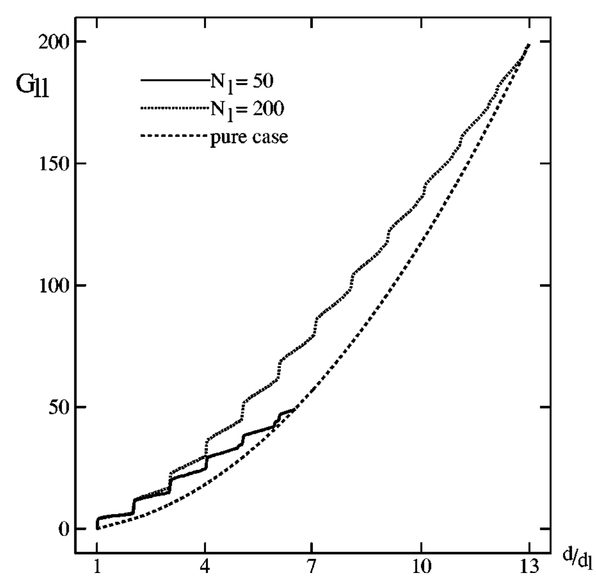

FIG. 4. Integrated two-point correlation functions for the dense system $\eta_l=\eta_s=0.30$ (cf. Fig. 2) for 50 and 200 large squares, respectively. $G_{ll}(r)$ directly counts the average number of large particles in a square of length $2r$ around a given large particle. The two curves are compared to the monodisperse system's correlation function.

A comparison of Fig. 4 with the data for the homogeneous mixture (cf. Fig. 1) at $\eta=0.44$ is very revealing. In the latter case (not shown), the difference between the mixed and the monodisperse system concerns mainly the region of small separation between the squares and would be unobservable on the scale of Fig. 4. The same observation was made in three dimensions. The effects at small separations r are already detectable by visual inspection of Fig. 1, since there are quite many ''bound'' pairs and triplets. We find that each large square has bound an average of 0.8 squares. This agrees very nicely with our observation in three dimensions, where we noticed the onset of the phase-separation instability as the additional binding was close to one.

We also performed simulations for mixtures of hard *disks*. Let us begin our discussion with an indirect heuristic argument, which connects transition parameters for squares and for disks (it supposes that the same type of transition appears). It has long been understood [2] that the overlap of excluded volumes entropically favors close contact of the large objects. The excluded volume (for a small square) around a big square consists in the area of the latter and a strip of width $d_s/2$ around it. Side-to-side contact between two squares leads to an overlap of excluded volume of the size $\Delta V_{\text{square}} \sim d_l \times d_s$. As the large objects touch, the volume available to the small particles and therefore their entropy increase. At the same time, contact of large objects *de*creases their contribution to the entropy of the complete system. The phase-separation transition appears when those two contributions compensate each other. As the decrease of entropy due to contact of large objects may be considered as independent of the ratio R of the size of the small and large objects and of the shape of objects, we may compare the increase of entropy due to larger available volume for small disks or squares. In fact, since the small particles' contribution to the entropy is $S \sim N_s \ln V_s$ (with V_s the available volume), one finds $\Delta S \sim (N_s/V)\Delta V_{\text{square}}$, and, therefore,

$$\Delta S_{\text{square}} \sim \eta_s d_l / d_s . \tag{1}$$

Repeating the same calculation for disks, we notice, of course, that the overlap of excluded volume $\Delta V_{\text{disk}} \sim \sqrt{r_s^3 r_l}$ and the number of concerned small disks are much smaller. This leads to

$$\Delta S_{\text{disk}} \sim \eta_s \sqrt{r_l / r_s}. \tag{2}$$

This order-of-magnitude argument tells us that (with a hard square transition at $d_s/d_l \sim 1/10$ for $\eta \simeq 0.5$) we can expect an analogous transition for disks at best for $r_s/r_l \sim 1/100$. Accordingly, our simulations for $r_s/r_l \gtrsim 1/100$ at $\eta=0.6$ have revealed no instability of the homogeneous phase. Even larger simulations at $r_s/r_l = 1/150$ (50 large and 1 125 000 small disks, $\eta=0.6$) did not converge, even though the additional binding has continuously increased in the course of a month-long simulation. In these simulations, the effective depletion potential between two large disks is very strong, but also extremely short-ranged. The Monte Carlo simulation of such ''golf-course'' potentials, where the interaction is felt in a tiny interval only, is of course extremely timeconsuming and often impossible.

In conclusion we have studied the problem of phase separation of two-dimensional systems (hard squares and hard disks) by direct Monte Carlo simulation. For hard squares, our Monte Carlo data leave little room to doubt a direct fluid to (solid fluid) transition. For hard disks, the stability of the homogeneous mixture seems established for any ''reasonable'' ratio of radii $r_s/r_l \gtrsim 1/100$. Our heuristic argument would, however, lead us to expect a transition for even more extreme ratios.

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