Elusiveness of Fluid-Fluid Demixing in Additive Hard-Core Mixtures

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The conjecture that when an additive hard-core mixture phase separates when one of the phases is spatially ordered, well supported by considerable evidence, is in contradiction with some simulations of a binary mixture of hard cubes on cubic lattices. By extending Rosenfeld's fundamental measure theory to lattice models we show that the phase behavior of this mixture is far more complex than simulations show, exhibiting regions of stability of several smectic, columnar, and solid phases, but no fluid-fluid demixing. A comparison with the simulations show that they are, in fact, compatible with a fluid-columnar demixing transition, thus bringing this model into the same demixing scheme as the rest of additive hard-core mixtures.

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The absence of a spinodal instability in the Percus-Yevick solution for additive mixtures of hard spheres ruled out for nearly 30 years the existence of demixing in this system [1]. That entropy-driven demixing is possible is evidenced by its appearance in nonadditive mixtures of particles [2–5]. But until 1991 [6], when the first signs of a spinodal instability were found by means of an integral equation theory, it was thought that additivity is insufficient to induce demixing. This first result was followed by an avalanche of theoretical [7–11], simulation [12–14], and experimental [15–18] results supporting the existence of demixing in binary mixtures of hard spheres when the large and small diameters are at least in the ratio 5 : 1. At the same time, it became clear that this demixing does not separate the system into two fluid phases, but at least one is always a crystal [10,11,13,14,16–18]. So the current scenario for binary hard-sphere demixing is no more a fluid-fluid one, but a fluid-solid one, or even (if the mixture is sufficiently asymmetric) a solid-solid one [13,14]. A binary mixture of parallel hard cubes, another additive hard-core mixture, also exhibits the same qualitative behavior [19–21].

Fluid-fluid demixing can, however, be found in nonadditive hard-sphere mixtures [22,23], as well as in mixtures of anisotropic hard particles [24], which are a particular case of nonadditive mixtures [25]. It is therefore very tempting to conjecture that nonadditivity is a requirement for a binary mixture of hard-core particles to exhibit fluid-fluid demixing. But, in an attempt to decide whether entropic fluid-fluid demixing can be observed in additive binary mixtures, Dijkstra and Frenkel performed some simulations on the (admittedly academic) model of hard cubes in a cubic lattice. According to these simulations, this kind of demixing occurs if the cube edges are at least in the ratio 3 : 1 [26]. The importance of this result (which justifies considering this rather academic model) is to disprove the above-mentioned conjecture and then to provide a model in which the mechanism for fluid-fluid demixing can be analyzed in order to determine whether it can also be observed in other more realistic additive mixtures.

The results of these simulations are, however, in frank contradiction with the predictions of Rosenfeld's fundamental measure theory for mixtures of parallel hard cubes in the continuum [20,21]. This notwithstanding, in this Letter we will show that the latter theory provides the correct picture. To this purpose we will extend fundamental measure theory to lattice models and apply it to the simulated mixture. We will show that the simulation results are, in fact, incompatible with a fluid-fluid demixing and that they are remarkably consistent with the phase behavior deduced from the theory.

The standard construction of a fundamental measure functional amounts to taking the following steps [27–29]: (i) decomposing the Mayer function into a sum of convolutions of one-particle ''measures''; (ii) defining a set of densities weighted with these measures and assuming that the local free-energy density is a function of them; (iii) determining the functional form of this function through the scaled particle assumption; (iv) forcing the exactness of the lowest order in the virial expansion of the direct correlation function; and (v) imposing dimensional reduction (i.e., the lower-dimensional functionals have to be recovered from the upper-dimensional ones by constraining the density to lie in a lower-dimensional space). There is some arbitrariness in the choice of the ''fundamental measures,'' step (i), and it can be shown that different choices reproduce different functionals proposed in the literature [27,30]. Once a set of measures has been selected, all the remaining steps go straightforward. Notice that it is not always possible to construct a fundamental measure functional because step (i) is not always achievable.

The difficulty to accomplish this program for a lattice model is that there is not a known scaled particle theory for such a system [31], so the process breaks down at step (iii). We have nevertheless been able to construct the functional

by exploiting an analogy with the system of parallel hard cubes [28,29]. The analogy is implied by the exact functional for a one-dimensional mixture of hard rods. For a single component mixture this functional has been derived several times, in different ways, in the literature [32–34]. However, extending it to mixtures seems more demanding, and, to the best of our knowledge, no one has ever reported this generalization. By following a similar procedure to that used by Vanderlick *et al.* for the continuum [35], we arrive at a free-energy functional whose excess (over the ideal gas) part can be written as

$$\beta\mathcal{F}_{\mathrm{ex}}[\{\rho_\alpha\}] = \sum_{x\in\mathbb{Z}} \mathcal{D}_k \phi^{(0)}(n^{(k)}(x)), \tag{1}$$

where β is the inverse temperature, $\phi^{(0)}(\eta) = \eta + (1-\eta)\ln(1-\eta)$ is the excess free energy of a zero-dimensional system [30], $n^{(k)}(x) = \sum_\alpha \sum_{x'\in\mathbb{Z}} \omega_\alpha^{(k)}(x-x')\rho_\alpha(x')$, with $k = 0, 1$, are weighted densities with weights $\omega_\alpha^{(k)}(x) = 1$ if $-\lfloor(\sigma_\alpha+1)/2\rfloor - k < x < \lfloor\sigma_\alpha/2\rfloor$ and 0 otherwise, σ_α being the diameter of the rod and $\rho_\alpha(x)$ the occupancy probability (density) of species α at point x, and, finally, $\mathcal{D}_k f(k) \equiv f(1) - f(0)$ is a difference operator acting on the weighted density index k. This is not the way in which this functional is normally written (for the monocomponent system) in the literature, but we have chosen to do it this way because this expression explicitly shows that (as it occurs for the continuum hard-rod model [28,29]) the one-dimensional excess free-energy functional can be obtained from the zero-dimensional one by applying a differential operator with respect to the particle sizes. Only in this case the differential operator is a difference operator instead, a consequence of the underlying lattice. For the system of parallel hard cubes, this zero-dimensional functional generates the d-dimensional one by successive applications of similar differential operators with respect to the size along every coordinate axis. In Ref. [28] it was proven that the functional so generated coincides with that obtained by accomplishing all the above described requirements, steps (i)–(v). Accordingly, for the equivalent lattice model we propose to generate the functional in a similar way, though this time using difference operators. Hence, the excess part will be given by

$$\beta\mathcal{F}_{\mathrm{ex}}[\{\rho_\alpha\}] = \sum_{\mathbf{x}\in\mathbb{Z}^d} \mathcal{D}_{\mathbf{k}} \phi^{(0)}(n^{(\mathbf{k})}(\mathbf{x})), \tag{2}$$

where now $\mathbf{k} \equiv (k_1, \ldots, k_d)$, $n^{(\mathbf{k})}(\mathbf{x})$ is the corresponding weighted function with weight $\omega_\alpha^{(\mathbf{k})}(\mathbf{x}) = \prod_{i=1}^d \omega_\alpha^{(k_i)}(x_i)$, and $\mathcal{D}_{\mathbf{k}} \equiv \prod_{i=1}^d \mathcal{D}_{k_i}$ denotes the same finite difference operator appearing in (1) but with respect to the particle sizes along every coordinate axis. This differentiation gives rise to a linear combination (with ± 1 coefficients) of the function $\phi^{(0)}(\eta)$ evaluated at the different weighted densities $n^{(\mathbf{k})}(\mathbf{x})$, according to the pattern

$$\mathcal{D}_{\mathbf{k}} \phi^{(0)}(n^{(\mathbf{k})}(\mathbf{x})) = \sum_{\mathbf{k}\in\{0,1\}^d} (-1)^{d-\sum_i k_i} \phi^{(0)}(n^{(\mathbf{k})}(\mathbf{x})).$$

A full account of the details of the theory can be found in Ref. [36].

We have checked that, indeed, this functional accomplishes the following items of the standard construction of a fundamental measure functional (see above): (i) a correct decomposition of the Mayer function as a sum of discrete convolutions of one-particle measures; (ii) an expression of the functional in terms of a set of densities weighted with these measures; (iv) the exact lowest order in the virial expansion of the direct correlation function; and (v) a consistent dimensional reduction to any lower dimension. Furthermore, this functional recovers, in the limit of vanishing lattice spacing, its continuum counterpart [28,29]. Also, this functional becomes exact in at least two cases: for the one-dimensional system [Eq. (1)] and for the ideal gas with site exclusion. As concerns step (iii), its presumed compatibility with the scaled particle theory may precisely provide an alternative route to formulate it. Research along this line is currently in progress.

As a first test of this "lattice fundamental measure functional" (LFMF), we have applied it to get the phase behavior of the lattice fluid of hard squares on a square lattice with second-neighbor exclusion. Results for the equation of state of this fluid are available from cluster expansions [37]. These results show a second order phase transition at packing fraction $\eta \approx 0.807$ from a fluid phase to a columnar phase. No direct simulations have, to our knowledge, ever been performed on this system, but the transition density can be inferred by extrapolating down to zero temperature the available simulations of the antiferromagnetic second-neighbor Ising model [38,39]. The transition density so obtained is $\eta \approx 0.84$. This result is rather close (within a 10% deviation) to the one the LFMF predicts, $\eta \approx 0.764$. Also the ordered phase is the correct one. For the sake of comparison we plot together in Fig. 1 both the equation of state derived from the LFMF and that of Ref. [37]. We can realize that, despite its simple derivation, the LFMF produces results as accurate as those obtained from more involved theoretical approaches.

We have further applied the LFMF to the system simulated in Ref. [26], namely, a binary mixture of hard cubes of sizes 6 and 2 lattice spacings on a cubic lattice. First of all, we have determined the spinodal line (the dotted line of Fig. 2) and the wave vector of the reciprocal lattice for which the structure factor diverges at this spinodal. It determines both the direction and the wavelength, λ, of the periodic inhomogeneous instabilities. For x from 0 up to the cusp in the spinodal it yields $\lambda = 2$, and from the cusp up to 1, $\lambda = 7$. Accordingly, to obtain the free energy of the inhomogeneous phases we have assumed periodicity in one, two, and three dimensions, corresponding to smectic (Sm), columnar (C), and solid (S) phases, respectively.

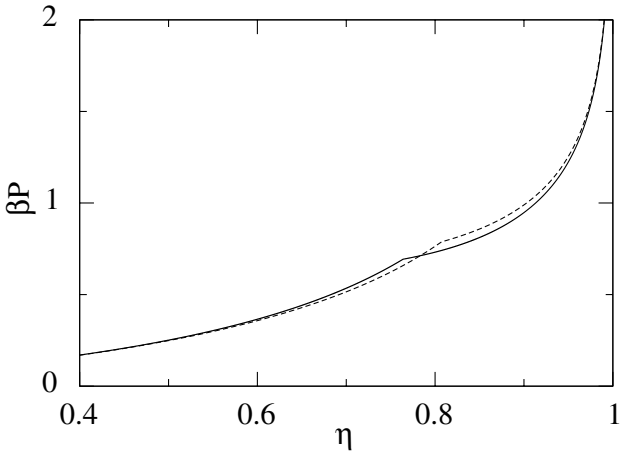

FIG. 1. Reduced pressure, βP, vs packing fraction, η, for the hard-square (2×2) model obtained from the present theory (solid line) and from cluster expansions [37] (dashed line). The former shows a second order fluid-columnar phase transition at $\eta \approx 0.764$, while the latter shows a second order fluid-solid phase transition at $\eta \approx 0.807$. The ordered phase is in both cases a columnar phase.

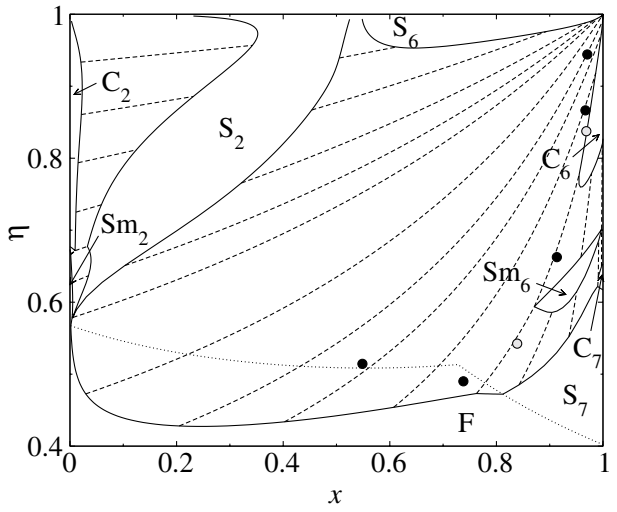

FIG. 2. Phase diagram of the binary mixture of hard cubes (size ratio 6 : 2), $\eta = \eta_L + \eta_S$ being the total packing fraction of the large (L) and small (S) cubes, and $x = \eta_L/\eta$. The phases are labeled F (fluid), S_α (solid), Sm_α (smectic), and C_α (columnar), where $\alpha = 2, 6, 7$ stands for the lattice parameter of the ordered phases. A bunch of coexistence lines are also drawn within the coexistence regions. The dotted line corresponds to the spinodal of the uniform fluid. For $0.81 \lesssim x$ it marks a stable continuous F-S_7 phase transition. The points are simulation results taken from from Ref. [26]; see text for details.

On the left of the cusp we have considered only period 2, but on the right we have considered periods 6 and 7. Then we have performed a free minimization with respect to the occupation probabilities at all points within the unit cell (taking into account the obvious symmetries in order to reduce the number of minimizing variables). Finally we have solved all possible phase equilibria by imposing equality of pressure and chemical potentials between the coexisting phases, resorting to the Gibbs free energy, whenever there was a doubt, to decide which was the most stable coexistence. The result of this laborious computation is summarized in Fig. 2.

As concerns our discussion, the most important conclusion one extracts from this phase diagram is that fluid-fluid demixing never occurs in this system. In fact, if we restrict the functional to homogeneous phases, it predicts stability of the mixture up to size ratios as large as 26 : 2 (a result, by the way, not very far from the value 10 : 1 obtained for the system of parallel hard cubes [19,21]). This contradicts the results of Ref. [26], according to which this system undergoes a fluid-fluid phase separation.

A second striking feature of the phase diagram is its extraordinary complexity. There appear regions of stability of smectic, columnar, and solid phases, rich in both small and large cubes, and the latter with lattice parameters 6 and 7. Triple points abound. Of course, our procedure does not exclude the possibility that phases with more complex structures are more stable than those considered, but it is almost impossible to guess them just from the form of the functional, without further knowledge.

Since this theory is just approximate and the complexity of the phase diagram arises from a subtle balance between the free energies of the different phases, many of the small stability regions may be incorrectly placed or may not exist at all. However, we do not expect the main regions to be very different from those appearing in Fig. 2, especially at high densities, where, by construction, the functional is more accurate [28]. And very likely, the true phase diagram will also be as complex (so much that many regions will probably be inaccessible to simulations as well).

In order to understand the discrepancy between the conclusions of Ref. [26] and our results, we have represented with circles in Fig. 2 the state points corresponding to the two coexisting fluids, according to the simulations, together with the inferred critical point. Filled circles correspond to data reported as being either true coexisting states or the critical point; open circles are other data, not reported as coexisting states, but lying very close to the fitted binodal. It is very remarkable that these points follow quite well a fluid-columnar (C_6) coexistence in our phase diagram. So, according to the present theory, the dense fluid in the simulation must be a C_6 columnar phase instead. This conclusion is supported by the fact that the presumed big-cube-rich fluid phase is actually too dense to be a fluid (packing fractions are around 0.8–0.9). The particular shape of these particles enhances the formation of spatial ordering: parallel hard cubes, for instance, crystallize at a packing fraction around 0.5 [40].

To summarize, we have reexamined the only known example so far of fluid-fluid demixing in additive hard-core mixtures: a simulation of a binary mixture of hard

cubes on a cubic lattice. We have shown convincing evidence that this transition corresponds most likely to a fluid-columnar phase separation rather than to a fluid-fluid phase separation. This scenario is consistent with the fluid-inhomogeneous phase scheme arising in all additive hard-core mixtures studied so far. Accordingly, only nonadditive models (or models with other degrees of freedom inducing nonadditivity, like orientational ones) are known to give rise to a true fluid-fluid phase separation in a binary mixture of hard particles. The explanation of this may rest in the fact that the range of the depletion potential is larger for nonadditive mixtures than for additive ones. A detailed discussion of this effect appears in Ref. [41].

As a by-product, on the way to achieve the above goal we have constructed a ''lattice fundamental measure theory'' for mixtures of hard cubes. Extensions of this theory to other particle shapes and other lattice structures are currently under exploration. However, the most promising feature of this theory is that it seems to patch the way to build a scaled particle theory for lattice systems, so far unknown.

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