Numerical Solution of Hard-Core Mixtures

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Liquid binary mixtures pose an important, yet easily formulated problem: Imagine a 3-dimensional box of size $L$ (volume $V = L^3$) occupied by objects of two different types $a, b$ with packing fractions $\eta_a$ and $\eta_b$. Will the system remain homogeneously mixed or will it phase-separate?

This demixing problem can be readily analyzed whenever there is an obvious free energy imbalance between the homogeneous and the phase-separated system. In many cases of practical importance, such an imbalance is due to the interactions, for example caused by electrostatic screening. Even in the absence of interactions (other than by a hard-core term), a free energy difference can be caused by an entropic contribution. In “non-additive” mixtures, the, say, demixed phase may be able to pack space more densely. At high overall packing fractions, the system will then be phase-separated.

Systems of impenetrable large and small spheres or cubes belong to the class of additive mixtures. In these systems, the distance $r_{ab}$ of closest approach between, say, two spheres of radii $r_a$ and $r_b$ satisfies: $r_{ab} = r_a + r_b$, so that the abovementioned simple entropic effect is absent. Nevertheless, it has been understood for a long time that even additive mixtures are subject to an entropic “depletion force” where two large particles may approach sufficiently closely for the small ones to be expelled from the interspace between them. In that situation, an osmotic (partial) pressure difference (of the small particles) builds up and pulls the big particles even closer together. The depletion force is strongly attractive at very short distances $r$ between the large particles (for $2 r_a < r \lesssim 2 r_a + r_b$), but finally turns out to be quite long-range in nature. Approaches to integrate out the small particles are thus problematic. As a prototype of additive mixtures, it is thus of great interest to completely analyze the microscopic model of large and small spheres or cubes and to understand whether it will eventually lead to phase separation. Precisely this question has remained hotly debated even in recent years.

The theoretical framework for the mixture problem has traditionally relied on the solutions of ‘closure approximations’ to the Ornstein-Zernicke integral equations. Classic work of Lebowitz and Rowlinson, performed more than 30 years ago, first showed that the Percus-Yevick closure of the integral equations did not lead to phase separation. This exact statement was thought to reflect the true behavior of the system until Biben and Hansen challenged the view by showing that an instability of the mixture was predicted by a different choice of the closure. Since the closure approximations are contradictory (and fundamentally uncontrolled), it is of prime importance to resort to independent checks. However, numerical simulations have been notoriously difficult, especially for objects very different in size. Numerical evidence for a phase transition has, to our knowledge, only been obtained in a lattice model of hard cubes.

The situation has thus been very confusing. One is lead to agree with the author of ref. where previous work (for systems two orders of magnitude smaller) remained inconclusive. Our method to us) where previous work (for systems two orders of magnitude smaller) remained inconclusive. Our method to agree with the author of ref. [7]: the field would benefit from an “Ising model of liquids”, an exactly solvable full-complexity model against which the concepts and the approximate theories could be checked. In the present paper, short of providing such an analytic solution, we obtain a very precise numerical solution to the problem of binary mixtures, by applying an extremely powerful cluster algorithm to the problem. Like the algorithms of Swendsen and Wang and Wolff for the case of the Ising model, the new method allows to obtain all the thermodynamic quantities with unprecedented accuracy. As a first important application, we actually establish the long sought for demixing transition both for spheres and for cubes.

In our algorithm, the convergence problems of ordinary Monte Carlo simulations are completely eliminated in a wide and physically interesting range of parameters. We have obtained convergence for up to $10^6$ particles (limited by the size of the computer memory available to us) where previous work (for systems two orders of magnitude smaller) remained inconclusive. Our method applies equally well to spheres, cubes or any other shape, and both to the continuum and the lattice.

At any step of the algorithm (cf. for details) one generates a new ‘copy’ of the ‘original’ by inverting the latter around a randomly chosen pivot point $x_p$. Original and copy are then superimposed. The combined system
presents ‘clusters’ of overlapping objects. Some of these clusters are then ‘flipped’; particles belonging to the original are assigned to the copy, and vice versa. Thereafter, the copy is discarded and a new pivot point is chosen. The algorithm can easily be set up for simulations at constant particle number. It is completely symmetric with respect to the operation: original $\mapsto$ copy, a property which implies detailed balance. The method works perfectly well as long as the combined system breaks up into at least a few sizeable clusters. In our previous work on hard spheres in two dimension, we located this purely algorithmic percolation threshold at a much lower packing fraction than would have been useful to study the 2-dimensional liquid-solid phase transition. In the present case of mixtures, the situation is vastly improved: we find that the percolation threshold (the optimal operation point of our algorithm) mainly depends on the combined packing fraction $\eta_a + \eta_b$, but not on the size ratio of the two species. This is radically different from the behavior of ordinary (local) Monte Carlo methods, where the diffusion of large particles becomes completely blocked by the nearby presence of many small ones. The lack of sensitivity of our algorithm to the size ratio of the particles is all the more interesting for a second reason: it has long been understood that the important physical phenomena (depletion and the tendency to phase-separate) quickly move to lower overall packing fractions as the particles become dissimilar in size. These two effects open up a large window of packing fractions and size ratios in which we can numerically solve the problem of liquid mixtures with the new algorithm.

Let us first consider the superposed system of monodisperse objects. In this case, the algorithm’s optimal point of operation turns out to be at $\eta_a = \eta_b \sim 0.23$ both for cubes and for spheres. The percolation threshold is thus located at a packing fraction corresponding to 1/4 of the close packing fraction for cubes and 1/3 for spheres. At $\eta_p$, the algorithm evenly flips clusters of any size. For larger packing fractions, intermediate cluster sizes will appear less often, since we either encounter the percolating cluster, or have to do with the algebraically decreasing distribution of small clusters. Above the threshold, the algorithm deteriorates ‘gracefully’, and it is quite possible to converge the monodisperse system (at, say, $N = 500$) for packing fractions up to $\eta \sim 0.4$.

We now introduce the very large number of small objects (cubes or spheres). As long as the system remains homogeneous, we notice that the percolation threshold moves to slightly larger overall packing fractions. During the simulation, we sample the partial distribution function of pairs of large particles $g_{ll}(r)$ [13]. The numerical noise is much reduced if we consider not $g_{ll}(r)$, but the integrated pair distribution function $G_{ll}(r) = 4\pi \rho_l \int_0^r dr' r'^2 g_{ll}(r')$ ($\rho_l$ is the density of large particles). $G_{ll}(r)$ determines the average number of large particles within a radius $r$ around a randomly chosen large particle. We also compare $g_{ul}(r)$ and $G_{ul}(r)$ to the pair distribution functions $g(r)$ and $G(r)$ of the monodisperse system (with $\eta_b = 0$) at the same value of $\eta_a$. Knowledge of the pair distribution functions for all $r$ is equivalent to the computation of the structure factor (its Fourier transform), which informs us about the system’s phase: for a homogeneous phase, $g_{ll}(r)$ is completely flat for large arguments ($G_{ll}(r)$ will follow the monodisperse system’s $G(r)$). In contrast, $g_{ul}(r)$ and $G_{ul}(r)$ for phase separated systems will be system-size dependent functions even for moderate $r$. This fact translates to the presence of phase regions of varying extension.

For spheres at a packing fraction $\eta_a = \eta_b = 0.1215$, and a ratio of radii $r_b/r_a = 1/10$, we determined the integrated pair distribution function $G_{ll}(r)$ and compared it to the monodisperse system ($\eta_b = 0$). In fig. 1, we present our results for $N_a = 62, N_b = 62,000$ and $N_a = 108, N_b = 108,000$ (upper), compared to the monodisperse case (lower). The packing fraction is $\eta_a = \eta_b = 0.1215$, the system is homogeneous.

FIG. 1. Integrated pair distribution function $G_{ll}(r)$ for spheres of radii $r_b/r_a = 1/10$ ($N_a = 62, N_b = 62,000$ and $N_a = 108, N_b = 108,000$) (upper), compared to the monodisperse case (lower). The packing fraction is $\eta_a = \eta_b = 0.1215$, the system is homogeneous.
the effect is strongest for values $2r_a < r \lesssim 2(r_a + r_b)$. Differentiating $G(r)$, we obtain $g_l(r)$, whose contact value at $r = 2r_a$ is increased by a factor of 8.5 with respect to the monodisperse case. $g_l(r)$ oscillates for larger arguments, reaches a first minimum at $r \sim 2(r_a + r_b)$, and eventually levels out to the expected value $g_l(r) \to 1$ for large $r$. For small $r$, the integrated function, $G_l(r)$, exceeds the monodisperse system’s $G(r)$ by about 0.4. In our opinion, this additional binding of an average 0.4 particles characterizes the strength of the depletion much better than the contact value $g_l(2r_a)$. We also suggest that a system with an additional binding of more than one particle should be unstable to phase separation.

The inset of fig. 1, as the main graph, contains in fact two sets of curves. On the scale of the figure, the curves for $N_a = 62$ cannot be distinguished from those at $N_a = 108$ (for $r < L/2$, neither can the data for $N_a = 864$, which we have also computed). As mentioned before, the close agreement testifies to the good convergence of the algorithm, but also indicates that finite-size effects are completely negligible at these values of the physical parameters. This is a key observation, which leads us to strongly suspect that we are far away from any second-order phase transition point (as the critical point of phase separation), which should lead to such effects.

Finally, at the combined packing fraction of $\eta = 0.243$, we are still below the percolation threshold for the system with $r_b/r_a = 1/10$, but clearly above the monodisperse system’s point of percolation. We believe that the local binding effects of the depletion force lead to a slight modification of the many-particle distribution functions, which is picked up in the distribution of cluster sizes.

The situation appears to be changed for a ratio of radii $r_b/r_a = 1/20$. For this case, our memory resources have allowed us to perform calculations at $N_a = 32, N_b = 256,000$ and $N_a = 62, N_b = 496,000$, again at $\eta_a = \eta_b = 0.1215$ ($L = 10.33 \times r_a$ and $L = 12.88 \times r_a$, respectively). Phase separation still does not seem to have taken place, but we notice the presence of important finite-size effects. For example, the system at $N_a = 32$ indicates an average ‘additional binding’ of 0.7 particles per sphere, while the larger system at $N_a = 62$ yields a binding of 0.8. Again, the finite-size effects go into the direction of an increased depletion for the larger size. Since we are already at the limit of our computer resources, we were unable to check the phase behavior at even larger numbers of particles.

Finally, we have performed simulations at $r_b/r_a = 1/30$, and $N_a = 32, N_b = 864,000$, again at the same packing fraction $\eta_a = \eta_b = 0.1215$. In these very large simulations, the system clearly has crossed into the separated phase: the distribution function $G_l(r)$ is suddenly very different from the monodisperse system’s $G(r)$ for all values of $r$, and the additional binding is clearly larger than 1. In this case, we usually observe the presence of one or two large aggregates [14] of large spheres which comprise most of them. In agreement with this observation we also notice a dramatic change in the behavior of our algorithm: the distribution of ‘cluster’ sizes is shifted towards very large clusters, since the presence of the dense phase of spheres (the ‘aggregate’) pushes the system locally beyond the percolation threshold.

Our algorithm is extremely powerful, but we have nevertheless reached the memory limits of today’s workstations. For spheres, the transition takes place at rather small size ratios $(r_b/r_a \sim 1/20)$: therefore, we simulate a very large total number of particles but the $G_l(r)$ belongs to a small system with only a few dozen large spheres. For spheres, the finite-size analysis, and the precise location of the critical point will have to be done on more powerful machines.

![FIG. 2. $G_l(r)$ for cubes of side lengths $d_b/d_a = 1/10$ (upper two curves at small $r$), compared to the monodisperse case (lower) for $N_a = 62, N_b = 62,000$ and $N_a = 108, N_b = 108,000$. The system, at a packing fraction of $\eta_a = \eta_b = 0.067$ is phase-separated.](image-url)
Simulations have revealed no signatures of an instability for a size ratio of \( \frac{d_b}{d_a} = 1/2 \) (at the accessible packing fractions below \( \eta_a + \eta_b = \eta_P \sim 0.23 \)). Finite-size effects are negligible. For a ratio of \( \frac{d_b}{d_a} = 1/10 \), at small packing fractions, the same holds true. However, for a packing fraction of \( \eta_a = \eta_b = 0.054 \), the system at \( N_a = 62; L = 10.5 \times d_a \) remains clearly homogeneous, with a very strong depletion and an ‘additional binding’ of about 0.9 particles. At the same packing fraction, at \( N_a = 496; N_b = 496.000; L = 21.0 \times d_a \), the \( G_b(r) \) has pulled away from the monodisperse case for all \( r \): the system has already undergone phase separation. In fig. 2, we present well-converged data for a slightly larger packing fraction \( \eta_a = \eta_b = 0.067 \), still at \( d_b/d_a = 1/10 \). Here, already the system at \( N_a = 62; L = 9.75 \times d_a \) is in the demixed phase. The data at \( N_a = 108; L = 11.73 \times d_a \) illustrate the large finite-size effects at moderate \( r_a \). The maximum difference of \( \langle d_{IL} - G \rangle \) is much larger for \( N_a = 108 \) than for \( N_a = 62 \), and is expected to diverge for \( N_a \to +\infty \). We stress again that these effects are specific of the phase-separated system, and in the present form of the fixed particle number system, in which actual phase coexistence is obtained. In the demixed system, one of the two phases will be ‘rich in cubes’. Unfortunately this phase will have a packing fraction above \( \eta_P \) (except very close to the critical point), and will be difficult to study with our algorithm. The route towards instability is not touched by this problem. Nevertheless, both systems seem to have converged. While we did not study the demixed phases in detail, we have noticed the appearance of aggregates which are all but closed packed.

In conclusion, we have studied the equilibrium phases of hard core mixtures. A superior algorithm has allowed us to establish and to access the demixed phase both for spheres and for cubes, and to investigate the subtle interplay between short-range depletion and long-range demixing. There are many questions and a large number of directions for further research, besides those already mentioned. Primarily, we think that the precise phase diagram needs to be established, especially the position of the critical point. In addition, the comparison with various closure formulas should be undertaken. We can already see that ref. 4 places the critical packing fraction for cubes much too high. For most closure approximations, the numerical applications were done at quite large values of the size ratio, probably since Monte Carlo simulations for very dissimilar objects were thought to be completely out of reach. Paradoxically, the opposite is true. We are much more at ease at large asymmetry, as long as the packing fraction is not too high. The comparison between the exact numerical points and the closures should of course be done directly on the observables, such as \( g_{II}(r) \), and not on the phase diagram. To encourage and simplify further work, we will make available via email the Fortran code used in this paper.

Finally, the question remains whether the artificial percolation threshold \( \eta_P \) presents an unsurmountable barrier to the numerical solution. Several ideas to go much beyond \( \eta_P \) have been formulated (cf. 3). Even in the very dense limit of importance in the two-dimensional melting problem, the flip of the percolating cluster can be avoided, but we have up to now been unable to transform this idea into a working algorithm 13. However, we are firmly convinced that \( \eta_P \) is not a hard boundary: many more difficult problems, such as melting, are also likely to fall under the attack of appropriate, while very specialized algorithms.

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