Fluid-fluid transitions of hard spheres with a very-short-range attraction

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Hard spheres with an attraction of range a tenth to a hundredth of the sphere diameter are constrained to remain fluid even at densities when monodisperse particles at equilibrium would have crystallized, in order to compare with experimental systems that remain fluid. They are found to have a fluid-fluid transition at high density. As the range of the attraction tends to zero, the density at the critical point tends toward the random-close-packing density of hard spheres.

I. INTRODUCTION

Argon forms a liquid because argon atoms attract each other and these dispersion attractions between the atoms are relatively long ranged; the volume over which one argon atom attracts another is comparable to the volume one argon atom of the pair excludes to another. If we could reduce the range of the attraction between argon atoms then the liquid phase would disappear from the equilibrium phase diagram when the volume over which the atoms attract was of order one-tenth of the volume they exclude to each other. Of course, we cannot change the interaction between argon atoms but there are well-established colloidal systems whose interactions we can change. The liquid phase disappears from the equilibrium phase diagram because the fluid-fluid transition is preempted by the crystallization of the fluid. But, although the fluid-fluid transition has disappeared from the equilibrium phase diagram of monodisperse particles, experiments often do not observe crystallization, presumably due to a combination of a large free energy barrier to crystallization and the destabilizing effect of small amounts of polydispersity on the crystalline phase. As crystallization does not occur it does not preempt the fluid-fluid transition, which is therefore observable. With this in mind, we study the behavior of spherical particles with a short-range attraction which are constrained to remain fluid. We study attraction ranges down to a hundredth of the diameter of the hard core—this is what we mean by very-short-range attractions. We find that as the range decreases the density at the critical point increases to very high values. For a sufficiently short range the critical point lies above the density of the kinetic glass transition observed in experiments on hard-sphere-like colloids. This will make direct observation of the phase separation difficult or impossible; however, this phase transition may still influence nonequilibrium behavior such as the formation of glasses and gels.

Here we will not consider the crystalline phase at all. Our results are for a system of particles that is constrained to remain fluid at all temperatures and pressures; see Refs. [1–3] for a discussion of the application of constraints to stabilize a phase that would otherwise be metastable or unstable. Although experiments on near-monodisperse colloidal spheres show that they crystallize readily, at least as long as the attraction is not too strong, polydisperse colloidal spheres often never crystallize [4] and the presence of a very-short-range attraction makes the crystalline phase even more sensitive to polydispersity [5]. By ''polydisperse'' spheres we mean that the spherical particles do not all have the same diameter but have a range of diameters. Our theory is a perturbation theory about a hard-sphere fluid and so completely neglects the crystal. Thus we will not need to explicitly apply a constraint within the theory. We do, however, need to assume that it is possible to apply a constraint to the system that has almost no effect on the fluid phase but completely prevents crystallization.

II. THEORY

We chose a simple potential with a hard-sphere core and an attraction in the form of a Yukawa function. The hard-sphere + Yukawa potential is a spherically symmetric pair potential so the interaction energy v depends only on the separation r of the centers of the two particles,

$$v(r) = \begin{cases} \infty, & r \leq \sigma \\ -\epsilon(\sigma/r)\exp[\kappa(1-r/\sigma)], & \sigma < r, \end{cases} \qquad (1)$$

where σ is the hard-sphere diameter and ϵ is the energy of interaction for touching spheres. With this potential the thermodynamic functions depend on the reduced temperature kT/ϵ and the reduced density $\eta = (N/V)(\pi/6)\sigma^3$, which is the fraction of the volume occupied by the cores of the particles. k, T, N, and V are Boltzmann's constant, the temperature, the number of particles, and the volume, respectively.

We require a free energy for this potential that is accurate up to very high densities, up to near random close packing, which is at a volume fraction $\eta \simeq 0.64 - 0.65$ [6,7]. Speedy [7] has obtained, from computer simulation data, an accurate equation of state of hard spheres up to random close packing. This enables us to use a perturbation theory, i.e., to start from the Helmholtz free energy in the infinite temperature limit of our model, which is hard spheres, and add on the energy as a perturbation. Then our expression for the Helmholtz free energy per particle a at a temperature T and a volume fraction η is

$$\beta a(\eta, T) = \beta a_{\mathrm{HS}}(\eta) + \beta u(\eta, T), \qquad (2)$$

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where a_{HS} is the Helmholtz free energy of hard spheres, u is the energy per particle, and $\beta = 1/kT$. As the energy of a fluid of hard spheres is zero, $\beta a_{HS} = -s_{HS}/k$, where s_{HS} is the entropy per particle of hard spheres, which is, according to Speedy [7,8],

$$\frac{s_{HS}}{k} = 1 - \ln \rho + C \ln(\eta_0 - \eta) + S_0 + N^{-1} \ln N_g(\eta_0), \quad (3)$$

where $C = 2.8$, $S_0 = -0.25$, and N_g is

$$N_g(\eta_0) = \exp\{N[\alpha - \gamma(\eta_0 - \eta_m)^2]\}, \quad (4)$$

where $\alpha = 2$, $\gamma = 193$, and $\eta_m = 0.555$. In these equations the value of η_0 at any density is determined by minimizing the free energy at that density. This form of the free energy is optimized for the dense fluid. Essentially, if we start from any configuration of the dense fluid and begin to expand all the spheres (so increasing the volume fraction) then at some point the spheres will touch and then the spheres cannot be expanded further. At this point the volume fraction is η_0; this can be seen from the logarithimic term in Eq. (3), which diverges when $\eta = \eta_0$. If we start from different configurations then after expansion of the spheres we may end up with a different value of η_0. The larger the difference $\eta_0 - \eta$ then the more room the spheres have, which increases the entropy. However, simulations show that there are few arrangements of the spheres that have a large η_0; therefore there is an entropic cost to being in an arrangement with a large η_0. $N_g(\eta_0)$, Eq. (4), is essentially the number of ways of arranging spheres such that the maximum possible volume fraction is η_0; it is maximal at $\eta_0 = \eta_m$. The competition between the third and fifth terms in Eq. (3) then determines the value of η_0. As the spheres touch when $\eta = \eta_0$ and if we assume that the expansion is isotropic, then the separation b of spheres at a given η and η_0 is

$$b/\sigma = (\eta_0/\eta)^{1/3}, \quad (5)$$

just as in a crystal. The energy of attraction is approximated by the energy of interaction of each sphere with its six neighbors [6] at a separation b

$$u = 3v(b) = 3v((\eta_0/\eta)^{1/3}). \quad (6)$$

As the energy depends on η_0, the total free energy, Eq. (2), is minimized to obtain η_0 at each density and temperature.

Guides to the accuracy of our free energy are obtained by comparison with existing simulation data. For $\kappa = 7$, Hagen and Frenkel [9] find a fluid-fluid critical point at $kT/\epsilon = 0.41$, $\eta = 0.26$, whereas we predict $kT/\epsilon = 0.54$, $\eta = 0.30$. The agreement is fair although not quantitative and we expect our theory to do better at higher densities. Applying an approximation of the type Eq. (6) to a face-centered-cubic (fcc) crystal [10] yields an fcc-crystal–fcc-crystal critical point when $\kappa = 100$ at $kT/\epsilon = 1.1$, $\eta = 0.69$. Bolhuis, Hagen, and Frenkel [11] using computer simulation and perturbation theory predict $kT/\epsilon = 0.70$, $\eta = 0.71$. Again, there is fair but not quantitative agreement.

We should note that our theory, although a perturbation theory, differs markedly from the conventional high temperature expansions used to study liquids [13]. These are
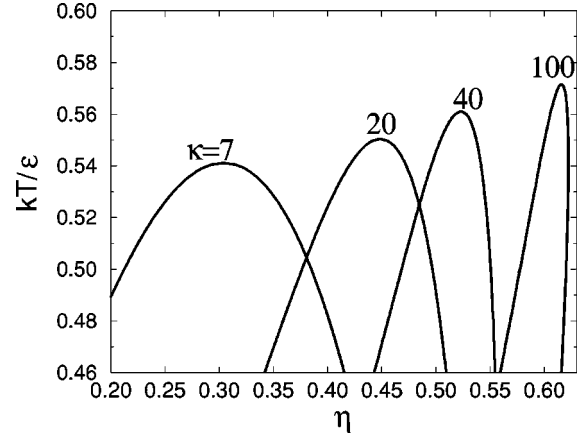

FIG. 1. The fluid phase diagrams in the temperature-density plane, for four different ranges. The curves are, from left to right, for inverse ranges $\kappa = 7$, 20, 40, and 100. In each case the curve encloses the fluid-fluid coexistence region and the critical point is the highest point on the curve.

most accurate for long-range attractions. The theory is closely related to simple theories of a crystal of spheres with a short-range attraction such as that of Daanoun *et al.* [14]. These theories should be as applicable to a fluid near random close packing as they are to a crystal. The crystal lattice enters a theory such as that of Ref. [14] only by fixing the close-packing density and the number of nearest neighbors. It relies on the fact that in a dense crystal each sphere just rattles around in a cage formed by its nearest neighbors. But this is also true in a glass and is true except for infrequent rearrangements in a very dense fluid [7,1].

III. RESULTS

Results for four short ranges are plotted in Fig. 1 [8]. A simple liquid such as argon is reasonably well modeled by an attraction of inverse range $\kappa = 1.8$ [12]. The results are for inverse ranges up to two orders of magnitude greater. The notable feature is that the critical densities and the densities of the liquid phase are high and move to higher density as the range decreases. At high density the particles are pushed together until they are within range of the attraction. This occurs at separations between the surfaces of the spheres $b - \sigma = O(\sigma \kappa^{-1})$. With the particles just within range of the attraction there is a clear energetic driving force toward phase separation: the fluid lowers its energy at fixed overall density by some of the fluid condensing into a dense fluid where all the spheres are well within the range of the attraction of their nearest neighbors. This is just what was observed by Bolhuis, Hagen, and Frenkel [11] in the fcc crystal. In the absence of the crystalline phase, due to polydispersity perhaps, the transition simply shifts over to a fluid-fluid transition, and it occurs at a lower density due to the fact that the random-close-packing density, which is the maximum density of amorphous spheres, is lower than the maximum density of spheres achievable in an fcc crystal. Because of the smaller number of neighbors in the dense fluid as compared to the crystal, the transition shifts to a lower temperature, but in both cases the critical temperature varies little with changing range.

We predict a critical point at a density that increases as the range decreases and at a temperature which is roughly constant. Although we cannot perform calculations at zero range, $\kappa = \infty$, extrapolation of our results together with the results of Bolhuis, Hagen, and Frenkel [11], who were able to study the zero-range limit in the crystal, suggests that in the zero-range limit there is a fluid-fluid critical point *at the* random-close-packing density and at $\epsilon/kT = O(1)$.

Baxter [15] solved the Percus-Yevick (PY) approximation for hard spheres with a zero-range attraction, $\kappa \to \infty$, and an infinite reduced well depth $\epsilon/kT \to \infty$. He defined a parameter τ, which is related to the second virial coefficient B_2 by

$$\tau = \tfrac{1}{4}(1 - B_2/B_2^{\text{HS}})^{-1}, \tag{7}$$

where B_2^{HS} is the second virial coefficient of hard spheres. This is an extreme model and Stell has shown that the fluid phase is unstable at *all* nonzero densities for finite τ [16]. Above we considered $\epsilon/kT = O(1)$, for which $\tau \to \infty$ as $\kappa \to 0$. Stell [16] showed that in the zero-range limit the virial expansion is pathological. See Refs. [11,16–18] for the equilibrium phase diagram in the zero-range limit. Within the PY approximation there are two routes to the thermodynamic functions. Both routes incorrectly predict a stable fluid; thus the PY approximation is qualitatively wrong for the equilibrium behavior. However, if the nucleation rate of the crystalline phase is very low even for an infinite reduced well depth then the fluid will be metastable [1] and the predictions of the PY approximation may be valid for this fluid [19]. The model is still an extreme one, ϵ/kT is divergent, and the PY approximation is an uncontrolled one, so it is difficult to place much faith in its predictions. The two routes both predict fluid-fluid critical points. If the compressibility route is used, the critical point is at the low volume fraction $\eta = 0.12$ and at $\tau = 0.098$, whereas via the energy route the prediction is $\eta = 0.32$ and $\tau = 0.12$ [20]. The prediction of the compressibility route in particular is surprising. Simulations find a critical density that increases as the range decreases. As we noted above, for $\kappa = 7$ Hagen and Frenkel [9] found a critical volume fraction $\eta = 0.26$, twice the value of a van der Waals fluid. Note that the PY approximation predicts a pressure that diverges only at $\eta = 1$; it is qualitatively wrong even for the fluid of hard spheres at densities near random close packing. Because of this the PY approximation can never predict a transition at random close packing. The PY approximation is qualitatively wrong for very dense fluids where the spheres are very close together but a short-range attractions favors precisely these configurations. We therefore suggest that its predictions be treated with caution.

In summary, the present theory predicts a fluid-fluid transition that is always at $\epsilon/kT = O(1)$ and occurs at a density that approaches that of random close packing as the range approaches zero. The PY approximation predicts a fluid-fluid transition in the zero-range limit, which is at quite low density, and $\epsilon/kT \to \infty$. We should note that these two predictions are not incompatible; it is possible that there are two fluid-fluid critical points. The present theory is restricted to $\epsilon/kT = O(1)$ and so cannot describe fluids with very-short-range attractions and small τ where $\epsilon/kT \gg 1$. Thus the fact that it does not predict another fluid-fluid transition at low τ and low density for very-short-range attractions is not evidence that there is no transition there. Ultimately, computer simulations or much more accurate theories will be required to prove whether or not either prediction is correct.

IV. CONCLUSION

In conclusion, we have determined the phase diagram of hard spheres with an attraction with a range of order 0.1 or 0.01 of the hard-core diameter, which are constrained not to crystallize. The fluid-fluid transition persists, according to our approximate theory, for all ranges of the attraction. As the range decreases the density at the critical point increases and can become very high near the random-close-packing density of hard spheres. As the density is so high, observing it will be difficult as the dynamics are very slow at these densities; the densities can exceed that of the glass transition of hard spheres. Due to these slow dynamics a glass-glass transition may be observed instead of a fluid-fluid transition, but again it may be impossible to observe directly. The difficulty in observing fully equilibrated coexistence does not mean that the transition has no observable consequences. Out of equilibrium systems tend to head toward equilibrium, and even if they do not reach equilibrium their final state may be, roughly speaking, the point on the path to equilibrium where the dynamics stop. One final point is that as the range decreases the critical point, with its associated large fluctuations and critical slowing down of the dynamics [21], will approach the kinetic glass transition. What effect this will have on the kinetic glass transition is unknown.

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