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

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Abstract

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 crystallised, in order to compare with experimental systems which 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 towards the random-close-packing density of hard spheres.

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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 crystallisation of the fluid. But although the fluid-fluid transition has disappeared from the equilibrium phase diagram of monodisperse particles, experiments often do not observe crystallisation, presumably due to a combination of a large free energy barrier to crystallisation and the destabilising effect of small amounts of polydispersity on the crystalline phase. As crystallisation does not occur it does not preempt the fluid-fluid transition, which is therefore observable. With this in mind we study the behaviour 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. Experiments on colloids with very short-range attractions have found a threshold beyond which diffusion ceases, and Poon, Pirie and Pusey have previously suggested that this is due to an arrested fluid-fluid phase separation. If as we find, the dense fluid has a density above that of the hard-sphere glass transition, then it is not surprising that the dynamics of phase separation become arrested.

Here we will not consider the crystalline phase at all. Our results are for a system of particles which is constrained to remain fluid at all temperatures and pressures; see refs. for a discussion of the application of constraints to stabilise a phase which would otherwise be metastable or unstable. Although experiments on near-monodisperse colloidal spheres show that they crystallise readily, at least as long as the attraction is not too strong, polydisperse colloidal spheres often never crystallise and the presence of a very short-range attraction makes the crystalline phase even more sensitive to polydispersity. 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 which has almost no effect on the fluid phase but completely prevents crystallisation.

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 centres of the two particles,

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

where $\sigma$ is the hard-sphere diameter and $\epsilon$ is the energy of interaction for touching spheres. With this potential the thermodynamic functions depend on the reduced temperature $kT/\epsilon$, 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 which is accurate up to very high densities, up to near random close packing which is at a volume fraction accurate up to very high densities, up to near random close packing. This enables us to use a perturbation theory, i.e., to start from the Helmholtz free energy per particle of our model, which is hard spheres, and add on the entropic cost to being in an arrangement with a large number of particles and the volume, respectively.

\[ \beta a(\eta, T) = \beta a_{hs}(\eta) + \beta u(\eta, T), \tag{2} \]

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, $a_{hs} = -s_{hs}/k$, where $s_{hs}$ is the entropy per particle of hard spheres, which is, according to Speedy \cite{9, 10}.

\[ \frac{s_{hs}}{k} = 1 - \ln \rho + C \ln(\eta_0 - \eta) + S_0 + N^{-1} \ln N_g(\eta_0), \tag{3} \]

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

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

where $\alpha = 2$, $\gamma = 193$ and $\eta_m = 0.555$. In these equations the value of $\eta_0$ at any density is determined by minimising the free energy at that density. This form of the free energy is optimised 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 $\eta_0$; this can be seen from the log 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 $\eta_0$. The larger the difference $\eta_0 - \eta$ then the more room the spheres have which increases the entropy. However, simulations show that there few arrangements of the spheres which have a large $\eta_0$, therefore there is an entropic cost to being in an arrangement with a large $\eta_0$. $N_g(\eta_0)$, eq. (4), is essentially the number of ways of arranging spheres such that the maximum possible volume fraction is $\eta_0$; it is maximal at $\eta_0 = \eta_m$. The competition between the third and fifth terms in eq. (3) then determines the value of $\eta_0$. 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 $\eta$ and $\eta_0$ is

\[ b/\sigma = (\eta_0/\eta)^{1/3}, \tag{5} \]

just as in a crystal. The energy of attraction is approximated by the energy of interaction of each sphere with its six neighbours \cite{5} at a separation $b$

\[ u = -3v(b) = -3v((\eta_0/\eta)^{1/3}). \tag{6} \]

As the energy depends on $\eta_0$, the total free energy, eq. (3), is minimised to obtain $\eta_0$ 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 \cite{12} 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. (4), to a face-centred-cubic (fcc) crystal \cite{13} yields an fcc-crystal–fcc-crystal critical point when $\kappa = 100$ at $kT/\epsilon = 1.1$, $\eta = 0.69$. Bolhuis, Hagen and Frenkel \cite{14} using computer simulation and perturbation theory predict $kT/\epsilon = 0.70$, $\eta = 0.71$. Again there is fair but not quantitative agreement.
Results for four, short, ranges are plotted in fig. 1. A simple liquid such as argon is reasonably well modeled by an attraction of inverse range $\kappa = 1.8$. 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 $b-\sigma = \mathcal{O}(\sigma\kappa^{-1})$. With the particles just within range of the attraction there is a clear energetic driving force towards 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 neighbours. This is just what was observed by Bolhuis, Hagen and Frenkel [1] 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 neighbours 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.

Grant and Russel [1], and Verduin and Dhont [2] have performed experiments on colloids which are hard-sphere-like at high temperature but as the temperature is reduced the solvent becomes a poor solvent for the alkane chains which are grafted to the surface of the colloids. There is then a very short-range attraction when the grafted layers of two colloids overlap. Verduin and Dhont [2] estimate the range of the attraction to be less than 1nm for colloids with a diameter 80nm. They assess the strength of the attraction via a parameter $\tau$ [16, 17] which is related to the second virial coefficient $B_2$ by

$$\tau = \frac{1}{4} \left(1 - B_2/B_{2}^{hs}\right)^{-1},$$

(7)

where $B_{2}^{hs}$ is the second virial coefficient of hard spheres. We have replotted the phase diagrams for $\kappa = 20$ and 100 in the density-$\tau$ plane in fig. 2. The experimental results are in the range $\tau = 0.1$ to 0.2, and $\eta = 0.1$ to $\eta = 0.4$. These densities and temperatures lie within the coexistence region for $\kappa = 100$. They locate both a spinodal and a ‘static percolation’ line where diffusion of the particles stops. At these densities and temperatures, the fluid is unstable with respect to phase separation into a more dilute phase and a very dense fluid phase — this phase has a volume fraction $\simeq 0.56$. Beyond a volume fraction of 0.56-0.58 [18], the relaxation time of a fluid of hard spheres exceeds typical experimental times which are of the order of 100s. This is referred to as a kinetic glass transition, above it the samples are not equilibrated on the experimental time scale and so are not an equilibrium fluid. Thus as phase separation proceeds and domains of this dense phase appear the phase separation dynamics may become arrested due to the very slow relaxation within these dense domains. This is the scenario suggested by Poon, Pirie and Pusey on the basis of their experiments on colloids with a longer range but still short-range attraction [3]. Alternatively, as Grant and Russel [1] have suggested the phase separation may be fluid-crystal phase separation.

We predict a critical point at a density which increases as the range decreases and at a value of $\tau$ which also increases as the range decreases. Although we cannot perform calculations at zero range, $\kappa = \infty$, extrapolation of our results together with the results of Bolhuis, Hagen and Frenkel [14] 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. The critical point would be at roughly the same temperature as the critical points in fig. 1, which implies that as in the crystal [14] it occurs at infinite $\tau$. Baxter [16] solved the Percus-Yevick (PY) approximation for hard-spheres with a zero-range attraction. Within the PY approximation there are 2 routes to the thermodynamic functions. If the compressibility route is used the critical point is at the low volume fraction $\eta = 0.12$ and at $\tau = 0.098$ [19], whereas via the energy route the prediction is $\eta = 0.32$ and $\tau = 0.12$ [19]. Our results suggest that the critical point predicted by the PY approximation may be an artifact of this approximation. Stell [17] has shown that the virial expansion is pathological for all finite $\tau$ in the limit of the range of the attraction tending to zero. However, this pathology originates in crystalline clusters which we have eliminated with our constraint that crystalline configurations are not allowed [4, 18]. So the pathological virial expansion shows that in the zero-range limit, the equilibrium, unconstrained, fluid is completely unstable at finite $\tau$; see Refs. [14, 17, 20, 21] for the equilibrium phase diagram in the zero-range limit.

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 crystallise. 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. This is our tentative interpretation of the results on colloids with a very short-range attraction [1,2]: the ceasing of diffusion observed is arrested fluid-fluid phase separation. One final point is that as the range decreases the critical point, with its associated large fluctuations and critical slowing down of the dynamics [22], will approach the kinetic glass transition. What effect this will have on the kinetic glass transition is unknown.

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Figure 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.

Figure 2: The fluid phase diagrams in the $\tau$-density plane, for two different ranges.