The stability limit of the fluid phase of polydisperse sticky spheres

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Abstract

It has been shown by Stell [J. Stat. Phys., 63, 1203 (1991)] that at low temperature monodisperse sticky spheres collapse to form coexisting close-packed solid and infinitely dilute gases. We show that polydisperse sticky spheres also collapse and calculate the collapse temperature. The polydisperse spheres separate into fractions with narrower polydispersities which can then solidify. This is perhaps the first example of a single-peaked polydisperse mixture phase solidifying and separating. It implies that a mixture of polydisperse large hard spheres with much smaller hard spheres does not show fluid–fluid coexistence.

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1 Introduction

Sticky spheres are hard spheres with a zero-ranged, ‘sticky’, attraction \([1]\). Their phase behaviour is straightforward, if a little peculiar. Above a certain temperature \(T_{\text{coll}}\) they behave as hard spheres (below close packing \([2]\)) and below this temperature, they phase separate into an infinitely dilute gas coexisting with a close-packed solid \([2, 3]\). As \(T_{\text{coll}}\) can be determined analytically (see below) the sticky sphere model is very attractive for doing simple analytic theory. So, if we wish to go beyond pure fluids and consider mixtures, and we wish to use analytic theory then the sticky sphere model is an obvious choice for generalisation to describe a mixture. As we will see below, even for a mixture we can determine the limit of its stability analytically. Of course, the model is an extreme one but we think that even so our analytic demonstration of its phase behaviour is useful. Our mixture is polydisperse which means that particles of a whole range of sizes are present. Within this range, particles of all sizes are found, i.e., the distribution of sizes of the particles is a continuous function \([4–6]\).

In terms of describing experiment, sticky spheres have been extensively used as a model for colloidal particles and proteins, for examples see Refs. \([3, 7, 8]\) and references therein. Also, the fractionation method of Bibette \([9, 10]\) for emulsions relies on behaviour which is similar to that which we find.

We find that at low temperature polydisperse sticky spheres, like monodisperse sticky spheres, phase separate into an infinitely dilute gas and close packed solid. But in order to solidify the polydisperse mixture fractionates: the original polydisperse mixture separates into a number of polydisperse mixtures with narrower polydispersities, each of which then solidifies. Thus there is not one solid phase but many solid phases, each formed from a different range of sizes of spheres. This fractionation occurs as highly polydisperse spheres cannot solidify into a single solid phase because a wide range of sizes of sphere cannot be accommodated within a solid lattice \([11–14]\). As in monodisperse sticky spheres the driving force for solidification is the lowering of energy when a particle is in contact with, and so interacting with, the 12 particles that surround it in a face-centered-cubic or hexagonal-close-packed lattice.

In the next section we examine monodisperse sticky spheres, then in section 3 we generalise the theory to polydisperse spheres. Finally we discuss our results and point out their relevance to mixtures of hard spheres.

2 Monodisperse sticky spheres

First, we define the sticky sphere potential of Baxter \([1]\). It is the spherically symmetric pair potential \(u(r)\) defined by

\[
  u(r) = \begin{cases} 
    \infty & r \leq 1 \\
    -\epsilon & 1 < r \leq 1 + \delta \\
    0 & r > 1 + \delta 
  \end{cases},
\]

(1)

in the limit \(\delta \rightarrow 0\). We have defined the diameter of the hard-sphere part of the potential to be equal to 1. The effect of the attractive part of the interaction, that between 1 and \(1 + \delta\), can be assessed using the second virial coefficient \(B_2\), which is

\[
  B_2 = \frac{2\pi}{3} - 2\pi\delta \exp(\epsilon/T),
\]

(2)

where the first term is simply \(B_2\) for hard spheres of unit diameter and the second term comes from the attractive interactions. We use temperature units such that Boltzmann’s constant \(k = 1\).
We can easily see that as we cool sticky spheres the attractive interactions contribute a significant amount to \( B_2 \) at temperatures of \( \ln(1/\delta) \) and below. In the limit \( \delta \to 0 \)

\[
B_2 = \begin{cases} 
\frac{2\pi}{3} & T > T_{B20} \\
-\infty & T < T_{B20}
\end{cases}
\]

where \( T_{B20} \) is

\[
\frac{T_{B20}}{e} = \lim_{\delta \to 0} \left( \frac{1}{\ln(1/\delta)} \right) .
\]

The temperature \( T_{B20} \) has no relevance for monodisperse sticky spheres [3], however, as we shall see, it may have for polydisperse sticky spheres. As \( B_2 \) diverges below \( T_{B20} \) Baxter [1, 15] studied sticky spheres in an infinitesimal temperature range at \( T_{B20} \). However, Stell and Williams [3, 7, 16, 17] found that the fluid phase of monodisperse sticky spheres is unstable at \( T_{B20} \). It is only stable above a higher temperature \( T_{coll} \) [3, 17], when the second virial coefficient is indistinguishable from that of hard spheres. We will now determine \( T_{coll} \) in a way that we will later generalize to polydisperse sticky spheres. The fluid becomes unstable with respect to a solid phase near close packing. This is demonstrated by comparing the free energy of a low density fluid phase with that of the solid. At low density the fluid has a free energy per particle \( a_f \) which is given by that of an ideal gas

\[
a_f = \ln \rho - 1 \quad \rho \ll 1,
\]

where \( \rho = N/V \) is the density of particles; \( N \) is the number of particles and \( V \) is the volume. We have neglected a term \( \ln \Lambda^3 \) where \( \Lambda \) is the de Broglie wavelength of a sticky sphere. This term is irrelevant as far as the phase behaviour is concerned. The free energy of the solid phase may be estimated using a cell theory [18]. The free energy per particle is, in a cell theory, obtained from the 1-particle partition function of a particle trapped in a cell formed from its neighboring particles fixed at the positions they occupy in an ideal lattice. This partition function \( q_1 \) is

\[
q_1 = v_f \exp(z\epsilon/(2T))
\]

for sticky spheres in a \( z \)-coordinate lattice with a lattice constant sufficiently small that the particle interacts with all \( z \) neighbours at any position in the cell. For sticky spheres this means that the lattice constant should be less than \( 1 + \delta/2 \). This constraint on the maximum value of the lattice constant implies that the density must be at least \( \rho_{cp}/(1 + \delta/2)^3 \), where \( \rho_{cp}(z) \) is the maximum possible density of the \( z \)-coordinate lattice. With a lattice constant \( \simeq 1 + \delta/2 \) a sphere can move a distance \( \simeq \delta/2 \) in any direction which yields a volume available to the centre of mass of the particle \( \simeq \delta^3/8 \). So, an accurate approximation to \( q_1 \) is given by

\[
q_1 = \frac{\delta^3}{8} \exp(z\epsilon/(2T)) \quad \rho > \frac{\rho_{cp}(z)}{(1 + \delta/2)^3},
\]

which gives a free energy per particle in the solid phase \( a_s \) of

\[
\frac{a_s}{T} = -\ln q_1 = -3\ln \delta - \frac{z\epsilon}{2T} \quad \rho > \frac{\rho_{cp}(z)}{(1 + \delta/2)^3},
\]

where we have neglected the factor of \( \ln 8 \) as being negligible. The free energy of the solid phase is lowest for the lattice with the highest coordination \( z \). Thus a close packed lattice, either face-centered-cubic or hexagonal-close-packed, with \( z = 12 \) is the stable solid phase. From now on we
always take \( z = 12 \). Here we are considering the \( \delta \to 0 \) limit and so Eq. (8) is only valid for a solid at close-packing, \( \rho = \rho_{cp} \).

In order to determine the stability of the fluid with respect to the close-packed solid we determine the free energy difference \( a_s - a_f \) in the \( \delta \to 0 \) limit. From Eqs. (5) and (8) it is, in the limit \( \delta \to 0 \),

\[
\frac{a_s - a_f}{T} = \begin{cases} 
\infty & T > T_{coll} \\
-\infty & T < T_{coll}
\end{cases},
\]

where \( T_{coll} \) is

\[
\frac{T_{coll}}{\epsilon} = \lim_{\delta \to 0} \left( \frac{2}{\ln(1/\delta)} \right),
\]

which is higher than \( T_{B20} \), Eq. (4). So, below \( T_{coll} \) the free energy is \(-\infty\) at close packing in the sticky limit: the dilute fluid, with free energy given by Eq. (5), then has a higher free energy than the close-packed solid phase for all nonzero densities and so is unstable with respect to this phase. Positivity of the pressure requires that the free energy be an increasing function of density at constant temperature so a phase is necessarily unstable with respect to a denser phase of lower free energy.

At this point we have not quite demonstrated that the fluid phase is stable above \( T_{coll} \) but collapses to the close-packed solid at this temperature; we have not considered the effect of the sticky attractions on the dense fluid phase and the solid phase at densities below close packing. We will now consider their effect on the solid phase; there should be no qualitative difference between it and the dense fluid phase. At densities below \( \rho_{cp}/(1 + \delta/2) \) a sticky sphere cannot be within \( \delta \) of all \( z \) of its neighbours and so at these densities the energy is higher. If the sphere rattles freely in the cell and the cell is much larger than \( \delta \) across then the energy is close to zero: the solid is almost indistinguishable from a solid of hard spheres. It is possible that while keeping the overall density fixed the sticky spheres could form chains or sheets of spheres in contact. Forming a chain incurs an entropy cost of \( \ln(1/\delta) \) and releases an energy \( \epsilon \). Thus the free energy change of chain formation becomes negative at \( T_{B20} \), as we would expect given the nature of the second virial coefficient approximation for the free energy of a fluid. So, as \( T_{coll} > T_{B20} \) chains are not favoured at \( T_{coll} \). Forming sheets costs \( 3\ln(1/\delta) \) and releases an energy \( z_s \epsilon/2 \) where \( z_s \) is the coordination number of the sheet. The highest coordination number for a sheet is \( z_s = 6 \), so sheets are never stable: their entropy is no higher than that of a close-packed solid but their energy is only half that of the close-packed solid. So, we conclude that at and above \( T_{coll} \) the free energy of sticky spheres is the same as that of hard spheres at all densities below close packing and that therefore at \( T_{coll} \) sticky spheres at any density below close packing phase separate into an infinitely dilute gas coexisting with a close-packed solid. The gas is infinitely dilute as its free energy per particle must be less than that of the close-packed solid which is \(-\infty\). Above \( T_{coll} \) the free energy of the solid diverges to \( \infty \) as we approach close packing: the solid behaves as a solid of hard spheres and the fluid–solid transition is at the same densities as found for hard spheres.

At higher temperatures, Bolhuis et al. have shown that at close packing there is an expanded-solid–condensed-solid transition which is analogous to a vapour–liquid transition. This transition persists up to a critical temperature \( T_c/\epsilon = \mathcal{O}(1) \). However, because this occurs at close packing this transition is isolated from the fluid phase; the solid which coexists with the fluid is at much lower density where the attractive interactions have no effect at a temperature \( T/\epsilon = \mathcal{O}(1) \).
3 Polydisperse sticky spheres

In a polydisperse mixture of sticky spheres, spheres with a range of diameters are present \[4–6\]. In the thermodynamic limit there is a continuous distribution of spheres of sizes with a density \(\rho x(s)ds\) of spheres of size \(s\). The fraction of spheres of size \(s\) is \(x(s)ds\). The width of the polydispersity is characterised by a width parameter \(w\). The larger is \(w\) the broader the distribution of sizes present in the mixture. In the limit \(w \to 0\) we recover a monodisperse system. Generally, this limit is straightforward but here of course, we are taking the limit \(\delta \to 0\) limit so we must take care in the limit of small \(w\) as then the ratio \(w/\delta\) may not be small and so the phase behaviour will depend on it \[3\]. In order to recover a monodisperse system the ratio of \(w\) to all other length scales must tend to 0.

Stell \[3\] realised that the phase behaviour of polydisperse sticky hard spheres depends strongly on the ratio \(r = w/\delta\). For \(r \ll 1\) then the spheres are effectively monodisperse and they behave as described in the previous section. However, in the opposite limit, sufficiently large polydispersity suppresses the collapse. However, Stell did not determine how large must the ratio \(r\) be in order to do so. This is what we do here. We will show that the width of polydispersity required to stabilise the fluid phase is a function of temperature. As the temperature decreases below the \(T_{coll}\) of Eq. (10) the width of the polydispersity required to suppress the collapse to a close-packed solid and so stabilise the fluid phase increases exponentially.

We will take the range of the attraction to be \(\delta\) and the well depth to be \(\epsilon\) for all spheres. This would be appropriate if the attraction is a depletion attraction induced by the presence of small spheres \[20–23\] and the polydispersity width \(w\) is much less than the diameter of the spheres. The functional form of the polydispersity should not matter too much; we select a very simple form, the hat function. The function \(x(s)\) is defined to be

\[
x(s) = \begin{cases} 
0 & s < 1 - w/2 \\
-1 & 1 - w/2 \leq s \leq 1 + w/2 \\
0 & s > 1 + w/2
\end{cases}
\] (11)

The interaction \(u(r, s, s')\) between a pair of spheres of species \(s\) and \(s'\) is

\[
u(r, s, s') = \begin{cases} 
\infty & r \leq (1/2)(s + s') \\
-\epsilon & (1/2)(s + s') < r \leq (1/2)(s + s') + \delta \\
0 & r > (1/2)(s + s') + \delta
\end{cases}
\] (12)

First, let us consider the low density fluid phase. The free energy per particle of a polydisperse ideal gas is \[4–6\]

\[
\frac{a_f}{T} = \ln \rho + \int x(s) \ln x(s)ds.
\] (13)

For the distribution of Eq. (11)

\[
\frac{a_f}{T} = \ln \rho - \ln w.
\] (14)

Now, it is observed that a solid of hard spheres can tolerate a polydispersity of approximately 10% \[11–14\] of the hard sphere diameter. This makes sense if we note that the lattice constant of the solid is at most of order 10% larger than the diameter of the hard spheres. Hard spheres melt at a fraction \(\simeq 0.74\) of close packing \[24\] which corresponds to a lattice constant \(\simeq 1.11\) times the hard sphere diameter. Only if the polydispersity is sufficiently narrow that few or no spheres are larger than this lattice spacing can the mixture solidify \[11\]. We assume that this is also true for polydisperse sticky spheres; that they can form a solid lattice if and only if the width of the
polydispersity is less than the difference between the lattice spacing and the average diameter. Sticky hard spheres solidify into a solid with a lattice constant $\simeq 1 + \delta/2$ and so polydispersity with a width less than $\delta/2$ should allow solidification. When $w \gg \delta$ the polydisperse spheres are unable to solidify into a single solid. However, if the polydisperse spheres fractionate, i.e., if they phase separate into fractions each with a width $< \delta/2$ then these fractions can individually solidify. Of course, this phase separation costs some ideal mixing entropy but at low temperatures this will be outweighed by the reduction in energy due to the spheres now being in a 12-coordinate lattice. The phase separation is to phases with a width $\simeq \delta/2$, so we have one phase with the spheres in the range of diameters $(1 - w/2)$ to $(1 - w/2 + \delta/2)$, one phase with the spheres $(1 - w/2 + \delta/2)$ to $(1 - w/2 + \delta)$, etc. This implies that a fluid with polydispersity of width $w$ solidifies into $2w/\delta$ solid phases. The free energy of these phases is equal to that for a monodisperse solid, Eq. (8) minus the mixing entropy for polydisperse spheres with a distribution of width $\simeq \delta/2$, obtained from Eq. (13). This is
\[
\frac{a_s}{T} = -4 \ln \delta - 6 \epsilon / T, \tag{15}
\]
where we have neglected a term $\ln 2$ as being negligible.

Now we can use the free energies of the fluid and solid phases, Eqs. (14) and (15), to determine the lowest temperature at which the fluid is stable with respect to the solid. In the limit $\delta \to 0$
\[
\frac{a_s - a_f}{T} = \begin{cases} 
\infty & T > T_{\text{poly}}^{\text{coll}} \\
-\infty & T < T_{\text{poly}}^{\text{coll}} 
\end{cases}, \tag{16}
\]
where $T_{\text{poly}}^{\text{coll}}$ is
\[
\frac{T_{\text{coll}}^{\text{poly}}}{\epsilon} = \lim_{\delta \to 0} \left( \frac{6}{\ln (r/\delta^3)} \right) \delta^{-1} \gg r \gg 1, \tag{17}
\]
where the lower bound on $r$ ensures that $r$ is large enough that the number of demixed phases is sufficiently large that it can be treated as a continuous variable without introducing significant error, and the upper bound ensures that the polydispersity width $w \ll 1$. So, below $T_{\text{coll}}^{\text{poly}}$ the polydisperse sticky spheres collapse to form $\simeq 2w/\delta$ solid phases, each with a narrow polydispersity width of $\simeq \delta/2$. $T_{\text{coll}}^{\text{poly}}$ is the lowest temperature at which the fluid phase is stable. This is the principal result of this work, that polydispersity delays but does not eliminate the collapse of sticky spheres, and that the collapse drives fractionation of the mixture. We see that as the ratio of the width of polydispersity to the range of the attraction, $r$, increases the collapse temperature $T_{\text{coll}}^{\text{poly}}$ decreases slowly; the variation is only logarithmic.

If we compare Eqs. (4) and (17) we see that as $r$ is at most $\ll \delta^{-1}$, then $T_{\text{coll}}^{\text{poly}}$ is always above $T_{B20}$. When the polydispersity of the spheres is not large in comparison with their diameter then they always collapse above the temperature at which the second virial coefficient starts to differ from that of hard spheres. This contradicts Stell’s speculation [3] that polydisperse sticky spheres may show ‘normal’ behaviour, such as a vapour-liquid transition. We have shown that this not so when $w \ll 1$. Actually, we have implicitly assumed that the thermodynamic limit is taken before the $\delta \to 0$ limit. If the order of the two limits is reversed, then as Stell has shown the dramatic collapse is prevented [3]. Even if we relax the constraint on $w$ and consider $w = \mathcal{O}(1)$, then so long as $\epsilon$ is the same for all spheres (which it will not be if the attraction is due to depletion) then Eq. (17) still holds and the fluid phase becomes unstable before the second virial coefficient starts to differ from its hard-sphere value. Thus, the phase behaviour first derived by Baxter using the Percus-Yevick (PY) approximation [1, 3, 15] is qualitatively incorrect even for polydisperse sticky spheres.
4 Discussion

We have found that polydispersity stabilises the fluid phase of sticky hard spheres. The larger the polydispersity the lower the temperature at which the fluid phase becomes unstable with respect to demixing and solidification into a number of coexisting solid phases. This is a straightforward consequence of the cost in mixing entropy incurred in phase separating to form fractions which are sufficiently monodisperse to solidify. Polydisperse mixtures have been studied before and the effect of polydispersity on transitions such as solidification \[12-14\], liquid crystal transitions \[25\] and on transitions in the fluid state \[3, 24\] has been studied. However, there has been no theoretical demonstration of coupled solidification and phase separation of a polydisperse mixture. See Ref. \[27\] for phase separation of polydisperse mixtures in the fluid phase.

Finally, we comment on the relevance of our findings to demixing in mixtures of hard spheres. There has been much recent interest in binary mixtures of hard spheres, see Refs. \[28-31\] and references therein. The question is: Does a binary mixture of small and large hard spheres ever phase separate to form two coexisting fluid phases? The answer appears from the latest work \[31\] to be no. Now, in a mixture of small and large hard spheres the small spheres can be integrated out, see Refs. \[20-22, 31\] for details. Then the binary mixture of hard spheres becomes a single component system of spheres interacting via a hard core plus an attraction with a range of order of the diameters of the small spheres. Thus in the limit that the ratio $\gamma$ of the diameter of the small spheres to that of the large spheres is zero the mixture becomes a single component system of sticky spheres. We know that sticky spheres do not exhibit fluid–fluid coexistence which implies that a binary mixture of hard spheres does not exhibit fluid–fluid coexistence in the $\gamma \to 0$ limit. This, of course, does not rule out coexistence for $0 < \gamma \ll 1$ but Dijkstra et al. \[31\] find that fluid–fluid demixing is metastable in this range. However, the analysis of our section 3 suggests that even polydisperse sticky spheres do not show fluid–fluid coexistence. This implies that a mixture of polydisperse large spheres and small spheres do not phase separate into two coexisting fluid phases.

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