Depletion induced demixing in polydisperse mixtures of hard spheres

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Abstract

Polydisperse mixtures are those in which components with a whole range of sizes are present. It is shown that the fluid phase of polydisperse hard spheres is thermodynamically unstable unless the density of large spheres decreases at least exponentially as their size increases. The instability is with respect to the large spheres crystallising out into multiple solid phases.

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Mixtures of hard spheres in which spheres with a wide range of diameters are present are a good first model of emulsions. Emulsions are suspensions of droplets of oil or fat in water; milk is perhaps the most familiar example. The droplets of an emulsion interact via a short ranged repulsion, which is well represented by a hard-sphere interaction. They are typically present with a wide range of diameters: from 0.1 to a few micrometers \[ 0.1 - 100 \mu m \]. Mixtures in which a continuous range of sizes are present are termed polydisperse. They are much less well understood than systems which contain only one or two components. For example, the phase behaviour of single component hard spheres \[ \sigma \] has been understood for thirty years: the fluid phase is stable up the point where the spheres occupy a little less than half the volume of the suspension, there is then a first order transition to a solid. In contrast there are no phase diagrams known for polydisperse hard spheres. Below, we examine polydisperse spheres with particular emphasis on the largest spheres. We show that unless their density decreases at least exponentially with increasing size, they crystallise out of the mixture at all densities. The mixture is then never stable as a single fluid phase. The crystallisation is driven by a depletion attraction \[ \sigma \] between the large spheres, due to the smaller spheres. Depletion-induced separation of the largest spheres has been observed in emulsions \[ \sigma \] but there the floating of the droplets to the surface due to gravity complicates the situation. Our demonstration applies to spheres at equilibrium.

Specifying a polydisperse mixture requires specifying the number density of spheres of every size. This is done with a distribution function \[ x(\sigma) \] \[ \sigma \]. The number density of spheres with diameter \( \sigma \) is then \( \rho x(\sigma) d\sigma \), where \( \rho \) is the total number density of spheres. Although our final result will apply to a whole class of distribution functions we choose a specific function for definiteness and because it is widely used to describe emulsions \[ \sigma \] and powders \[ \sigma \]. The distribution is called the log-normal distribution, and it is defined by

\[
x(\sigma) = \frac{1 + w^2}{\sigma \sqrt{2\pi \ln(1 + w^2)}} \times \exp \left( -\frac{\left[ \ln(\sigma/\sigma) + (3/2) \ln(1 + w^2) \right]^2}{2 \ln(1 + w^2)} \right),
\]

where \( \sigma \) is the mean diameter and \( w \) is the standard deviation in units of \( \sigma \). Note that for this distribution there is no upper limit on \( w \); its lower limit is zero and corresponds to a one component system. In the canonical ensemble a polydisperse mixture of hard spheres is completely specified by \( x(\sigma) \) and the total number density of spheres \( \rho \); for hard spheres the temperature is not a relevant variable.

In order to make progress in understanding a polydisperse mixture of hard spheres with a broad distribution of sizes we distinguish between the spheres with diameters close to or less than the average diameter \( \sigma \) and spheres with much greater diameters. Due to the large differences in size and number density of these two sets of spheres we will treat them differently. Not only is the number density of the large spheres much less than that of the spheres with diameters near \( \sigma \) but the fraction of the fluid’s volume they occupy is much less. This is so because \( x(\sigma) \), Eq. \( \sigma \), decays much faster than \( \sigma^{-3} \) at large \( \sigma \).

Consider the very large spheres of the distribution, those with diameters \( \sigma \gg \sigma \). These spheres are immersed in a ‘sea’ of spheres much smaller than themselves, for each large sphere there are many spheres with diameters of the
same order as $\sigma$ or smaller. These smaller spheres induce an effective attraction between the large spheres of the polydisperse mixture: the well-known depletion attraction first described by Asakura and Oosawa [1]. This effect has been extensively studied both theoretically [2,3,4] and in experiments on colloids which accurately model (polydisperse) hard spheres [5,6,7].

The depletion attraction is entropic in origin (it cannot have any other origin as in hard spheres there is no energy of interaction and so there is nothing but entropy). When two spheres approach each other then the volumes they exclude to the other spheres overlap. Thus the volume this pair of spheres denies to the other spheres decreases and so the volume available to the other spheres increases, increasing their entropy. This is particularly pronounced for a pair of large spheres surrounded by many small spheres, then when the large spheres touch the entropy of very many small spheres increases.

For a pair of spheres of diameter $\sigma$ immersed in an ideal gas of spheres all of diameter $\sigma' \ll \sigma$ the range of the depletion attraction is $\sigma + \sigma'$. The attraction increases from zero when the surfaces of the large spheres are $\sigma'$ apart to a maximum when the large spheres touch. The strength of the effective attraction can be measured by its value at contact divided by the thermal energy $kT$, $u$. This is the increase in the entropy of the small spheres of size $\sigma'$ when a widely separated pair of spheres of size $\sigma$ is brought into contact with each other. It is given by

$$u = -\rho_s v_{ov},$$

where $\rho_s$ is the density of the small spheres. Each large sphere excludes the smaller spheres from a spherical volume of diameter $\sigma + \sigma'$, shown in Fig. 1 by the thick lines around the spheres. When two large spheres are touching, the two volumes which they exclude to the small spheres overlap. The volume of overlap of these two volumes is $v_{ov}$. In Fig. 1 we see that this volume is equal to that of two caps, each an end of a sphere of diameter $\sigma + \sigma'$ and of height $\sigma'/2$. We are considering the limit of small $\sigma'/\sigma$ and so the caps are very flat. Then the height of one of the caps a distance $x$ from a line drawn between the centres of the two large spheres is $(\sigma'/2)(1 - x^2/r^2)$ where $r$ is the radius of a cap at its base; $r^2 = \sigma\sigma'/2$. The total volume of the two caps

$$v_{ov} = 2\int_0^\sigma 2\pi x \left(\frac{\sigma'}{2}\right) \left(1 - \frac{x^2}{r^2}\right) dx = \frac{\pi}{4} \sigma'\sigma^2.$$ (3)

Now, for polydisperse spheres distributed according to Eq. (4) the number density of spheres with diameter $\sigma'$ is $\rho x(\sigma') d\sigma'$ and so for a pair of spheres of diameter $\sigma \gg \sigma_c$ the depletion attraction due to spheres with diameters $\leq \sigma_c$ is

$$u(\sigma) = -\frac{\pi}{4} \sigma^2 \int_0^{\sigma_c} x(\sigma')\sigma'^2 d\sigma',$$ (4)

which depends on the cutoff $\sigma_c$. However, if $\sigma$ is sufficiently large that $\sigma \ll \sigma_c \ll \sigma$ then the integral depends only weakly on $\sigma_c$ because $x(\sigma')\sigma'^2$ is small for values of $\sigma' \geq \sigma_c$. Indeed we can extend the upper limit of integration to infinity without introducing a significant error. The fact that we can do so justifies our splitting of the distribution into two parts. Then we have

$$u(\sigma) = \frac{3}{2} \frac{\eta}{(1 + w^2)^2} \frac{\sigma}{\sigma} \sigma \gg \sigma,$$ (5)

where we have used the relation $\eta = (\pi/6)\rho^3(1 + w^2)^3$ which holds when $x(\sigma)$ is given by Eq. (4). The physical content of this approximation is that very large spheres only notice spheres with diameters around $\sigma$ and less; the density of the larger spheres is too small to add significantly to the depletion effect. Note that the attraction increases linearly with the size of the spheres $\sigma$.

By using the idea of a depletion attraction we have reduced our polydisperse mixture to the large $\sigma$ tail of the distribution interacting via an effective interaction which is the sum of a hard-core interaction plus the short ranged attraction of Eq. (5). The attraction of Eq. (4) favours condensed phases where the large spheres are within the range of the attraction of each other. Competing against this attraction is the translational entropy of the large spheres, which favours dilute phases. This competition is the same as that involved in the vapour-liquid transition of a simple substance such as argon. The translational entropy of the large spheres is just that of an ideal gas mixture, so per large sphere of size $\sigma$ it is

$$s_F(\sigma) = 1 - \ln[\rho x(\sigma)] \\ \sim \text{const.} - \ln(\rho/\sigma) \\ - (3/2) \ln(\sigma/\sigma) + \frac{[\ln(\sigma/\sigma)]^2}{2 \ln(1 + w^2)},$$ (6)

where the second expression is obtained by substituting Eq. (4) in the first and the constant is a function only of $w$. The entropy $s_F$ increases with sphere size $\sigma$ because the density decreases. But it only increases as the square of a log, which is a slower than linear increase.

The stability of the dilute fluid phase with respect to condensation into a phase in which the density of large spheres is much higher, is determined by the relative entropy of the dilute and condensed phases. Therefore, we require the entropy of the condensed phase. The range of the depletion attraction is $\sim \sigma$. For spheres of diameter $\sigma \gg \sigma$, this is very small in comparison to the size of the sphere, $\sigma$. In the $\sigma \rightarrow \infty$ limit, the ratio of the range of the attraction to the size of the sphere, $\sigma/\sigma$, tends to zero.

This is the sticky-sphere limit introduced by Baxter [7]. Thus the large spheres are all near this sticky-sphere limit and as $\sigma$ diverges the spheres tend towards the limit. Stell has shown [8,9] that as the strength of the attractions is increased, a fluid of sticky spheres does not condense to form a liquid but collapses to form a close-packed solid, see also Refs. [10,11]. So, we look not for condensing of the large spheres into a dense, liquid-like, phase but for collapse into a dense solid. We therefore require the entropy in the dense solid phase. By dense we mean sufficiently close to
the close packed density that the sphere is within the range of
the depletion attraction of its neighbours.

The entropy per large sphere, \( s_K \) of a dense solid phase has
two parts. The first is the entropy associated with the
motion of the large sphere, and the second is the entropy
gain of the small spheres when a large sphere is brought
close to twelve neighbouring spheres, as it is in a dense
face-centred-cubic or hexagonal-close-packed lattice. The
first part is easily obtained from a cell theory \([21, 22]\). This
assumes that each sphere is restricted to a cage formed by
its neighbours, which are taken to be fixed at their lattice
positions. For a solid with a lattice constant \( a \), the centre
of mass of a sphere can move a distance \( \sim (a - \sigma) \) from
its lattice position without bumping into any of its neigh-
bours. The solid is formed due to attractive interactions so
the spheres must be close enough to each other to attract
each other throughout the cage which its neighbours form.
For this to be true \( a \) must satisfy \( a < \sigma + c \sigma / 2 \), and so
\( a - \sigma = c \sigma \), where \( c \) is a parameter in the range \((0, 1/2)\).
For monodisperse spheres the entropy is simply the loga-

\[
\Delta s(\sigma) \simeq \text{const.} + \ln \left( c^4 \sigma^3 \right) + (3/2) \ln(\sigma / \sigma) \sim \frac{[\ln(\sigma / \sigma)]^2}{2 \ln(1 + w^2)} + \frac{\eta}{(1 + w^2)^2} \sigma \sigma \gg \sigma (9)
\]

When the volume fraction \( \eta \) is non-zero, this is positive for
sufficiently large \( \sigma \). In fact it is positive for any \( x(\sigma) \) which
decreases more slowly than exponentially with \( \sigma \). There-

very Cuesta \([27]\) has shown that within the
Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) \([4]\)
approximation polydisperse hard spheres with a log-normal
distribution with a sufficiently large standard deviation \( w \)
have a spinodal. Warren has also found a spinodal within
the BMCSL approximation \([18]\). A spinodal is where the
fluid phase becomes unstable with respect to an infinitesi-
mal density and composition fluctuation. The difference
between Cuesta’s result and ours is probably due to one or
both of two factors. The first factor is the nature of the
transition we have found. It is very strongly first order and
so the transition occurs much before the spinodal. The sec-
ond factor is the accuracy of the BMCSL approximation.
It may be poor when there are spheres of widely different
sizes present \([21]\).

In comparing our result with experiment it should be
remembered that in an emulsion there will be some upper
size limit, beyond which there are essentially no particles.
Obviously, the number of phases which separate out is then
not infinite. In addition, at sufficiently low volume frac-
tions the fluid phase of the emulsion will be stable. The
fluid phase can be destabilised by adding small spheres to
the distribution, so increasing the strength of the deple-
tion attraction. For emulsions, micelles can be added and
indeed this is done in Bibette’s \([3]\) procedure for fraction-
ating emulsions.

To summarise, polydisperse hard spheres with a non-
zero volume fraction and distributed according to a dis-
tribution function which decays more slowly than expo-
nentially are thermodynamically unstable. Spheres above
some lower size limit crystallise due to the depletion attraction induced between them by the presence of the smaller spheres of the distribution. We have not determined this lower limit but it is much larger than the average size  over the range of spheres which crystallise. The lower limit to the sizes of spheres which crystallise is clearly finite as a solid phase will form so long as it reduces the entropy by any non-zero amount. The sub-linear increase with of the translational entropy in the fluid is the crucial factor in destabilising the fluid phase. It inevitably leads to the fluid being unstable when the attractions grow linearly with sphere diameter.

Finally, we conjecture that the instability we have found is not restricted to spheres or to attractions which arise from depletion. Consider a general polydisperse fluid with a number density  and the range of spheres which crystallise is from this lower limit to infinity. Thus, the number of solid phases which form is infinite. This seems surprising at first but in the large it is much larger than the average size of elements condensing out to form a dense phase in the fluid being unstable when the attractions grow linearly with sphere diameter.

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References

[1] K. J. Packer and C. Rees, J. Coll. Int. Sci. 40, 206 (1972).
[2] P. J. McDonald, E. Ciampi, J. L. Keddie, M. Heidenreich and R. Kimmich, Phys. Rev. E, in press.
[3] J. Bibette, J. Coll. Int. Sci. 147, 474 (1991).
[4] J. J. Salacuse and G. Stell, J. Chem. Phys. 77, 3714 (1982).
[5] W. G. Hoover and F. H. Ree, J. Chem. Phys. 49, 3609 (1968).
[6] S. Asakura and F. Oosawa, J. Chem. Phys. 22, 1255 (1954); J. Polymer Sci. 33, 183 (1958).
[7] A. Vrij, Pure Appl. Chem. 48, 471 (1976).
[8] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. 47, 2200 (1976).
[9] A. P. Gast, C. K. Hall and W. B. Russell, Faraday Discuss. Chem. Soc. 76, 189 (1983).
[10] M. Dijkstra, R. van Roij and R. Evans, Phys. Rev. Lett. 81, 2268 (1998).
[11] W. C. K. Poon and P. N. Pusey, Proceedings of the International School of Physics ‘Enrico Fermi’ Course CXXIX, edited by M. Baus, L. F. Rull and J. P. Ryckaert (Kluwer, Dordrecht, 1995).
[12] H. N. W. Lekkerkerker, P. Buining, J. Buitenhuis, G. J. Vroege and A. Stroobants, ibid..
[13] P. D. Kaplan, L. P. Faucheux and A. J. Libchaber, Phys. Rev. Lett. 73, 2793 (1994).
[14] A. D. Dinsmore, A. G. Yodh and D. J. Pine, Phys. Rev. E 52, 4045 (1995).
[15] A. D. Dinsmore, A. G. Yodh and D. J. Pine, Nature 383, 239 (1996).
[16] A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. 75, 1662 (1995).
[17] R. J. Baxter, J. Chem. Phys. 49, 2770 (1968).
[18] G. Stell, J. Stat. Phys. 63, 1203 (1991).
[19] P. C. Hemmer and G. Stell, J. Chem. Phys. 93, 8220 (1990).
[20] P. Bolhuis, M. Hagen and D. Frenkel, Phys. Rev. E 50, 4880 (1994).
[21] R. P. Sear, Mol. Phys., in press; cond-mat/9805201 (http://xxx.lanl.gov).
[22] R. J. Buehler, R. H. Wentorf, J. O. Hirschfelder and C. Curtiss, J. Chem. Phys. 19, 61 (1951).
[23] R. P. Sear, Europhys. Lett., in press; cond-mat/9806205 (http://xxx.lanl.gov).
[24] P. Bartlett, cond-mat/9809131 (http://xxx.lanl.gov).
[25] P. N. Pusey, J. Phys. (France) 48, 709 (1987).
[26] J. L. Barrat, and J. P. Hansen, J. Phys. (France) 47, 1547 (1986).
[27] J. A. Cuesta, cond-mat/9807030 (http://xxx.lanl.gov).
[28] P. B. Warren, cond-mat/9807117 (http://xxx.lanl.gov).
[29] T. Coussaert and M. Baus, J. Chem. Phys. 109, 6012 (1998).

Figure caption

Fig. 1. A schematic of two large touching spheres of diameter , the shaded discs, with the volumes they exclude to smaller spheres of diameter . These volumes are outlined by the heavy circles and they overlap when the large spheres touch.
