Depletion-Induced Demixing in Polydisperse Mixtures of Hard Spheres

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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 crystallizing into multiple solid phases. [S0031-9007(99)09203-0]

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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-range 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 [1–3]. Mixtures in which a continuous range of sizes are present are termed polydisperse [4]. They are much less well understood than systems which contain only one or two components. For example, the phase behavior of single component hard spheres 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 study a dilute fluid phase and show that, unless the density of the largest spheres decreases at least exponentially with increasing size, they crystallize out of the mixture at all densities. The mixture is then never stable as a single fluid phase. The crystallization is driven by a depletion attraction [5–7] between the large spheres, due to the smaller spheres. Depletion-induced separation of the largest spheres has been observed in emulsions [3] 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 $x(\sigma)$ [4]. The number density of spheres with diameter σ is then $\rho x(\sigma) d\sigma$, where ρ 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 because it is widely used to describe emulsions [1,2] and powders [8]. The distribution is called the log-normal distribution, and it is defined by

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

where $\overline{\sigma}$ is the mean diameter and w is the standard deviation in units of $\overline{\sigma}$. 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 ρ; for hard spheres the temperature is not a relevant variable. We can also use the total volume fraction occupied by the spheres η instead of ρ; we will start from a dilute fluid and therefore η will be small. Temperature affects the de Broglie wavelength of each species, but as usual these wavelengths do not depend on density or composition and so have no effect on the phase behavior [4].

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 $\overline{\sigma}$ and spheres with much greater diameters. Because of 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 $\overline{\sigma}$ but the fraction of the fluid's volume they occupy is much less. This is so because $x(\sigma)$ [Eq. (1)] decays much faster than σ^{-3} at large σ.

Consider the very large spheres of the distribution, those with diameters $\sigma \gg \overline{\sigma}$. 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 $\overline{\sigma}$ 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 [5]. This effect has been extensively studied theoretically [6,9,10] and in experiments on colloids which accurately model (polydisperse) hard spheres [11–13].

The depletion attraction is entropic in origin (it cannot have any other origin because in hard spheres there is no energy of interaction and so there is nothing but entropy). When two spheres approach each other, 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; when the large spheres touch, the entropy of very many small spheres increases.

For a pair of spheres of diameter σ immersed in an ideal gas of spheres all of diameter, $\sigma' \ll \sigma$, the range of the depletion attraction is $\sigma + \sigma'$. 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 σ' when a widely separated pair of spheres of size σ is brought into contact with each other. It is given by [5–7]

$$u = -\rho_s v_{\text{ov}}\,, \tag{2}$$

where ρ_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 σ'/σ and so the caps are very flat. Then the height of one of the caps a distance x from a line drawn between the centers 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

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

Now, for polydisperse spheres distributed according to Eq. (1) the number density of spheres with diameter σ' 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

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

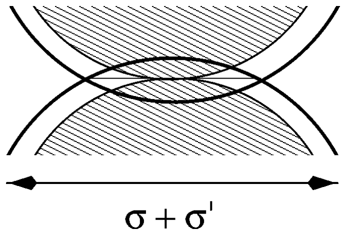

FIG. 1. A schematic of two large touching spheres of diameter σ, the shaded disks, with the volumes they exclude to smaller spheres of diameter σ'. These volumes are outlined by the heavy curves and they overlap when the large spheres touch.

which depends on the cutoff σ_c. However, if σ is sufficiently large so that $\overline{\sigma} \ll \sigma_c \ll \sigma$, the integral depends only weakly on σ_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. We then have

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

where we have used $\eta = (\pi/6)\rho\overline{\sigma}^3(1 + w^2)^3$. The physical content of this approximation is that very large spheres only notice spheres with diameters around $\overline{\sigma}$ 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 σ.

By using the idea of a depletion attraction we have reduced our polydisperse mixture to the large σ tail of the distribution interacting via an effective interaction which is the sum of a hard-core interaction plus the short-range attraction of Eq. (5). The attraction of Eq. (5) favors 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 favors dilute phases. The translational entropy of the large spheres is just that of an ideal gas mixture, so that, per large sphere of size σ, it is [4]

$$s_F(\sigma) = 1 - \ln[\rho x(\sigma)]\,, \tag{6}$$

$$\sim \text{const} - \ln(\rho/\overline{\sigma}) - (3/2)\ln(\sigma/\overline{\sigma}) + \frac{[\ln(\sigma/\overline{\sigma})]^2}{2\ln(1 + w^2)}\,, \tag{7}$$

where the second expression is obtained by substituting Eq. (1) into the first and the constant is a function only of w. The entropy s_F increases with sphere size σ 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 $\sim\overline{\sigma}$. For spheres of diameter $\sigma \gg \overline{\sigma}$, this is very small in comparison to the size of the sphere σ. In the $\sigma \to \infty$ limit, the ratio of the range of the attraction to the size of the sphere $\overline{\sigma}/\sigma$ tends to zero. Stell has shown [14,15] that, as the strength of the attractions is increased, a fluid of spheres with a zero-range attraction does not condense to form a liquid but collapses to form a close-packed solid (see also Refs. [16,17]). Therefore, we look not for condensing of the large spheres into a dense, liquidlike, 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 neighbors.

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 neighboring spheres, as it is in a dense face-centered-cubic or hexagonal-close-packed lattice [18]. The first part is easily obtained from a cell theory [17,19]. This assumes that each sphere is restricted to a cage formed by its neighbors, which are taken to be fixed at their lattice positions. For a solid with a lattice constant a, the center of mass of a sphere can move a distance $\sim(a - \sigma)$ from its lattice position without bumping into any of its neighbors. 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 their neighbors form. For this to be true, a must satisfy $a - \sigma = c\overline{\sigma}$, where $c \lesssim \frac{1}{2}$. For monodisperse spheres the entropy is simply the logarithm of the volume $(c\overline{\sigma})^3$, which is available to the center of mass of a sphere [19].

When the spheres are polydisperse the situation is more complicated. There is an upper limit to the range of sizes of spheres a single solid phase can tolerate [20]. A lattice can only accommodate spheres up to about its lattice constant a in diameter; larger spheres cannot fit into the lattice position without overlapping with their neighbors. Spheres with diameters less than $\sim(a - \overline{\sigma})$ are so small that they cannot be within the range of the depletion attraction of all of their neighbors [17]. This means that the large spheres cannot all crystallize into a single solid phase. In order to crystallize they first fractionate into many fractions, each containing spheres with only a narrow range of diameters. The fractions can then crystallize individually to produce separate solid phases, each containing spheres of a different size. The combined fractionation and crystallization of polydisperse spheres with zero-range attraction is discussed in Ref. [17]. The range of diameters is roughly $a - \sigma = c\overline{\sigma}$. This width of distribution contributes an amount $\simeq\ln(c\overline{\sigma})$ to the entropy of the solid [4,17].

The parameter c will be determined by a competition between the depletion attraction which tends to reduce it and the motion of the large sphere which tends to increase it. However, our results are not sensitive to the exact value of c and so we merely take it to be much less than one. Then the depletion attraction is almost equal to its value at contact [Eq. (5)], and the gain in entropy of the small spheres per large sphere which solidifies is closely equal to minus six times Eq. (5). The entropy per large sphere of a solid phase of large spheres of size σ,

$$s_K(\sigma) \simeq 4\ln(c\overline{\sigma}) - 6u(\sigma), \qquad \sigma \gg \overline{\sigma}, \qquad c \ll 1\,. \tag{8}$$

The solid phases are much denser than the fluid phase and so can be formed without increasing the volume occupied by the system. Thus if the solid phases have a higher entropy than the dilute fluid, the dilute fluid cannot be the equilibrium phase, as the entropy can be increased at fixed volume by forming the solid phases. We now compare the entropies of the fluid and solid phases. The entropy change per large sphere Δs, when spheres of average diameter σ separate from an ideal gas to form a crystal phase with a polydispersity of order $c\overline{\sigma}$, is Eq. (8) minus Eq. (7)

$$\begin{aligned}\Delta s(\sigma) \simeq{}& \text{const} + \ln(c^4\rho\overline{\sigma}^3) + (3/2)\ln(\sigma/\overline{\sigma}) \\ &- \frac{[\ln(\sigma/\overline{\sigma})]^2}{2\ln(1+w^2)} + 9\frac{\eta}{(1+w^2)^2}\frac{\sigma}{\overline{\sigma}}\,, \\ &\sigma \gg \overline{\sigma}\,. \end{aligned}\tag{9}$$

When the volume fraction η is nonzero, this is positive for sufficiently large σ. In fact, it is positive for any $x(\sigma)$ which decreases more slowly than exponentially with σ. Therefore, *any* fluid phase of hard spheres with a distribution which decreases more slowly than exponentially is *unstable* with respect to the largest spheres crystallizing into solid phases with narrow polydispersities. This is true however low η is, as long as it is nonzero; this justifies *a posteriori* our use of the Asakura-Oosawa approximation for the depletion attraction, which is only valid at low densities of the small spheres. A single solid phase can contain only a narrow slice, of width a fraction of $\overline{\sigma}$, of the original distribution $x(\sigma)$, but spheres with diameters ranging from infinity down to some large but finite limit crystallize. Thus, an infinite number of solid phases form, each phase with a different range of sphere sizes. For the sake of clarity, when we say that the fluid phase is unstable we mean that the solid phases have higher entropies. The fluid phase will, however, be metastable, i.e., stable with respect to infinitesimal perturbations.

Very recently, Cuesta [21] 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 [22]. A spinodal is where the fluid phase becomes unstable. 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 second factor is the poor accuracy of the BMCSL approximation when there are spheres of widely different sizes present [23]. Kofke and Bolhuis [24] have also studied the freezing of polydisperse hard spheres. Their polydisperse mixture contains a much narrower distribution of spheres and thus the small spheres, which are driving the behavior we have observed via the depletion attraction, are absent. As a result they observe very different behavior. Very high pressures need to be exerted on the spheres in order for them to freeze, and the fluid phase is stable with respect to the solid phase up to higher volume fractions than are monodisperse hard spheres.

In comparing our result with experiment it should be remembered that in an emulsion there will be some upper size limits, beyond which there are essentially no particles.

Obviously, the number of phases which separate is then not infinite. In addition, at sufficiently low volume fractions the fluid phase of the emulsion will be stable. The fluid phase can be destabilized by adding small spheres to the distribution, thus increasing the strength of the depletion attraction. For emulsions, micelles can be added and indeed this is done in Bibette's [3] procedure for fractionating emulsions.

In summary, a dilute suspension of polydisperse hard spheres with a nonzero volume fraction and distributed according to a distribution function which decays more slowly than exponentially is thermodynamically unstable. Spheres above some lower size limit crystallize 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 $\overline{\sigma}$. The solid phase can only tolerate a very limited polydispersity [17,20], and the range of spheres which crystallize 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 σ tail of the distribution, the depletion attraction is increasing more rapidly than the translational entropy in the fluid phase and so there is no upper limit to the sizes of spheres which crystallize. The sublinear increase with σ of the translational entropy in the fluid is the crucial factor in destabilizing the fluid phase. It inevitably leads to the fluid being unstable when the attractions grow linearly with sphere diameter. At high volume fractions, effects not considered here may become important, in particular, interactions between the spheres with diameters around $\overline{\sigma}$; the small spheres may even freeze. Thus our conclusions apply only to a dilute suspension in which the volume fraction is small.

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 $\rho x(l)dl$ of elements of size l, then the translational entropy increases as minus the logarithm of $x(l)$. If the attractive energy (over kT) $u(l)$ between elements increases faster than $\ln x(l)$,

$$\frac{d|u(l)|}{dl} > -\frac{d[\ln x(l)]}{dl}, \tag{10}$$

then the attractive energy is much larger than the translational entropy for sufficiently large l. When this is true we expect the mixture to be unstable with respect to the largest elements condensing out to form a dense phase in order to minimize the energy.

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