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The effect of polydispersity on colloidal phase transitions

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Abstract A polydisperse hard-sphere mixture contains particles with a continuous ranges of diameters. It is shown that the observed phase behaviour depends sensitively upon the kinetics of size fractionation. Two limiting situations are considered. In the quenched case, where the size distribution is fixed, the fluid–crystal transition is reentrant at low polydispersities and disappears altogether at high polydispersities. If size partitioning is allowed it is shown that the polydisperse crystal is spinodally unstable to small fluctuations in polydispersity. The direction of the instability suggests that equilibrium corresponds to a set of multiple crystal phases, each containing spheres with a narrow range of diameters.

Key words Colloids · Polydispersity · Hard spheres · Phase transitions

Introduction

A polydisperse mixture of hard spheres with a continuous range of sizes is a simple model of many colloidal suspensions. A well-known example [1] is poly(methyl methacrylate) (PMMA) stabilised by a thin polymeric layer of poly(12-hydroxystearic acid) and dispersed in a good solvent such as decalin. The colloidal particles in this suspension interact via a short-range repulsion, which is well represented by a hard-sphere interaction. While many of the properties of uniform hard spheres have been known for at least 30 years our understanding of polydisperse mixtures is much less developed. Most of the theoretical effort to date has concentrated on exploring the consequences of polydispersity for scattering [2]. In contrast, virtually no theoretical work on polydisperse phase diagrams has been reported (until recently [3–9]) despite the fact that many industrial products are frequently very polydisperse. It is, however, clear that as soon as a suspension is allowed to enjoy a significant degree of polydispersity several interesting new phenomena arise. First, increasing polydispersity can suppress certain phase transitions.

For instance, the fluid–crystal phase transitions reported in dispersions of latex particles of PMMA are only found if the particles have a narrow range of sizes. Pusey reported [1] that while PMMA spheres with a polydispersity, σ, of about 0.075 displayed a fluid–crystal transition similar to that reported for identically sized hard spheres, on increasing σ to about 0.12 no crystallites were found even after several months of observation. Second, those transitions which still remain in polydisperse systems are frequently accompanied by a fractionation of the particle size distribution between coexisting phases [7]. Finally, polydispersity can induce new transitions, not found for monodisperse systems [8].

Despite both the practical importance and the potential richness of polydisperse phase behaviour, the mathematical complexity of treating a mixture with essentially an infinite number of components makes a first-principles determination of a polydisperse phase diagram a formidable task. We examine a simple model for a system of polydisperse hard spheres with the aim of developing some generic insight into the thermodynamics of polydisperse transitions. We calculate the phase
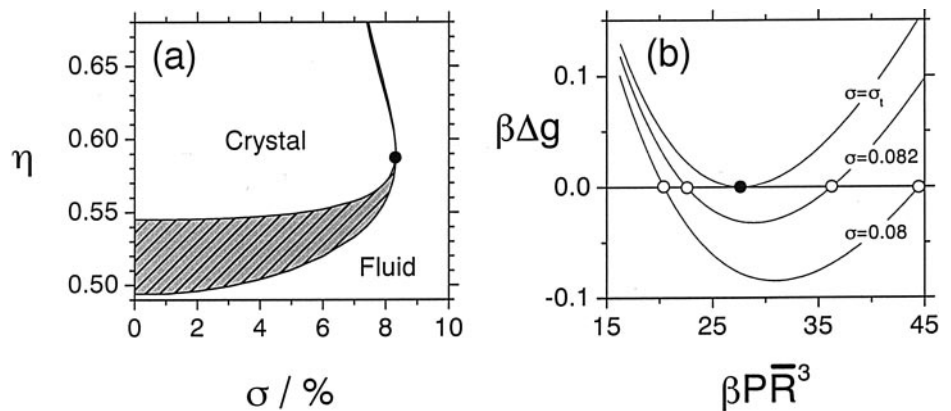
behaviour in two limits: the quenched limit, where the size distribution in each phase is fixed, and the corresponding annealed limit, where particles redistribute so as to minimise the total free energy. The physical significance of these two limits is clear if we remember that in a dense colloidal suspension collective diffusion is appreciably faster than self-diffusion [1], so fractionation will be slow. This difference in time scales implies that freezing could occur in two stages in a polydisperse suspension. First, a metastable suspension will relax its density rapidly to equilibrium by growing a crystal without fractionation (quenched behaviour). Then, over much longer times, self-diffusion will occur and the size distributions will relax towards the completely annealed state [9]. We find very different results for the phase behaviour in these two limits. In the quenched situation, the polydisperse crystal is stable at low polydispersities with the fluid–crystal transition only vanishing at polydispersities above a certain terminal level, σ_t. In contrast, in the annealed limit, the polydisperse crystal is thermodynamically unstable and separates into several solid phases, the number of which grows without limit as the polydispersity increases.

The model

The size of each particle in a polydisperse mixture can take any one of a set of essentially continuous values distributed according to a distribution function $x(R)$. The number density of spheres with diameter R is then $\rho x(R)\mathrm{d}R$, where ρ is the total number density. Since we do not expect our final results to depend significantly on the exact form of $x(R)$ we choose a specific function for definiteness. The generalised-exponential distribution is widely used to describe suspensions and is defined by

$$x(R) = \frac{(\sigma^{-2})^{\sigma^{-2}}}{\Gamma(\sigma^{-2})}\left(\frac{R}{\bar{R}}\right)^{\sigma^{-2}-1}\exp\left(-\sigma^{-2}\frac{R}{\bar{R}}\right) \ , \tag{1}$$

where $\bar{R}$ is the mean diameter and σ is the standard deviation in units of $\bar{R}$.

The polydisperse phase equilibrium is calculated using the finite-moment approximation introduced by Sollich and Cates [3] and Warren [4]. The justification for this approximation is the recognition that the excess free energy in a polydisperse hard-sphere mixture depends only on a limited set of moment densities, quantities such as $\phi_n = \rho m_n$, where the nth moment m_n is defined by $\int R^n x(R)\mathrm{d}R$, rather than by the explicit form of $x(R)$. The central idea is to treat the ϕ_n as independent thermodynamic density variables. Since the moment variables are simply linear combinations of species densities they acquire many of the properties of conventional particle densities. So, for instance, at equilibrium the moment chemical potentials (defined by analogy to the particle potentials), $\mu_n = \partial f/\partial\phi_n$ ($f = F/V$), are equal in all coexisting phases. The accurate equation of state (EOS) suggested by Boublik and Mansoori et al. [10] is used for the polydisperse fluid, while the crystal is approximated by a recently introduced EOS [11].

Quenched phase behaviour

In the quenched limit there is no size fractionation. The polydisperse system now behaves essentially as a one-component system with effective properties fixed by the polydispersity. The free energies of the polydisperse fluid and the crystal phases are formally only a function of ρ since m_n are fixed at their initial values. Phase boundaries are located by equating P and $\mu_\rho = \partial f/\partial\rho$. In the monodisperse limit we recover the expected transition from a fluid phase at a volume fraction of $\eta = (\pi/6)\phi_3 = 0.49$ to a crystalline phase at the higher volume fraction $\eta = 0.55$. This is the only transition in the monodisperse limit. Figure 1a shows how the phase boundaries shift with increasing polydispersity. The first effect increasing σ has is to progressively narrow the fluid–crystal coexistence region until it eventually vanishes at the

Fig. 1a, b Quenched phase behaviour for polydisperse hard spheres. a Phase boundaries in the polydispersity (σ)–volume fraction (η) plane. The miscibility gap vanishes at the azeotrope, marked by the *filled circle*. b The Gibbs-free-energy difference per particle, $\Delta g = g_s - g_f$, as a function of the dimensionless pressure. The *circles* mark the fluid–crystal transitions and the *filled circle* marks the position of the azeotrope

terminal point $\sigma_t = 0.083$ and $\eta_t = 0.59$. At high polydispersities, the free-energy difference between the crystal and fluid phases is a nonmonotonic function of the density or equivalently of the pressure (Fig. 1b). This indicates that at high densities there is an additional transition in the polydisperse system from the crystal back to a disordered phase. The range of densities over which the crystal is stable shrinks with increasing polydispersity until, at the terminal polydispersity, it has disappeared completely from the equilibrium phase diagram [5].

Annealed phase behaviour

The phase diagram depicted in Fig. 1a describes quenched freezing where m_n are fixed at their initial values. A natural question is what happens if we relax this constraint and allow particles to redistribute? This is more difficult to answer on two counts: first, because we have to deal with an effective four-component free energy $f(\rho, \phi_1, \phi_2, \phi_3)$ and second, the expression derived by Warren [4] for the reduced entropy, s, is intractable analytically for two or more moments. Here, we do not attempt to derive the equilibrium phase diagram from first principles. Instead, we investigate the stability of the polydisperse crystal phase to small fluctuations in moment densities. We find that a polydisperse crystal is always stable against fluctuations in the total number density but, above a certain density, is unstable against polydispersity fluctuations. This instability suggests that the equilibrium annealed state is one in which the broad initial diameter distribution is split into several narrower fractions. We confirm this hypothesis by comparing the free energies of polydisperse fluid, crystal and multiply fractionated solid phases and find that multiple crystal phases are stable over large regions of parameter space.

The criterion for stability of the polydisperse crystal is the standard one that the matrix of second partial derivatives of f with respect to the moment densities (including $\phi_0 = \rho$ amongst these) should be positive definite. The plane in the moment space where the determinant $|\partial^2 f / \partial \phi_i \partial \phi_j| = 0$ defines the position of the mean-field spinodal. Generally, the determinant is always positive except at high densities and polydispersities. The numerically determined spinodal with the instability region increasing as the degree of polydispersity increases is shown in Fig. 2. The origin of the instability is revealed by the direction in moment space along which the fluctuations diverge as the spinodal plane is crossed. The instability direction is defined by the eigenvector of the matrix $\partial^2 f / \partial \phi_i \partial \phi_j$ whose eigenvalue vanishes at the spinodal. The arrows on the spinodal line in Fig. 2 indicate the direction of the rapidly growing fluctuations, projected into the (σ, η)
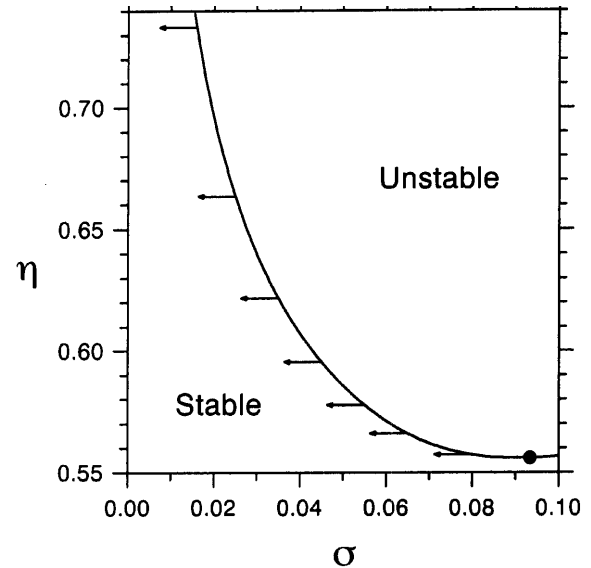

Fig. 2 The annealed spinodal (*solid line*) and critical point (*filled circle*) of the polydisperse hard-sphere crystal in the σ–η plane. The *arrows* indicate the spinodal instability direction

plane. The arrows are almost parallel to the σ-axis so the system is unstable towards a composition fluctuation in which σ and not ρ changes. The physical interpretation of this instability is straightforward. A close-packed crystal of monodisperse hard spheres has a maximum density of $\eta_{cp} \sim 0.74$ at which each sphere contacts its 12 equally sized nearest neighbours. In a polydisperse crystal, by contrast, there is a finite chance that one of the neighbouring spheres will be larger than the mean and these two spheres will then touch at a density $\eta < \eta_{cp}$. Consequently, increased polydispersity lowers the packing efficiency of the crystal. Compressing a polydisperse crystal results in phase separation since at some density the reduction in excess free energy as fractionation occurs will exceed the resulting loss of entropy of mixing.

The physical picture that emerges is that a crystalline lattice can only accomodate spheres with a narrow range of sizes, the width of the sizes being determined by the density. At high densities not all the differently sized spheres can crystallise into a single solid phase. In order to crystallise they must first fractionate before crystallising individually into separate solid phases each containing spheres of a different size. To confirm this picture we compare the free energies at each point in the (σ, η) plane of the polydisperse fluid, the unfractionated crystal (of polydispersity σ) and m coexisting solid phases (each with a polydispersity of σ/m). The resulting stability diagram is shown in Fig. 3. It is clear that there are large regions of parameter space where fractionated crystal phases are stable.
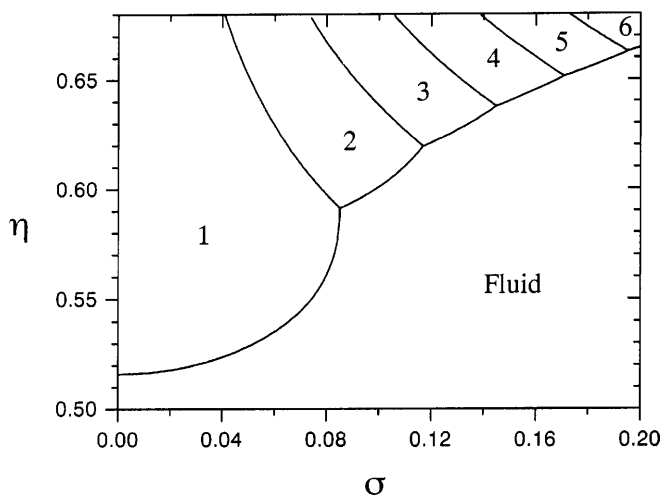
Fig. 3 The stability boundaries of the polydisperse hard-sphere system. The *caption* indicates the number of multiply fractionated crystal phases stable at each η and σ

Conclusions

We have shown that the effect of small levels of polydispersity is to narrow the width of the region of fluid–crystal coexistence. At higher levels of polydispersity, however, the phase behaviour predicted depends sensitively on the time scale for fractionation. If the kinetics of fractionation is slow compared with crystal nucleation and growth, as we conjecture should be the case for dense suspensions, then the fluid–crystal transition is reentrant. Above some density the polydisperse crystal melts back to an amorphous phase and the range of densities over which the polydisperse crystal is stable shrinks rapidly as one approaches a critical level of polydispersity. If there is either no significant separation between the time scales for the relaxation of the total density and the polydispersity or we are interested in the long-time properties then we expect very different behaviour. In this case the polydisperse hard-sphere crystal is thermodynamically unstable with a tendency to separate into multiple crystal phases, each containing spheres of a different size. Finally we comment on the relevance of our predictions to experiment. Although it is not clear yet from the limited experimental data available which (if either) of these two extreme limits is appropriate to the freezing of real colloidal systems our key result is the demonstration that the kinetic behaviour of polydisperse systems could prove to be very rich. Its elucidation remains a challenge to experimentalists.

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