Freezing in polydisperse colloidal suspensions

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Abstract.   The phase behaviour of a polydisperse mixture of hard spheres is examined within a moment-density approximation. The role of size fractionation and the difference between quenched and annealed phase behaviour is outlined. The quenched phase diagram shows a terminal level of polydispersity above which no fluid–crystal transition occurs. It is demonstrated that this singularity arises from the re-entrant nature of the freezing transition at high polydispersities. In the annealed situation by contrast, the polydisperse crystal is spinodally unstable with respect to fluctuations in polydispersity. The direction of the instability suggests that the equilibrium annealed state is a fractionated crystal.

1. Introduction

In contrast to atomic or molecular fluids, colloidal systems remain poorly understood states of matter. One of the major stumbling blocks on the route to a better understanding of colloids is the phenomenon of polydispersity. In a colloidal suspension every constituent particle is subtly different from every other. For instance the size, charge, and the interaction potential vary essentially *continuously* in a suspension. Experiments reveal that as soon as a suspension is allowed to enjoy a significant degree of polydispersity, several interesting new phenomena arise. Phase boundaries are shifted [1]—in some cases totally suppressed [2] and accompanied frequently by fractionation [3]. Despite the practical importance of polydispersity, the mathematical complexity of treating a mixture of infinitely many components has meant that to date most theories of colloidal phase behaviour have ignored polydispersity.

In this work, we examine the effect of size polydispersity on the freezing transition of hard spheres (HS). The hard-sphere model is a very good representation of the properties of spherical colloidal particles which interact via steeply repulsive steric interactions [2]. The equilibrium phase is fluid at volume fractions $\eta < 0.494$ and crystalline at $\eta > 0.545$, with the two phases coexisting between these densities. The main complication of introducing polydispersity into this model is the possibility that different sized species will partition between phases. The rate of such fractionation will, in general, be slow since it requires large-scale individual particle motion which must occur by self-diffusion. In dense colloidal systems, collective diffusion is some two orders of magnitude faster than self-diffusion [2], so we expect freezing in a polydisperse suspension to occur in two stages. First, a metastable suspension will relax its density rapidly to equilibrium by nucleating 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 [4].

Given the simplicity of the hard-sphere model it is not surprising that the effect of polydispersity has been investigated extensively [5, 6]. Most of the calculations [5] have

assumed that the size distributions in coexisting phases are equal and so have essentially calculated quenched behaviour. (The exception is the recent work of Kofke and Bolhuis [6] who have studied the annealed phase diagram using Monte Carlo techniques.) Given the diversity of theoretical approaches used to tackle the quenched system, there is a remarkable uniformity in their predictions. On increasing the polydispersity σ from zero, defined as the standard deviation of the size distribution divided by its mean, the density discontinuity at the transition decreases, vanishing altogether at a 'terminal' polydispersity, $\sigma = \sigma_t$, above which no fluid–crystal transition is found. These previous studies have left unanswered a number of key questions. First, why do the densities of the coexisting phases converge as $\sigma \to \sigma_t$ and second, what is the nature of the fluid–solid transition at σ_t? In this paper we summarize the results of a recent study [7] in which these questions were addressed. We then go on to consider how the annealed phase diagram may differ from the quenched limit.

2. Moment densities

Our starting point is the recognition that the excess free energy in a polydisperse HS system is a function of a limited number of moments of the diameter distribution $p(R)$. For instance, if we define the moment densities as quantities like

$$\phi_n = \rho m_n = \rho \int R^n p(R) \, \mathrm{d}R \tag{1}$$

then successful fluid equations of states (EOS) including those suggested by Boublik and Mansoori *et al* (BMCSL) [8] are functions solely of the density ρ and the three moment densities ϕ_1, ϕ_2 and ϕ_3. Our knowledge of the polydisperse crystal is, by contrast, rather sketchy with only one limited simulation study [6] reported so far. Given the scarcity of data, we have resorted to a simple *ansatz* to construct an equation of state for a polydisperse crystal. Our *ansatz* is motivated by the fluid in that we assume that the EOS of the crystal will be a function also of ρ and the three moment variables. A binary mixture has four degrees of freedom (the diameters and densities of each of the species), so it is straightforward to construct a binary mixture with values of ρ and ϕ_1 to ϕ_3 the same as those of any polydisperse mixture. We assume that these two systems have the same excess free energy. Using this idea and simulation data for face-centred-cubic binary HS crystals [9], we have constructed an empirical EOS for the substitutionally disordered polydisperse crystal [10]. Comparison with polydisperse simulation data [6] shows good agreement.

The central idea is to treat the ϕ_n as independent thermodynamic density variables. Since moment variables are simply linear combinations of species densities, they acquire many of the properties of conventional particle densities. For instance, at equilibrium the moment chemical potentials, $\mu_n = \partial f / \partial \phi_n$ ($f = F/V$), must be equal in all coexisting phases. The immediate use of moment densities is prevented however by the ideal entropy of mixing:

$$s_{\mathrm{mix}} = - \int p(R) \ln p(R) \, \mathrm{d}R$$

which depends explicitly upon the distribution. Sollich, Cates and Warren [11, 12] showed that this term can, under certain conditions, be replaced by a reduced entropy of mixing $s(\{\phi_n\})$ which depends on the moment densities alone. The price for this simplification is that only approximate results for phase coexistence are obtained if finite amounts of several phases coexist. But in those situations where the diameter distribution in the majority phase is negligibly perturbed, for instance at spinodal and critical points, the results are, by contrast, *exact*. The reduced free energy

$$f^{(\mathrm{red})} = \rho k_{\mathrm{B}} T \ln \rho + f^{(\mathrm{ex})}(\rho, \{\phi_n\}) - T s(\{\phi_n\}) \tag{2}$$

is now a function only of moment densities. Analytical expressions for $s(\{\phi_n\})$ have been given by Warren [12] for a variety of common distributions. In the limit $\sigma \to 0$ the entropic term $s(\{\phi_n\})$ reduces to a constant and the phase diagram of the polydisperse mixture reduces to the pure hard-sphere result.

3. The quenched phase diagram

In the quenched limit no size fractionation is allowed. The reduced free energy (2) is formally now only a function of ρ since the moment variables are fixed at their initial values. The combinatorial entropy s is simply a constant which does not affect the phase behaviour and so may be dropped. We have calculated the resulting phase diagram using the excess free energy from the empirical equation of state for the polydisperse crystal outlined above (and described in greater detail in [10]) and the BMCSL approximation for the fluid. The parent distribution is taken as a Schulz distribution of polydispersity σ. The crystal and fluid phases are both stable against small density fluctuations (i.e. $\partial^2 f/\partial\rho^2 > 0$), so the quenched phase diagram contains neither spinodal or critical points. The only phase changes are first-order fluid–crystal transitions which are located by equating P and $\mu_\rho = \partial f/\partial\rho$, the chemical potential of the mean-sized particle. Figure 1(a) shows the calculated phase boundaries in the σ–η plane, with the volume fraction $\eta = (\pi/6)\phi_3$. The phase diagram contains two distinctive features. At low polydispersities there is a single fluid-to-crystal transition with a coexistence gap that reduces with increasing polydispersity, eventually vanishing at the terminal point $\sigma_t = 0.083$ and $\eta_t = 0.59$. At high polydispersities the situation is more complicated with a second transition from the polydisperse crystal back to a disordered phase appearing in the phase diagram. The range of densities over which the crystal is stable shrinks with increasing polydispersity until, at the terminal polydispersity, it disappears completely from the equilibrium phase diagram. The polydisperse fluid and crystal phases remain microscopically distinct at all points in the
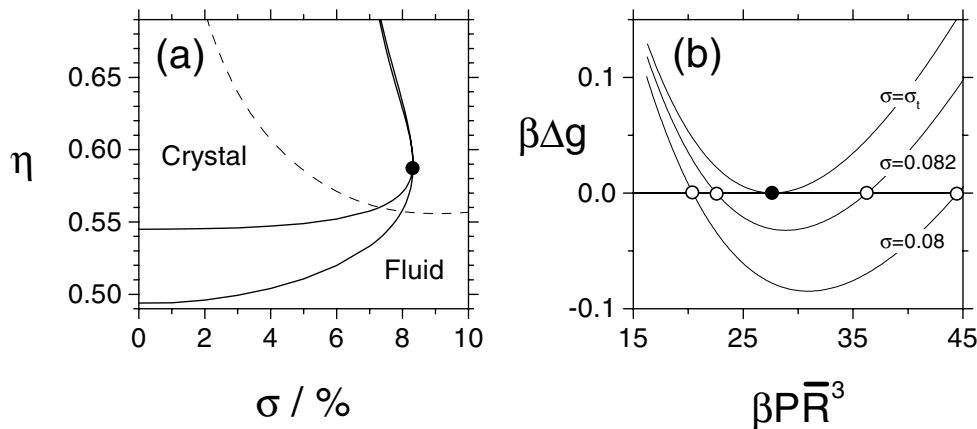
Figure 1. Quenched phase behaviour for Schulz-distributed hard spheres. (a) Phase boundaries in the polydispersity–volume fraction (σ–η) plane. The miscibility gap vanishes at the point of equal concentration, marked by the filled circle. The portion of this diagram accessible to experiment is restricted by a polydisperse glass transition at $\eta_g \sim 0.58$. The dashed line indicates the position of the spinodal instability, calculated in section 4. (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 the position of the point of equal concentration. The density jump on freezing, $\Delta\eta = \eta_s - \eta_f$, is proportional to the slope of the plot.

$\sigma - \eta$ plane, so the singularity at the point (σ_t, η_t) is a polydisperse analogue of the point of equal concentration [13] seen in molecular mixtures and is not a critical point. The reason for the vanishing density discontinuity in the vicinity of the point of equal concentration can be understood with the aid of figure 1(b) where the free-energy difference between crystal and fluid phases is plotted as a function of pressure. At $\sigma < \sigma_t$ the re-entrant nature of the crystal is clearly visible, with stability occurring over a limited range of pressures. The coexistence gap $\Delta \eta$ is proportional to the slope of the free-energy curve at the point $\Delta g = 0$. Increasing polydispersity stabilizes the fluid and destabilizes the crystal, displacing the Δg curve vertically and reducing the gap $\Delta \eta$, until at the point of equal concentration the crystal touches the fluid free-energy curve at a single point and the tangent becomes horizontal, so $\Delta \eta = 0$.

4. Annealed behaviour

The phase diagram depicted in figure 1 describes the initial stages of freezing where the moments m_n are quenched. How different is the later stage where the particles redistribute between phases to relax the 'slow' moment variables? 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 expressions derived by Warren [12] for the combinatorial entropy are intractable analytically for two or more moments. Here we limit ourselves to a simpler task, that of investigating the stability of the polydisperse fluid and crystal phases against small fluctuations in the moment densities. The criterion for stability 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 $\left| \partial^2 f / \partial \phi_i \, \partial \phi_j \right| = 0$ defines the position of the mean-field spinodal.

Cuesta [14] has already considered a polydisperse HS fluid in the BMCSL approximation and shown that it remains stable at the level of polydispersity relevant here (although a phase separation is indeed observed at significantly higher degrees of σ). Using the approximation outlined in section 2 we have investigated the stability of the polydisperse HS crystal as a function of the volume fraction η and polydispersity σ. Generally the determinant is always positive except at high densities and polydispersities. Figure 2 shows the numerically determined spinodal with the instability region increasing as the degree of polydispersity increases. The origin of the instability is revealed by the direction in moment space along which the fluctuations become strong 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 figure 2 indicate the direction of the unstable fluctuations, projected into the $\sigma - \eta$ plane. The arrows are almost parallel to the σ-axis, so the system is unstable towards a composition fluctuation in which the polydispersity σ and not the overall density ρ changes. The precise nature of the unstable composition fluctuation is shown in the inset of figure 2 where it is clear that the fluctuation reduces the numbers of particles in the tails of the distribution. The direction of the instability suggests that the equilibrium annealed state is one in which the initial diameter distribution is split into two narrower fractions, with one or both of the phases crystalline.

Why should polydispersity have this effect? The instability in the polydisperse crystal may be understood in terms of packing. A close-packed fcc or hcp crystal of monodisperse hard spheres has a maximum density of $\eta_{cp} \sim 0.74$ at which each sphere contacts its twelve equal-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
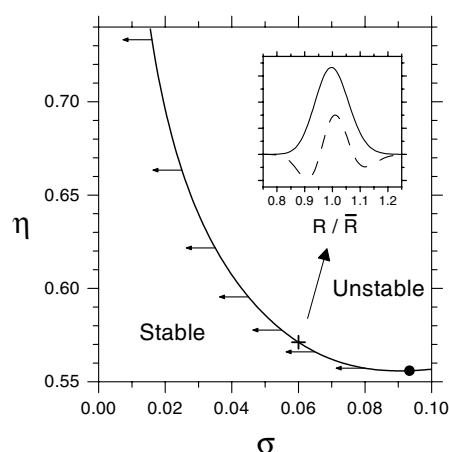
Figure 2. The annealed spinodal (solid line) and critical point (filled circle) of the polydisperse hard-sphere crystal in the polydispersity–volume fraction (σ–η) plane. The arrows indicate the spinodal instability direction. The inset shows the unnormalized size distribution (solid line) and the nature of the unstable fluctuation (dashed line) which develops at the point (+). The scaling is arbitrary.

at some density the reduction in excess free energy as fractionation occurs and the crystal polydispersity reduces will exceed the loss of entropy of mixing. What is remarkable is that the approximate crystal equation of state used here seems to capture this effect without being specifically designed to.

5. Concluding remarks

The significant differences found in the stabilities of the polydisperse crystal in the quenched and the annealed moment spaces demonstrate that the effects of polydispersity can be subtle, nontrivial and difficult to predict from first principles. Unfortunately it is not yet clear which (if either) of these two limiting situations is appropriate to the freezing of real colloidal systems. The limited experimental results available [15] on the freezing of polydisperse hard-sphere colloids show, for instance, no significant fractionation between phases, in line with the quenched predictions, but do not reveal the narrowing of the coexistence region with polydispersity predicted by the quenched calculations.

Acknowledgments

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