Reentrant Melting in Polydispersed Hard Spheres

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The effect of polydispersity on the freezing transition of hard spheres is examined within a moment description. At low polydispersities a single fluid-to-crystal transition is recovered. With increasing polydispersity we find a density above which the crystal melts back into an amorphous phase. The range of densities over which the crystalline phase is stable shrinks with increasing polydispersity until, at a certain level of polydispersity, the crystal disappears completely from the equilibrium phase diagram. The two transitions converge to a single point which we identify as the polydisperse analog of a point of equal concentration. At this point, the freezing transition is continuous in a thermodynamic sense. [S0031-9007(99)08638-X]

Freezing and melting are probably the most common and striking physical changes observed in everyday life. All experiments, to date, demonstrate that the crystallization of a simple liquid is a first-order transition, in three dimensions. So for instance, the sharp Bragg peaks of the crystal, which reflect the long-range spatial modulation of the density $\rho(r)$ and which distinguish a crystal from a liquid, disappear *abruptly* as a crystal melts [1]. This sharp microstructural change is also mirrored by discontinuities in the first derivative of the free energy so that experimentally, melting is accompanied by a finite density and entropy change.

Although the experimental situation is clear, in an early analysis Landau [2] argued that, under certain conditions, a crystal can transform *continuously* into a liquid. In a simple Landau-Alexander-McTague theory [3] the excess free energy of the crystal (relative to the isotropic liquid) has the following form:

$$f_{\text{sl}} = r(T,P) \sum_{G} |n_G|^2$$
$$- u_3(T,P) \sum_{G_1,G_2,G_3} n_{G_1} n_{G_2} n_{G_3} \delta_{G_1+G_2+G_3,0} + \cdots$$
(1)

where the order parameters n_G are the Fourier components of the crystal density, $\rho_s(r) = \rho_s + \delta\rho(r)$, at the reciprocal lattice vector G (ρ_s is the uniform crystal density) and the coefficients of the expansion are analytic functions of the temperature T and pressure P. Equation (1) contains cubic terms because the order parameter sets $\{n_G\}$ and $\{-n_G\}$ describe physically distinct crystals with different energies. As a consequence, the freezing transition is generally first order. However, since *both* T and P can be independently varied the possibility exists that r and u_3 can be made to vanish at a single point in the T-P plane. At the resulting Landau point the liquid-solid transition is continuous in a mean-field description [4]. Landau theory makes two further distinctive predictions. First, the Landau point must lie at the intersection of, at least, three first-order lines of transitions [2] which separate the liquid from two conjugate crystalline phases, C_+ and C_-, with identical symmetry but which differ in the sign of $\delta\rho(r)$. Second, in three dimensions, symmetry considerations should uniquely favor a bcc structure [3].

In spite of these interesting predictions it is not clear if, in a liquid-solid system, the point at which the cubic coefficient u_3 vanishes is experimentally accessible. On the face of it, one of the most promising candidates is a system of polydisperse hard spheres where the constituent particles have different sizes. The freezing of polydisperse hard spheres has been studied extensively in recent years [5–14] motivated, in part, because it is a realistic model of a colloidal suspension [15]. These studies have focused mainly on the effect of size polydispersity σ, defined as the ratio of the standard deviation to the mean of the diameter distribution, upon the fluid-solid transition. Calculations have been made using a variety of theoretical and computational techniques, for various size distributions, and in both two and three dimensions. Yet the picture that has emerged is remarkably similar. On increasing σ, from zero the density discontinuity at the transition $\Delta\rho = \rho_s - \rho_l$ decreases, vanishing altogether at a "terminal" polydispersity [16], $\sigma = \sigma_t$, above which no liquid-solid transition is found. A number of key questions have, however, been left unanswered. First, why do the densities of the coexisting phases converge as $\sigma \to \sigma_t$? If the liquid-solid transition is continuous, then the singularity at σ_t must correspond to a Landau point. The phase diagram should therefore contain *two* crystal phases, in contradiction with the theoretical work to date. Furthermore, while the C_+ crystal has the normal bcc structure with spheres at the cube corners and center, the C_- crystal has particles at interstitial sites. The unfavorably low packing of the C_- crystal ($\phi_m \sim 0.20$)

makes it unlikely that this phase could be important in a dense system. If the vanishing density discontinuity at σ_t is not critical in origin, then what is its true nature? And finally, why is the polydisperse phase behavior apparently universal? In this Letter we reexamine the freezing of polydisperse hard spheres using simple mean-field models for the polydisperse crystal and liquid phases. *Our results suggest that the polydisperse solid-liquid transition at σ_t is not critical.* We show that the vanishing of the density discontinuity at the terminal polydispersity is a consequence of a *reentrant* solid-liquid transition in a polydisperse system.

Our model consists of N hard sphere particles in a volume V, at an overall density of $\rho = N/V$. Each particle has a diameter R drawn from a distribution $\rho(R)$ so that $\rho = \int dR\rho(R)$. The distribution $\rho(R)$ is conveniently characterized by the set of generalized moments $m_i = \int dR\rho(R)w_i(R)$ where the weight function $w_i(R) = (R/\bar{R} - 1)^i$. The zeroth moment is simply the total number density ρ. The "shape" of the diameter distribution, $\tilde{\rho}(R) = \rho(R)/\rho$, is taken here for simplicity, as the Schultz distribution, $\tilde{\rho}(R) = \gamma^\alpha R^{\alpha-1}\exp(-\gamma R)/\Gamma(\alpha)$ with $\alpha = 1/\sigma^2$ and $\gamma = \alpha/\bar{R}$. The (excess) chemical potential $\mu^{\mathrm{ex}}(R)$ in a polydisperse system is in general a complex and unknown function of the particle size. But with the assumption that there is no critical point at σ_t the excess chemical potential must, first of all, be an analytic function of R. Formally, $\mu^{\mathrm{ex}}(R)$ may be calculated from the probability, $W(R)$, for insertion [17] of a test sphere of diameter R. At large R, the leading term in $\mu^{\mathrm{ex}}(R)$ is the *PV* work required to generate a cavity sufficiently large to accommodate the test sphere. This contribution varies as R^3. Motivated by this we assume that in a hard-sphere crystal or fluid $\mu^{\mathrm{ex}}(R)$ has the simple analytic form

$$\mu^{\mathrm{ex}}(R) = -k_B T \ln W(R)$$
$$\approx \lambda_0 + \lambda_1 R + \lambda_2 R^2 + \lambda_3 R^3, \quad (2)$$

where consistency demands that the coefficients λ_i depend only on the four moments $m_0, \ldots, m_3$ of the polydisperse distribution [12]. Two of the four unknown coefficients may be determined from the known small and large R limits of $W(R)$. This fixes $\beta\lambda_0 = -\ln(1 - \phi)$ and $\lambda_3 = \frac{\pi}{6}P$ with ϕ the volume fraction and $\beta = 1/k_B T$.

Having specified the general form expected for $\mu^{\mathrm{ex}}(R)$, we now outline the calculation of the size-dependent chemical potential in the crystal. From Eq. (2) the probability to insert an arbitrary-sized test particle into any two hard-sphere systems will be equal if the two distributions have the same first four moments [12]. In this sense the two systems may be termed "equivalent." Since a binary mixture can always be chosen so as to match any four moments we look at the "equivalent" binary substitutionally disordered crystal, for which simulation data is available [18]. By looking at test particles with sizes equal to the

two species in the binary mixture, for which the chemical potentials are known, the remaining two unknown coefficients (λ_1 and λ_2) in the general expression for $\mu^{\mathrm{ex}}(R)$ are determined. The resulting predictions for the polydisperse crystal have been compared with simulation data previously [12]. Agreement is good.

For the polydisperse fluid accurate expression for $\mu^{\mathrm{ex}}(R)$ is available. We use the approximate BMCSL [19] equation of state which for a Schultz distribution has the closed form

$$\frac{\pi}{6}\beta P_f \bar{R}^3 = \frac{\xi}{1 + \sigma^2} + \frac{3\xi^2}{1 + \sigma^2} + (3 - \phi)\xi^3, \quad (3)$$

where $\xi = (\frac{1}{1+\sigma^2})\frac{\phi}{1-\phi}$. The excess free energy per particle is found by integrating Eq. (3). Differentiation then yields an expression for the particle potential $\mu^{\mathrm{ex}}(R)$ which is of the form of Eq. (2).

The total polydisperse free energy f (with $f = F/V$) consists of ideal and excess terms, $f = f^{\mathrm{id}} + f^{\mathrm{ex}}$, which depend in a very different manner on the distribution $\rho(R)$. The excess free energy, $f^{\mathrm{ex}} = \int dR\rho(R)\mu^{\mathrm{ex}}(R)$, is a function only of the four moments variables $m_0, \ldots, m_3$. The ideal term $\beta f^{\mathrm{id}} = \int dR\rho(R)\ln[\rho(R)]$, by contrast, depends upon the detailed shape of the function $\rho(R)$ so formally, at least, the total free energy f resides in an infinite dimensional space. Sollich, Cates, and Warren [20] have shown that the full polydisperse phase diagram can be approximated by replacing the ideal free energy by a projected term $\widehat{f^{\mathrm{id}}}(\{m_i\})$ which includes only those contributions that depend on a *finite* set of moment variables. The remaining contributions to the ideal free energy, from those degrees of freedom of $\rho(R)$ which can be varied without affecting the selected moments, are chosen to minimize the free energy. The power of this approach is that by including more moment variables the calculated phase diagram approaches, with increasing precision, the actual phase diagram. The position of equilibrium is fixed by the equality of the "moment" chemical potentials, $\mu_i = \partial\widehat{f}/\partial m_i$ and the pressure P among all phases with $\widehat{f}$ the projected free energy. For polydisperse hard spheres the excess moment chemical potentials are simply combinations of the (known) coefficients $\{\lambda_i\}$ in $\mu^{\mathrm{ex}}(R)$ [Eq. (2)] since $\mu(R) = \delta\widehat{f}/\delta\rho(R) = \sum_i(\partial\widehat{f}/\partial m_i)w_i(R) = \sum_i \mu_i w_i(R)$. The first two ideal moment potentials are [20], ignoring unimportant factors, $\mu_0^{\mathrm{id}} = \ln\rho - \alpha\ln\bar{R}$ and $\mu_1^{\mathrm{id}} = -\alpha\bar{R}$.

In order to understand the qualitative features of the polydisperse transition, we consider first the simplest description in which only the lowest moment (m_0) is retained in the projected free energy. In this limit, there is no size fractionation so the normalized diameter distribution, $\tilde{\rho}(R)$, is fixed and equal in all phases. The location of the fluid-solid transition is determined by equating P and μ_0, the chemical potential of the mean-sized particle, in each of the crystal and fluid phases. In this way we

obtain the phase diagram of Fig. 1. At low densities we find, in qualitative agreement with previous work [5–10,12–14], that the density discontinuity at freezing $\Delta\rho$ reduces with increasing polydispersity and eventually vanishes at the point $\sigma_t = 0.0833$ and $\rho_t = 1.111$. However, at high polydispersity, the calculated diagram contains a novel feature. For $0.07 \leq \sigma \leq 0.083$ we find a further transition from the crystal back to a disordered phase [21]. The location of this polydispersity-induced-melting transition varies sharply with polydispersity. The range of densities for which a crystal is found shrinks with increasing polydispersity until at σ_t the crystal of density ρ_t disappears completely from the phase diagram. At the point (ρ_t, σ_t) the line of fluid-to-crystal transitions intersects an upper line of crystal-to-amorphous transitions. At all points in the (ρ, σ) plane the freezing transition remains first order so the singularity at (ρ_t, σ_t) is equivalent to the *point of equal concentration* [22] seen in molecular mixtures and is not a critical point—so providing an answer to the second of our questions.

We now turn to the vanishing density discontinuity in the vicinity of the point of equal concentration. The Gibbs free energy difference $\Delta g = g_s - g_l$ (with $g = G/N$) between the solid and liquid phases as a function of pressure for three fixed values of σ is shown in Fig. 2. The reentrant nature of the freezing transition is very evident with a stable crystal appearing only in an intermediate range of pressures bounded by the two transitions where $\Delta g = 0$. The density change $\Delta\rho$ at the liquid-solid transition is given by the slope of the free energy curve at the point $\Delta g = 0$ since $\partial\Delta g/\partial\rho = (1/\rho_s) - (1/\rho_l)$. Increasing the polydispersity raises the free energy of the solid relative to the fluid, displacing the Δg curve ver-

tically and as is evident from Fig. 2 reduces the density jump at the transition. At the terminal polydispersity the solid just touches the fluid curve so the tangent is horizontal and $\Delta\rho = 0$. In a system of hard spheres (where the internal energy is constant) the condition $\Delta\rho = 0$ necessarily requires the entropy change at this point to also vanish. Clearly while the underlying microscopic transition remains first order the first derivatives of the thermodynamic potential are continuous at σ_t. A conventional classification of this transition, following the ideas of Ehrenfest [23], is clearly inappropriate.

Retaining more moments in the projected free energy allows the possibility of different-sized particles to be partitioned between phases. To establish the effect of fractionation we have recalculated the phase equilibria with *two* moment variables. The phase diagram, now given by equating P and the moment potentials μ_0 and μ_1 in all phases, is unchanged in topology from Fig. 1. The point of equal concentration is retained although shifted slightly to $(\rho_t, \sigma_t) = (1.115, 0.0831)$. Hence our prediction of a reentrant freezing transition seems to be robust. The extent of fractionation is generally small, although increasing as $\sigma \rightarrow \sigma_t$, with the larger particles preferentially found in the crystal phase. Details of our calculations are given elsewhere [24].

The appearance of an equilibrium amorphous phase may be understood simply from maximum packing arguments. For uniform-sized spheres the maximum density of a randomly packed Bernal glass ($\rho_{rcp} \simeq 1.22$) is significantly smaller than the geometric limit of a close-packed hexagonal of fcc crystal ($\rho_{cp} = \sqrt{2}$). The greater packing efficiency of the crystal ensures that at high densities, particles have more freedom and so a higher
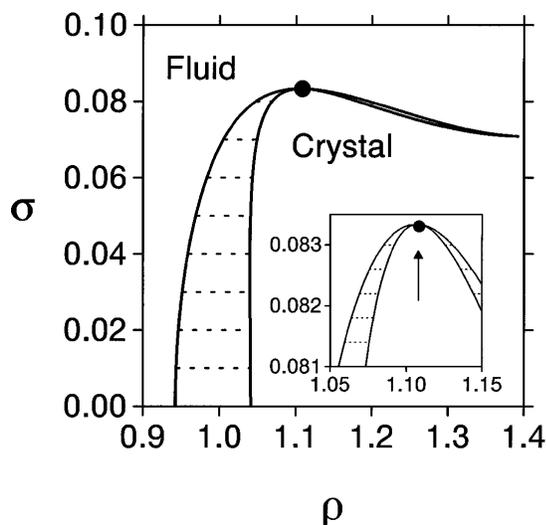

FIG. 1. Phase diagram of a polydisperse system of hard spheres showing the reentrant freezing transition. The density discontinuity $\Delta\rho = \rho_s - \rho_l$ vanishes at the *point of equal concentration*, marked by the filled circle. The inset shows the phase boundaries near this point in greater detail.
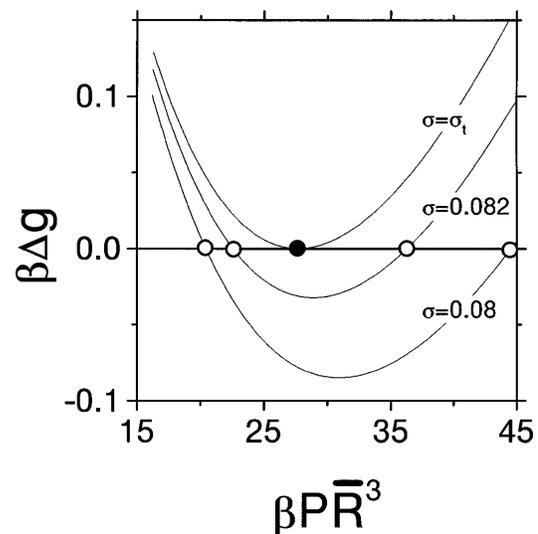

FIG. 2. The Gibbs free energy difference (per particle) Δg between crystal and fluid phases as a function of the pressure, for different polydispersities. The circles are the first-order fluid/solid transitions. The filled circle marks the point of equal concentration.

entropy than those in the fluid phase [25]. The stable high density phase of uniform hard spheres is therefore crystalline. Polydispersity affects crystalline and disordered phases in different ways. In an amorphous phase, small particles pack in the cavities between large particles and ρ_{rcp} increases with σ while the constrained environment of a fixed repeating unit cell causes the maximum density of a crystal ρ_{cp} to decrease with σ. Computer simulations [11,26] indicate that the limiting densities of amorphous and crystalline structures become equal at $\sigma \approx 0.05$. For higher polydispersities disordered structures fill space more efficiently than ordered ones. Consequently, the appearance of an equilibrium amorphous phase and the ensuing reentrant freezing transition should be a universal feature of all polydisperse systems—so answering the last of our questions.

In conclusion, we have presented a simple mean-field model of polydisperse hard spheres which suggests that the equilibrium state at high polydispersities and densities is amorphous. An equilibrium crystal is found only at intermediate densities. The growing stability of the fluid phase with polydispersity causes a singularity in the density-polydispersity phase diagram which we identify as a point of equal concentration. Finally, although we use mean-field theory, our results should be robust with respect to fluctuation effects since the transition we find is not critical and the thermodynamic functions are not singular at this point.

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