

Diffusive growth of polydisperse hard-sphere crystals

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Unlike atoms, colloidal particles are not identical, but can only be synthesised within a finite size tolerance. Colloids are therefore polydisperse, i.e., mixtures of infinitely many components with sizes drawn from a continuous distribution. We model the crystallization of hard-sphere colloids (with/without attractions) from an initially amorphous phase. Although the polydisperse hard-sphere phase diagram has been widely studied, it is not straightforwardly applicable to real colloidal crystals, since they are inevitably out of equilibrium. The process by which colloidal crystals form determines the size distribution of the particles that comprise them. Once frozen into the crystal lattice, the particles are caged so that the composition cannot subsequently relax to the equilibrium optimum. We predict that the mean size of colloidal particles incorporated into a crystal is smaller than anticipated by equilibrium calculations. This is because small particles diffuse fastest and therefore arrive at the crystal in disproportionate abundance.

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I. INTRODUCTION

How many ways are there to pack balls into a box? The answer, of course, is infinitely many, since each ball can be placed in a continuum of different positions. However, if one tried to count the different arrangements, one would notice that many of them are very similar. The predominant packing arrangements for a given concentration ϕ (the fraction of the total volume occupied by the balls) are summarized by the hard-sphere equilibrium phase diagram, which is well known when all spheres are of equal size [1]. A face-centered-cubic (fcc) crystal phase exists for any concentration from close packing at $\phi = \pi/\sqrt{18}$ [2] down to $\phi = 0.545$. For $\phi < 0.494$ a fluid phase exists in which configurations are amorphous, and between these two concentrations statistical weight is dominated by systems partitioned into fluid and crystalline regions. On the other hand, when differently sized balls are considered, the full phase diagram is not known. It may seem at first surprising that such a straightforward question is still a field of active research.

The subject is not merely of idle interest. Many real substances, particularly colloids, are composed of spherical particles with negligible energetic interactions except for a hard repulsion at contact. For a further, very large class of substances, the hard-sphere model is a useful starting point for more accurate theories [3]. Studying their configurations is of central importance to our understanding of matter, and has implications for the development of new materials.

It is often assumed that the configurations observed in a real material, such as a hard-sphere colloid, are those of highest entropy (lowest free energy for non-hard-sphere interactions), i.e., those that dominate the counting of all possible arrangements. On this equilibrium assumption, many efforts have been devoted to exploring the elaborate phase diagram of hard-sphere mixtures. Since the particles never exchange potential energy, temperature does not influence their configurations, only their speeds. So the phase diagram has only as many axes as there are different sizes of sphere in the mixture, each axis representing the concentration of one type of particle. When just two species of balls are mixed, the diagram is already complicated, with theory [4] and ex-

periment [5] finding regions of fluid, pure crystals, and crystalline alloys of the A and B type particles in the ratios AB , AB_2 , or even AB_{13} depending on the size ratio. In the ‘‘polydisperse’’ hard-sphere phase diagram, for systems such as real colloids, in which each particle is slightly different from every other, an infinite number of axes is needed to span the space of all possible compositions. A small corner of this phase diagram has been charted by experiments [6], simulations [7], and theories based on phenomenological free energies [8], integral equations [9], cell theory [10], and perturbation about a monodisperse system [11,12]. When the overall concentration of particles is low, an amorphous fluid phase inevitably results. At higher concentrations, it is expected that crystals of quite monodisperse (similarly sized) particles can form, even when the overall size distribution is broad [7], in which case, particles of the wrong size to be included in the crystal remain in a coexisting fluid phase. Many predictions exist for the equilibrium distribution of particle sizes in a polydisperse crystal at coexistence with a fluid.

We shall argue that such equilibrium states are not as straightforwardly applicable to colloidal systems as might be expected, and shall calculate an alternative distribution of particle sizes, which we expect to comprise the crystallites observed in real suspensions. The size distribution of particles incorporated into colloidal crystals is determined by the kinetics of their formation and, as we shall explain, never relaxes to the equilibrium distribution, remaining instead as a relic of that process. Despite the fact that the state of the system evolves while the crystals are growing, we shall show that a large temporal regime exists during which the distribution of species incorporated into a growing crystal is invariant with time. Hence, during this regime, there exists a unique solution for the distribution constituting the crystal. We expect this kinetically mediated distribution to be trapped within colloidal crystallites in laboratory samples that are quiescent and therefore *appear* to have reached equilibrium. We shall find that the particles buried deep within a crystallite are on average *smaller* than would be expected from an equilibrium calculation. If attractions exist between

the hard particles, the effect can be so marked as to swamp the thermodynamic driving force that favors *larger* than average particles in the equilibrium crystal phase.

The rest of the article is organized as follows. In the next section we shall discuss the formal procedure for obtaining the equilibrium phase diagram of an n -component hard-sphere system. We then go on to discuss the evidence that experimental hard-sphere systems are not at equilibrium. In Sec. IV we construct the most general equations of motion for diffusive growth of a polydisperse hard-sphere crystal, and show that there exists a time regime during which the distribution of particles dynamically incorporated into the crystal has a time-invariant solution. It will transpire that the crystalline distribution is one that appears on the phase boundary in the *equilibrium* phase diagram, but is not located on the expected tie line, due to temporary violation of the lever rule. Using a low-concentration approximation for the diffusion coefficients in the fluid phase, we shall derive, in Sec. V, a simple replacement for the lever rule, which yields the appropriate distributions for this nonequilibrium situation. In Sec. VI we derive the conditions for local mechanical and chemical balance at the crystal-fluid interface (equivalent to finding binodals in the equilibrium phase diagram) using, for convenience, a perturbative approximation that is valid for narrow distributions. Section VII contains our results, and we conclude in Sec. VIII.

II. EQUILIBRIUM PHASE DIAGRAMS

As explained above, the phase diagram of single sized (monodisperse) hard spheres is well known. The phase behavior may be calculated via a theoretical treatment in the following way. First, an expression for the Helmholtz free energy of the fluid and crystalline phases must be found. From this, one has knowledge of all thermodynamic quantities. The phase boundaries are then determined by finding the values of ϕ for which the pressure and chemical potential are equal in two phases, signaling mechanical and chemical equilibrium between the phases. The volumes of the two coexisting phases may be found by application of the lever rule,

$$\phi_c V_c + \phi_f V_f = \phi_p V \quad (1)$$

in terms of the system volume $V = V_c + V_f$. The subscript c refers to a quantity in the crystal phase, f refers to the fluid phase, and p to the overall, or *parent*, composition. The lever rule follows from conservation of material in the system.

The situation is immediately complicated if we consider a system containing differently sized particles, although the formal procedure is wholly analogous. We illustrate this first by a glance at a system of binary hard spheres. The phase diagram is now two dimensional, so the task of finding coexisting phases is a problem in four variables, because one must determine the concentrations of two species for each of the two phases. Coexisting phases must have equal pressures, as well as equal chemical potentials for each species. These three constraints on four unknowns lead to a locus of fluid (crystal) states in the phase diagram that can coexist with a crystal (fluid) phase. We now have two lever rules,

one for each species, which supply the extra constraints needed to fix coexisting points, and to fix the volume of the crystal phase.

In the case of an n -component system, there are $n+1$ constraints arising from equality of pressure and n chemical potentials. The problem of finding two coexisting points in the n -dimensional space of the phase diagram is a $2n$ -dimensional problem, leaving us with $(n-1)$ -dimensional phase boundaries. There are now n lever rules, one for each species, allowing us to fix coexisting points on the phase boundaries, as well as the ratio of phase volumes. We note that, in the continuously polydisperse case, the equations remain closed despite the infinite number of thermodynamic variables. Therefore, in principle at least, we know how to calculate the equilibrium phase behavior of any hard-sphere system. The practicalities of phase separation in real systems are a different matter, which we now proceed to discuss.

III. COLLOIDAL SYSTEMS

In a polydisperse hard-sphere system each particle has a slightly different size. In a given sample, then, there will be a thermodynamically large number of species present, and thus the free energy is a function of the same number of concentration variables. As such a system tends toward equilibrium, it must minimize its free energy with respect to these variables. The minimization in this case is obviously much more complicated than in the monodisperse situation, where there is only one relevant parameter.

To reach the equilibrium state from some initial state that an experimenter prepares by mixing and homogenizing, the system must separate itself into distinct regions of coexisting phases. Even in the relatively simple case of monodisperse phase separation, there are many pathways by which the phase separation may occur [13]. In the polydisperse case, the situation is complicated further, as the densities of individual species need not relax at the same rate as the overall density. One could conceive a situation whereby phase equilibrium is approached by a two-stage process, as has been suggested previously for polymeric systems [14]. In such a scenario, the polydisperse system initially lowers its free energy by a quick and expedient demixing of material to form the separate phase regions. Subsequently, the distributions of species within the phases are further optimized to attain the absolute minimum of free energy, which requires particles to be exchanged between the separate regions. Alternatively, it would be possible for the system to separate into the two phases with the optimum particle distribution right from the start. Perhaps more realistically, the separation could proceed along a path somewhere between these two extremes.

A clue to how the separation does occur is found in experiments on colloids of attractive particles. Colloidal systems may, given a sufficiently long ranged interparticle attraction, exhibit two fluid phases, analogous to the liquid and gas phases of atomic systems. Observations of the fluid-fluid phase separation reveal that the process is approximately as swift in the polydisperse case as in the (near) monodisperse [6]. Given that minimization of the polydisperse free energy

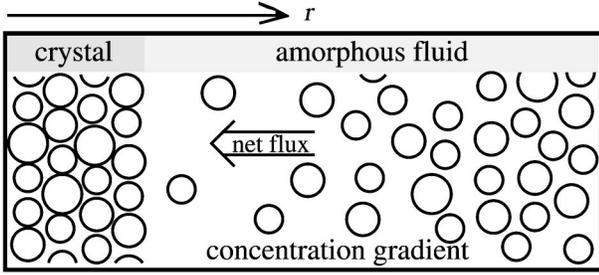


FIG. 1. Schematic illustration of the crystal growth mechanism.

must be carried out with respect to many more variables, it might be expected that the additional “sorting” required would result in a slower relaxation to equilibrium. This suggests that the initial phase separation is not the end of the story—the systems are relaxing to equilibrium by a two-stage process, with an initial fast separation of material, followed by particle exchange to absolutely minimize the free energy.

Such an optimization stage is feasible between two fluid phases as, given sufficient time, particles can diffuse between phases. In a hard-sphere fluid-crystal phase separation, however, the system has a problem. The caging of particles by their neighbors suppresses diffusion within the crystal to a very low rate, mediated only by lattice defects. Optimizing the population of particles in the crystal, by exchanging a macroscopic amount of material with the adjacent fluid region, is therefore unachievable on experimental time scales. Hence we expect the crystalline population to be arrested in a nonequilibrium state, so that the footprint of the initial, expedient stage of phase separation remains observable at late times.

Therefore, if we wish to make predictions as to the phase behavior of hard-sphere colloids, we need to move away from equilibrium predictions and model the process of crystal growth. We now develop such a model, with a view to predicting the size distribution that forms within a polydisperse hard-sphere crystal.

IV. CRYSTAL GROWTH PROCESS

In this section, we outline the treatment of the kinetic process during crystal-fluid phase separation. We begin by considering a size-polydisperse sample of colloidal particles suspended in solvent, prepared with a composition lying in the fluid-crystal coexistence region of the phase diagram. The sample is assumed to be initially homogeneous. Eventually, a crystal will randomly nucleate somewhere in the fluid, creating a concentration gradient in the fluid, as the immediate vicinity of the growing crystal is depleted of particles. Particles will diffuse down this gradient toward the crystal, with the smaller particles diffusing more quickly. The situation is illustrated in Fig. 1. It should be noted that the latent heat released during the crystal formation does not hinder crystallization. This is because the solvent acts as a heat bath, keeping the temperature of the system constant.

We wish to find the composition of the crystal, for which we require the time- and position-dependent composition of

the surrounding fluid. Let us characterize each particle species by its radius a . The number density $\rho(a, \mathbf{r}, t) da$ is a function of position and time, as is the diffusive flux $\mathbf{j}(a, \mathbf{r}, t) da$, for particles with sizes in the interval $a \rightarrow a + da$. We begin with an expression of continuity,

$$\frac{\partial \rho(a)}{\partial t} = -\nabla \cdot \mathbf{j}(a), \quad (2)$$

and a generalization of Fick’s law to polydisperse particles, to describe the diffusive dynamics of the fluid phase,

$$\mathbf{j}(a, \mathbf{r}, t) = -\int D(a, a', [\rho(a)]) \nabla \rho(a', \mathbf{r}, t) da', \quad (3)$$

which tells us that the flux of a particular species depends on the concentration gradients of *all* species. The diffusion coefficient $D(a, a', [\rho(a)])$ is a functional of the composition $\rho(a)$. Later, we will introduce a particular form for D , but for now we continue with the general case.

We must also describe the physics of the interface between the fluid and crystalline regions. First, we demand conservation of material. If r_0 is the position of the interface, in unit time the interface advances a distance \dot{r}_0 . In this time, unit area of the crystal surface “swallows up” a volume \dot{r}_0 of the fluid, requiring an additional $\dot{r}_0 \Delta \rho$ particles, where $\Delta \rho$ is the (positive) difference in densities across the interface. So \dot{r}_0 is related to the flux across the interface by

$$\mathbf{j}(a) = -\hat{\mathbf{n}} \dot{r}_0 \Delta \rho(a), \quad (4)$$

where $\hat{\mathbf{n}}$ is a unit normal to the interface.

Various empirical approximations exist for the flux across the interface between nonequilibrium phases. In the following, the details of the approximation will turn out to be unimportant. We choose the standard Wilson-Frenkel law [16] which, for a monodisperse system, is given by

$$\mathbf{j} = -\hat{\mathbf{n}} \nu D_s \frac{(\exp \Delta \mu) - 1}{\Lambda},$$

where ν is a constant, D_s is a short-time self-diffusion coefficient, $\Delta \mu$ is the chemical potential difference across the interface (with units such that $k_B T \equiv 1$), and Λ is the interfacial width. We generalize it for our polydisperse system to

$$\mathbf{j}(a) = \frac{-\hat{\mathbf{n}}}{\Lambda} \int \Gamma(a, a', [\rho(a)]) \{ \exp \Delta \mu(a') - 1 \} da', \quad (5)$$

where $\Gamma(a, a', [\rho(a)])$ is a mobility for particles of radius a due to a chemical potential difference in particles of radius a' . The mobility is a functional of the whole set of concentrations present.

We now search for a solution to our equations. For simplicity, let us assume that the crystal grows with spherical symmetry, neglecting the possibilities of faceting or dendritic growth. We try a solution in which lengths scale as $t^{1/2}$, the validity of which will be examined *a posteriori*. We may then replace $r \rightarrow Rt^{1/2}$. With this assumption, we can write

the density of particles of radius a as $\rho(a,r,t) = \rho(a,R)$. At a given value of R , the density remains constant in time; the diffusive flux, however, will fall off as $t^{-1/2}$, as it is proportional to density gradients. We write the flux as $\mathbf{j}(a,r,t) = t^{-1/2}\mathbf{J}(a,R)$. Let us use these variables to rewrite the relevant equations. The generalized Wilson-Frenkel law becomes

$$\mathbf{J}(a,R) = -\hat{\mathbf{n}} \int \Gamma(a,a',[\rho(a)]) \left\{ \frac{\exp \Delta\mu(a') - 1}{\Lambda t^{-1/2}} \right\} da'.$$

Note that Λ , the width of the interface, is the only length that does not scale as $t^{1/2}$. Since the flux \mathbf{J} is now independent of t ; the right-hand side (RHS) must also be time independent, so we have

$$\exp \Delta\mu(a) - 1 = g(a)t^{-1/2}$$

with some (unknown) function $g(a)$, which gives

$$\Delta\mu(a) \rightarrow g(a)t^{-1/2} \rightarrow 0 \quad (6)$$

at late times, confirming our expectation that the interface tends to local equilibrium. The Wilson-Frenkel law has demonstrated the relevant physics, that lengths controlling sub-interfacial dynamics remain microscopic and therefore become irrelevant.

The equation of continuity may also be written in terms of the scaled variables. As spherical symmetry is assumed, we transform to d -dimensional spherical coordinates. Hence Eq. (2) becomes

$$\frac{\partial \rho(a,R)}{\partial R} = \frac{2}{R} \left(\frac{\partial}{\partial R} + \frac{d-1}{R} \right) J(a,R). \quad (7)$$

Similarly, we write Fick's law [Eq. (3)] as

$$J(a,R) = - \int D(a,a',[\rho(a)]) \frac{\partial \rho(a',R)}{\partial R} da'. \quad (8)$$

From Eq. (4), we obtain

$$J(a,R_0) = - \frac{1}{2} R_0 [\rho_c(a) - \rho(a,R_0)], \quad (9)$$

where $\rho_c(a)$ is the density distribution in the crystal and R_0 is the value of R at the interface. Note that $\rho_c(a)$ is independent of position and time. Our scaling solution yields a unique answer (although not the equilibrium one) for the crystalline composition (for a given system and parent). In other words, the crystal grows uniformly.

We now have a closed pair of time-independent equations [Eqs. (7,8)], with the boundary condition at $R=R_0$ given by Eq. (9) and, from Eq. (6), local thermodynamic equilibrium across the interface. The boundary condition at $R \rightarrow \infty$ is $\rho(a,R) \rightarrow \rho_p(a)$ since the *parent* distribution $\rho_p(a)$ exists in the bulk. The fact that this asymptote remains time independent is a consequence of our scaling solution, for which all lengths vary as $t^{1/2}$. We see, then, that this scaling solution describes the regime of growth *before* the distant composi-

tion of the supersaturated fluid has been depleted (i.e., while condensation nuclei grow as if isolated), but *after* the crystal-fluid interface has locally equilibrated following the initial transients of nucleation.

V. A MODIFIED LEVER RULE

In order that an analytic solution is possible, we now make the simplest possible choice of the diffusion coefficient present in Fick's law, and write

$$D(a,a') = D_0(a) \delta(a-a') = \frac{kT}{2d\pi\eta a} \delta(a-a'), \quad (10)$$

where $D_0(a)$ is the monodisperse diffusion coefficient of a particle of size a , taken to be of Stokes-Einstein form. In making this approximation, our generalized Fick's law reduces to the ordinary form for each species independently. This neglects the flux of a given species due to density gradients of all other species. This becomes correct in the low-density limit [15], but will be incorrect at the large densities required for coexistence in a hard-sphere system. Here, the generalized Fick's law has been discarded, but a more sophisticated treatment could utilize it along with a more accurate approximation to the diffusion coefficient, such as the expression given in Ref. [15] to second order in concentration. The consequences of our low-density approximation and the likely effects of the neglected interactions are discussed in Sec. VIII.

We now wish to solve our system of equations. We begin with Eq. (8),

$$-J(a,R) = D_0(a) \frac{\partial \rho(a,R)}{\partial R}. \quad (11)$$

Substituting in Eq. (7), and with a little work, we find

$$J(a,R) = J_0(a) \left(\frac{R}{2\sqrt{D_0(a)}} \right)^{(1-d)} \exp\left(-\frac{R^2}{4D_0(a)} \right)$$

with $J_0(a)$ appropriately defined. Now using the expression of continuity of particles at the interface (9), we fix $J_0(a)$, leaving us with

$$J(a,R) = - \frac{1}{2} R_0 [\rho_c(a) - \rho_f(a)] \frac{R_0^{d-1}}{R} \exp\left(\frac{R_0^2 - R^2}{4D_0(a)} \right), \quad (12)$$

where the density distribution in the fluid at the interface has been written as $\rho_f(a)$. Integrating Eq. (11), and applying the boundary condition at $R \rightarrow \infty$, we obtain for $\rho(a,R)$

$$\rho(a,R) = \rho_p(a) + \int_R^\infty \frac{J(a,R')}{D_0(a)} dR'.$$

On substitution from Eq. (12), we obtain

$$\frac{\rho_p(a) - \rho(a, R)}{\rho_c(a) - \rho_f(a)} = \frac{R_0}{2D_0(a)} \int_R^\infty \left(\frac{R_0}{R'}\right)^{d-1} \exp\left(\frac{R_0^2 - R'^2}{4D_0(a)}\right) dR'. \quad (13)$$

This yields a closed form expression for $\rho(a, R)$. For our present purposes, we evaluate Eq. (13) at $R=R_0$. With a change of variables to $u \equiv R'/R_0$, we find

$$\chi(a) \equiv \frac{\rho_p(a) - \rho_f(a)}{\rho_c(a) - \rho_f(a)} = f_d \left(\frac{R_0}{2\sqrt{D_0(a)}} \right), \quad (14)$$

where

$$f_d(x) \equiv 2e^{x^2} x^d \int_x^\infty \frac{\exp(-u^2)}{u^{d-1}} du = \begin{cases} \sqrt{\pi} x e^{x^2} \operatorname{erfc} x & \text{for } d=1 \\ 2x^2(1 - \sqrt{\pi} x e^{x^2} \operatorname{erfc} x) & \text{for } d=3. \end{cases} \quad (15)$$

This is an important result in our treatment of the kinetics. Recall that, in a system *at equilibrium*, conservation of material is expressed by the lever rule [Eq. (1)], which may be reexpressed as

$$\frac{\rho_p(a) - \rho_f(a)}{\rho_c(a) - \rho_f(a)} = \frac{V_c}{V}, \quad (16)$$

where V and V_c are the overall system volume and the volume of the crystalline phase, respectively. The densities have the same meanings as in Eq. (14), with the exception that here $\rho_f(a)$ refers to the equilibrium fluid, which will be the same throughout that phase, while in the nonequilibrium case the subscript f refers only to the fluid at the interface. We stress that the lever rule does *not* hold in the situation under consideration. Rather, on comparing Eqs. (16) and (14), we note that Eq. (14) may be considered an alternative to the lever rule in our nonequilibrium system. Obviously we must conserve matter in the nonequilibrium system as a whole, but here we are only considering a certain region, into which there is a flux of material.

In the same way as the lever rule closes the set of equations governing equilibrium phase behavior (and fixes V_c/V), Eq. (14) closes the same set of equations in the nonequilibrium case (and fixes R_0). As we are not conserving material in this case, the tie lines predicted in the nonequilibrium phase diagram, using Eq. (14), need not be straight. In summary, the crystal formed has a composition that lies on the equilibrium phase boundary, since it coexists with a local region of fluid, but this composition appears at the end of the ‘‘wrong’’ tie line.

So now we have an alternative to the lever rule for our nonequilibrium system. Using this, along with conditions of local equilibrium at the crystal fluid interface, we shall predict the phase behavior of our polydisperse system.

VI. LOCAL EQUILIBRIUM

In order to solve Eq. (6) for the locally coexisting density distributions that ensure chemical (and mechanical) balance across the crystal-fluid interface, we need a technique by which to calculate phase equilibria in a polydisperse system. This is a difficult task, even in the simplest case of an equilibrium system for which the free energy is known, since the free energy is a function(al) of an infinity of concentration variables. Several different approaches have been developed to tackle the problem [17], most relying on a numerical stage to the solution. In pursuit of a concise result, we adopt a perturbative approach that yields analytic answers in a closed form. The method has previously been applied to equilibrium problems [11,12]. We shall adapt the mathematics to deal with the nonequilibrium aspects of the system, by replacing the lever rule with our nonequilibrium equivalent.

We take a monodisperse system as a reference state, and treat the polydispersity as a perturbation. This permits us to deal with systems in which the degree of polydispersity is, in some sense, small, and will be applicable only if the polydisperse system behaves similarly to the monodisperse limit. In particular, we expect to find coexistences corresponding to those present in the monodisperse system, with binodal concentrations and other properties altered a little by the polydispersity. For details of the method, the reader is directed to Ref. [12].

Let us briefly explain the notation used. For a species of particle of radius a , we define a small, dimensionless number $\epsilon \equiv (a - a_0)/a_0$, to quantify its deviation from the radius a_0 of particles in the monodisperse reference system. We denote the number density of particles of ‘‘size’’ ϵ as $\rho(\epsilon)d\epsilon$. Normalized distributions are denoted $p(\epsilon)$, and subscripts label the relevant population of particles, be it that of the crystal (c), fluid (f), or parent (p). Angular brackets denote averages over the relevant distribution. We choose the reference size a_0 to be the mean of our parent distribution so that, by definition, $\langle \epsilon \rangle_p$ is identically zero.

Our approach is as follows. We wish to find the conditions for equality of pressure and chemical potentials across the interface between crystal and fluid. The pressure of a phase is a functional of the whole distribution of densities within it. Likewise, the chemical potential of a species is a functional of the density distribution, and is also a function of the particular species in question, characterized by its size deviation ϵ . So we need to solve the infinity (plus one) of equations

$$P[\rho_f(\epsilon)] = P[\rho_c(\epsilon)], \quad (17)$$

$$\mu(\epsilon, [\rho_f(\epsilon')]) = \mu(\epsilon, [\rho_c(\epsilon')]) \quad \forall \epsilon, \quad (18)$$

the latter of which is the late-time limit of Eq. (6). These relations between $\rho_f(\epsilon)$ and $\rho_c(\epsilon)$ define the phase boundaries of an equilibrium phase diagram in $\rho(\epsilon)$ space. Simultaneously applying the modified lever rule [Eq. (14)] then fixes uniquely the coexisting distributions. To solve Eqs. (17,18), we expand their slowly varying parts in ϵ . At zeroth order, this yields the conditions for local equilibrium in the monodisperse system, for which solutions are known. A

problem exists in expanding Eq. (18). In the reference system, species for which $\epsilon \neq 0$ are unpopulated, so their chemical potential is negative infinity. This singularity is logarithmic in the density, as is the case for an ideal gas, $\mu^{\text{id}}(\epsilon) = \ln \rho(\epsilon)$. To circumvent the problem, we shall subtract off this singular part, and work with the excess chemical potential $\mu^{\text{ex}} \equiv \mu - \mu^{\text{id}}$, in terms of which Eq. (18) becomes

$$\rho_f(\epsilon) \exp \mu_f^{\text{ex}}(\epsilon, [\rho_f(\epsilon)]) = \rho_c(\epsilon) \exp \mu_c^{\text{ex}}(\epsilon, [\rho_c(\epsilon)]), \quad (19)$$

which may be substituted into Eq. (14), the modified lever rule, to yield

$$\rho_c(\epsilon) = \frac{\rho_p(\epsilon)}{\chi(\epsilon) + [1 - \chi(\epsilon)] \exp[\mu^{\text{ex}}(\epsilon, [\rho(\epsilon)])]_f^c} \quad (20)$$

where the notation $[x]_f^c$ denotes the difference in quantity x between the phases, i.e., $x_c - x_f$, and we have written $\chi(\epsilon)$ for $\chi((1 + \epsilon)a_0)$ as defined in Eq. (14).

If we now express each density distribution $\rho(\epsilon)$ in terms of its normalization ρ and moments $\{\langle \epsilon \rangle, \langle \epsilon^2 \rangle, \dots\}$ then the excess chemical potential, appearing on the RHS of Eq. (20) can be expanded as [12]

$$\mu^{\text{ex}}(\epsilon, [\rho(\epsilon)]) = \mu_0^{\text{ex}}(\rho, \langle \epsilon \rangle) + \frac{A(\rho)}{\rho} \epsilon + O(\epsilon^2) \quad (21)$$

in terms of its value μ_0^{ex} for the mean species in the phase (which differs a little [12] from the overall mean at $\epsilon=0$) and the function $A(\rho)$ that parametrizes the variation of excess chemical potential with size. Note that $A(\rho) = \rho d\mu^{\text{ex}}/d\epsilon$, with the derivative evaluated in the limit of a narrow distribution.

Expanding the exponential in Eq. (20), and writing $\chi(\epsilon) = \chi_0 + \epsilon\chi_1 + O(\epsilon^2)$, we obtain

$$\rho_c(\epsilon) = \frac{\rho_p(\epsilon)(\xi + 1)}{1 + \chi_0\xi} \left\{ 1 - \epsilon \frac{\chi_1\xi + (1 - \chi_0)[A/\rho]_f^c}{1 + \chi_0\xi} + O(\epsilon^2) \right\}, \quad (22)$$

where $\xi \equiv \exp(-[\mu_0^{\text{ex}}]_f^c) - 1$, with $\rho_f(\epsilon)$ given, from Eq. (14), by $(\rho_p - \rho_c\chi)/(1 - \chi)$. The overall density in either phase is then given by integration over all sizes. This allows one to obtain an expression for *normalized* size distributions. The difference in this distribution between phases is thus found to obey an expression that is independent of kinetic parameters,

$$[p(\epsilon)]_f^c = -p_p(\epsilon) \{ \epsilon [A/\rho]_f^c + O(\epsilon^2) \}. \quad (23)$$

Combining this result with the modified lever rule [Eq. (14)] recovers expressions for the normalized size distributions on either side of the crystal-fluid interface,

$$p_c(\epsilon) = p_p(\epsilon) \left(1 + \left\{ (\chi_0 - 1) \frac{\rho_f}{\rho_p} [A/\rho]_f^c - \chi_1 \frac{(\rho_c - \rho_f)}{\rho_p} \right\} \epsilon + O(\epsilon^2) \right), \quad (24)$$

$$p_f(\epsilon) = p_p(\epsilon) \left(1 + \left\{ \chi_0 \frac{\rho_c}{\rho_p} [A/\rho]_f^c - \chi_1 \frac{(\rho_c - \rho_f)}{\rho_p} \right\} \epsilon + O(\epsilon^2) \right). \quad (25)$$

Note that Eq. (17) for equality of pressure was not required. It affects the results only at higher order in ϵ .

In order to employ these equations, we need expressions for χ_0, χ_1 [which depend on $D_0(\epsilon)$ and the unknown R_0], and the densities of each phase in the nonequilibrium polydisperse system. Consider the behavior of R_0 , the scaled position of the interface. This controls the rate of growth, via $r_0 = R_0 t^{1/2}$. Physically, R_0 must depend on the composition of the system, i.e., on the density distribution $\rho_p(\epsilon)$, so $R_0 = R_0(\rho_p, \langle \epsilon \rangle_p, \langle \epsilon^2 \rangle_p, \dots)$. Assuming that R_0 can be smoothly expanded about its monodisperse value thus:

$$R_0 = R_m(\rho_p) + R_1(\rho_p) \langle \epsilon \rangle_p + R_{11}(\rho_p) \langle \epsilon \rangle_p^2 + R_2(\rho_p) \langle \epsilon^2 \rangle_p + \dots,$$

we find that, to first order, it is unchanged from the monodisperse value, since $\langle \epsilon \rangle_p \equiv 0$. We may therefore use the monodisperse value of R_0 in our first order calculation. Hence, we can take χ_0 to be the monodisperse value of $f_d(R_0/2\sqrt{D_0}(\epsilon))$, given by Eq. (14). That is,

$$\chi_0 = \frac{\rho_p - \rho_f^m}{\rho_c^m - \rho_f^m}, \quad (26)$$

i.e., χ_0 is the distance of the quench from the monodisperse phase boundary, as a fraction of the width of the coexistence region. The unknown crystal growth rate R_0 is then given, in terms of the inverse of the function f_d , by

$$R_0 = 2\sqrt{D_0} f_d^{-1}(\chi_0) + O(\langle \epsilon^2 \rangle_p) \quad (27)$$

with D_0 evaluated at $\epsilon=0$. Taylor expansion of Eq. (14) then gives

$$\chi_1 = \frac{d\chi(\epsilon)}{d\epsilon} = -\frac{R_0 D_0'}{4D_0^{3/2} f_d'} \left(\frac{R_0}{2\sqrt{D_0}} \right),$$

where $D_0' = dD_0/d\epsilon$ is evaluated at $\epsilon=0$.

By integration of Eq. (22), one finds that (to first order) the overall densities of each phase are unchanged from the monodisperse values. Hence, on the RHS of Eqs. (24) and (25), we may use the monodisperse, equilibrium values of these quantities.

VII. RESULTS

The formal expressions obtained are now applied to the case study of nonattracting polydisperse hard spheres, for which the value of the parameter $[A/\rho]_f^c$ has been determined previously [12,7] as -3.55 in units of kT .

Equations (13), (24), and (25) allow calculation of density profiles in our system. An example is plotted in Fig. 2, which shows density profiles calculated for a nonattractive hard-sphere system in $d=3$ spatial dimensions. One can see that

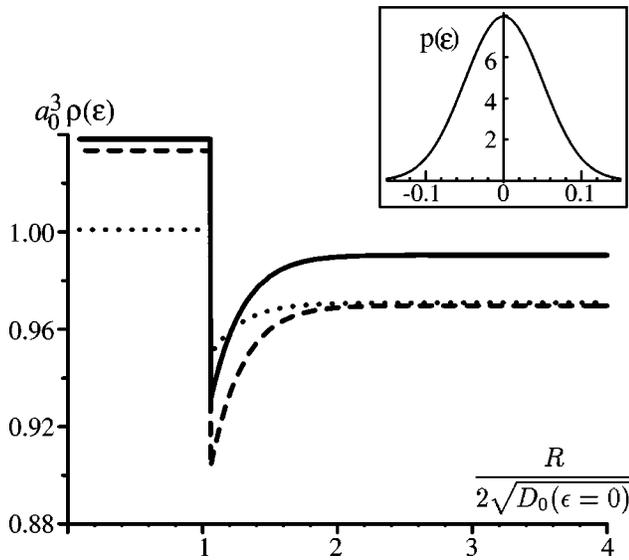


FIG. 2. Density profiles for three of the infinite number of species in the hard-sphere system: the mean sized species ($\epsilon=0$, solid line), a large species ($\epsilon=0.01$, dashed), and a small species ($\epsilon=-0.01$, dotted). The normalized parent distribution is Gaussian (inset), with standard deviation $\sqrt{\langle\epsilon^2\rangle}=0.05$; the parent concentration is $\phi_p=0.52$.

the diffusion process transports small particles to the crystal-fluid interface in relatively greater abundance than it does large particles (relative to the numbers in the parent distribution). Thus, when thermodynamic effects (of local equilibrium at the crystal-fluid interface) decide which particles are incorporated into the crystal, the choice is made from a biased version of the parent. The result of this is that the crystal is made up of particles that are, on average, smaller than would be the case in equilibrium.

Equation (24) allows us to calculate the size distribution in the crystal, given any narrow parent. As an example we use a Gaussian parent. For comparison the resulting distributions in the fluid and crystal, for a system that has reached thermodynamic equilibrium (as predicted by the equilibrium perturbation theory [12]) are displayed in Fig. 3. We note that the crystal has a preference for larger particles, telling us that entropy is maximized if the particles are partitioned in this way. Heuristically, this is because the particles' positional entropy in the fluid phase is increased if more space is

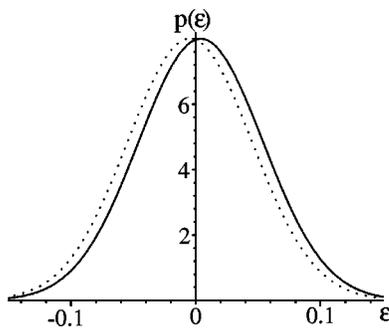


FIG. 3. The *equilibrium* size distribution in the crystal (solid line) and fluid (dotted).

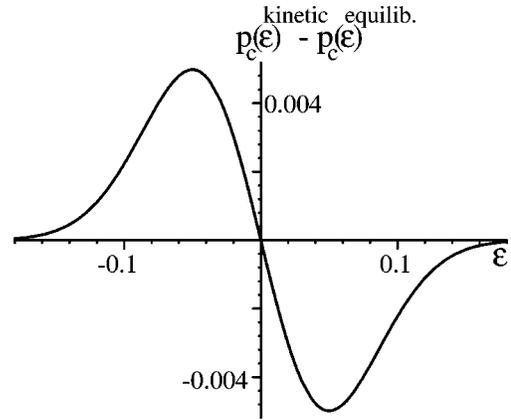


FIG. 4. The difference in normalized size distributions in the crystal between that calculated using the present kinetic model, and that of the equilibrium theory (for the parent used in Fig. 2).

made available by removing the larger particles to the crystal phase. What then is the effect of the growth process on the size distributions? The effect can be seen by plotting the difference between size distributions in the crystal as predicted by the kinetic and equilibrium calculations. This is shown in Fig. 4.

We see the effect of kinetics is to bias the distribution in the crystal toward smaller sizes. We take the first moment of Eq. (24) to find the mean size $\langle\epsilon\rangle_c$ in the crystal, which is a function of the overall concentration in the system. It is plotted in Fig. 5 as a function of the relative supersaturation χ_0 beyond the fluid phase boundary.

At $\chi_0=0$, the system is at equilibrium, at its cloud point, since the fluid is not supersaturated, and the crystal phase at coexistence occupies an infinitesimal volume. As a result, the growth rate R_0 vanishes, and the mean size deviation in the crystal attains its equilibrium value $\langle\epsilon\rangle_c=3.55\langle\epsilon^2\rangle_p$. As the supersaturation of the initial fluid state increases, the mean particle size in the crystal becomes smaller, in an almost (although not quite) linear fashion. In the limit where the initial state is so dense that crystallization induces no density change, the mean size in the crystal equals that in the parent ($\langle\epsilon\rangle=0$).

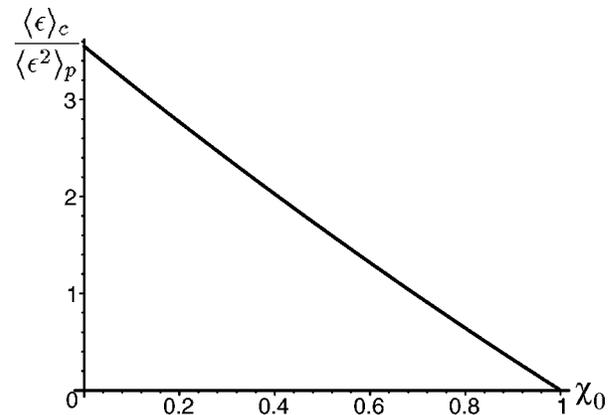


FIG. 5. The mean size deviation of particles in the crystal, in units of the overall variance $\langle\epsilon\rangle_c/\langle\epsilon^2\rangle_p$, as a function of relative supersaturation of the initial fluid phase χ_0 .

Note that, in the hard-sphere system, although the effect of kinetics is to reduce the mean particle size in the crystal, it remains larger than the overall parental mean, i.e., $\langle \epsilon \rangle_c \geq 0$. Hence, in a sense, the thermodynamic effects of crystal-fluid partitioning win over the kinetics. We find that this is a consequence of the small density change at the hard-sphere crystal-fluid phase transition ($\rho_c/\rho_f - 1 \approx 10\%$). In a second case study (not presented here), we have substituted into Eq. (24) parameters appropriate to a system of hard spheres with attractive interactions [12] (in particular, the ‘‘depletion’’ interaction arising in colloid-polymer mixtures [18]). In that case, the coexistence region can become much broader since, with strong attractions, even a very dilute gas of hard spheres can crystallize. Then we find a range of values of χ_0 for which crystals form from particles *smaller* on average than the mean composition of the system, i.e., $\langle \epsilon \rangle_c < 0$, signaling the dominance of the kinetic effects presented here.

VIII. CONCLUSION

The kinetics of polydisperse systems are sufficiently complex that few analytical or even numerical studies have been attempted. Exceptions are Refs. [14] and [19].

We have argued that colloidal hard-sphere systems (which are inevitably polydisperse) form crystals whose composition is not at equilibrium, i.e., does not maximize the entropy of the two-phase ensemble. Instead, particles are caged in the crystalline structure. In practice, some small-scale rearrangements within the crystal can take place in the presence of lattice defects, but the rate of particle diffusion is negligible (particularly with interparticle attractions) compared to that in the fluid phase. As a result, the distribution of particle sizes frozen into a colloidal crystal remains as a relic of its growth mechanism.

The establishment of chemical equilibrium requires a significant fraction of each chemical species to be exchanged many times between the crystal and fluid phases. A hypothetical system in which this occurs, so that phase space is fully explored and distributions are optimized, would preferentially partition more large particles into the crystal phase, so that particles in the coexisting fluid have more space in which to enjoy positional entropy. In contrast, the diffusive growth process biases the crystalline composition toward small particles, since they can travel most quickly from the distant bulk of the ambient fluid. While the mean particle size at the crystal-fluid interface must be larger in the crystal side than in the adjacent fluid, the largest, most sluggish particles remain predominantly in the fluid bulk.

The regime for which we were able to find analytical solutions of the equations of motion was at intermediate times, when all relevant lengths scale with time as $t^{1/2}$. That is, after transients associated with the initial random nucleation event have passed so that, on the scale of the interfacial width (a few particle diameters), the phases are at local equilibrium, but before the fluid zone of depleted concentration around each condensation nucleus begins to overlap with its neighbors, so that the distant fluid composition still asymptotes to that of the initial (‘‘parent’’) mixture. Once these

depleted regions do significantly overlap, the supersaturation of the fluid phase is soon exhausted. The remaining mix of predominantly large particles, which have remained in the fluid, will eventually coat each crystallite, and growth will cease when no concentration gradient remains in the fluid. Hence, in laboratory samples, we expect the inert colloidal crystallites to have an unknown core of a few particles that collected together during the early nucleation stage, a significant bulk of the uniform composition we have calculated, and a nonuniform coating of larger particles. Happily, equilibrium phase diagrams, that have previously been calculated are not redundant, as the uniform composition from the scaling regime of crystal growth does lie on the equilibrium phase boundary, although not on the tie line specified by the usual lever rule. For our calculation to be useful, the core region of each crystallite, whose composition we do not know, must be small compared with the whole crystallite, which requires a low concentration of condensation nuclei to appear in the system.

The above scenario should hold, no matter how the diffusion matrix (which determines the flux of each species induced by concentration gradients of any other species) varies with concentration. Although collective motions and many-body interactions lead to a nonlinear diffusion equation for the fluid [15], this affects details of the shape of the concentration profiles in Fig. 2, but does not alter the $t^{1/2}$ growth law or the conditions of local interfacial equilibrium, leading to a uniform crystalline composition. Also, the qualitative principle remains, that small particles diffuse most quickly.

To find quantitative solutions, however, we were compelled to make two approximations. The first, in order to diagonalize the diffusion matrix, was a low-concentration approximation which, although it has a regime of validity near the fluid phase boundary of attractive systems, is otherwise quantitatively poor. In its favor, it yields qualitatively significant results. The trend in Fig. 5, for instance, is correct, tending as it does from an equilibrium result at the fluid phase boundary (zero supersaturation, $\chi_0=0$) to a total absence of demixing at the crystal boundary ($\chi_0=1$). More accurate analysis reveals complex physics. The diffusion coefficient for smaller particles may be attenuated more [15] or less [20] than for larger ones as concentration increases, depending on details of the mixture. However, in experiments on binary colloids [21], the long-time self-diffusion coefficients of the small/large particles were found to remain in approximately the same ratio over a wide range in concentration. This, together with intuition based on effective medium theory, leads us to believe that the small particles will always tend to diffuse more quickly.

Our second approximation holds true for many experimental systems. Hard-sphere colloids can be synthesised [22] with a narrow distribution of particle sizes (typically 2–10% tolerance in the radii), for which perturbation about a monodisperse reference state, to first order in size deviations, has been shown to yield accurate results for two-phase equilibrium [11,12], which is local in this case. The perturbation expansion holds, given that the perturbation (i.e., the

width of the distribution) is sufficiently small. With increasing polydispersity, the system is expected to exhibit singular behavior, partitioning its particles into several coexisting crystal phases of more uniformly sized particles [23], or forming alloys with more complex unit cells [4,5], to avoid costly lattice interstitials of very mis-sized particles. In that case, the growth may be controlled by the kinetics of segre-

gation at interfaces, leading to different physics from the diffusion-limited regime calculated here.

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