Correlations and Freezing in Steadily Settling Suspensions

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(version of October 8 1998 draft 5; printed May 18, 2018)

We study the liquid-solid transition in a collection of interacting particles moving through a dissipative medium under the action of a constant, spatially uniform external force, e.g. a charge-stabilized suspension in a fluidized bed or a flux-point lattice moving through a thin, current-carrying slab of type II superconductor. The mobility of a given region in these systems is in general a function of the local concentration. We show that the structure factor peak is suppressed in an anisotropic manner as a result of this effect, resulting in a shift of the crystalline-liquid phase boundary towards the crystal side. A nonequilibrium phase diagram is presented.

05.40+j, 64.70.Dv, 82.70.Dd, 47.15.Gf,

I. INTRODUCTION AND RESULTS

How a liquid freezes to form a solid is a problem of longstanding interest to physicists. Freezing at thermal equilibrium can now be said to be quite well understood in terms of a first-principles order-parameter theory [1]. The effect of steady nonequilibrium driving on the freezing transition has been studied in the context of sheared colloids [2,3]. A uniformly driven state, with no gradients on the average, as would arise in steady sedimentation [4] or the fluidized bed [5,6] is conceptually simpler: unlike in shear flow, an order-parameter description of the mean state of the driven crystal is straightforward. Nonetheless, we know of no studies, experimental or theoretical, of the effect of sedimentation on the liquid-solid phase boundary in a suspension settling uniformly under gravity, or of the freezing of moving flux lattices in the absence of quenched disorder.

A study of freezing in the presence of uniform driving is also of interest as a problem in the general class of driven diffusive systems. Most of the investigations in this field [4] are either away from any equilibrium phase transition or in the neighbourhood of a second order phase transition. The effect of uniform driving on a first order phase transition has received very little attention [7,8], the freezing transition, in particular holds interesting possibilities since the ordering is at non-zero wavenumber.

In this paper we consider a collection of interacting particles in a liquid state, i.e., with strong short-range translational correlations, and ask what happens to the liquid-solid transition in the presence of an imposed steady mean translational motion of the particles with respect to the ambient medium. Our model should apply not only to charge-stabilized colloidal suspensions [3,9], but also to the effect of a steady current on the freezing transition of flux-point liquids [10] in thin slabs of clean type II superconductors. The main ingredient in our theory is the concentration dependence of the mobility of particles in a suspension, or of the flux-points in a superconductor. In colloidal suspensions, this dependence arises as a result of the hydrodynamic interactions between particles, while in the flux-liquid, it is the electromagnetic interaction that is primarily responsible for the effect. Although our approach is fairly general, we use parameter values appropriate to the specific case of sedimenting colloidal suspensions in the rest of the paper.

Our main results are as follows: As the mean concentration of the suspension is increased, the hydrodynamic interaction causes it to settle more slowly [3,9,11,12]. We show that this leads to a nonlinearity in the equations of motion whose effect is to reduce the height of the structure factor relative to its equilibrium value. The suppression is strongly anisotropic, largest for wavevectors along the direction of mean drift, and vanishing for wavevectors normal to it. The reduction is most pronounced at the location of the peak, which means the strong short-range correlations in the liquid, which are the precursor of translational order, are suppressed. This inevitably leads to a shift of the phase boundary towards the crystal side (i.e., favours the liquid over the crystalline phase), by an amount proportional to the square of the Péclet number, in a manner reminiscent of a proposed mechanism [13] for shear-induced melting. This nonequilibrium phase transition now assumes additional importance in the wake of recent experiments on charged fluidized beds [14,15,16], where it should be possible to test our predictions. Constraints on the types of systems to which our theory should apply are discussed at the end of section VII.

The paper is organised as follows. Section II gives an overview of equilibrium freezing. The equations describing the motion of a sedimenting suspension are derived in section III. In section IV we discuss in a general setting the prescription used in this paper to describe a nonequilibrium phase transition. The perturbative calculation leading to the equal time correlation function in the driven system is the content of section V, and
our numerical results for the structure factor are given in section VII. In section VII we derive our results for the freezing transition, and conclude in section VIII.

II. EQUILIBRIUM FREEZING

The equilibrium phase-transition from a liquid to a crystal is the spontaneous appearance of a static, spatially periodic modulation in the density field of the liquid. An order parameter theory of this transition [17,18] is obtained by writing down the free-energy cost of such a modulation as a functional of the density field.

The free energy cost of an inhomogeneous density field \( \rho(x) \) relative to the uniform liquid state of density \( \rho_0 \) is given by

\[
\tilde{F} = F/k_B T = \frac{1}{2} \int dx c(|x - x'|)(\rho(x) - \rho_0)(\rho(x') - \rho_0)
+ \int dx \left[ \rho(x) \ln \frac{\rho(x)}{\rho_0} - (\rho(x) - \rho_0) \right],
\]

(2.1)

where \( c(r) \) is the direct correlation function of the liquid. The second term in (2.1) is an ideal gas entropy, whereas the first comes from correlations in the interacting system. Expanding the logarithm and stopping at the second order in the density fluctuation \( \phi = \rho - \rho_0 \), gives the quadratic part of the free-energy in terms of the Fourier modes \( \phi(k) \) as:

\[
\tilde{F} = \frac{1}{2} \int \frac{dk}{(2\pi)^d} \frac{1}{\rho_0 S_0(k)} |\phi(k)|^2
\]

(2.2)

in terms of the dimensionless structure factor

\[
S_0(k) = \frac{1}{1 - \rho_0 c(k)}.
\]

(2.3)

The density correlation function at equilibrium is related to the structure factor by the relation

\[
\langle \phi(k)\phi(-k) \rangle = V \rho_0 S_0(k)
\]

(2.4)

where \( V \) is the system volume.

All information about temperature and mean density is encoded in the liquid-state direct correlation function \( c(r) \). For a given \( c(r) \), \( \rho(r) \) corresponding to the thermodynamically stable state, within mean-field theory, is the global minimum of \( F[\rho] \), obtained in principle by solving \( \frac{dF}{d\rho} = 0 \), and choosing that solution for which \( F \) is the smallest. At low densities and high temperatures, the global minimum is \( \rho(r) = \rho_0 \). For sufficiently dense, cold systems, this uniform liquid state is unstable relative to a spatially periodic \( \rho(r) \), the crystal. Terms in \( F \) of order higher than quadratic in \( \phi(r) = \rho(r) - \rho_0 \) are clearly essential to give such a solution. Although the best theories of freezing [1] go the whole log, we shall sacrifice accuracy in favour of simplicity, and use a quartic polynomial approximation to \( F \). Since we are looking for periodic density waves, it is convenient to work with \( \{ \phi_G \} \), the weights of the Bragg peaks at the reciprocal lattice vectors \( G \), defined by

\[
\phi(k) = \sum_G \phi_G \delta(k - G).
\]

(2.5)

Since the peak of the liquid-state structure factor at its first maximum \( G = 2\pi/a \) is much higher than the subsequent peaks, we restrict ourselves to Fourier amplitudes of \( \phi(k) \) close to this peak. This is equivalent to considering only the first shell of reciprocal lattice vectors for the crystal. Only the form of the \( S(k) \) near the peak matters then, and \( S^{-1}(G) \) can be replaced by a Lorentzian

\[
S^{-1}(G) = a + \sigma(G^2 - k_0^2)^2
\]

(2.6)

so that the peak height is

\[
S(k_0) = a^{-1}.
\]

(2.7)

The Landau Free energy per particle is then given by

\[
\tilde{F} = \frac{1}{N} \sum_G \left[ a + \sigma(G^2 - k_0^2)^2 \right] \frac{\phi_G \phi_G^*}{\rho_0^2} - \frac{1}{3!} B \rho_0^2 \sum_{G_1,G_2,G_3} \frac{\phi_{G_1}\phi_{G_2}\phi_{G_3}}{\rho_0^2} \delta_{G_1+G_2+G_3,0}
+ \frac{1}{4!} C \rho_0^3 \sum_{G_1\ldots G_4} \frac{\phi_{G_1}\phi_{G_2}\phi_{G_3}\phi_{G_4}}{\rho_0^3} \delta_{G_1+G_2+G_3+G_4,0}.
\]

(2.8)

If \( \sigma G_0^4 \gg a \), then free energy costs strongly discourage the Fourier amplitudes to stray from the peak of the structure factor, i.e \( |G| = k_0 \). The free energy can then be expressed as a function of a single scalar order parameter

\[
r = n^{1/2}(\rho_G/\rho_0)
\]

(2.9)

where \( n \) is the number of reciprocal lattice vectors in the set (i.e. 6 for a triangular lattice, 12 for bcc etc). Note that at nonzero wavevector \( G \), \( \phi_G \) and \( \rho_G \) are identical. The free energy per particle per \( k_B T \) is thus a polynomial

\[
f = \frac{F}{N k_B T} = \frac{1}{2} ar^2 - \frac{1}{3!} b r^3 + \frac{1}{4!} c r^4,
\]

(2.10)

with

\[
b = 2 p^{-1/2} \rho_0^2 B
\]

(2.11a)

\[
c = 6 \left[ 1 + \frac{q}{n} \right] \rho_0^3 C.
\]

(2.11b)

Here \( p \) and \( q \) are numbers that depend on the type of lattice being considered: \( p \) is the number of such triplets or triangles that each RLV belongs to, and \( q \) is the number
of non-planar diamonds that the RLVs can form among themselves [18]. The value of $a$ at which the transition occurs is found by demanding that the free energy be zero at the crystalline minimum. This leads to the value of $a$ at the transition,

$$a_c = \frac{b^2}{3c}.$$ (2.12)

The cubic term favours lattice structures in which the RLVs form triangles in sets of three. The candidate lattices, within the one order parameter theory, are the ones whose RLVs correspond to edges of regular polyhedra or polygons with triangular faces, i.e. planar triangular (whose RLVs form a pair of triangles), face centred cubic (octahedron) and icosahedral (icosahedron) lattices. The theory predicts that all crystals should be triangular lattices in two dimensions and body centred cubic (which has a face centred cubic reciprocal lattice) in three dimensions. Given the lack of sophistication, the theory is reasonably successful as almost all two dimensional crystals are triangular lattices, and many, if not all elemental solids in three dimensions are indeed BCC, at least close to freezing [19].

The theory discussed above has several drawbacks: it neglects all structure in S(k) except that at the peak and assumes that all wavevectors have the same order parameter amplitude. These assumptions can be relaxed and a more complete theory written down, but the Landau expansion itself is questionable, in fact inaccurate, since the order parameter jump at freezing is large. It would doubtless be better to generalize the first-principles density-wave approach of Ramakrishnan and Yussouff [1] to include the effects of sedimentation. In the present work, however, we have attempted only a nonequilibrium generalizations of the simple and intuitive Landau-Alexander-McTague theory, as a first step in taking into account the effect of sedimentation on freezing. An extension of our approach to more realistic freezing theories should be fairly straightforward.

III. EQUATIONS OF MOTION

The frictional force on a spherical particle of radius $R$ moving slowly in a fluid with shear viscosity $\eta$ with a uniform speed $v$ is given by [20]

$$\mathcal{F} = 6\pi\eta Rv.$$ (3.1)

The dimensionless parameter which gives a measure of the relative importance of sedimentation with respect to Brownian motion is the Péclet number, defined as the ratio of the time taken by the particle to diffuse a characteristic distance $\ell$ to the time taken to settle the same distance under gravity, without diffusing. In terms of the mean settling speed $v_{\text{Stokes}}$ of the particle, the Péclet number is given by

$$Pe = \frac{v_{\text{Stokes}} \ell}{D}.$$ (3.2)

The appropriate dimensionless measure (which we will continue to call the Péclet number) of the relative importance of drift versus diffusion for this problem, will turn out to be proportional to the Péclet number defined at the scale of an interparticle spacing, but will incorporate certain collective effects whose nature will become clear below after we construct our equations of motion.

Although the single particle problem was solved in 1851 [21], the sedimentation speed of a suspension was theoretically obtained as recently as 1972 [21], and that too in the dilute limit. The speed of a strictly random suspension of volume fraction $\phi$ turns out to be less than that of a single sphere:

$$v_\phi = (1 - 6.55\phi + O(\phi^2))v_{\text{Stokes}}$$ (3.3)

Thus, at a volume fraction of 10%, the settling speed is reduced to 35% of the Stokes value. It has been also observed experimentally [22, 23] that the mean settling speed of a suspension is less than that of a single particle, and a decreasing function of the concentration of suspended particles. In other words, the mobility of a region is a function of the local concentration.

The sedimenting suspension that we speak of is an idealized bottomless tube of infinite height containing a solvent in which there is a steady downward flow of particles (denser than the solvent). An ‘infinite’ tube is realized in real life by means of a setup known as a fluidized bed [8–10, 15], a vertical tube through which fluid is pushed up at a steady rate by an externally maintained pressure head, with particles suspended stably on the average by the balance between gravity and the viscous drag of the upflow of fluid. The problem of the steadily sedimenting particle in the comoving frame of reference is identical, in the infinite container limit, or far from the walls of the container, to the fluidized bed problem in the lab frame. For very dilute solutions, the reduced weight of the particle (i.e. the weight minus the buoyant force) is balanced by the single particle Stokes friction. At higher concentrations, hydrodynamic interactions between the spheres [23, 24] becomes important, leading to a hindered settling speed, the effect of which we investigate.

Consider now a collection of interacting particles, on the average in a liquid state with uniform number density $\rho_0$, moving through a frictional medium. In the absence of external forces (such as gravity) the number density $\rho(x)$ follows the equation:

$$\frac{\partial \rho}{\partial t} = \Gamma_0 \nabla^2 \delta F + \eta,$$ (3.4)

where $\Gamma_0$ is the collective diffusion constant, $\eta$ is a Gaussian white noise consistent with thermal equilibrium:

$$\langle \eta(x, t)\eta(x', t') \rangle = 2k_B T \Gamma_0 \nabla^2 \delta(x - x')\delta(t - t'),$$ (3.5)

and $F$ is the free-energy functional defined in [21]. This equation is simply the equation of continuity.
The equation of motion for the concentration field \( \rho \) in a constant external force field \( \mathbf{g} = g \mathbf{z} \), the particles sediment with a steady mean drift velocity \( \mathbf{v} = \mu(\rho)mg \) [24], where \( \mu \) is the concentration-dependent mobility, which in the low density limit, is expected to go to the Stokes value \( \frac{m}{3\ell_{\text{p}}^2} \). The current then acquires an extra piece \( \rho \mathbf{v} \) leading to an additional term of the form

\[
-mg \frac{\partial}{\partial z}[\rho \mu(\rho)]
\]

on the right hand side of equation (3.4). Here \( mg \) is the reduced or Archimedean weight of the solute particles,

\[
mg = m_0 g - m_{\text{displaced}} g,
\]

with \( m_0 \) being the mass of the particle, and \( m_{\text{displaced}} \) the mass of solvent displaced by submerging it.

Let us now consider concentration fluctuations in the suspension around the mean density \( \rho_0: \rho = \rho_0 + \delta \rho \). Taylor expanding the mobility about the mean value \( \mu_0 \) to second order, we find the equation of motion for the density field to be

\[
\frac{\partial}{\partial t} \delta \rho + mg(\mu_0 + \rho_0 \left( \frac{\partial \mu}{\partial \rho} \right)_{\rho_0}) \frac{\partial}{\partial z} \delta \rho = \Gamma_0 \nabla^2 \delta \overline{F} - \mu_2 \frac{\partial}{\partial z} \delta \rho^2 + \eta,
\]

where

\[
\mu_2 = mg \frac{\left( \frac{\partial \mu}{\partial \rho} \right)_{\rho_0} + \rho_0 \left( \frac{\partial^2 \mu}{\partial \rho^2} \right)_{\rho_0}}{\rho_0},
\]

\[
= \frac{\mu_0 mg}{\rho_0} \frac{\partial^2 \left( \frac{\mu}{\rho_0} \right)}{\partial \left( \ln \left( \frac{\rho}{\rho_0} \right) \right)^2}_{\rho_0}.
\]

The left hand side of (3.10) is simply the Eulerian derivative for a reference frame moving with a velocity

\[
\mathbf{v}_{\text{frame}} = g(\mu_0 + \left( \frac{\partial (\ln \mu)}{\partial \rho} \right)_{\rho_0} \frac{\partial}{\partial z} ) \hat{z}.
\]

In the rest of this paper, we will do all our calculations in this reference frame, so that the left hand side of (3.10) can be replaced by a time derivative. Note that this frame is not the frame in which the mean velocity of the particles is zero. For a colloidal suspension, since \( \mu \) decreases on increasing concentration, the frame moves with a velocity less than the mean velocity. Thus one would see a net drift along gravity in this frame. However, the quantities of interest to us, i.e., equal time correlation functions, are invariant under a Galilean transformation, so it doesn’t matter in which frame we do our calculation.

Before beginning the calculations, we change variables to the non-dimensionalized fluctuation of the concentration from the mean, \( \phi = \frac{\rho - \rho_0}{\rho_0} \), and the dimensionless free energy \( \overline{F} = F/k_B T \), in terms of which the equation of motion in the comoving frame becomes

\[
\frac{\partial \phi}{\partial t} = \overline{D} \nabla^2 \delta \overline{F} + \lambda \frac{\partial}{\partial z} \phi^2 + \eta,
\]

\[
\langle \eta(x,t) \eta(x',t) \rangle = -\overline{D} \nabla^2 \delta(x-x') \delta(t-t'),
\]

where

\[
\overline{D} = \frac{k_B T T_0}{\rho_0} \tag{3.14}
\]

is the collective diffusion constant, and

\[
\lambda = -\mu_0 mg \frac{\partial^2 \left( \frac{\mu}{\rho_0} \right)}{\partial \left( \ln \left( \frac{\rho}{\rho_0} \right) \right)^2}_{\rho_0} \tag{3.15}
\]

is a velocity scale set by the Stokes velocity modified by the concentration-dependence of the mobility. Note that the piece \( \mu_0 mg \) outside the brackets is the mean settling speed. The term within the brackets is a dimensionless number that vanishes in the dilute limit. For sedimenting suspensions, the mobility is a decreasing function of concentration, so \( \lambda > 0 \). Since \( \overline{D} \) and \( \lambda \) are a diffusion constant and a velocity respectively, together they give the appropriate dimensionless coupling (which we will call the Péclet number \( Pe \)) for the problem:

\[
P e = \frac{\lambda \ell}{\overline{D}} \tag{3.16a}
\]

\[
= \left( \frac{\mu_0 mg \ell^2 \rho_0^2}{k_B T T_0} \right) \frac{\partial^2 \left( \frac{\mu}{\rho_0} \right)}{\partial \left( \ln \left( \frac{\rho}{\rho_0} \right) \right)^2}_{\rho_0}, \tag{3.16b}
\]

where \( \ell \) is the average interparticle spacing in the suspension. Note that we are using \( \ell \) rather than the particle size as the length scale to define the Péclet number. This is reasonable since we are considering collective rather than single particle effects. In terms of the single particle diffusion constant \( D_0 \), which is related to the bare
mobility by the Einstein relation $D_0 = k_B T \mu_0$, the Péclet number can be written as

$$P_e = \left( \frac{D_0}{D} \right) \left( \frac{\ell}{R} \right) \left[ \frac{\partial^2 \left( \frac{\rho}{\rho_0} \right)}{\partial \left( \ln \left( \frac{\rho}{\rho_0} \right) \right)^2} \right] \left( \frac{mgR}{k_B T} \right). \quad (3.17)$$

The last piece (in parentheses) in (3.17) is the particle-size Péclet number for a single sphere, which is simply the ratio of the gravitational potential energy drop across the size of the particle to the thermal energy $k_B T$. The other three terms are dimensionless numbers that bring in the collective effects.

The hydrodynamic interactions appear through the third piece in (3.17) (in square brackets). It should be noted that this term is indeed nonzero even if the mobility is a linear function of concentration.

We pause here to do some power-counting. The change in mobility due to a number density fluctuation depends on the change in volume fraction. The Taylor expansion of mobility, for example, is given by $\mu = \mu_0 \left[ 1 - \alpha R^d (\rho - \rho_0) + \ldots \right]$ in $d$ dimensions, where $\alpha$ is a dimensionless number that can be found from experiments. To the lowest order in the polyball size $R$, therefore, the piece in square brackets in (3.17) is proportional to $R^d$. The Péclet number thus goes as $mR^d$ for particle of mass $m$ and radius $R$. As $R \to 0$, the hydrodynamic interaction between the spheres goes away, and the Péclet number goes to zero as $R^d$ if we keep the mass fixed, and as $R^{2d}$ if we change the radius of the particle keeping the density fixed.

The equation of motion (3.13) of the density fluctuation is the equilibrium dynamical equation with an additional nonlinearity of the Burgers type [26]. Qualitatively, the nonlinear term may be understood in terms of a lattice gas model [11], where particles are driven in one direction by a constant field, but a particle is allowed to hop to the next site only if it is empty (no double occupancy). This microscopically models a mobility depending on the local density – in regions where the density is large, the probability of hopping being obstructed by the presence of other particles is larger, and hence the mobility smaller. The current at site $n$ is then proportional to $\rho_n (1 - \rho_{n+1})$, where $\rho_n$ is the discretized density in a bin at $n$. On coarse graining this will give two terms: a term $\sim \phi$, which can be removed by a Galilean transformation; and another $\sim -\phi^2$, which persists even in the comoving frame.

Before moving on to use (3.13) to calculate the correlations in the suspension, let us briefly discuss the limitations of our model. First, we have only considered one effect of sedimentation, namely the dependence of concentration on mobility. This is a coarse-grained description of the hydrodynamic interactions, reliable only at long wavelengths. A better theory should consider, for example, gradient-dependence in the mobility, i.e., the diffusivity at wavenumber $k$ should have corrections of $O(kR)$ for a suspension of particles of size $R$. Since we are interested in ordering phenomena at finite wavevectors $\sim k_0$, our theory should give reliable results for $k_0 R \ll 1$ which is satisfied, for example, for strongly charge stabilized colloids where the ordering length scale $k_0^{-1}$ is of order the screening length, $\xi \gg R$. In addition, we have ignored the dependence of the mobility on more detailed aspects of the local distribution of particles, e.g., its anisotropy, a point which we comment on at the end of this paper.

Secondly, we have also ignored the concentration-dependence of the diffusion constant $\tilde{D}$ in (3.13). Strictly speaking, $\tilde{D}$ should have the same concentration dependence as $\mu_0$, since the two are related by the Einstein formula. A correct formulation of the problem with $\tilde{D}(\phi)$ would require a multiplicative noise (of the form $\nabla \cdot [\sqrt{\tilde{D}(\phi) f}$ where $f$ is a spatiotemporally white noise with unit variance) to make the equations of motion consistent with equilibrium. This problem is technically much more difficult [27,28], and we believe it shouldn’t change the results dramatically for the following reason. A concentration-dependent diffusion constant coupled with a consistent noise of the above type is an equilibrium effect, and an (effective) concentration independent $\tilde{D}$ with ordinary Gaussian noise leads to the same equilibrium distribution. The nonlinear term in (3.13) is the only driving term arising from concentration dependence. In any case, (3.13) is the simplest driven-diffusive model with a liquid-solid transition and the correct equilibrium limit, and thus merits study in its own right.

Lastly, we have also ignored the long-ranged effects of the hydrodynamic interaction. Our description corresponds to a quasi two-dimensional suspension confined between parallel walls with spacing $h$. The walls cut off the hydrodynamic forces on lateral scales much larger than $h$, making them effectively short range. The local effects of the hydrodynamic interactions are, however, accounted for by the concentration dependent mobility. To describe the three dimensional problem we have to explicitly include the the hydrodynamic velocity-field of the suspension in the description. Although this could have far-reaching effects at small wavenumber, it should be relatively unimportant for the statics of crystallization, whose physics is dominated by wavenumbers near the structure-factor peak.

IV. PHASE TRANSITIONS IN A NONEQUILIBRIUM PROBLEM

Since we are interested in the freezing transition, we set up the equation of motion (3.13) for the density field, with a free energy functional that leads to a freezing transition in equilibrium. The simplest of these is the Landau-Alexander-McTague free energy functional which we have discussed in section I. A spatially inhomogeneous density fluctuation $\phi(r)$ (Fourier transform
\[ \phi(k) \text{ has, relative to the uniform fluid, a free energy} \]
\[ F[\phi(k)] = \frac{1}{2} \int \frac{dk}{(2\pi)^d} \frac{1}{\rho_0 S_0(k)} \phi(k)\phi(-k) \]
\[ -\frac{1}{3!} b \int \frac{dk}{(2\pi)^d} \int \frac{dp}{(2\pi)^d} \phi(-k)\phi(p)\phi(k-p) \]
\[ + \frac{1}{4!} c \int \frac{dk}{(2\pi)^d} \int \frac{dp}{(2\pi)^d} \int \frac{dp'}{(2\pi)^d} \times \phi(-k)\phi(p)\phi(p')\phi(k-p-p') \]  
(4.1)

where \( S_0(k) \) is the equilibrium structure factor of the suspension. The density correlation function at equilibrium calculated using the above free energy is, to quadratic order,

\[ \langle \phi(k_1)\phi(k_2) \rangle = \rho_0 S_0(k) \delta(k_1 + k_2). \]  
(4.2)

The equation of motion (3.13) becomes in reciprocal space

\[ \begin{aligned}
\frac{\partial}{\partial t} \phi(k) &= -(2\pi)^d \tilde{D} \rho_0 k^2 \frac{\partial F}{\partial \phi(-k)} \\
&+ i \frac{\lambda}{\rho_0} k z \int \frac{dp}{(2\pi)^d} \phi(p)\phi(k-p) + \eta(k), \\
\langle \eta(k, t)\eta(k', t') \rangle &= (2\pi)^d 2\tilde{D} k^2 \rho_0 \delta(k+k')\delta(t-t'). 
\end{aligned} \]  
(4.3a)

Using the form (4.1) for the free energy, the equation of motion (4.3a) becomes

\[ \begin{aligned}
\frac{\partial}{\partial t} \phi(k) &= -\tilde{D} k^2 S_0(k) \phi(k) + i \frac{\lambda}{\rho_0} k z \int \frac{dp}{(2\pi)^d} \phi(p)\phi(k-p) \\
&+ \eta(k). 
\end{aligned} \]  
(4.4)

where the contribution of anharmonic terms in the free energy have not been put in. This is because we are interested in the corrections to the equilibrium bare correlation functions due to the driving term.

It is easy to see that the additional nonlinear term in equation (3.13) or (4.4) cannot be expressed in a form so as to be absorbed into an additional term in the free energy. This is done by checking that the functional curl of the term is nonvanishing. We will call this term in (4.4) the sedimentation nonlinearity.

To describe phase transitions in this nonequilibrium problem, we follow earlier work on critical phenomena in the presence of shear [2] and shear-induced melting of colloidal crystals [4]. We assume that the Fokker-Planck equation that derives from the above Langevin equation (4.4) has a steady solution in the long time limit, which we write as

\[ P[\phi] \sim e^{-\Gamma[\phi]} \]  
(4.5)

and expand the functional \( \Gamma[\phi] \) in a Taylor expansion

\[ \Gamma[\phi] = \frac{1}{2} \Gamma_2(1,2)\phi(1)\phi(2) + \frac{1}{3!} \Gamma_3(1,2,3)\phi(1)\phi(2)\phi(3) + \ldots \]  
(4.6)

where 1, 2 etc. are arguments, for example spatial positions \( x_1, x_2 \) etc. The summation convention is implied for repeated arguments. The \( \Gamma_n \) are the vertex functions. The calculation of moments from this probability functional gives, for the connected parts, the relations [30]

\[ \langle \phi(1)\phi(2) \rangle = \frac{\Gamma_2(1,2)}{2}, \]

\[ \langle \phi(1)\phi(2)\phi(3) \rangle = -\frac{\Gamma_3(1',2',3')\phi(1')\phi(1')}{3}, \]

\[ \langle \phi(2)\phi(2') \rangle \langle \phi(3)\phi(3') \rangle, \]  
(4.7a)

and so on, which are the usual relations between the connected correlation functions and vertex parts. The only difference here is that the steady state probability distribution is not the inverse exponential of the equilibrium free energy functional. The vertex functions \( \Gamma_i \) above have to be therefore calculated from the steady state probability distribution \( P \). However, the correlation functions can be calculated from the Langevin equation itself by demanding that the time derivative of all correlation functions can be calculated from the Langevin equation [3].

\[ \langle \phi(k_1)\phi(k_2) \rangle = \tilde{\Gamma}_2(k_1,k_2)^{-1}, \]

\[ \langle \phi(k_1)\phi(k_2)\phi(k_3) \rangle = \tilde{\Gamma}_3(k_1,k_2,k_3)^{-1}, \]

\[ \langle \phi(k_1')\phi(k_1) \rangle \langle \phi(k_2')\phi(k_2) \rangle \langle \phi(k_3')\phi(k_3) \rangle. \]  
(4.8a)

The second of these relations can be rewritten in terms of the structure factor as

\[ \langle \phi(k_1)\phi(k_2)\phi(k_3) \rangle = -\tilde{\Gamma}_3(k_1,k_2,k_3)\rho_0^3 S(k_1)S(k_2)S(k_3). \]  
(4.9)

At thermal equilibrium, i.e., in the absence of driving, the vertex functions calculated to tree level are simply the inverse correlation function and the higher vertices in the free energy:

\[ \Gamma_2(k_1,k_2) = \frac{1}{\rho_0 S_0(k)}, \]

\[ \Gamma_3(k_1,k_2,k_3) = -\delta(k_1 + k_2 + k_3), \]

\[ \Gamma_4(k_1,k_2,k_3,k_4) = c\delta(k_1 + k_2 + k_3 + k_4). \]  
(4.10a)

We calculate the perturbative correction to the vertices due to the sedimentation nonlinearity, from which we obtain the steady state probability distribution [5]. This \( P \) can be treated as a mean-field probability distribution which may be maximized to find the stable phase at any given temperature. In other words, \( \Gamma[\phi] \) can be treated as a nonequilibrium free energy. Thus the perturbative corrections to the vertices can be interpreted as additional terms generated by sedimentation in an effective free energy.
V. PERTURBATION THEORY

We start with the linearized equation of motion (4.4) for the density field with only the sedimentation nonlinearity,

\[ \frac{\partial}{\partial t} \phi(k) = -\frac{\tilde{D}k^2}{S_0(k)} \phi(k) + i\frac{\lambda}{\rho_0} k_z \int \frac{dp}{(2\pi)^d} \phi(p) \phi(k-p) + \eta(k), \tag{5.1} \]

and calculate perturbative correction to the vertex functions. The noise statistics is as given in (4.3b) which, for momentum labels \( k \) and \(-k\), reads

\[ \langle \eta(k,t)\eta(-k,t') \rangle = 2\tilde{D}k^2\rho_0 V \delta(t-t') \tag{5.2} \]

where \( V \) is the volume of the system. To the lowest (i.e. first) order, there is a correction to the three-point vertex, whereas the structure factor gets modified at second order in Péclet number. The four-point vertex \( \Gamma_4 \) will also have a correction at second order, but we ignore this correction as this is simply a stabilizing term and small changes in it will not affect the physics of freezing significantly.

In this section, we set up a hierarchy of equations for the moments of \( \phi \), which we close by decoupling the four-point function into a product of two two-point functions (Hartree approximation). Multiplying the equation of motion (4.4) by \( \phi(k) \), symmetrizing in \( k, -k \) and setting time derivative of the two-point function to zero, we obtain for equal time a relation between the two-point and the three-point functions:

\[ 2\tilde{D}k^2 \left( \phi(-k)\phi(k) \right) = i\frac{\lambda}{\rho_0} k_z \int \frac{dp}{(2\pi)^d} \left[ \langle \phi(p)\phi(k-p)\phi(-k) \rangle - \langle k \rightarrow -k \rangle \right] + 2N\tilde{D}k^2, \tag{5.3} \]

where we have used the equal-time correlation between the noise and the density fluctuation,

\[ \langle \phi(-k,t)\eta(k,t) \rangle = N\tilde{D}k^2, \tag{5.4} \]

which is proved in detail in the appendix. Here \( N = \rho_0 V \) is the total number of particles in the system. Since the correlation function is symmetric under interchange of \( k \) and \(-k\), (5.3) can be rewritten as

\[ \frac{\tilde{D}k^2}{S_0(k)} \langle \phi(-k)\phi(k) \rangle = i\lambda k_z \int \frac{dp}{(2\pi)^d} \langle \phi(p)\phi(k-p)\phi(-k) \rangle + N\tilde{D}k^2, \tag{5.5} \]

Similarly, multiplying with two fields \( \phi \) at different wavevectors but equal times, we obtain a relation involving the third and fourth moments:

\[ \tilde{D} \langle \phi(k_1)\phi(k_2)\phi(k_3) \rangle = \left( \frac{k_1^2}{S_0(k_1)} + \frac{k_2^2}{S_0(k_2)} + \frac{k_3^2}{S_0(k_3)} \right) \sum_{i=1}^3 \frac{k_i^2}{S_0(k)} + \frac{i\lambda k_z}{\rho_0} \int \frac{dp}{(2\pi)^d} \langle \phi(p)\phi(k_1-p)\phi(k_2)\phi(k_3) \rangle. \tag{5.6} \]

To obtain this equation we have used the fact that the correlation of two fields \( \phi \) and one noise \( \eta \) vanishes at equal time (see appendix). If we proceed in this manner we will keep obtaining higher-order correlations in terms of the lower ones. We are, however, interested only in the lowest-order correlations, so we close the hierarchy by replacing the four-point function by a product of two two-point functions. Only pairings of \( p \) with \( k_2 \) or \( k_3 \) give nonzero contributions, because of the \( k_1 \) prefactor, so the dummy index \( p \) on the right hand side of (5.6) can only take the values \(-k_2 \) and \(-k_3 \). The two terms thus obtained are identical, and we arrive at the following relation between the three-point and two-point functions:

\[ \delta \Gamma_3(k_1,k_2,k_3) = -\frac{2i\lambda}{\tilde{D}\rho_0^2} \sum_{i=1}^3 \frac{k_i^2}{S_0(k)} \delta(k_1+k_2+k_3). \tag{5.7} \]

Using this in combination with (4.3) we obtain the correction to the three-point vertex from sedimentation:

\[ \delta \Gamma_3(k_1,k_2,k_3) = -\frac{2i\lambda}{\tilde{D}\rho_0^2} \sum_{i=1}^3 \frac{k_i^2}{S_0(k)} \delta(k_1+k_2+k_3). \tag{5.8} \]

Combining (5.3) with (5.7), we obtain the correction to the structure factor as an integral over wavevectors. In the limit of infinite volume, the sum over wavenumbers goes from 0 to an upper cutoff determined by the smallest length scale in the problem. Our coarse-grained model breaks down on scales of order the particle radius \( R \); the upper cutoff is therefore \( 2R/\pi \). Non-dimensionalizing the momentum argument in the integral with the \( 1/\rho_0 \) outside, i.e. by multiplying all momenta by the average interparticle spacing \( \ell \), we finally obtain

\[ S(k) = S_0(k) - 2\left( \frac{\lambda}{\tilde{D}} \right)^2 S_0(k) \frac{k_z}{k^2} \int \frac{2d\ell}{0} \frac{d^dk}{(2\pi)^d} S_0(k) S_0(|k - p|). \]
where all the wavevectors in the above equation, including the \( k \)'s multiplying the integral, are non-dimensionalized by multiplying with \( \ell \).

Note that the upper cutoff and hence the integral goes to \( \infty \) in the limit \( R \rightarrow 0 \). Let us calculate how the structure factor correction behaves in this limit. The integrand, for large arguments, \( \sim \frac{1}{p} \) (note that \( S(p) \rightarrow 1 \) for large \( p \)), so by power counting, the integral \( \sim R^{(1-d)} \).

This apparent divergence is however controlled by the powers of \( R \) in the Péclet number, which was \( R^{2d} \). We are thus left with a correction that \( \sim R^{(1+d)} \), which vanishes as \( R \rightarrow 0 \) for all \( d \). This is consistent with the fact that in this limit there are no hydrodynamic interactions.

The results of this section can also be obtained using diagrammatic perturbation theory \([31]\). The correlation function calculated to one loop without self consistency and the three point vertex at tree level give results identical to those obtained above.

**VI. THE STRUCTURE FACTOR**

![Figure 1](image1)

**FIG. 1.** The correction \( \frac{S(k) - S_0(k)}{S_0(k)} \) as a function of \( k \) for different angles with respect to the sedimentation direction, in two dimensions: \( \theta = 90^\circ \) (dotted line) showing no change; \( \theta = 60^\circ \) (dash-dot); \( \theta = 30^\circ \) (dashed line); and \( \theta = 0^\circ \) (continuous line). Clearly, the correlations are reduced near the peak, and the reduction is the largest along the sedimentation direction.

We computed the structure factor of the sedimenting suspension by numerically computing the integral in Eq. (5.9). We used a 40-point Gaussian quadrature routine \([33]\) and took the large \( k \) cutoff of the integral, \( \frac{2\pi a}{\nu} \), to be 20, corresponding to \( \frac{k}{P} \sim 3 \). The integral has reflection symmetry about \( \theta = \pi/2 \), so that the structure factor at an angle \( \alpha \) from the horizontal \( (\theta = \pi/2 - \alpha) \) is the same as that at an angle \( -\alpha \) from the horizontal \( (\theta = \pi/2 + \alpha) \). This follows from the invariance of the integral under \( k_z \rightarrow -k_z \).

The numerical results are presented in Figs. 1 and 2. The first shows the fractional change in the structure factor per unit Péclet number as a function of wavenumber and angle. The reduction happens to be a maximum at the peak itself, and is a monotonic function of the angle between the horizontal (where it is maximum) and the vertical (where it goes to zero). In Fig. 2 we show the numerically computed structure factor in two dimensions. The equilibrium structure factor has been taken from Monte Carlo simulations of a two-dimensional system of particles interacting via a screened Coulomb potential, just above freezing \([34]\). The peak of the equilibrium \( S(k) \) was at \( k = 7.3 \) (which is close to the average interparticle separation \( k_0 \sim 2\pi \) in the units we are using) and the peak value was \( S_0(k_0) = 4.947 \). We have chosen the Péclet number \( \frac{\Delta \nu a}{D} = 1 \) for these plots. This is a rather large number, and our calculation, which goes only up to leading order in perturbation theory is probably not accurate for such large driving. The large value has been chosen to make the deviations from the equilibrium structure easily visible.

![Figure 2](image2)

**FIG. 2.** \( S(k) \) for a sedimenting colloidal suspension in two dimensions as a function of \( k \), at \( Pe = 1 \) for four different angles with respect to the sedimentation direction: \( \theta = 90^\circ \) (dotted line) which is the same as the undistorted structure factor; \( \theta = 60^\circ \) (dash-dot); \( \theta = 30^\circ \) (dashed line); and \( \theta = 0^\circ \) (continuous line).

It is important to note that the split-peak in \( S(k) \) is a high Péclet number effect. Since the correction to \( S(k) \) is peaked at the same place as \( S(k) \) itself, there can be no shift in the position of the peak of the extremum. At low Péclet number, therefore, the structure factor has a global maximum at \( k \sim 7.3 \), which becomes a local minimum at a sufficiently large \( Pe \). At what value of \( Pe \)
this happens depends on the angle, the required driving force going to infinity as the horizontal direction is approached.

We have studied the freezing transition only in two dimensions (section VII), but we present structure factor data for three dimensions as well (Figs. 3 and 4). In three dimensions the integral in (5.9), and also the structure factor correction, have an azimuthal symmetry. In addition there is the reflection symmetry about θ = π/2 as in the two-dimensional case. For this case we used a 30-point Gaussian quadrature routine [33], and checked that the answer does not change significantly between 28-point and 30-point. The structure factor after the sedimentation correction is shown in Fig. 4. For the equilibrium structure factor we have used Monte Carlo results for a 1/π liquid [34], made continuous by suitable interpolation. The Péclet number is once again Pe = 1.

FIG. 3. The correction $\frac{S(k)-S_0(k)}{S_0(k)}$ as a function of $k$ for different angles with respect to the sedimentation direction, in three dimensions; θ = 90° (dotted line) showing no change; θ = 60° (dash-dot); θ = 30° (dashed line); and θ = 0° (continuous line). As in the two-dimensional case, the correlations are reduced near the peak, and the reduction is the largest along the sedimentation direction.

FIG. 4. The three dimensional $S(k)$ as a function of $k$ after sedimentation correction, at $Pe = 1$ for different angles with respect to the sedimentation direction: θ = 90° (dotted line) ⊂ the undistorted structure factor; θ = 60° (dash-dot); θ = 30° (dashed line); and θ = 0° (continuous line).

VII. FREEZING

The effect of the corrected three-point vertex as well as the structure factor correction have to be considered while describing the liquid-solid transition in the presence of sedimentation. The latter has a relatively simple effect: since $S(k)$ is reduced in all directions, there is a tendency towards melting. The correction (5.8) to the three-point vertex, being imaginary, has more interesting implications. Combining (5.8) with (1.10) we conclude that the nonequilibrium effects shift the cubic vertex,

$$ B \rightarrow B \rightarrow B - \frac{2i}{\rho_0} \left( \frac{\lambda^2}{D} \right) \sum_{i=1}^{3} \frac{k_{iz}^2}{S_0(k)} \cdot \sum_{i=1}^{3} \frac{k_i^2}{S_0(k)} \cdot (7.1) $$

where we have scaled all wavevectors by multiplying with the average interparticle separation $\ell$. With reference to (2.11), we can find the cubic term in the Landau expansion for the nonequilibrium system,

$$ -b \rightarrow -b - (2\pi n^{-1/2}) \frac{2i\lambda}{D} \sum_{i=1}^{3} \frac{k_{iz}^2}{S_0(k)} \cdot \sum_{i=1}^{3} \frac{k_i^2}{S_0(k)} \cdot (7.2) $$

Introducing a real dimensionless quantity which is first order in Péclet number,

$$ \beta_1 = 2 \left( \frac{\lambda a}{D} \right) \sum_{i=1}^{3} \frac{k_{iz}}{S_0(k)} \cdot \sum_{i=1}^{3} \frac{k_i^2}{S_0(k)} \cdot (7.3) $$

we rewrite (7.2) as

$$ b \rightarrow b + i(2\pi n^{-1/2})\beta_1 \cdot (7.4) $$

The correction to the Landau parameter $b$ is entirely imaginary, and makes the effective $b$ complex. The free energy is a real, positive quantity, so a complex coefficient $B$ in (2.8) would imply that the complex Fourier amplitudes $\phi(k)$ pick up phases. In equilibrium, when $B$ is real (and positive by construction), the phases of $\phi(-k), \phi(p)$ and $\phi(k-p)$ add up to $2\pi$ so as to make the cubic term as negative as possible. In other words, if we write the amplitude as
\[ \phi(k) = |\phi(k)|e^{i\theta(k)} \]  
(7.5)

then

\[ \theta(k_1, k_2, k_3) = \theta(k_1) + \theta(k_2) + \theta(k_3) = 2\pi \]  
(7.6)

for sets of vectors that form triangles, i.e. satisfy \( k_1 + k_2 + k_3 = 0 \). Note that the cubic term is always real, whatever the phases of the wavevectors, since for any set \( \{k_1, k_2, k_3\} \) there is another with all wavevectors reversed which has exactly the opposite total phase \( \theta \). However the contribution to the free energy from two such terms is \( 2\cos \theta \), which should be = 2 to minimize the free energy.

![Diagram of possible orientations of inner shell reciprocal lattice vectors in a sedimenting colloidal crystal.](image)

This ‘phase shift’ in the order parameters may be visualized in real space as a shift of one set of lattice planes relative to its equilibrium position. Note that scattering experiments measure only the squared modulus \( |\phi(k)|^2 \), and will not see a phase shift.

Freezing is determined by the modulus of the modified coefficient of the cubic term, which is

\[ b \longrightarrow \sqrt{b^2 + 4p^2n^{-1}b_1^2}. \]  
(7.8)

The prefactor multiplying \( b_1^2 \) is a number that depends on the type of lattice. For a triangular lattice in two dimensions, \( n = 6 \) (six reciprocal lattice vectors in the first shell) and \( p = 1 \) (each reciprocal lattice vector belongs to one of the two triangles). Thus

\[ b \longrightarrow \sqrt{b^2 + \frac{2}{3}b_1^2} \]  
(7.9)

Clearly, the magnitude of \( b \) can only increase due to sedimentation. Thus, as far as this term is concerned, sedimentation seems to favour ordering. This effect has to compete with the reduction of the structure factor and only a quantitative analysis can decide their combined effect.

In the rest of this section we present results for the simplest case, that of a planar triangular lattice. We have described the equilibrium freezing with a one-order parameter Landau theory, choosing the Landau coefficients to match the structure factor peak height at coexistence for our data, i.e. \( S_0(k_0) = 4.947 \). Our Landau parameters were \( b = 6, c = 59.364 \) and, at coexistence, \( a = a_0 = 0.20214271 \), giving a polynomial

\[ F = 0.10107ar^2 - r^3 + 2.5r^4 \]  
(7.10)

where \( r \) is the reduced order parameter, defined in (7.3).

Note that the correction \( b_1 \) [eqn. (7.3)] vanishes if the reciprocal lattice vectors remain on the shell \( |G| = G_0 \), and the structure factor remains unchanged. This follows from (7.2) and the fact that the sum of \( k_i \) has to be zero. Thus, to benefit from the free energy reduction that an increase in \( b \) can cause, the lattice may like to distort, thus sending one of the vectors out of the shell while keeping the sum equal to zero by rotating the other two towards or away from each other. We have considered two such distortions in our analysis, as shown in Fig. 3, which seem to be most likely from the symmetry of the problem. It is also imaginable that the lattice distorts to an asymmetric state with two degenerate minima of the free energy; we have not made a complete scan of all possible distortions to rule out such possibilities, but looked at only the above two on grounds of plausibility.

Such distortions apart, the structure factor is itself affected by the driving, so \( b_1 \) is nonzero even without pushing the reciprocal lattice vectors out of the shell.
The undistorted crystal is therefore also a strong candidate. The crucial issue is the relative importance of the two effects: $\beta_1$ and $S(k)$. Though the correction to the three-point vertex is first order in $Pe$, the correction to $b$ for small $Pe$ goes as $Pe^2$ as can be seen simply by binomially expanding the square-root in (7.9). For this reason, combined with the fact that the numerical value of $\beta_1$ is rather small at modest driving rates, the $\Gamma_3$ effect is negligible compared to the structure factor reduction. For the Landau potential chosen, we have found numerically that the structure factor reduction makes the free energy function go unstable well before $b$ can change significantly.

\[ |G_1| = G_0(1 + \Delta), \quad (7.11) \]

and the others rotating towards the $x$ axis so as to keep the sum of the vectors zero. If the Péclet number is not too large, $S(k)$ continues to have a peak at $k_0$ even in the presence of sedimentation (section V), so that there is a free energy cost to pay for the expanding $G_1$ which is moving off the peak. The other two, however, have moved closer to the horizontal, i.e. in a direction such that the driving affects them less, and the peak height at these wavevectors is higher than it would have been had they not rotated at all. There is a competition between these two effects, and its not a priori clear which will win, so we computed the free energy of distorted crystals at coexistence to find the most favourable value of the distortion or angle. Note that in any case the liquid is the favoured phase, but we can still search among all the crystalline phases and find which of them has the lowest free energy. This, as we demonstrate shortly, gives us some hint as to what to expect at other temperatures.

We found that for low Péclet numbers the undistorted crystal is favoured, but at around $Pe = 0.72$ a distorted crystal becomes favourable (Fig. 6). There seems to be a first order jump in what we might call the distortion order parameters $\Delta$. This is not surprising, as we may regard the nonequilibrium free energy coming out of our analysis as a function of $\Delta$, whose power series expansion will have odd order terms since $\Delta \rightarrow -\Delta$ is not a symmetry of the problem.

The distorted crystal appears at rather high Péclet number (Fig. 6), certainly well beyond the range of validity of our perturbation theory. The reason for the sudden distortion is probably related to the original peak $k_0$ becoming a minimum and two peaks developing on either side (Fig. 3). The several plateaus that appear at even higher $Pe$ are even more intriguing. The intriguing results regarding split peaks (Figs. 2, 4) and distortions are however somewhat speculative in the absence of a reliable theory for large driving.

We have also compared the configurations shown in Figs 5(a) and 5(b) and found, as expected, that the latter has a lower free energy at all values of the driving. Thus one immediate consequence of our theory is that the crystal, when it forms, will form with the orientation shown in Fig. 5(b), i.e. with lattice planes parallel to the sedimentation direction. This agrees with intuition, since there are shocks [24,36,37] travelling along the sedimentation direction.
the equilibrium freezing temperature $T_c$, and find how the melting Péclet number depends on $T - T_c$. Strictly speaking this requires structure factor data in the supercooled liquid, which one should use in (5.9) to compute the corrected $S(k)$. Such data, however, is not readily available, and in particular for the case of the planar triangular lattice that we are considering, it is very hard to sustain a supercooled liquid for too long in a simulation with monodisperse systems.

We therefore attempt the following approximate theory. Near $T_c$, the structure factor is that at coexistence plus a perturbative correction. The critical Péclet number $Pe_c$ at which the crystal melts is an object which is itself perturbative in $T - T_c$. In calculating $Pe_c$, if we neglect the perturbative corrections to $S_0(k)$, we will be making an error only at a higer order. We can therefore legitimately do a Landau theory at a $T$ below but close to $T_c$ using the structure factor at coexistence. The $S(k)$ corrections will all be calculated using this $S_0(k; T_c)$, the temperature entering only in the Landau parameter $a$. The result is shown in Fig. 7.

Finally, one would like to look at the system below the equilibrium freezing temperature $T_c$, and find how the melting Péclet number depends on $T - T_c$. Strictly speaking this requires structure factor data in the supercooled liquid, which one should use in (5.9) to compute the corrected $S(k)$. Such data, however, is not readily available, and in particular for the case of the planar triangular lattice that we are considering, it is very hard to sustain a supercooled liquid for too long in a simulation with monodisperse systems.

We therefore attempt the following approximate theory. Near $T_c$, the structure factor is that at coexistence plus a perturbative correction. The critical Péclet number $Pe_c$ at which the crystal melts is an object which is itself perturbative in $T - T_c$. In calculating $Pe_c$, if we neglect the perturbative corrections to $S_0(k)$, we will be making an error only at a higer order. We can therefore legitimately do a Landau theory at a $T$ below but close to $T_c$ using the structure factor at coexistence. The $S(k)$ corrections will all be calculated using this $S_0(k; T_c)$, the temperature entering only in the Landau parameter $a$. The result is shown in Fig. 7.

VIII. CONCLUDING REMARKS

We have shown that a uniform drift, as in steady-state sedimentation, reduces translational correlations in a suspension of interacting Brownian particles, as a result of local hydrodynamic interactions that reduce the mobility of a dense region. This reduction is largest in the direction of sedimentation. At sufficiently high Péclet number, the first peak of the structure factor splits due to the fact that the reduction is strongest where the initial correlation was largest.

For the freezing transition we find that the phase boundary in a charge stabilized colloidal suspension shifts towards the crystal side. The shape of the phase boundary is quadratic in $Pe$ as shown in Fig. 1.

Let us now make some estimates for Péclet numbers in realistic experimental situations to see whether the values of $Pe$ in Fig. 7 are accessible. The Péclet number for a dense suspension, at the scale of the particle radius, is given by Eq. (8.1) which can be rewritten as

$$
Pe = \left( \frac{D_0}{D} \right) \left( \frac{v}{R} \right) \left[ \frac{\partial^2 \left( \frac{v}{R} \right)}{\partial \left( \ln \left( \frac{v}{R} \right) \right)} \right]_{\rho_0} \left( \frac{m g R}{k_B T} \right),
$$

where $D$ is the diffusion coefficient, $v$ is the velocity of the particles, $\rho_0$ is the volume fraction used in our calculations, $D_0$ is the diffusion coefficient at the temperature $T_0$, and $R$ is the particle radius.

provided the hindered settling speed (or the mobility) is roughly linear in the volume fraction in the range of interest. Taking the specific case of polystyrene spheres of diameter $15.5 \mu m$ in water [13], we note that this is true for volume fraction between 0.1 and 0.3 [38]. The volume fraction used in our calculations ($\frac{v}{R} \sim 0.16$) falls within this range. From the data presented in [38], the term within the square brackets in (8.1) is found to be of order 1.5.

The first term $\left( \frac{D_0}{D} \right)$ in (8.1) is the ratio of the bare to the collective diffusion constant, which has a value of about 10 near the freezing transition of a colloidal suspension [19]. The ratio of the interparticle spacing to the radius of the polyballs, $\left( \frac{v}{R} \right)$, is $\sim 3$. The product of the first three factors in (8.1) is thus $10 \times 3 \times 1.5 = 45$. Finally, we have to estimate the bare Péclet number $\frac{m g R}{k_B T}$. This turns out to be $\sim 0.5$ for polystyrene [14]. The Péclet number for the interacting suspension is therefore 22.5. This is rather large, which means that our lowest-order theory is probably not reliable here. It does however suggest that the effect of steady-state sedimentation on freezing should be large for this system.

In general, in choosing a system on which to test our results, two competing needs must be kept in mind. On the one hand, the ordering length scale should be large compared to the particle size, so that the simple concentration-dependence of the mobility (see the remarks towards the end of section 11 in our model is valid. On the other hand, the particle size itself should be large enough to give an appreciable Péclet number.

A comparison with shear induced melting is tempting, since a perturbation theory similar in spirit to the present approach [2] is known to give a shift in the phase boundary that is quadratic in the shear rate. There are essential differences however: firstly the only significant effect of shear is to suppress correlations, whereas for a sedimenting suspension, there are nontrivial corrections to the three point vertex. The effect of these latter corrections happens to be negligible on the freezing transition as we have shown, making the phase boundary shift in a manner similar to the shear case. Secondly, the sheared
colloidal crystal at low shear-rates is a slightly distorted crystal essentially stuck in a statically sheared configuration. At low shear therefore (where perturbation theory is valid), the crystal is essentially in an equilibrium state, and its properties can be derived from an equilibrium picture \[43–45\]. For uniform driving, however, there are nonzero currents even at low Péclet numbers, making it a more genuinely nonequilibrium problem.

An interesting feature of our theory is that the sign of \(\frac{\partial \phi}{\partial \rho}\) does not figure in the results. Thus even if we have a suspension whose settling speed increases due to many body effects, our theory will still predict a reduction in the correlations and a consequent shift in the phase boundary towards the crystal side.

Finally, a few caveats. In \[41,42\] we have shown that a sedimenting colloidal crystalline lattice is likely to be unstable at long wavelength. The theory proposed in this paper is probably nonetheless applicable to the formation of the crystalline phase at least at low Péclet numbers, since the physics of freezing is centred primarily around the ordering wavenumber. The coupling of concentration and shear (tilt) considered in \[41,42\] may also be important in the liquid state. The detailed consequences will be different because shear stresses have a finite lifetime in the liquid, in contrast to that in a solid where it lasts for ever if the strain is present. The effect of the sedimentation instability is thus very different in a liquid. This is an additional aspect that we have totally ignored in the above treatment, and one that a more sophisticated approach must address. However, further development of the theory should be motivated by experiments, which we eagerly await.

**APPENDIX A: FIELD-NOISE CORRELATIONS AT EQUAL TIME**

Consider a set of Langevin equations of the form

\[
\dot{\phi}_\alpha = f(\phi) + \eta_\alpha, \quad \langle \eta_\alpha(t) \eta_\beta(t') \rangle = 2k_B T \delta_{\alpha\beta} \delta(t-t').
\]

where \(\phi\) stands for \(\{\phi_1, \phi_2, \ldots, \phi_n\}\), and \(f\) can be an arbitrary function, in general nonlinear. We shall calculate the field-noise correlations using Novikov’s theorem \[43\ \[44\], which states that for any functional of the noise \(A[\eta]\),

\[
\langle A[\eta](t) \rangle = 2T \delta_{\alpha\beta} \left( \frac{\delta A}{\delta \eta_\lambda(t)} \right).
\]

We first calculate the average of the product of one field with one noise, which by \[42\] is

\[
\langle \phi_\alpha(t) \eta_\lambda(t') \rangle = \left\langle \frac{\delta \phi_\alpha(t)}{\delta \eta_\lambda(t')} \right\rangle.
\]

The equation \[A1\] can be formally solved to give

\[
\phi_\alpha(t) = \int_{t_0}^{t} dt' f(\phi(t')) + \int_{t_0}^{t} dt' \eta_\lambda(t')
\]

where the \(\eta_\lambda\) dependence in the first term is present through \(\phi(t)\), which depends on the noise amplitudes at all past times but not those of the future. The derivative

\[
\frac{\delta \phi_\alpha(t)}{\delta \eta_\lambda(t')} = \int_{t_0}^{t} dt'' \frac{\partial f}{\partial \phi_\beta}(t'') \frac{\delta \phi_\beta(t'')}{\delta \eta_\lambda(t')} + 1.
\]

For \(t = t'\), all the arguments \(t''\) in the integral are times before \(t'\), so the functional derivative inside the integral, and hence the integral itself vanishes. Thus the forward derivative is simply equal to 1. The backward derivative is zero, therefore

\[
\frac{\delta \phi_\alpha(t)}{\delta \eta_\lambda(t')} = \theta(t-t').
\]

At equal time this is discontinuous, but we recall that the delta function noises are nothing but limits of Gaussians, so the theta function is not really a discontinuous function at the origin, but rather rises smoothly from 0 to 1 taking the midpoint value \(1/2\) at the origin. Thus

\[
\frac{\delta \phi_\alpha(t)}{\delta \eta_\lambda(t')} = \frac{1}{2}.
\]

which, combined with \[A2\] gives

\[
\langle \phi_\alpha(t) \eta_\lambda(t') \rangle = k_B T \Gamma_{\alpha\lambda}.
\]

This can be shown with more rigour by starting from a Gaussian distribution, calculating the equal time correlation and then taking the width of the Gaussian to zero \[45\]. In section V we have used an analogous result for reciprocal space variables.

Let us now consider the product of two fields and a noise. Again, using \[A2\], we have

\[
\langle \phi_\alpha(t) \phi_\beta(t) \eta_\lambda(t') \rangle = \langle \phi_\beta(t) \frac{\delta \phi_\alpha(t)}{\delta \eta_\lambda(t')} + \phi_\alpha(t) \frac{\delta \phi_\beta(t)}{\delta \eta_\lambda(t')} \rangle.
\]

where we have used the chain rule for functional derivatives. Now each of the partial derivatives = \(1/2\), therefore

\[
\langle \phi_\alpha(t) \phi_\beta(t) \eta_\lambda(t') \rangle = \frac{1}{2} \langle \phi_\beta(t) + \phi_\alpha(t) \rangle.
\]

In section V we do a perturbation theory about the liquid phase, calculating liquid state correlations, so the first
moments of $\phi$ are all zero, thus making all averages of the form $\langle \phi \phi \rangle$ vanish.

For completeness we explicitly check the vanishing of the first moment in the presence of driving. Averaging over noise, and setting the time derivative of the field average to zero (steady state), we have

$$\frac{D_S^2}{\tilde{S}_0(k)} \langle \phi(k) \rangle = i \frac{\Lambda}{\rho_0} k \int \frac{dp}{(2\pi)^d} \langle \phi(p) \phi(k-p) \rangle. \quad (A12)$$

The second moment on the right is nonzero only if $-p = k-p$, i.e. $k = 0$, so that the first moment $\langle \phi(k) \rangle$ vanishes for all $k \neq 0$. But since $\phi$ is a deviation variable, its $k = 0$ component is zero by construction.

**APPENDIX: ACKNOWLEDGMENTS**

We would like to thank Mustansir Barma, Pinaki Majumdar, Rajaram Nityananda and Rahul Pandit for discussions and Sushan Konar for the use of interpolation software. The second moment is nonzero only if $-p = k-p$, i.e. $k = 0$, so that the first moment $\langle \phi(k) \rangle$ vanishes for all $k \neq 0$. But since $\phi$ is a deviation variable, its $k = 0$ component is zero by construction.

Most of the work was done when R.L. was at the Physics Department, Indian Institute of Science, Bangalore. The facilities of the institute are acknowledged, including the the computational resources of the Supercomputer Education and Research Centre. R.L. was supported by CSIR (India) during the same period.

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[40] Bare Peclet number at the scale of particle radius:

\[ \frac{mgR}{k_BT} = \frac{\Delta \rho \rho_R \pi R^3 gR}{k_BT} = \frac{\Delta \rho (1 \text{ to } 2) 4 \times 10^{-16} \pi R^3 10^3}{k_BT} \]

In cgs units \( k_BT \sim 4 \times 10^{-14} \). For polystyrene, \( \frac{\Delta \rho}{\rho_0} \sim 0.05 \) and \( \rho \sim 1 \), giving \( Pe = 5 \).

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