Dynamical Criterion for Freezing of Colloidal Liquids

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A simple dynamical criterion for crystallization of a colloidal fluid which undergoes Brownian motion is proposed, similar in spirit to the classic Lindemann melting rule. It states that the ratio of the long-time and short-time self-diffusion coefficients is a universal number very close to 0.1 along the freezing line. This phenomenological crystallization rule is confirmed both by Brownian dynamics simulations of a Yukawa liquid and by forced Rayleigh scattering experiments on charge-stabilized colloidal suspensions.

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The crystallization of a liquid into a regular crystal is a classic example of a first-order phase transition with spontaneous breaking of the continuous translational symmetry of the homogeneous liquid. Since the last century, phenomenological and molecular aspects of this fascinating and important phase transformation have been studied and, during the past decade, new experimental and theoretical techniques have greatly advanced our understanding of the freezing transition [1]. Well-characterized colloidal suspensions of nearly monodisperse spherical macroparticles are excellent representatives of simple liquids on a mesoscopic length scale which also exhibit a crystallization transition [2]. They permit an investigation by optical methods which give insight into details of freezing on an interparticle length scale [3]. Furthermore, density functional theories were developed which describe freezing as a condensation of liquid density modes providing a microscopic theory for freezing of hard-sphere-like systems [4].

Despite these recent advances there is still no complete "*ab initio*" theory of freezing in three dimensions which works for arbitrary interparticle potentials of a one-component liquid. However, there are two important empirical rules of melting and freezing. The first phenomenological criterion was put forward as early as 1910 by Lindemann [5]. It states that the ratio L of the root-mean-square displacement and the average interparticle distance at the melting line of the solid has a value of roughly 0.15. The second criterion was formulated in 1969 by Hansen and Verlet [6]. For a Lennard-Jones system, they found that the first maximum of the liquid structure factor $S(k)$ has a constant amplitude of $\simeq 2.85$ along the freezing line. Both simple criteria were tested and found to hold for different interparticle interactions and are, in this sense, universal; especially the static structure factor criterion was strongly confirmed by scattering experiments on real liquids. Thus these criteria are very helpful in locating approximately the freezing and melting lines for a given system without doing any free-energy calculation. In particular, both rules (and also some generalizations of them [7]) are based on static properties, i.e., they are independent of the dynamics of the system.

In this Letter, we report a third phenomenological criterion for freezing in colloidal suspensions which is of *dynamical* origin. The motion of a colloidal particle embedded in a bath of solvent is characterized by two different self-diffusion constants. On a time scale that is short compared to a time τ_m which is a macroparticle needs to move over its own radius R, but large compared to that of microscopic solvent kicks, the macroparticle motion is diffusive with a short-time self-diffusion coefficient D_S. In a dilute suspension of spherical colloidal particles, D_S is given by the Stokes-Einstein value D_0, i.e., $D_S = D_0 \equiv k_B T / 6\pi\eta R$, where T is the temperature and η the viscosity of the solvent. This relation is actually only valid for highly charged, salt-free colloidal liquids where freezing occurs even at very low packing fractions of the macroparticles; in dense sterically stabilized or strongly screened charged colloids, however, D_S is also strongly affected by solvent-mediated hydrodynamic interactions. There is a second self-diffusion coefficient, D_L, for times long compared to τ_m, which can be defined as

$$D_L = \lim_{t \to \infty} \frac{1}{6t} [\mathbf{r}(t) - \mathbf{r}(0)]^2 , \qquad (1)$$

where $\mathbf{r}(t)$ is a time-dependent trajectory of a colloidal particle. In general, due to direct interparticle interactions, D_L is smaller than D_S. In the following we give evidence that the ratio D_L/D_S provides a suitable quantity for a dynamical freezing rule: *D_L/D_S equals a fixed universal value of* $\simeq 0.98$ *along the freezing line of a colloidal suspension.* This constitutes a dynamical analog to the usual (static) Lindemann criterion.

Evidence for this dynamical rule is given by extensive Brownian dynamics computer simulations along the freezing line of a liquid interacting via a pairwise Yukawa potential which is a reasonable simple model for a charged colloidal suspension [3]. Furthermore we present systematic measurements of the self-diffusion coefficient across the fluid-solid phase transition of a dilute charged colloidal fluid, using the method of forced Rayleigh scattering, which also strongly confirm the dynamical freezing rule for real colloidal suspensions.

As regards the simulated part, we take $N=500$ particles in a periodically repeated cubic box (whose volume V is governed by the particle concentration $c_P=N/V$) and integrate the stochastic Langevin equations of motion for the particle positions $\{\mathbf{r}_i(t),\ i=1,\dots,N\}$ with a finite time step Δt. Neglecting any hydrodynamic interactions, we use the finite difference algorithm [8]

$$\mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\frac{k_BT}{D_0}\mathbf{F}_i(t)\Delta t+(\Delta\mathbf{r})_R+\cdots, \qquad (2)$$

where $(\Delta\mathbf{r})_R$ is a random displacement due to solvent collisions which is sampled from a Gaussian distribution with zero mean and variance $6D_0\Delta t$. Furthermore, $\mathbf{F}_i(t)$ is the total interparticle force on particle i derived from the Yukawa potential $V(r)=V_0\exp[-\kappa(r-2R)]/r$. As a function of the inverse screening length κ, the Yukawa potential exhibits quite different shapes: For $\kappa=0$, the soft interaction of a one-component plasma (OCP) is recovered whereas for $\kappa\rightarrow\infty$ the interaction equals a hard-sphere (HS) potential. Simulations were done for six different values of κ along the freezing line including the two extreme cases of the OCP and HS. The OCP freezes isochorically if the dimensionless coupling parameter $\Gamma\equiv(4\pi c_P/3)^{1/3}V_0/k_BT$ equals 178 [9], whereas the hard-sphere liquid is characterized solely by its packing fraction $\phi=4\pi c_PR^3/3$ and shows a strongly first-order crystallization transition at $\phi=0.494$ [10]. The freezing line of a Yukawa liquid was calculated recently for four different values of κ by Meijer and Frenkel [11]. Using these data for the freezing line, the long-time self-diffusion coefficient D_L was calculated with Einstein's formula (1) for finite times and extrapolated to infinite time. It was carefully checked that the time step Δt of the Brownian dynamics simulations was small enough such that the results were independent on a further reduction of Δt which is particularly important for hard spheres [12]. Results for the ratio D_L/D_0 are given in Table I. For comparison, we have also shown the corresponding data for the Lindemann parameter L and the first maximum of the liquid structure factor, $S(k_m)$. As the shape of the potential varies from soft to hard repulsions, the ratio D_L/D_0 remains practically constant and has a value of 0.098. This demonstrates that it is a suitable universal quantity for a general freezing rule. The Lindemann parameter L, on the other hand, has much larger variations (of about 30%) whereas the Hansen-Verlet criterion is fulfilled extremely well.

Experimental values of D_L were determined by forced Rayleigh scattering (FRS) [13] which measures the self-diffusional decay of an absorption grid produced by a UV interference pattern in a suspension containing small amounts of UV sensitized, but otherwise equal, particles [14]. We used commercial particles (LOT 2011M9R, Seradyn, In. USA) of titrated charge number $Z_{\mathrm{titr}}=920\pm20$ and of hydrodynamic radius $R=50$ nm [15]. The dyed particles were carefully examined to have equal radius and surface charge number to the undyed ones. The hydrodynamic radius R was obtained from the Stokes-Einstein relation using dynamical light scattering data for the self-diffusion constant D_0^0 in a highly diluted ($\phi=0.0001$) and practically noninteracting sample with an excess salt concentration $c_s=10^{-3}$ mol/l. In this noninteracting sample, all self-diffusion coefficients D_0^0, D_S, and D_L are equal. The actual measurements were done for interacting, but still diluted samples ($\phi\leq0.004$), where we may safely assume that hydrodynamic interactions enter into the calculation of D_S via $D_S=D_0(1-1.73\phi)$ [3]. Therefore, for all our measurements, D_S is very well approximated by D_0^0. The suspensions were prepared by the recently reported method of continuous deionization [16] which allows fast and reproducible access to ordered colloidal systems at low volume fraction and practically no excess salt. This has the advantage that self-diffusion measurements are even feasible in the formerly inaccessible range of suspension parameters where crystallization occurs for such low packing fractions while hydrodynamic interactions are absent.

TABLE I. Comparison of the Lindemann, Hansen-Verlet, and the dynamical rule for freezing of a Yukawa system. The Lindemann parameter L of the coexisting solid, the value of the first maximum in the liquid structure factor, $S(k_m)$, and the ratio of the long- and short-time diffusion coefficients, D_L/D_0, are shown for six different points on the freezing line of a Yukawa liquid including OCP and HS. The freezing line data for the Yukawa system are characterized by the average particle distance $a=c_P^{-1/3}$ measured in units of $1/\kappa$ and a scaled temperature $T^*=k_BTa\exp(a-2\kappa R)/\kappa V_0$ [11]. With increasing a, the repulsion becomes steeper. The number in parentheses gives the error of the last digit. Data for the Lindemann parameter L are from Refs. [24] (OCP), [11] (Yukawa), and [25] (HS).

System	Freezing line data	L	$S(k_m)$	D_L/D_0
OCP	$\Gamma=178$	0.186(6)	2.82(3)	0.097(3)
Yukawa	$a=2.95, T^*=0.079$	0.185(8)	2.82(3)	0.099(3)
Yukawa	$a=3.87, T^*=0.116$	0.188(8)	2.84(3)	0.097(3)
Yukawa	$a=5.39, T^*=0.200$	0.164(5)	2.82(3)	0.100(3)
Yukawa	$a=6.87, T^*=0.286$	0.150(4)	2.83(3)	0.100(3)
HS	$\phi=0.494$	0.133(2)	2.85(3)	0.099(3)

Another advantage of our experimental technique compared to usual dynamical light scattering is that FRS is insensitive to multiple scattering.

The process of preparation leaves the suspension in a metastable fluid state, which crystallizes if the concentration of excess salt NaCl, c_s, is low and the particle concentration c_P is high enough. To scan the phase diagram several experimental runs both at constant volume fraction ϕ and at constant c_s were performed. All the FRS data were measured in the fluid state, which was either an equilibrium fluid or a metastable shear molten fluid. Care was taken in the latter case that measurements were completed before significant crystallization had occurred such that the data were not affected by the much slower diffusion in the solid phase [13]. Figure 1 shows a ϕ-κR diagram of our results; $\kappa = [e^2(c_P Z_{\text{titr}} + 2c_s)/\epsilon_0\epsilon_r k_B T]^{1/2}$ being the inverse Debye-Hückel screening length where $\epsilon_r = 78$ is the dielectric constant of water at room temperature $T = 295$ K and e the elementary charge. The results for several experimental runs are shown in comparison with the phase boundaries of our system (solid lines) which were determined independently by static light scattering and torsional resonance detection [17]. We only present the coordinates of samples with $D_L/D_S = 0.098 \pm 0.010$ and further discriminate between those showing only deviations on the order of the experimental error ($D_L/D_S = 0.098 \pm 0.005$) (solid circles) and those showing higher (0.108 ± 0.005) (circles with dots) or lower values (0.088 ± 0.005) (circles with crosses) of D_L/D_S. It can be noticed that irrespective of the stability of the fluid phase D_L/D_S decreases smoothly across the phase boundary. As is clearly demonstrated, within the experimental errors of 5% in D_L, 5% in c_s at micromolar concentrations, and less than 2% in the particle concentration, the coexistence region coincides with the region of $D_L/D_S = 0.098 \pm 0.005$.

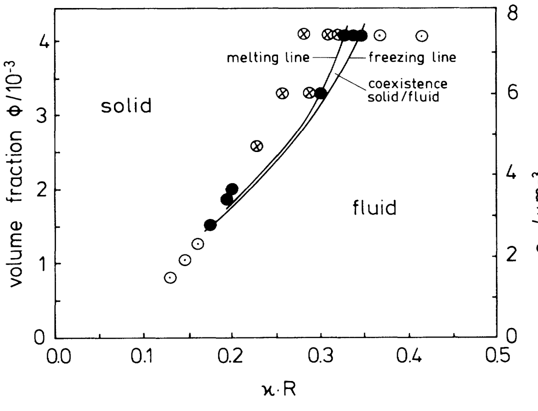

FIG. 1. Phase diagram of a suspension of charged particles in terms of their volume fraction ϕ (respectively their concentration c_P) and the dimensionless Debye-Hückel screening parameter κR. The solid curves represent the freezing and melting lines. Symbols show the coordinates of samples with D_L/D_S fulfilling the following criteria: ●: $0.093 \le D_L/D_S < 0.103$; ⊗: $0.083 \le D_L/D_S < 0.093$; ⊙: $0.103 \le D_L/D_S < 0.113$. The width of these intervals was set by the experimental error in D_L/D_S of 5%.

In conclusion, computer simulations on the Yukawa model and experiments on real colloidal suspensions both indicate that the ratio of short- and long-time self-diffusion constants has a universal value of ≈ 0.098 on the freezing line. This universality of a dynamical quantity for Brownian systems is surprising, since dynamical quantities usually depend much more sensitively on details of the interparticle interaction than their static counterparts in terms of which the Lindemann and the Hansen-Verlet melting rules are defined. Although the ratio D_L/D_S is sensitive even to small variations in the liquid density near the freezing lines, its value along the freezing line is remarkably universal. It also does not depend on the lattice structure of the coexisting crystal which is bcc for soft and fcc for hard repulsions.

It is also instructive to compare the self-diffusive behavior of colloidal liquids with that of *atomic* liquids along the freezing line. The marked difference to Brownian dynamics is that now the particle mass M enters in the equations of motion and sets the time scale. Since the short-time dynamics is ballistic, the short-time diffusion coefficient is zero and a simple scale for D_L is missing. For molecular dynamics (MD), the most natural scale for D_L is $D^* \equiv c_P^{-1/3}(k_B T/M)^{1/2}$; another possible scale uses the state-dependent Einstein frequency ω_E of a corresponding fcc crystal [18] $D^{**} \equiv c_P^{-2/3}\omega_E/2\pi$. We have also performed MD simulations for the same states as given in Table I. As a result, the ratio D_L/D^* is rather constant [0.027(2)] for the OCP [19] and moderately steep Yukawa potentials but decreases from strong repulsive potentials to 0.013(4) [20] for HS. On the other hand, D_L/D^{**} is 0.0084(3) for the OCP and increases for increasing steepness of the repulsion; it is 0.0106(4) for the fourth Yukawa system ($a = 6.87$) and diverges for the completely anharmonic HS system. Consequently, none of the two scales can be used to define a dynamical freezing criterion for MD which includes both extreme soft and hard repulsions. It is only in the case of Brownian dynamics where the short-time diffusion sets a suitable scale for the long-time diffusion that a general dynamical freezing rule holds. So, contrary to the static criteria, the dynamical criterion cannot be extended to atomic systems governed by reversible dynamics.

We end with three remarks on the stability of the dynamical freezing criterion with respect to several features important for colloidal suspensions: First, in dense colloidal suspensions, the dynamics (including both D_S and D_L) are strongly affected by hydrodynamic interactions. These interactions could be safely ignored for our experimental system and were also neglected in the Brownian dynamics (BD) simulations. Medina-Noyola [21] suggested the scaling $D_L = D_S D_L^0/D_0$ where D_L^0 is the long-time self-diffusion coefficient for a system without hydrodynamic interactions. This was checked and confirmed in recent experiments of dense colloidal liquids [22]. Thus the ratio D_L/D_S is universal also with regard to hydrodynamic interactions. In one sample of Ref. [22], D_L/D_0 was found to be significantly lower than 0.1 at freezing, but a rescaling with D_S/D_0 again leads to a value of D_L/D_S that is compatible with our prediction of ≈ 0.1 (within the experimental error of Ref. [22]). Second, real colloids have a small intrinsic polydispersity in their size and surface charge. In order to check the dependence of D_L/D_0 on polydispersity we have performed BD simulations with a polydisperse Yukawa model. We assumed a constant surface charge density, coupling size and surface charge polydispersities, and also included different scattering amplitudes of big and small particles. For an effective charge polydispersity $\leq 10\%$ we have not seen a systematic deviation from 0.1 for D_L/D_0 along the freezing line. This is consistent with our experimental findings, as our particles show an intrinsic size polydispersity of about 10% [15]. Thus the dynamical Lindemann criterion is also robust against small intrinsic polydispersity. Finally, our experimental results also indicate that further details in colloidal suspensions, like the van der Waals attraction, effective many-body forces between the macroions induced by nonlinear counterion screening [23], and corrections due to nonspherical bodies, which we ignored in the simple picture used in the BD simulations, also do not have any strong influence on D_L/D_S at freezing.

Direct consequences of the dynamical Lindemann criterion are twofold: First, it gives a theoretical insight into the self-diffusional behavior at melting, proving that the behavior is universal. It also couples dynamical quantities to the free energies which determine the coexistence lines. This demonstrates a dynamical self-similarity of the freezing process. Second, for a real colloidal suspension, it allows a determination of the liquid-solid coexistence line with a single self-diffusion measurement, and has the advantage of a robust rule of thumb in estimating the coexistence lines in a simple yet accurate manner. This is of prime importance for systems allowing no direct optical access to their phase diagram, e.g., micelles or other very small particles.

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