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Dynamical criterion for two-dimensional freezing

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The dynamical criterion for freezing of three-dimensional colloidal fluids recently proposed by Löwen, Palberg, and Simon [Phys. Rev. Lett. **70**, 1557 (1993)] states that the ratio of the long-time to short-time self-diffusion coefficients has the universal value 0.1 along the fluid freezing line. Based on Brownian dynamics computer simulations of two-dimensional fluids interacting via different inverse-power pair potentials, it is shown that this criterion also holds for two-dimensional freezing. It is thus the only freezing criterion that holds simultaneously in three and two dimensions.

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Since the famous works of Kosterlitz and Thouless [1], Halperin and Nelson [2], and Young [3] (KTHNY), it is known that freezing in two spatial dimensions (2D) may be fundamentally different from the usual bulk freezing in three dimensions. In particular, 2D freezing may be a two-stage process of continuous phase transitions with an intermediate hexatic phase possessing algebraically decaying orientational order which contrasts to the three-dimensional case where freezing is known to be a first-order transition. Despite enormous effects during the last decade there is no true unambiguous proof of the existence of the hexatic phase, either in experiments on liquid layers absorbed onto a solid substrate or in computer simulations of two-dimensional liquids; see, e.g., Strandburg, for a review [4]. The reason is that in most experiments the liquid layers are not truly two dimensional and that in computer simulations effects stemming from a finite system size as well as insufficient equilibration exclude any clear conclusion about the stability of a hexatic phase. Although the exact nature of the freezing transition is still controversial in computer simulation, the fluid freezing line can be located with high precision for a given model of the interaction.

Recently, colloidal suspensions [5] confined between two parallel plates [6] have gained an increasing interest since they represent excellent two-dimensional model liquids on a mesoscopic length scale [7]. Another big advantage is that the interaction parameter can be controlled experimentally and that direct images can be taken and even whole sets of two-dimensional particle trajectories can be followed by videoimaging [8,9] methods and the freezing transition can be observed directly in real space. Although there are some hints on the existence of the hexatic phase in such colloidal suspensions [10], the statistical error resulting from the finite number of images is still too large to demonstrate clearly the algebraic decay of the orientational correlation function.

The present paper is concerned with a dynamical phenomenological rule of two-dimensional freezing. Such empirical criteria have played a major role in three dimensions. One of them is the celebrated Lindemann melting rule [11] which predicts that the ratio 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. A second criterion, formulated in 1969 by Hansen and Verlet [12], states that the amplitude of the first maximum of the liquid structure factor $S(k)$ has a constant value of $\simeq 2.85$ along the freezing line. Recently a dynamical criterion for freezing of colloidal fluids undergoing Brownian dynamics was put forward by Löwen, Palberg, and Simon (LPS) [13]. It states that the ratio of the long-time and short-time self-diffusion coefficient is 0.1 along the freezing line. These three simple criteria were also tested to hold for different interparticle interactions and are, in this sense, universal. Thus they are very helpful in locating approximately the freezing and melting lines for a given system without doing any free energy calculation.

If one tries to look for such empirical melting and freezing laws in the case of two-dimensional melting and freezing much less is known. The root-mean-square displacement of a two-dimensional solid does not exist because of long-wavelength phonon fluctuations [14]. Hence there is no Lindemann criterion in two dimensions. Furthermore, near two-dimensional freezing, the amplitude of the first maximum of the liquid structure factor is 5.5 [15] rather than 2.85 which excludes again the validity of the Hansen-Verlet rule in the two-dimensional case. Another criterion for two-dimensional melting follows from KTHNY theory: The dimensionless combination $K=4\tilde{\mu}(\tilde{\mu}+\tilde{\lambda})/(2\tilde{\mu}+\tilde{\lambda})$ of the two scaled elastic Lamé constants $\tilde{\lambda}=\lambda a_0^2/k_BT$ and $\tilde{\mu}=\mu a_0^2/k_BT$ in the triangular crystal is predicted to adopt the universal value 16π on the melting line of the solid. Here, λ and μ are the bare Lamé constants of the solid, a_0 is the triangular lattice spacing, T the temperature, and k_B Boltzmann's constant. This criterion, which been checked by computer simulation [15,16], is based upon static quantities. Unfortunately it is designed only for two-dimensional melting and does not possess any three-dimensional counterpart.

In this paper I show that the dynamical LPS criterion is valid for two-dimensional freezing. It is thus the only criterion known to date that describes both two- and three-dimensional freezing. In fact, this was already partially anticipated by recent measurements of Grier and Murray [17] in colloidal suspensions confined between two smooth walls in nonequilibrium. They indeed found consistency of their freezing data with the LPS criterion. Using Brownian dynamics simulations, the ratio D_L/D_0 of the long-time to short-time self-diffusion coefficient is computed for different soft-sphere fluids at freezing. Here the short-time diffusion constant is defined via

$$D_0 \equiv \lim_{t\to\infty} \frac{1}{4t}\Delta(t), \tag{1}$$

where

$$\Delta(t) = \sum_{i=1}^{N} \frac{1}{N}\langle[\vec{r}_i(t) - \vec{r}_i(0)]^2\rangle \tag{2}$$

is the mean-square displacement, $\langle\ \rangle$ denoting a canonical average. D_0 defines the natural time scale $\tau = \sigma^2/D_0$ of the Brownian fluid. For times much larger than τ, the long-time self-diffusion coefficient D_L is defined as

$$D_L = \lim_{t\to\infty} \frac{1}{4t}\Delta(t). \tag{3}$$

In the simulations it is found that D_L/D_0 is about 0.086 ± 0.014 at freezing only slightly depending on the softness of the interaction.

The soft-sphere pair interaction is described by an inverse-power pair potential with exponent n

$$V(r) = \epsilon\left(\frac{\sigma}{r}\right)^n, \tag{4}$$

where ϵ sets the energy scale and the soft-sphere diameter σ is the natural length scale. Due to scaling properties of the inverse-power potential, all structural and thermodynamic quantities only depend on the scaled density

$$\tilde{\rho} = \left(\frac{\epsilon}{k_B T}\right)^{2/n} \rho\sigma^2, \tag{5}$$

where $\rho = N/A$ is the particle concentration, i.e., the number of particles per unit area. Considering the limit $n\to\infty$, also the interaction of hard disks with pure excluded area is included. In this case the area packing fraction or the scaled particle density $\tilde{\rho} = \rho\sigma^2$ is the only relevant variable.

The two-dimensional freezing transition was studied for different exponents n. Particularly, for $n = \infty, 12, 6, 3$ high-precision results for $\tilde{\rho}$ are available in the literature which we briefly summarize below.

(1) $n=\infty$. Extensive computer simulations have revealed that hard disks exhibit a first-order freezing transition with a coexisting fluid density of $\tilde{\rho} \equiv \tilde{\rho}_f = 0.887$ [18–20]. Recently it was found that the freezing scenario is not in accordance with KTHNY theory [20].

(2) $n=12$. This potential was investigated in great detail by Broughton *et al.* [15] as a simple model fluid to investigate the 2D fluid-solid transition. They cut the interparticle potential off at a distance $r = 2.5\sigma$. The coexisting fluid density is $\tilde{\rho}_f = 0.986$. Recently, Anderson *et al.* [21] found accordance with the KTHNY scenario of melting.

(3) $n=6$. Solid-fluid phase transitions for this inverse-power potential, also cutoff at the distance $r = 2.5\sigma$, were studied by Allen *et al.* [16]. They found $\tilde{\rho}_f = 1.513$ with indications for the validity of KTHNY theory.

(4) $n=3$. Finally the very soft $1/r^3$ potential is used to model the dipolar interaction between two colloidal spheres at the air-water interface [22,23]. Kalia and Vashishta [23] found a fluid-solid transition at $\tilde{\rho}_f = 5.0 \pm 0.2$. However, in their simulations they use a small system size with $N = 256$ particles. Recent simulations with a higher number of particles ($N = 961$) [24] indicate a freezing transition at $\tilde{\rho}_f = 5.29$. At present it is unclear whether the KTHNY scenario is followed in this case.

Henceforth I assume Brownian dynamics of the colloidal particles embedded in the solvent. Relying on a complete time-scale separation between the colloidal and the solvent particles and neglecting any hydrodynamic interactions, the usual way to model the dynamics is to introduce stochastic forces in the equations of motion for the two-dimensional time-dependent trajectories $\{\vec{r}(t)\}$ of the colloidal particles [25–27]. A finite difference algorithm describing these dynamics is [28]

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \frac{D_0}{k_B T}\vec{F}_i(t)\Delta t + (\Delta\vec{r}_i)_R + \cdots, \tag{6}$$

where Δt is a finite time step and $(\Delta\vec{r}_i)_R$ is a random displacement due to solvent collisions which is sampled from a Gaussian distribution with zero mean and variance $4D_0\Delta t$. Furthermore, $\vec{F}_i(t)$ is the total interparticle force on particle i derived from the soft-sphere potential $V(r)$. One easily sees that the motion is diffusive on "short" time scales (which of course have to be much larger than the microscopic solvent motion) with the short-time diffusion constant D_0 defined via (1).

From low-density expansions [25] the long-time diffusion coefficient D_L is known to exist and to be positive in a Brownian fluid. It is quite natural to measure D_L in terms of its short-time counterpart D_0. For an inverse power-law interaction (4), the ratio D_L/D_0 only depends on $\tilde{\rho}$. In the dilute or high-temperature limit ($\tilde{\rho}\to 0$), $D_L/D_0 = 1$. For increasing $\tilde{\rho}$, D_L/D_0 decreases due to the repulsive direct interparticle interactions. If a first-order freezing transition occurs, D_L/D_0 jumps from a finite value at the fluid freezing line to a very small value in the crystalline phase. If the transition is continuous, KTNHY theory predicts that D_L/D_0 drops *continuously* [29] to zero via the hexatic and the solid phase.

Brownian dynamics simulations have been performed at freezing for different exponents n ($n = \infty, 12, 6, 3$). $N = 961$ particles were confined in a periodically repeated square whose area A is governed by the particle concentration $\rho = N/A$. The stochastic Langevin equations of motion were integrated for the particle positions $\{\vec{r}_i(t),\ i = 1, \ldots, N\}$ with a finite time step Δt according to (6). The simulation technique is well known from Refs. [26,27]. Provided the system has been equilibrated long enough, there are three possible sources of error in calculating D_L/D_0.

(i) The time step $\Delta t/\tau$ has to be very small.

(ii) One needs to extrapolate the mean-square-displacement data to infinite time.

(iii) The usual statistical error which is large for long-time correlations has to be taken into account properly.

TABLE I. Ratios of long-time and short-time self-diffusion coefficients, D_L/D_0, at freezing for an inverse-power potential $V(r)=\epsilon(\sigma/r)^n$ with different exponents n: $n=\infty$ (hard disks) and $n=12,6,3$ (soft disks). The number in parentheses gives the error of the last digit. Also given are the dimensionless fluid density $\tilde{\rho}_f=(\epsilon/k_BT)^{2/n}\rho_f\sigma^2$ and the dimensionless derivative $q=(1/D_0)dD_L/d\tilde{\rho}$ at fluid-solid coexistence.

n	$\tilde{\rho}_f$	D_L/D_0	q
∞	0.887	0.072(4)	−1.3(2)
12	0.986	0.099(3)	−1.1(1)
6	1.513	0.087(3)	−0.6(1)
3	5.29	0.086(3)	−0.07(3)

The error due to a finite time step is most notable for hard disks [30] where an explicit extrapolation to a time step zero is required. For $n=\infty$, this extrapolation was controlled using a small time step of $\Delta t=0.000\,02\tau$ and an ultrashort time step of $\Delta t=0.000\,000\,5\tau$ while for $n=12,6,3$ a time step of $\Delta t=0.000\,02\tau$ was sufficiently small.

Fitting the mean-square displacement data by a suitable analytical form, the extrapolation to infinite times can be performed. Two different expressions have been proposed. The first is from the author [26]:

$$\Delta(t)=4tD_L+\frac{At}{t+t_0}, \tag{7}$$

and the other stems from the analytic solution for a semidilute suspension [25] and was suggested by Cichocki and Felderhof [31]

$$\Delta(t)=4tD_L+A\ \ln(t/t_0). \tag{8}$$

In both formulas, D_L, A, and t_0 are fitting parameters. Testing these formulas against the simulational data, it turned out that both expressions can be used to extract D_L properly. If the fitted data are in a small time window, Eq. (7) is superior to Eq. (8) since the long-time tail $\propto\ln(t/t_0)$ has only a small amplitude. Another way of reducing the effort of the extrapolation to infinite time is to compute the differential quantity $\frac{1}{4}d\Delta(t)/dt$ which turns much more rapidly to D_L than $(1/4t)\Delta(t)$. Consistency between these different ways to perform the long-time limit was found.

Finally the statistical error was controlled by a large simulation time typically being 50τ and by redoing the calculations with a different starting configuration and checking that the results do not change.

Results for the ratio D_L/D_0 at freezing are given in Table I for different exponents n. Indeed the data reveal that D_L/D_0 adopts values close to 0.1. Hence the LPS criterion is fulfilled also in two dimensions. The actual values for D_L/D_0 depend a bit on n, i.e., on the softness of the interaction. In fact, the data scatter more in two than in three dimensions. Based on our data one can state that $D_L/D_0=0.086\pm0.01$ for two-dimensional freezing while the value 0.098 ± 0.003 was found in three dimensions [13]. Particularly for hard disks, D_L/D_0 deviates most (about 26%) from the three-dimensional value. Still it is reasonable to speak about the validity of the LPS criterion and this 2D freezing rule may be used to get a simple estimate of the freezing line for different interactions. In contrast the *variation* of D_L/D_0 with $\tilde{\rho}$ as embodied in the derivative $q=(1/D_0)dD_L/d\tilde{\rho}$ is nonuniversal at freezing (see again Table I).

In conclusion, Brownian dynamics computer simulations on the two-dimensional soft-sphere model reveal that D_L/D_0 is close to its three-dimensional universal value 0.1 at freezing. This constitutes a freezing rule which is valid both in three and two dimensions. This is quite remarkable since there is evidence that the two-dimensional freezing process differs from that in three dimensions. The "universal" value of 0.086 ± 0.01 for D_L/D_0 seems to be unaffected by the detailed nature of the freezing process, i.e., it does not matter whether freezing occurs continuously via a hexatic phase or is a conventional first-order transition.

I finish with a couple of remarks: First it would be interesting to perform a theoretical mode-coupling analysis to check whether the universal value of 0.1 near freezing comes out of a theory. The attempts that have been performed to check this in three dimensions [32,33] can in principle be carried out to two dimensions. A mode-coupling-like theory for a two-dimensional Brownian fluid of moderate density was already presented recently by Aranda-Espinoza *et al.* [34].

Second, one should study more realistic pair potentials for charged colloidal suspensions between highly charged plates such as, e.g., the Debye-Hückel (or Yukawa) interactions [26,35,36] where also the image charges can be taken into account [37].

Thirdly, following the pioneering work of Grier and Murray [17], one should perform more detailed and more quantitative dynamical measurements for two-dimensional colloidal suspensions in order to check the universality of the diffusion coefficient ratio for different interactions.

Next I would like to comment on the fact that hydrodynamic interactions are neglected. This is certainly well justified for dilute but highly interacting charged suspensions with a low excess salt concentration. For a high amount of excess salt or for sterically stabilized neutral suspensions, hydrodynamic interactions mediated by the velocity field of the solvent are important. But there is reason to believe that they do not alter much the ratio of the short-time and long-time diffusion coefficient; see the discussion in Ref. [13].

Finally I remark that two-dimensional molecular liquids exhibit Newtonian dynamics rather than Brownian. In this case there is no generalization of a dynamical freezing rule since the long-time self-diffusion coefficient does not exist for two-dimensional molecular dynamics [38].

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