Dynamic Criteria for Melting in Two Dimensions

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The two-dimensional (2D) melting transition is analyzed on the basis of the long-time behavior of a modified Lindemann parameter in 2D $\gamma_L(t)$ and the bond-angular correlation function $g_6(t)$. Using video microscopy complete positional data are obtained over five decades in time for an ensemble of superparamagnetic colloidal particles confined to an air-water interface. We find that each of the three phases (solid/hexatic/isotropic liquid) is uniquely characterized by the long-time behavior of $\gamma_L(t)$, $g_6(t)$, and the non-Gaussian parameter of the relative neighbor-neighbor displacement.

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Ever since the work of Kosterlitz and Thouless [1] and—inspired by the latter—of Halperin, Nelson, and Young [2,3] the melting transition in two dimensions (2D) has been a continuous matter of debate. Their theory, referred to as KTHNY theory, suggests that a 2D crystal melts via two continuous transitions to the isotropic liquid with an intermediate hexatic phase. Both transitions are mediated by the pairwise creation of topological defects. First the disassociation of dislocations drives the system to the hexatic phase while the creation of disclinations induces a transition to the isotropic liquid. However, KTHNY only predicts the temperatures where the system becomes unstable to formation of the defects and does not rule out the possibility of a first-order melting transition (without hexatic phase) preempting the KTHNY scenario [4].

While experiments with electrons on helium [5] and with colloidal particles in quasi-2D systems [6–9] were in favor of the KTHNY theory, the situation is much more controversial concerning computer simulations. Both for hard sphere and Lennard-Jones systems the odds were for a long time against KTHNY until recently very large systems were studied [10,11]. So far all simulations and experiments focused on the static correlation functions of the particle ensemble at melting. This may be due to the fact that the mean square displacement $\langle \Delta \mathbf{u}^2(t) \rangle$ [with $\Delta \mathbf{u}(t) = \mathbf{u}(t) - \mathbf{u}(0)$ [12]] is not an appropriate measure to distinguish between the solid and the liquid phases in 2D, since it diverges at long times with increasing system size [13]. In fact, an alternative is to replace $\langle \Delta \mathbf{u}^2(t) \rangle$ by the relative neighbor-neighbor displacement [14] or the displacement with respect to a local coordinate system defined by different neighbor shells [15]. In addition there are theoretical predictions for the bond-angular correlation function in *time* $g_6(t) = \langle \exp[i6\theta(t)] \rangle$, which suggest an algebraic decay in the hexatic phase similar to spatial correlations [16].

In the present Letter video microscopy is used to study the dynamic properties of an ensemble of colloidal particles in a quasi-2D system over 5 decades in time. We show that the 2D Lindemann criterion of melting [14,15] is applicable and that the behavior of $g_6(t)$ is in fact as predicted in [16]. Finally the glide of free dislocations leads to a dramatic increase of a non-Gaussian parameter as the system enters the hexatic phase. To our knowledge the present data represent the first results on the *dynamic* behavior of a 2D solid at melting. The characterization and preparation of the samples and the realization of the experiments followed precisely the procedure described in [9]. Therefore we only briefly summarize the essentials here: Superparamagnetic spherical colloids [17] of diameter $d = 4.5\ \mu$m and mass density 1.7 kg/dm^3 are confined by gravity to a water/air interface. The latter is formed by a cylindrical drop suspended by surface tension in a top-sealed ring. The flatness of the water-air interface ($\varnothing = 8$ mm) is controlled within $\pm 1\ \mu$m [18]. For weak magnetic fields B applied perpendicular to the interface the induced magnetic moment M depends linearly on B, i.e., $M = \chi B$ with an effective magnetic susceptibility χ [18]. The repulsive magnetic dipole-dipole potential dominates the interaction and is absolutely calibrated by the interaction strength $\Gamma = (\mu_0/4\pi)(\chi B)^2(\pi n)^{3/2}/kT$ (n denotes the 2D volume fraction of the particles).

The experiments were carried out as follows: At high Γ, in the crystalline phase, the system was equilibrated by application of small ac magnetic fields in the particle plane. Next, the temperature $T = 1/\Gamma$ was increased by steps, each increase followed by an equilibration time [9]. Coordinates of typically 10^3 particles (the entire sample contains $\approx 10^5$ particles) were recorded using digital video microscopy and evaluated on a PC later on. While the data in Refs. [9,18] were rather limited in time we are now able to track 2000 particles in time steps of $\Delta t = 0.2$ s over arbitrary long times. This is possible by tracking and *labeling* all particles using the minimum time step Δt, but recording data and corresponding labels only on a logarithmic time scale $\Delta t_n = 2^n \Delta t$. The value of n is increased by 1 after every 1000 data records. This reduces the otherwise unmanageable large amount of data to be stored. The labeling of particles in subsequent records allows one to find the corresponding coordinates even if Δt_n becomes large.

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The dynamic behavior of the particle ensemble is analyzed in terms of the bond-order correlation function and the above mentioned Lindemann melting criterion applicable to 2D. In Fig. 1 (top) the $\Delta\mathbf{u}(t)$ values of some few hundred particles at a temperature of $1/\Gamma = 0.0160$ (about 4% below melting) are shown. Initial particle positions are indicated by a dot and the lines correspond to the diffusion over a time of about 2000 s. Long wavelength fluctuations involving hundreds of particles induce absolute displacements of the order of the lattice constant. In Fig. 1 (bottom) the relative motion of the colloids with respect to their first neighbor shell is drawn [15]. Obviously this quantity more appropriately describes the crystal-like dynamics and is independent of the sample size. In a forthcoming paper we will show that this "neighbor-shell" approach is qualitatively identical to the use of the relative displacement of neighboring particles (indices j and $j+1$) $\gamma_M = \langle(\mathbf{u}_j - \mathbf{u}_{j+1})^2\rangle/a^2$, the lattice constant being denoted by a [14]. For the following we will generalize γ_M to a time correlation function as already introduced in [9]:

$$\begin{aligned}\gamma_L(t) &= \langle(\Delta\mathbf{r}_{\mathrm{rel}}(t))^2\rangle/2a^2 \\ &= \langle(\Delta\mathbf{u}_j(t) - \Delta\mathbf{u}_{j+1}(t))^2\rangle/2a^2, \qquad (1)\end{aligned}$$

where we refer to $\Delta\mathbf{r}_{\mathrm{rel}}(t)$ as the relative neighbor-neighbor displacement. In the crystal $\gamma_L(t)$ is bound at long times, its limit value being equal to γ_M: This follows if Eq. (1) is rewritten as

$$\begin{aligned}\gamma_L(t) = \{&\langle(\mathbf{u}_j(t) - \mathbf{u}_{j+1}(t))^2\rangle + \langle(\mathbf{u}_j(0) - \mathbf{u}_{j+1}(0))^2\rangle \\ &- 2\langle(\mathbf{u}_j(t) - \mathbf{u}_{j+1}(t))\,(\mathbf{u}_j(0) - \mathbf{u}_{j+1}(0))\rangle\}/2a^2. \qquad (2)\end{aligned}$$

As the displacements of the particles are not correlated over long times the last term in Eq. (2) vanishes as $t \to \infty$. On the other hand, in the liquid phase the displacements $\Delta\mathbf{u}(t)$ of particles j and $j+1$ are uncorrelated at long times and $\gamma_L(t)$ is therefore proportional to the mean square displacement [19]. In Fig. 2 $\gamma_L(t)$ is shown as a function of time for various values of $1/\Gamma$. The long time behavior clearly distinguishes between the solid [$\gamma_L(t)$ finite] and the liquid [$\gamma_L(t) \to \infty$] phases. In the inset the data are drawn in linear scale to illustrate the difference in the behavior of $\gamma_L(t)$ observed at melting. At times below 0.2 s all the curves merge as the motion corresponds to free diffusion [18]. In the liquid phase the diffusive behavior—represented by a linear increase of $\gamma_L(t)$ with t—is recovered at long times.

We demonstrated in [9] that our crystalline system melts into the hexatic phase, which is characterized by a quasi-long-range orientational order [16]. Here we analyze the bond-order correlation function in time, i.e., $g_6(t) = \langle\exp[i6\theta(t)]\rangle$, where $\theta(t)$ denotes the angle fluctuation of a *fixed* bond over time t. In Fig. 3 $g_6(t)$ is drawn as a function of $1/\Gamma$ in a log-log diagram. Three different t dependencies can be distinguished: In the solid phase ($1/\Gamma \leq 0.0160$) $g_6(t)$ tends to a constant close to 1 at long times, while it decays exponentially to zero in the isotropic liquid $1/\Gamma \geq 0.0183$. In the hexatic phase $1/\Gamma = 0.0168/0.0176$ the decay is algebraic with an exponent compatible with the prediction [16], i.e., one-half of the value found for the spatial correlation function $g_6(\mathbf{r})$ usually denoted by $\eta_6(T)$. This can be seen for $1/\Gamma = 0.0176$ where the system is close to the transition to the isotropic liquid phase ($T_i = 1/\Gamma_i = 0.0179$):

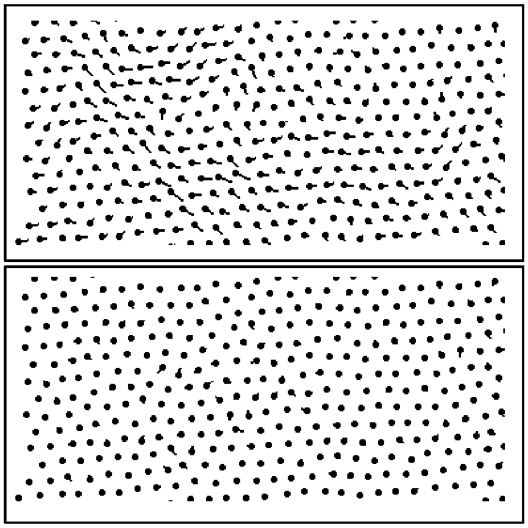

FIG. 1. (top) Part of the sample showing the absolute displacement of some few hundred particles at a value of $1/\Gamma = 0.0160$, which is about 4% below melting. The particles may undergo excursions about their equilibrium positions of the order of the lattice spacing. If the relative displacement with respect to the first neighbor shell is plotted (bottom), the excursions are significantly smaller.

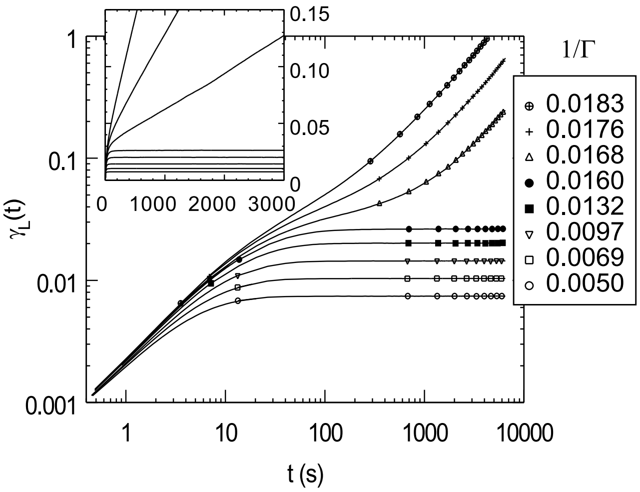

FIG. 2. Dynamic Lindemann parameter as a function of the temperature $1/\Gamma$. In the crystalline phase the long-time limit of $\gamma_L(t)$ is bounded while it diverges in the liquid phases ($1/\Gamma \geq 0.0168$). The inset shows the data in a linear plot to illustrate the change in the behavior of $\gamma_L(t)$.

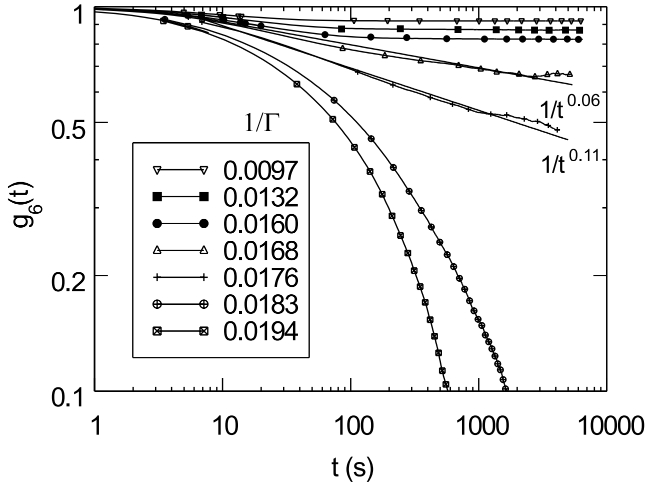

FIG. 3. The bond-order correlation function in *time* $g_6(t)$ as a function of $1/\Gamma$. Clearly three long-time regimes of $g_6(t)$ can be distinguished: In the solid $g_6(t)$ tends to a constant; in the hexatic and the isotropic liquid, respectively, an algebraic and an exponential decay is found.

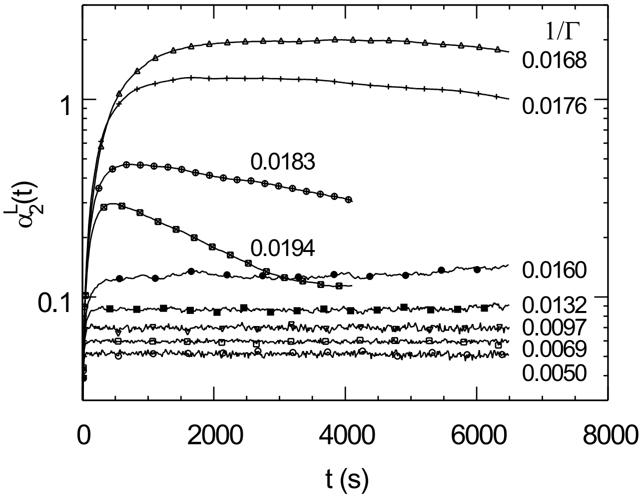

FIG. 4. The non-Gaussian parameter $\alpha_2^L(t)$ for the relative neighbor-neighbor displacement as a function of $1/\Gamma$. From the solid to the hexatic phase the maximum of $\alpha_2^L(t)$ increases by a factor of about 20. This behavior is further discussed in Fig. 5.

We found $\eta_6(T_i) = 1/4$ [9] as compared to 2×0.11. As stated above the functions $\gamma_L(t)$ and $g_6(t)$ clearly characterize the different phases of a 2D system. The use of time correlation functions instead of spatial ones has the advantage that due to the limited field of view the latter cannot be obtained over a large dynamic range, while the former can, in principle, over arbitrarily many decades.

Additional insight into the melting process is obtained by the calculation of the non-Gaussian parameter of the relative neighbor-neighbor displacement, defined as $\alpha_2^L(t) = \langle \Delta\mathbf{r}_{\mathrm{rel}}^4(t)\rangle / 2\langle \Delta\mathbf{r}_{\mathrm{rel}}^2(t)\rangle^2 - 1$ in 2D. It is a measure of the deviation of a random variable from a pure Gaussian behavior and large values are attributed to spatial or dynamic heterogeneities, as, e.g., for supercooled liquids close to the glass transition. It is convenient to analyze $\alpha_2^L(t)$ together with the self-part of the corresponding van Hove correlation function $\mathrm{G}_s^L(r,t)$ defined as

$$\mathrm{G}_s^L(r,t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \Delta\mathbf{r}_{\mathrm{rel}}(t)) \right\rangle, \tag{3}$$

where N denotes the number of particles. The dependence of $\alpha_2^L(t)$ upon $1/\Gamma$ is represented in Fig. 4 (note the logarithmic scale of the y axis) and the van Hove functions $\mathrm{G}_s^L(r,t)$ are shown in Fig. 5. There open and filled symbols correspond, respectively, to times $t = 1000$ s and $t = 6000$ s (for $1/\Gamma = 0.0160$ the two curves coincide). In the solid phase $1/\Gamma \le 0.0160$ $\alpha_2^L(t)$ increases within the first 300 seconds from 0 to a constant value ≤ 0.15, i.e., the behavior is well described by a Gaussian. The increase of $\alpha_2^L(t)$ as $1/\Gamma$ approaches melting is mostly due to the presence of pairs of bound dislocations which, as shown in [9], are already present in the solid phase. These lead to nonzero values of $\mathrm{G}_s^L(r,t)$ for distances r of the order of the lattice spacing a. For $1/\Gamma = 0.0160$, however, these are too small to be resolved in Fig. 5. The situation dramatically changes when the system enters the hexatic phase. The maximum of $\alpha_2^L(t)$ increases by more than an order of magnitude which is caused by the appearance of a peak in $\mathrm{G}_s^L(r,t)$ at $r \approx a$. Apparently two species of colloids are present: particles diffusing around their equilibrium position (peak at $r \approx 0.25a$) and particles displaced

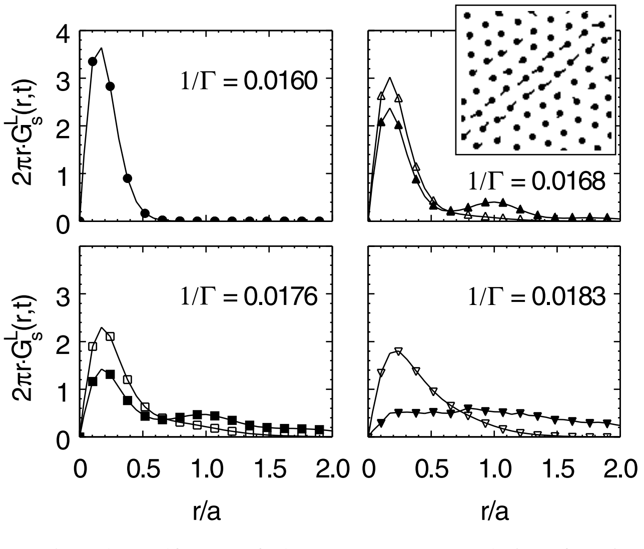

FIG. 5. The self-part of the van Hove correlation function $\mathrm{G}_s^L(r,t)$, r being the relative neighbor-neighbor displacement. The open and filled symbols correspond, respectively, to times $t = 1000$ s and $t = 6000$ s. In the hexatic phase ($1/\Gamma = 0.0168/0.0176$) two peaks can be distinguished corresponding to particles moving around their equilibrium position ($r_{\mathrm{max}} \approx 0.25a$) and particles displaced with respect to each other through the glide of dislocations ($r_{\mathrm{max}} \approx a$) (as illustrated in the inset).

with respect to each other by the glide of free dislocations ($r \approx a$). In the following we will call them, respectively, slow and fast particles. In the inset the glide of a dislocation through the system is represented in terms of the relative neighbor-neighbor displacement of the particles [only the maximum of the six possible values of $\Delta\mathbf{r}_{\mathrm{rel}}(t)$, corresponding to six different neighbors, for a given particle is drawn] [20]. Obviously, at a given time the system is spatially inhomogeneous. The glide of a dislocation involves the collective motion of several colloids and therefore the fast colloids will appear in clusters. However, at long time we did not observe any inhomogeneity. Analysis of the particles trajectories over long times ($t \approx 10^4$ s) reveals that basically all colloids took part in the glide of a free dislocation during the time interval investigated.

In summary, the two-dimensional melting transition of a quasi-2D ensemble of superparamagnetic colloidal particles is analyzed using the long-time behavior of dynamic correlation functions. Real time video microscopy and image processing on a PC enable one to record complete positional data of 2000 particles over five decades in time. The divergence of the long-time limit of a modified Lindemann criterion in 2D, which analyzes the relative neighbor-neighbor displacement $\Delta\mathbf{r}_{\mathrm{rel}}(t)$, determines the melting point of the system. The bond-angular correlation function in time $g_6(t)$ is shown to decay algebraically in the hexatic phase and exponentially in the isotropic liquid, in agreement with theoretical predictions of the KTHNY theory. In addition, the analysis of the van Hove function $G_s^L(r,t)$, which gives the probability that the relative displacement $\Delta\mathbf{r}_{\mathrm{rel}}(t)$ is equal to the distance r at time t, and the corresponding non-Gaussian parameter reveal that the dynamics in the hexatic phase is governed by the glide of free dislocations. Thus our measurements represent additional strong evidence for the occurrence of the KTHNY melting scenario in 2D for $1/r^3$-type interaction potentials.

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[20] In fact, the sample shown corresponds to a crystalline phase during the equilibration process. It has been used for reasons of clarity because in the hexatic phase the appearance of other free dislocations would blur the effect.