# Two-Stage Melting of Paramagnetic Colloidal Crystals in Two Dimensions

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(Received 5 October 1998)

A novel two-dimensional system of colloidal particles with absolutely calibrated magnetic interaction is used to investigate static and dynamic properties at the 2D crystal to liquid phase transition. We observe two successive transitions from the solid to the liquid phase with an intermediate hexatic phase, in perfect agreement with the theory of Kosterlitz and Thouless. The absolute values of the transition temperatures are given, and we demonstrate that they depend neither on the system size nor on the cooling rate. [S0031-9007(99)08831-6]

PACS numbers: 64.70.Dv, 61.72.Lk, 82.70.Dd

Since the work of Mermin [1] it is known that the density-density correlation function in a two-dimensional (2D) crystal decays algebraically to zero with distance, in contrast to the 3D case where a finite value is attained. Therefore, Kosterlitz and Thouless [2] pointed out that the nature of the melting transition in 2D is different from 3D and suggested crystal melting via a continuous transition mediated by the dissociation of dislocation pairs. Later it was shown [3,4] that the resulting phase is not an isotropic liquid, and a second transition induced by the formation of disclinations is necessary to drive the system from the so-called hexatic phase into the isotropic liquid. This two-stage melting scenario is referred to as the Kosterlitz-Thouless-Halperin-Nelson-Young theory (KTHNY). This theory predicts the temperature where the system becomes unstable and topological defects (dislocations or disclinations) are formed. However, these transitions might be preempted by other processes leading to a single first order transition as in 3D [5]. Several computer simulations and experiments have been performed [6], leading to inconsistent results. So far it seems that the melting scenario in 2D is not universal but depends on the specific properties of the systems, e.g., the core energy of the dislocations [7].

In this Letter we use a novel 2D setup of colloidal particles with absolutely calibrated magnetic interaction [8] to investigate statics and dynamics at the crystal to liquid phase transition with "atomic" resolution. The results unambiguously demonstrate that a 2D system of interacting dipoles melts via a two-stage scenario in agreement with KTHNY. In addition, for the first time absolute values of the transition temperatures are given. Furthermore, we study the system size dependence of the transition and the question of thermal equilibrium.

Spherical colloids of diameter $d = 4.7\ \mu$m and mass density 1.7 kg/m$^3$ are confined by gravity to a water/air interface formed by a cylindrical drop suspended by surface tension in a top-sealed ring. We control the flatness of the entire interface (o.d. = 8 mm) up to $\pm 1\ \mu$m [8]. The particles are superparamagnetic due to $Fe_2O_3$ doping [9], and a magnetic field $B$ applied perpendicular to the interface induces magnetic dipole moments $M$ leading to a repulsive interparticle potential. For the weak field intensities used we find $M = \chi_{\text{eff}} B$ with an effective magnetic susceptibility of the particles $\chi_{\text{eff}} = (7.62 \pm 0.2) \times 10^{11}$ A m$^2$/T [8]. This setup has considerable advantages over colloidal model systems previously used [10–12]: It can be regarded an almost ideal 2D model system as the out-of-plane motion of the particles corresponds to less than 1% of their diameter. The only relevant contribution to the interaction potential is the magnetic dipolar repulsion which is conveniently and reversibly adjustable by the external field $B$ and absolutely calibrated by the dimensionless interaction amplitude (or inverse temperature) $\Gamma = (\mu_0/4\pi)(\chi_{\text{eff}} B)^2 (\pi n)^{3/2}/kT$ ($n$ denotes the 2D volume fraction of the particles). Finally, the system size and the equilibration time can easily be varied and their influence on the transitions studied.

The experiments were carried out as follows: At high field $B$, i.e., in the crystalline phase, the system was equilibrated for several days up to a week. In addition, small ac magnetic fields in the particle plane were superimposed to $B$ to anneal lattice defects. After this procedure the entire sample [13] consisted of one single crystalline domain with a few (one per several thousand particles) isolated dislocations left. The field of view of size $520 \times 440\ \mu$m$^2$, which corresponds to typically $10^3$ particles (the entire sample contains $\approx 10^5$ particles), was chosen without any defect to minimize influences on the phase transition. Finally, the temperature $T = 1/\Gamma$ was increased by steps, each increase followed by an equilibration time of the order of an hour. After equilibration the particle coordinates were determined using digital video-microscopy and recorded for later evaluation on a PC.

For the analysis of the static properties the density-density [Eq. (1)] and bond-angular [Eq. (2)] correlation functions have been calculated,

$$g_G(|\mathbf{r} - \mathbf{r}'|) = \langle \exp\left(i\mathbf{G} \cdot [\mathbf{u}(\mathbf{r}) - \mathbf{u}(\mathbf{r}')]\right) \rangle , \quad (1)$$

$$g_6(|\mathbf{r} - \mathbf{r}'|) = \langle \exp\left(i6[\theta(\mathbf{r}) - \theta(\mathbf{r}')]\right) \rangle . \quad (2)$$

  

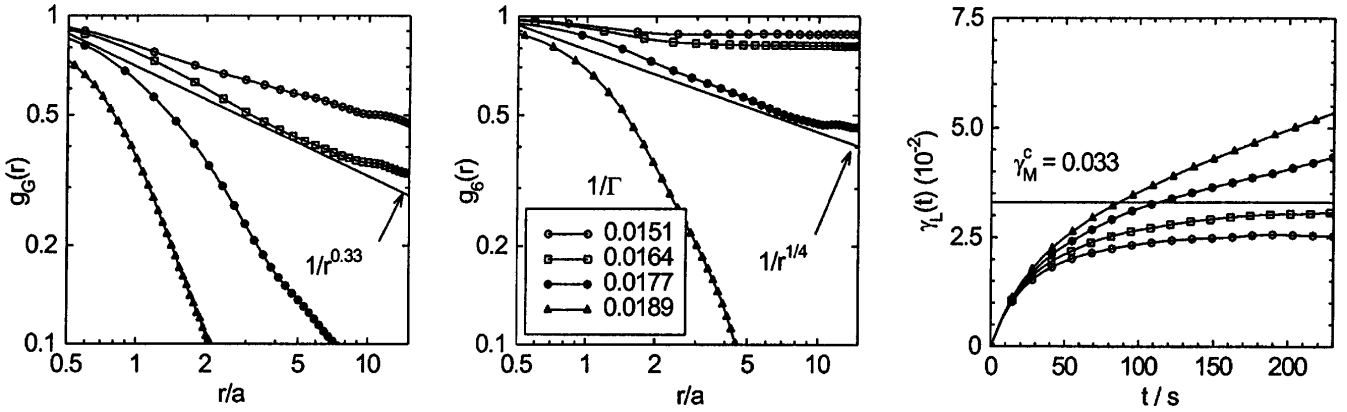


FIG. 1. The behavior of the density-density (left) and bond-angular (middle) correlation functions and the Lindemann parameter (right) for different temperatures $1/\Gamma$ are in agreement with KTHNY (see text).

$\mathbf{G}$ denotes a reciprocal lattice vector, $\mathbf{u}(\mathbf{r})$ is the particle displacement field, and $\theta(\mathbf{r})$ represents the angle, with respect to the $x$ axis, of the bond centered at position $\mathbf{r}$. For a 2D crystal KTHNY predicts an algebraic decay of $g_G(r) \sim 1/r^{\eta(T)}$ while $g_6(r)$ remains finite at large $r$. At the melting temperature $T_m$ one finds $\eta(T_m) = (\mathbf{G}^2 a^2/64\pi^2)(1 + \sigma_R)(3 - \sigma_R)|_{T_m}$. Here $a$ is the lattice constant and $\sigma_R$ the 2D Poisson's ratio (evaluated at $T_m$) related to the Lamé elastic constants by $\sigma_R = \lambda/(\lambda + 2\mu)$ [4]. In our system the interaction potential is known precisely, and thus $\lambda, \mu$ at $T = 0$ can be determined. We determined the renormalized values (at $T = T_m$) of $\lambda, \mu$ as described in [4] and obtained $\eta(T_m) = 0.33$. In fact, these values hardly differ from the values at $T = 0$ [14]. In the hexatic phase an exponential decay is expected for $g_G$ and an algebraic decay for $g_6(r) \sim 1/r^{\eta_6(T)}$. The exponent $\eta_6$ tends towards $1/4$ as the system approaches the transition to the isotropic liquid. There both functions decay exponentially.

To analyze the dynamics we refer to the 2D Lindemann melting criterion introduced by Bedanov and Gadiyak [15]. As the mean square displacement $\langle \mathbf{u}^2 \rangle$ diverges in a 2D crystal they suggested the Lindemann parameter

$$\gamma_M = \langle (\mathbf{u}_j - \mathbf{u}_{j+1})^2 \rangle / a^2, \tag{3}$$

where the indices $j$ and $j + 1$ refer to neighboring particles. At the melting point these authors found a critical value $\gamma_M^c = 0.033$ [16]. We generalize their definition to be time dependent as

$$\gamma_L(t) = \langle [\Delta \mathbf{u}_j(t) - \Delta \mathbf{u}_{j+1}(t)]^2 \rangle / 2a^2, \tag{4}$$

where $\Delta \mathbf{u}(t) = \mathbf{u}(t) - \mathbf{u}(0)$. In the crystal $\gamma_L(t)$ is bound at long times, its limit value being equal to $\gamma_M$ [17]. 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 proportional to the mean square displacement $\langle \Delta \mathbf{u}^2(t) \rangle$.

Figures 1–3 summarize the behavior of the system at four different temperatures $1/\Gamma$ around the melting transition. They show, respectively, the functions as defined

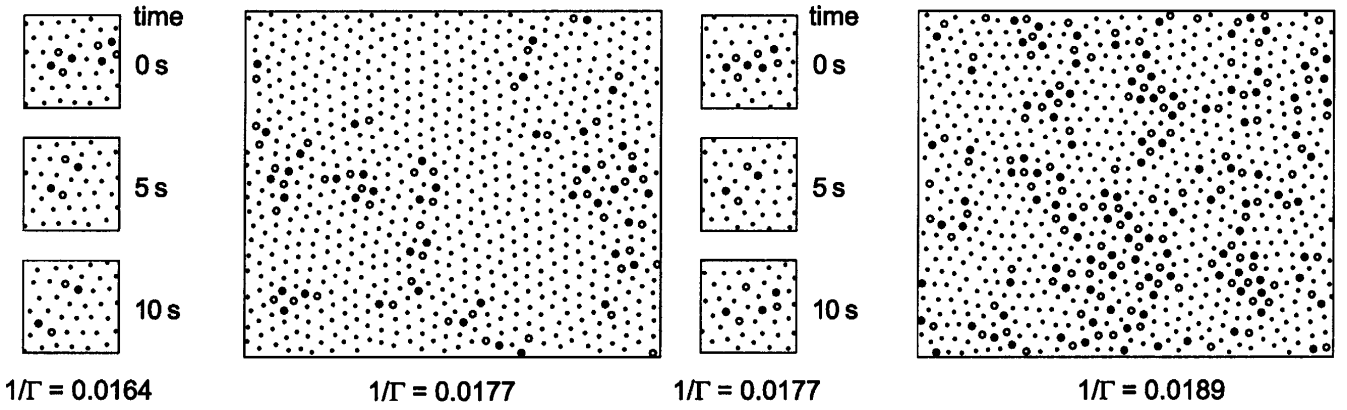


FIG. 2. The analysis of the defect structure (codes of $n$-fold coordinated sites: small black dots $n = 6$; open circles $n = 7$; filled circles $n = 5$) reveals for the solid, just before melting ($1/\Gamma = 0.0164$), the occurrence of weakly bound pairs of dislocations. In the hexatic phase ($1/\Gamma = 0.0177$) free dislocations appear (left) and disclinations start to be weakly bound (right). Finally, the isotropic liquid phase ($1/\Gamma = 0.0189$) can be characterized by the existence of free disclinations.

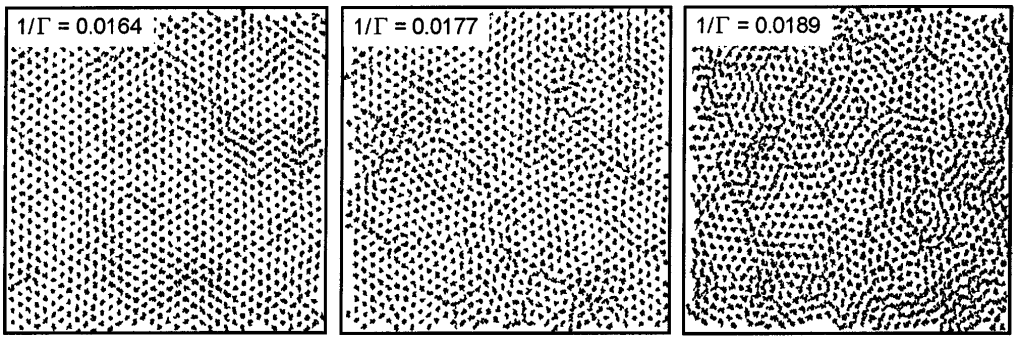


FIG. 3. Trajectories of particles integrated for a time $t = 300$ s taken at three different temperatures $1/\Gamma$. These correspond (from left to right) to the solid phase close to melting, the hexatic, and the isotropic liquid phase.

in Eqs. (1), (2), and (4) (from left to right), the defect structure determined by the Voronoi construction, and the trajectories of the particles integrated over 300 s. In the following these figures will be discussed simultaneously for the different $1/\Gamma$ values.

At the lowest temperature $1/\Gamma = 0.0151$ an algebraic decay is found for $g_G(r)$ while $g_6(r)$ is finite for large $r$. $\gamma_L(t)$ is bound at large times and no defects at all are present (not represented in Figs. 2 and 3). All this indicates a crystalline phase. At the higher temperature 0.0164 the behavior of $g_G(r)$, i.e., the exponent of the algebraic decay, is close to the predicted value $\eta = 0.33$ at the melting transition. Similarly, $\gamma_L(t)$ approaches the transition value $\gamma_M^c = 0.033$ but remains finite at long times. The analysis of the defects reveals the appearance of pairs of dislocations, which start to unbind (one example in Fig. 2, left). However, these pairs always annihilate after a few seconds and no free dislocation is present. Thus the overall analysis indicates a crystalline phase very close to the melting transition. Next, the temperature was increased to 0.0177. As the long time behavior of $\gamma_L(t)$ and the trajectories (Fig. 3) demonstrate, the particles now leave their positions in the lattice, their mean square displacement diverging as a function of time. In addition, free dislocations are present (Fig. 2) which were observed to move freely through the sample. All this is strong evidence for a liquidlike phase. However, contrary to $g_G(r)$ which is of short range, $g_6(r)$ remains quasi long range, its behavior being compatible with an algebraic decay. In addition, Fig. 2 ($1/\Gamma = 0.0177$, right part) demonstrates that disclinations are created by a dissociation process similar to the creation of dislocations. An isolated particle having seven neighbors is created leaving a particle with five neighbors plus an adjacent dislocation in its neighborhood. However, these defects are always found to annihilate after a few seconds and only at a higher temperature 0.0189 are free disclinations stable (Fig. 2, right). Therefore we claim that the phase corresponding to $1/\Gamma = 0.0177$ is hexatic and a second transition drives the system into the isotropic liquid ($1/\Gamma = 0.0189$), which is characterized by the exponential decrease of both $g_G(r)$ and $g_6(r)$. Thus the melting scenario proposed by KTHNY corresponds perfectly to the measurements presented.

In addition, we are able to give the absolute values of the transition temperatures $1/\Gamma_m, 1/\Gamma_i$: As a melting criterion to determine $1/\Gamma_m$ we claimed that the long time limit $\gamma_M$ of the Lindemann parameter $\gamma_L(t)$ should be equal to the critical value $\gamma_M^c = 0.033$. In Fig. 4 (main part) $\gamma_M$ is plotted as a function of $1/\Gamma$ for various lattice constants $a$. Intersection of these curves with $\gamma_M^c$ gives $1/\Gamma_m = 0.0167$. Even if the values of $\gamma_M$ above the melting temperature are no longer well defined, this should not have a considerable influence on the point where the curves intersect. This value is in good agreement with the simulations [15] cited earlier [18]. As a criterion to determine the temperature of the hexatic-liquid transition we used the point where $g_6(r)$ started to decrease faster than $1/r^{(1/4)}$ and found $1/\Gamma_i = 0.0179$.

In addition, Fig. 4 enables us to investigate another aspect of the transition. In the inset the values of $\gamma_M$ are represented as a function of the magnetic field, for various lattice constants $a$. As the size of the sample was kept

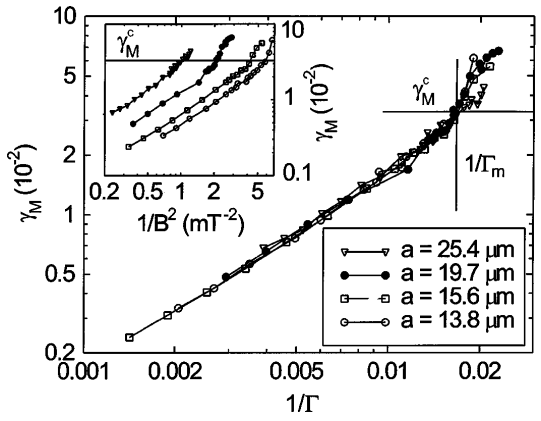


FIG. 4. The long time limit $\gamma_M$ of the Lindemann parameter as a function of the magnetic field (inset) and the temperature $1/\Gamma$ for different lattice constants $a$. $\gamma_M$ scales only with $1/\Gamma$ and no dependence on the number of particles (a consequence of the fixed system size for various $a$) is observed.

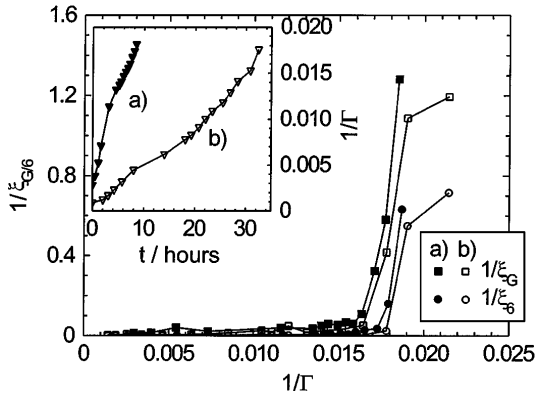


FIG. 5. The inverse of lengths $\xi_G, \xi_6$ (see text) vs $1/\Gamma$ (main part) for two melting transitions at different heating rates (inset). No considerable change in the transition temperatures is seen.

constant, increasing $a$ from 13.8 to 25.4 $\mu$m corresponds to reducing the number of the particles—i.e., the size of the system—by more than a factor of 3. However, in the main part of Fig. 4 all curves collapse to a single master curve when plotted as a function of $1/\Gamma$. This shows that within the range of system sizes considered there is no size dependence of the transition.

Finally the question of thermal equilibrium during the melting transition is investigated. In Fig. 5 the inverse of the lengths $\xi_G, \xi_6$ (given by the $1/e$ value of $g_G, g_6$) vs $1/\Gamma$ are compared for two melting experiments performed at different heating rates (inset). No considerable change in the transition temperatures were observed between experiment (a) and (b). Thus we conclude that we are working close to thermal equilibrium. The reason for this lies in the high diffusion constant of the dislocations $D_0^{\mathrm{dis}}$ close to melting (Fig. 2, left) which is about 100 times faster than the diffusion of the individual particles ($D_0 = 0.1\ \mu\mathrm{m}^2/\mathrm{s}$). As the dissociation of dislocation is the driving mechanism $D_0^{\mathrm{dis}}$ determines the time scale for thermal equilibrium.

In summary, analyzing the static and dynamic properties of a 2D system of colloidal particles with absolutely calibrated (dipole-dipole) interaction potential a two-stage melting transition in perfect agreement with theory (KTHNY) and simulations was observed. Absolute values of the transition temperature were determined and additional investigations show no system-size or heating-rate dependence of the transitions in the parameter range studied.

We acknowledge fruitful discussions with N. Rivier.

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[17] This follows if Eq. (4) is rewritten as

$$\gamma_L(t) = \{\langle[\mathbf{u}_j(t) - \mathbf{u}_{j+1}(t)]^2\rangle + \langle[\mathbf{u}_j(0) - \mathbf{u}_{j+1}(0)]^2\rangle - 2\langle[\mathbf{u}_j(t) - \mathbf{u}_{j+1}(t)] \cdot [\mathbf{u}_j(0) - \mathbf{u}_{j+1}(0)]\rangle\}/2a^2. \quad (5)$$

As the motion of the particles is not correlated over long times the last term in Eq. (5) vanishes for $t \to \infty$.
[18] The fact that Bedanov and Gadiyak find a single first-order transition is not too surprising regarding their small system size (about 500 particles).