Melting of microgel colloidal crystals

Yi Peng, Ziren Wang and Yilong Han
Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, China
E-mail: yilong@ust.hk

Abstract. We experimentally studied the melting of colloidal crystals composed of diameter-tunable microgel spheres by bright-field and confocal video microscopies at the single-particle level. Thick (\(>4\) layers) and thin (\(\leq4\) layers) films exhibited dramatically different melting kinetics. Thick films melted heterogeneously from grain boundaries in polycrystals and from surfaces in single crystals, while thin films melted homogeneously even in polycrystals. A novel heterogeneous melting at dislocation was observed in 5- to 12-layer films. The equilibrium phase behaviors in three thickness regimes were all different: thick films had a crystal-liquid coexistence regime which decreased with the film thickness and vanished at 4 layers, thin crystalline films melted into liquids in one step, while monolayers melted in two steps with an intermediate hexatic phase.

1. Introduction

Two-dimensional (2D) and three-dimensional (3D) crystals have qualitatively different melting behaviors. 2D melting often exhibits two continuous phase transitions with an intermediate hexatic phase as predicted by the KTHNY theory \([1, 2]\), while 3D melting is a one-step first-order transition. The crossover between 2D and 3D melting, i.e. the thin-film melting, has not been well studied because it is difficult in theory and challenging in simulation and experiment. In particular, the strong long-wavelength fluctuations in low dimensions make the finite-size effect difficult to estimate \([2]\). Recent simulations show that at least \(10^6\) particles are necessary for measuring the melting behaviors of hard disks in 2D \([3]\). For multilayer systems, such large-scale simulations become challenging. Thin-film melting has been measured experimentally in some molecular systems, but these films simply melted heterogeneously from film-vapor interfaces as expected \([4, 5]\). In contrast, the non-trivial melting of thin films fully wrapped by solid substrates has not been explored. Recently we studied the melting of colloidal thin films confined between two flat glass walls \([6, 7]\). Here we review those results and discuss in detail the annealing techniques used and the surface melting observed in single crystals.

Besides the dimensionality, melting behavior is strongly affected by defects and surfaces \([8]\). For 3D crystals, melting always starts heterogeneously from surfaces and progresses into the bulk. If a 3D crystal is fully covered by flat solid substrates, then melting will only start from grain boundaries \([9]\) which suppresses the melting from other defects. Here we explore the role of grain boundaries, dislocations and film-wall interfaces in 2D, thin-film and 3D melting. In fact, there lacks a quantitative theory about heterogeneous melting from defects in thin films. For example, all of the 2D melting theories including the KTHNY theory \([1, 2]\), the grain-boundary-mediated melting theory \([10]\) and the geometrical-defect-mediated melting theory \([11]\)
describe the homogenous melting of a single crystal. The defect-mediated melting theory for 3D crystals also focuses on the precursor defects in the homogenous melting of a single crystal without preexisting surfaces or defects. In real systems, however, crystals almost always melt heterogeneously from surfaces and preexisting defects. Hence the measurement of heterogeneous melting at the single-particle level is of practical interest and theoretical importance.

2. The experimental system
The colloidal crystals consisted of monodispersed N-isopropylacrylamide (NIPA) microgel spheres in aqueous solution. As temperature increases, NIPA polymers become less hydrophilic so that the diameter of the microgel sphere would decrease [12]. The pair potentials, \( u(r) \), were directly measured from the liquid structure of a dilute (area fraction \( \sim 10\% \)) monolayer of spheres [13, 14], see Fig. 1. The effective diameter \( \sigma \) is defined as \( u(\sigma) = \frac{1}{k_B T} \). For a typical batch of colloids, \( \sigma \) varies linearly from 1.27 \( \mu m \) at 24.1\(^\circ\)C to 1.14 \( \mu m \) at 28.0\(^\circ\)C.

![Figure 1. The pair potentials, \( u(r) \), of NIPA spheres at 24.1\(^\circ\)C, 26.0\(^\circ\)C and 28.0\(^\circ\)C.](image)

Hard spheres confined between two walls exhibit a cascade of phases as the wall separation increases [15]: \( 1\triangle - 2\square - 2\triangle - 3\square - 3\triangle - 4\square \) and so on. Here \( n\triangle \) denotes an \( n \)-layer triangular lattice (i.e. the (111) plane of a face-centered cubic (FCC) lattice), \( n\square \) denotes an \( n \)-layer square lattice (i.e. the (100) plane of an FCC lattice). We observed such a cascade of phases in thin films of soft NIPA spheres. We found that films of more than 8 layers only have triangular lattices in the xy plane.

Colloidal suspensions were sucked into thin glass cells by a capillary force. Such a capillary flow can anneal crystals of > 30 layers into mm- or cm-sized large FCC crystalline domains with the (111) plane along the xy direction. For crystals of <8 layers, however, the domain size was only about 10 to 100 \( \mu m \), see Fig. 2(a). We further annealed the sample by increasing the temperature to nearly the melting point so that the polycrystal would become soft. Then we manually oscillate the microscope objective in the z direction to slightly deform the coverslip and induce a periodic water flow in the sample. Such a flow can effectively anneal an area of 0.1 \( mm^2 \). Then we moved the stage in the xy plane to anneal the neighboring areas and achieved crystalline domains of >1 \( mm^2 \) with > \( 10^6 \) particles per layer, see the subarea in Fig. 2(b). Such a large domain size is important for the melting study because long wavelength fluctuations and finite-size effects are important in low dimensions.

The sample temperature was increased in steps of 0.2\(^\circ\)C. At each temperature, 5 minutes of video were recorded by bright-field microscopy, 2 to 4 minutes of video were recorded for each layer by confocal microscopy, and several confocal scans of the 3D static structure were taken along the z direction. Video rates were 30 frames/sec for bright-field microscopy and 7.5 frames/sec for confocal microscopy. The particle positions in each frame were obtained using standard 2D and 3D image analysis algorithms [16]. More than 100 layers of (111) planes can be seen through even in the bright field [9]. This unique advantage of microgel particles is due
to the fact that the refractive index of NIPA spheres is close to that of water and the diffraction of a triangular lattice in the xy plane matches the image of a neighboring (111) plane in an FCC crystal quite well.

3. Results of the experiment

3.1. Thick films (> 4 layers)

3D NIPA colloidal polycrystals melt only from grain boundaries [9]. Particles near smaller defects such as dislocations and partial dislocations have stronger motions than the bulk crystalline particles [9], but they never melt into small liquid domains. We observed that melting from dislocations became possible when the film thickness was between 5 to about 12 layers, see the coexistence of two liquid “lakes” melted from dislocations and one liquid strip melted from a grain boundary in Fig. 3. At the melting point, all the grain boundaries melt into liquid strips, and some dislocations melt into cylindrical liquid lakes with uniform cross-sections along the z direction. If the dislocation does not penetrate through the film, then neither does the lake, see Fig. 4.

The dislocation melting is often suppressed by a neighboring liquid strip or lake within about 20 lattice constants. A large crystalline domain can contain multiple lakes (see Fig. 3). Dislocations melt more easily in thinner films and in larger crystalline domains under higher heating rates. For example, 12-layer films do not melt from dislocations unless the heating rate is very high (∼ 0.1°C/sec), whereas 5- to 7-layer films with domains of more than 100 µm in size always melt from dislocations. This indicates that the difference in energy between the grain-boundary melting and the dislocation melting is comparable to the thermal energy.

The liquid strips and lakes have interesting interactions and dynamics. Unlike a dislocation which mainly glides along its Burgers vector at a relatively high speed, a lake randomly diffuses at a much lower speed independent of the direction of its Burgers vector. There is either an attraction or repulsion between two neighboring lakes, depending on which of the following two effects is dominant: 1) the surface tension at the liquid-crystal interfaces induces an effective attraction especially at a distance of less than 10 lattice constants; 2) the Burgers vectors of the two neighboring lakes usually differ by π/3, and such an acute angle between the effective “dipoles” will induce repulsion. We did not observe neighboring lakes with opposite Burgers vectors because their corresponding dislocations can be easily annihilated in the crystal phase before they melt into lakes. Lakes slowly diffuse and irreversibly merge into liquid strips. Large crystalline domains and large liquid strips coexist in the final equilibrium.

The 3D melting behaviors were observed in 300-layer samples. The crystal-liquid coexistence
regime is about 6% in volume fraction [6], which is close to the 5% coexistence regime (from 49.5% to 54.5%) in the well-known 3D hard sphere phase diagram [17]. This 1% difference is likely due to the fact that our NIPA spheres are soft and the volume fraction cannot be rigorously defined. Interestingly, the crystal-liquid coexistence regime decreases with the film thickness and vanishes at the critical thickness of 4 layers, see Fig. 5.

![Figure 5](image5.png)

**Figure 5.** The liquid-solid coexistence regime (expressed as the temperature interval $\Delta T$ or volume fraction interval $\Delta \phi$) decreases with the film thickness and vanishes at 4 layers.

So where does the melting start if there are no grain boundaries? We carefully annealed thick films of > 30 layers and made cm-sized single crystals. These single crystals melted from glass walls and formed droplets, see Fig. 6. The droplets had different sizes and contact angles with the glass walls because the dislocations had different lengths, see Fig. 7(a). As the temperature
was increased, the droplet became larger and then the whole surface layer melted as shown in Fig. 7(b). We never observed cylindrical lakes which can penetrate through the z direction as depicted in Fig. 4. Dislocations cannot melt if they are not connected to the walls. Melting from other defects is completely suppressed by such interfacial melting in films of > 30 layers.

![Figure 6](image-url)  
**Figure 6.** The single crystal melted from film-wall interfaces and formed liquid droplets. The cross-sections of a liquid droplet at the 3rd, 9th, 13th and 19th layers are shown.

3.2. Thin films (2-4 layers)  
Thin films (≤ 4 layers) do not have any preferential sites for melting as thick films do. They melt homogenously from everywhere in the xy plane, see the particle trajectories in Fig. 8. Increasing the temperature by just 0.2°C caused the whole crystalline structure to break down from the inside of domains. Disordered particles form small unstable defect clusters, but they never nucleate into large stable liquid domains such as lakes and strips. Since the melting is homogenous, we chose (60 µm)² (~2300 particles) representative areas in the centers of large domains and searched for the hexatic phase. In the KTHNY theory [1, 2], 2D crystals melt in two steps, from the crystal to the hexatic phase and then from the hexatic to the liquid phase. The intermediate hexatic phase has short-range translational and quasi-long-range orientational orders. The 2D crystal phase has quasi-long-range translational and long-range orientational orders. The liquid phase has short-range translational and orientational orders. Orders are characterized by the correlation functions of the order parameters as shown in Table 1. The correlation functions are defined in Table 2 and have three types of behaviors: approaching a
Figure 7. Surface melting of 3D single crystals with some dislocations. Dashed lines: dislocations. Yellow shaded area: liquid phase. (A) Melting starts from the intersection between dislocations and wall surfaces, forming lakes around the dislocations. No lake can penetrate through the film. Dislocations not connected to the walls cannot melt. (B) Further increasing the temperature results in melting from wall surfaces.

Figure 8. Typical 10-second trajectories of the homogenous melting in 2△ (a-c) and 3□ (d-f) films. Each figure is a subarea of a surface layer. (a) Crystal at 26.6°C; (b) At the melting point of 28.6°C; (c) Liquid phase at 28.8°C; (d) Crystal at 26.0°C; (e) At the melting point of 27.9°C; (f) Liquid phase at 28.1°C.

Table 1. In the KTHNY theory, the 2D crystal, hexatic and liquid phases are characterized by different exponential or power-law correlations.

| 2D crystal | Hexatic | Liquid |
|------------|---------|--------|
| \( g_6(r) \) | nonzero constant at \( r \to \infty \) | \( \sim r^{-\eta_6}, 0 < \eta_6 \leq 1/4 \) | \( \sim e^{-r/\xi_6} \) |
| \( g_6(t) \) | nonzero constant at \( t \to \infty \) | \( \sim r^{-\eta_6t}, 0 < \eta_6t = 2\eta_6r \leq 1/4 \) | \( \sim e^{-t/\tau} \) |
| \( g_T(r) \) | \( \sim r^{-\eta_T}, 1/4 < \eta_T \leq 1/3 \) | | \( \sim e^{-r/\xi_T} \) |

finite constant (long-range order); power-law decay (quasi-long-range order); and exponential decay (short-range order).

We have observed the hexatic phase in the melting of 2D microgel crystals in ref. [18]. For
melting. Thin films (2-4 layers) melt homogenously in one step without a middle tetratic crystals (>30 layers) melt from film-wall interfaces and suppress other types of heterogeneous melting. Thick films (>4 layers) melt heterogeneously with a crystal-liquid coexistence regime which decreases with the film thickness and vanishes at a critical thickness of 4 layers [6]. Moreover, 5- to 12-layer films exhibit a novel heterogeneous melting from dislocations and form lakes embedded in crystalline domains. Single crystals (>30 layers) melt from film-wall interfaces and suppress other types of heterogeneous melting. Thin films (2-4 layers) melt homogeneously in one step without a middle tetratic multilayer thin films, we measured the structures layer by layer because the particles were well stratified into separate layers even in the dense liquid phase near the melting point. From the particles’ trajectories, we calculated their global order parameters, correlations and susceptibilities as defined in Table 2. The results for 2Δ film melting are shown in Fig. 9. The correlations in Fig. 9(b) clearly show a crystal phase at 28.7°C and that 6 peak at the same point (Fig. 9(a)) and that 6 and 4 face peak at the same point (Fig. 9(c)). Bulk layers and surface layers have similar correlations and susceptibilities, indicating that they melt at the same temperature. These results in 2Δ melting were also observed in 3Δ, 3□, and 4□ film melting.

4. Summary and Discussion
Thick, thin and monolayer films exhibit different melting behaviors. Thick films (> 4 layers) melt heterogeneously with a crystal-liquid coexistence regime which decreases with the film thickness and vanishes at a critical thickness of 4 layers [6]. Moreover, 5- to 12-layer films exhibit a novel heterogeneous melting from dislocations and form lakes embedded in crystalline domains. Single crystals (>30 layers) melt from film-wall interfaces and suppress other types of heterogeneous melting. Thin films (2-4 layers) melt homogeneously in one step without a middle tetratic

| Table 2. Translational and orientational order parameters, susceptibilities and correlations. |  |
|---|---|
| Local order parameter | \( \psi_{ij}(r) = e^{iG \cdot r_j} \) |
| Global order parameter | \( \psi_T = |\langle \psi_{ij} \rangle| \) |
| Spatial correlation | \( g_T(r) = \langle \psi_{ij}(r_j) \psi_{ij}(r_j) \rangle \) |
| Time autocorrelation | \( g_6(t) = \langle \psi_{ij}^*(t_0) \psi_{ij}(t_0 + t) \rangle \) |
| 6-fold: \( \psi_{6j}(r) = (\sum_{k=1}^m e^{i\theta_{jk}})/nn \) | \( \psi_6 = |\langle \psi_{6j} \rangle| \) |
| 4-fold: \( \psi_{4j}(r) = (\sum_{k=1}^4 e^{i\theta_{jk}})/nn_4 \) |

Figure 9. 2Δ-crystal melting measured from one of the two surface layers. (a) 2D translational and orientational order parameters, \( \psi_T, \psi_6 \) as a function of sample temperature \( T \) and volume fraction \( \phi \). The jumps at 28.7°C indicate the melting transition. (b) Orientational correlation functions \( g_6(t) \) in time. Open symbols: liquid phase. Solid symbols: solid phase. (c) Translational susceptibility \( \chi_T \) and orientational susceptibility \( \chi_6 \). The peaks show the melting temperature at 28.7°C.

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or hexatic phase. Monolayers melt homogenously in two steps with an intermediate hexatic phase \[18\]. Thinner films are softer and the extra long-wavelength fluctuations in low dimensions \[2\] may break the large crystalline domains from the inside and result in homogenous melting. These melting behaviors are robust for NIPA spheres of different sizes, but they are sensitive to particle interactions. Our preliminary experiments show that if particles have attractions, the critical thickness may be less than 4 layers or even exhibit crystal-liquid coexistence in monolayers.

The microgel colloid is a versatile system for melting and freezing studies. The surface effects can be avoided by focusing a beam of light into a single crystal to achieve local superheating and melting. By tuning the beam of light, we have been able to control the size and shape of a liquid domain embedded in a single crystal or of a crystalline island embedded in liquid phase. This setup can provide a more controllable way to explore the superheating, melting and freezing in 3D.

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