Frank’s constant in the hexatic phase

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Using video-microscopy data of a two-dimensional colloidal system the bond-order correlation function $G_b$ is calculated and used to determine the temperature-dependence of both the orientational correlation length $\xi_b$ in the isotropic liquid phase and the Frank constant $F_A$ in the hexatic phase. $F_A$ takes the value $72/\pi$ at the hexatic ↔ isotropic liquid phase transition and diverges at the hexatic ↔ crystal transition as predicted by the KTHNY-theory. This is a quantitative test of the mechanism of breaking the orientational symmetry by disclination unbinding.

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The theory of melting in two dimensions (2d) developed by Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY-theory) suggests a two-stage melting from the crystalline phase to the isotropic liquid. The first transition at temperature $T_m$ is driven by the dissociation of thermally activated dislocation pairs into isolated dislocations breaking the translational symmetry $\mathbb{Z}_2$. The fluid phase directly above $T_m$ still exhibits orientational symmetry and is called the hexatic phase. It may be viewed as an anisotropic fluid with a six-fold director $\hat{d}$ which is characterized by a finite value of Frank’s constant $F_A$, the elastic modulus quantifying the orientational stiffness. At the second transition at $T_i > T_m$, the dissociation of some of the dislocations into free disclinations destroys the orientational symmetry. Now, the fluid shows ordinary short-range rotational and positional order as it is characteristic of an isotropic liquid.

Following an argument given in [1, 2], $T_m$ and $T_i$ can be estimated using the defect interaction Hamiltonian $H_d$ between a pair of disclinations ($d = \text{disc}$) and a pair of dislocations ($d = \text{disl}$) which for both defect pairs and at large distances goes like $H_d \sim c_d \log r$ with the dimensionless strength parameter $c_d$ dependent on the defect type. Defect dissociation is completed at a temperature where the thermally averaged pair distance $\langle r^2 \rangle$ diverges. Evaluating this expression for $H_d$ one generally finds divergence if $c_d = 4$. The unbinding condition $c_d = 4$ translates into $\lim_{T \to T_i} \beta \xi_b(T) a_0^2 = 16\pi$ for dislocation pairs ($\beta = 1/k_B T$; $a_0$ is lattice spacing) and into $\lim_{T \to T_i} \beta F_A(T) = 72/\pi$ for disclination pairs, where $K$ is the Young’s modulus of the crystal. Connecting thus the defect pair unbinding condition to the two transition temperatures $T_i$ and $T_m$, two expressions are obtained that summarize the microscopic explanation of the KTHNY theory for two-stage melting.

In this Letter we study the temperature-dependence of Frank’s constant of a 2D system in the hexatic phase. We first determine the hexatic ↔ isotropic fluid transition temperature $T_i$ and then check if Frank’s constant takes the value $72/\pi$ at $T_i$, thus testing the KTHNY theory and its prediction that disclination unbinding occurs at $T_i$. In addition, we analyze the divergence behavior of the orientational correlation length at $T_i$ and of Frank’s constant at $T_m$.

Different theoretical approaches invoking grain boundary induced melting [4] or condensation of geometrical defects [5, 6] suggest one first order transition. However some simulations for Lennard-Jones systems indicate the hexatic phase to be metastable [9, 10]. The transition in hard-core systems seem to be first-order probably due to finite-size effects [11]. Simulations with long-range dipole-dipole interaction clearly show second order behavior [12]. Experimental evidence for the hexatic phase has been demonstrated for colloidal systems [14, 15, 16, 17, 18, 19], in block copolymer films [20, 21], as well as for magnetic bubble arrays and macroscopic granular or atomic systems [22, 23, 24, 25, 26]. Still the order of the transitions is seen to be inconsistent. The observation of a phase equilibrium isotropic/hexatic [17, 21] and hexatic/crystalline [17] indicates two first order transitions. In our system we find two continuous transitions.

The experimental setup is essentially the same as in [27]. Spherical and super-paramagnetic colloids (diameter $d = 4.5 \mu m$) are confined by gravity to a water/air interface formed by a water drop suspended by surface tension in a top sealed cylindrical hole of a glass plate. The field of view has a size of $835 \times 620 \mu m^2$ containing typically up to $3 \times 10^5$ colloids (out of $3 \times 10^5$ of the whole sample). A magnetic field $\vec{H}$ is applied perpendicular to the air/water interface inducing in each particle a magnetic moment $\vec{M} = \chi \vec{H}$. This leads to a repulsive dipole-dipole pair-interaction with the dimensionless interaction strength given by $\Gamma = \beta (\mu_0/4\pi) (\chi H)^2 (\pi \rho)^{3/2}$. Here $\chi$ is the susceptibility per colloid while $\rho$ is the 2d particle density and the average particle distance is $a = 1/\sqrt{\pi}$. The interaction strength can be externally controlled by means of the magnetic field $H$; it can be interpreted as an inverse temperature and is the only parameter controlling the phase behavior of the system. For each $\Gamma$ the coordinates of the colloids are recorded.
via video-microscopy (resolution of particle position $dr = 100$ nm) and digital image processing over a period of 1–2 h using a frame rate of 250 ms.

To set the stage we first visualize in Fig. 1 the three phases and their symmetries by plotting the structure factor

$$S(\vec{q}) = \frac{1}{N} \left\langle \sum_{\alpha, \alpha'} e^{-i\vec{q}(\vec{r}_{\alpha} - \vec{r}_{\alpha'})} \right\rangle,$$

as calculated from the positional data of the colloids for three different temperatures. Here, $\alpha, \alpha'$ runs over all $N$ particles in the field of view while $\langle \rangle$ denote the time average over 700 configurations. In the liquid phase, concentric rings appear having radii that can be connected to typical inter-particle distances. The hexatic phase, on the other hand, is characterized by six segments of a ring which arise due to the quasi long-range orientational order of the six-fold director [28]. In the crystalline phase the Bragg peaks of a hexagonal crystal show up with a finite width that is due to the quasi long-range character of the translational order.

To quantify the six-fold orientational symmetry the bond-order correlation function

$$G_6(r) = \langle \psi(\vec{r})\psi^*(\vec{0}) \rangle,$$

is calculated with $\psi(\vec{r}) = \frac{1}{N_j} \sum_{j} e^{i\theta_{ij}(\vec{r})}$. Here the sum runs over the $N_j$ next neighbors of the particle $i$ at position $\vec{r}$ and $\theta_{ij}(\vec{r})$ is the angle between a fixed reference axis and the bond of the particle $i$ and its neighbor $j$. $\langle \rangle$ here denotes not only the ensemble average which is taken over all $N(N-1)/2$ particle-pair distances for each configuration (resolution $dr = 100$ nm) but also the time average over 70 statistically independent configurations.

KTHNY theory predicts that

$$\lim_{r \to \infty} G_6(r) \neq 0$$

crystal: long range order

$$G_6(r) \sim r^{-\eta_6}$$

hexatic: quasi long range

$$G_6(r) \sim e^{-r/\xi_6}$$

isotropic: short range

where $\eta_6 < 1/4$ and takes the value $1/4$ right at $T = T_i$. All three regimes can be easily distinguished in Fig. 2 showing $G_6(r)$ for a few representative temperatures. Note, that $G_6(0)$ is not normalized to 1.

We next fit $G_6(r)$ to $r^{-\eta_6}$ and $e^{-r/\xi_6}$ to extract $\eta_6$ and $\xi_6$. The fits are performed for radii $r/a \in \{0..20\}$ [29]. To check for the characteristic of the orientational correlation function, the ratio of the reduced chi-square

$$\chi^2 = \frac{\sum_{i} \left( \frac{G_6(r_i)^{\text{fit}} - G_6(r_i)^{\text{exp}}}{\sigma_{G_6(r_i)}} \right)^2}{\degofr}$$

K

FIG. 1: Structure factor $S(\vec{q})$ of our colloidal system at three different inverse temperatures $\Gamma$ corresponding to the isotropic liquid ($\Gamma = 52.4$), the hexatic phase ($\Gamma = 59.6$) and the crystalline ($\Gamma = 61.0$) phase. The central cross is an artifact of the Fourier-transformation.

FIG. 2: Orientational correlation function $G_6(r)$ as function of the inverse temperature $\Gamma$ in a log-log plot. From top to bottom: Three curves for the crystalline phase showing the long-range orientational order ($\lim_{r \to \infty} G_6(r) \neq 0$), two curves showing the quasi long-range order of the hexatic phase ($G_6(r) \sim r^{-\eta_6(\Gamma)}$) and three curves showing the short-range order typical of the isotropic liquid ($G_6(r) \sim e^{-r/\xi_6(\Gamma)}$).
χ² goodness-of-fit statistic of the algebraic (χ²_{alg}) and exponential (χ²_{exp}) fit is shown in Fig. 3 as a function of Γ for three different measurements. For melting, a crystal free of dislocations was grown at high Γ and then Γ was reduced in small steps. For each temperature step the system was equilibrated 1/2 h before data acquisition started. This was done at different densities: melt_1 with average particle distance of a = 11.8 µm and melt_2 with a = 14.8 µm containing 3200 respectively 2000 particles in the field of view. The measurement denoted freeze in Fig. 4 (a = 11.8 µm) started in the isotropic liquid phase and Γ was increased with an equilibration time of 1 h between the steps. For χ²_{alg}/χ²_{exp} > 1 an exponential decay fits better than the algebraic and vice versa for χ²_{alg}/χ²_{exp} < 1. We observe in Fig. 3 that the change in the characteristic appears at Γ_i = 57.5 ± 0.5. This value is the temperature of the hexatic ↔ isotropic liquid transition.

In the vicinity of the phase transition, approaching Γ_i from the isotropic liquid the orientational correlation length ξ_i should diverge as

$$\xi_i(\Gamma) \sim \exp \left( \frac{b}{1/\Gamma - 1/\Gamma_i} \right),$$  \(\text{Eq. 3}\)

with b a constant and ν = 1/2. This behavior is observed in Fig. 4a. ξ_i indeed increases dramatically near Γ_i = 57.5 ± 0.5 irrespective of whether the system is heated or cooled. Before discussing this feature we first address the finite size effect. To this end, we have computed G₆(r) and ξ_i for subsystems of different size ranging from 720 × 515 µm², 615 × 405 µm², 505 × 300 µm², 400 × 190 µm² to 390 × 80 µm². The resulting data-points are plotted as triangles in Fig. 4 and belong to the black filled squares which they converge to. No finite size effect is found for Γ < 56, but a considerable one at Γ = 56.9 close to Γ_i where we obviously need the full field of view to capture the characteristic of the divergence. At Γ = 58.0 there is a huge finite size effect indicating that ξ_i is much larger than the field of view. However, inside the hexatic phase, ξ_i is no longer well defined as the decay is algebraic. We fit our data to eq. 3 in the range 49 < Γ < 57.5 and find the critical exponent ν = 0.5 ± 0.03 and Γ_i = 58.9 ± 1.1, a value which due to the finite-size effect is slightly larger than Γ_i obtained from Fig. 3.

The exponent η_i is related to Frank’s constant F_A as

$$\eta_i(\Gamma) = \frac{18k_B T}{\pi F_A(\Gamma)}.$$  \(\text{Eq. 4}\)

So the critical exponent η_i(Γ_i) = 1/4 corresponds to βF_A(Γ_i) = 72/π at the hexatic ↔ isotropic liquid transition. This quantity is plotted in Fig. 4b. Indeed, F_A crosses the value 72/π at Γ_i = 57.5 ± 0.5 exactly at that temperature which in Fig. 4 has been independently determined to

![FIG. 4: Correlation length ξ_i (a) and Frank constant F_A (b) as a function of the inverse temperature. ξ_i diverges at Γ_i and F_A at Γ_m. In between the system shows hexatic symmetry. The solid lines are fits to eq. 3 and 4, resulting in critical exponents ν = 0.5 ± 0.03 and η_i = 0.35 ± 0.02 respectively. Triangles are shifted by 0.1 Γ for clarity.](image-url)
be the transition temperature $T_{\Gamma}$. For $\Gamma < \Gamma_1$, $F_A$ should jump to zero which is not completely reproduced. We note that since $\eta_0$ is not well defined in the isotropic fluid, it becomes problematic to extract $F_A$ from eqn. 4 below $\Gamma_1$. At $\Gamma_m$, at the hexatic $\rightarrow$ crystalline transition, $F_A$ must diverge which indeed it does. This divergence can be identified with the divergence of the square of the translational correlation length $\xi_+^2$,

$$F_A(\Gamma)/k_B T \sim \xi_+^2 \sim \exp \left( \frac{2c}{|1/\Gamma - 1/\Gamma_m|^\nu} \right),$$

where $c$ is again a constant and $\nu = 0.36963$. Fitting the values of $F_A$ to the expression in eqn. 4 in the range $57.5 < \Gamma < 61$ we obtain $\nu = 0.35 \pm 0.02$ and $\Gamma_m = 61.3 \pm 0.4$ as an upper threshold. Again triangles represent evaluation of our data in sub-windows of variable size (same sizes as above). The finite size effect for $\Gamma = 57.0$ is negligible. Close to $\Gamma_m$ it increases but the values saturates for $\Gamma = 59.1$ and $\Gamma = 60.8$ and remain within the error-bars for the biggest sub-windows.

In conclusion, we have checked quantitatively the change of quasi-long-range to short-range orientational order and extracted the correlation length $\xi_6$ in the isotropic fluid and Frank’s constant $F_A$ in the hexatic phase from trajectories of a 2d colloidal system. We find a hexatic $\leftrightarrow$ isotropic liquid transition at $\Gamma_1 = 57.5 \pm 0.5$. Three observations support this result: (i) the change of the distance dependence of $G_6(r)$ (Fig. 3), (ii) the condition $F_A(\Gamma_i) = 72/\pi$ for Frank’s constant and (iii) the divergence of $\xi_6$. For the transition hexatic $\leftrightarrow$ crystal $F_A$ diverges at $\Gamma_m$. Both divergencies (extracted from just one correlation function) lead to critical exponents that are in good agreement with the KTHNY-theory. The measurements for melting and freezing support each other; so we may conclude that there is no hysteresis effect of the phase-transitions. At the two transitions, the order parameters are observed to change continuously (within the resolution of $\Gamma \propto 1/T$); no indication of a phase-separation (as for example strong fluctuations of the order parameters) has been found as has been reported by \cite{17, 21}. So we believe that in our system - having a well-defined, purely repulsive pair-potential and a confinement to 2D that is free of any surface roughness - the transitions are second order.

In \cite{31, 32} we verified that the Young’s modulus becomes $16\pi$ at $T_m$. We have now checked that $F_A$ takes the value $72/\pi$ at $T_1$. These two findings together confirm the two-stage KTHNY melting scenario with its underlying microscopic picture of breaking the translational symmetry by dislocation-pair- and orientational symmetry by disclination-pair-unbinding.

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\item The segments will merge to rings, if the systems size tends towards infinity.
\item The upper value is motivated by the maximum value of the histogram of distances and $r/a = 0$ is excluded in the algebraic case to avoid the singularity. The histogram over distances is used as statistical weight of the fit-function taking into account the different frequency of occurrence of the data-points in the minima and maxima of $G_6(r)$.
\item We indeed do see a local clustering of dislocations as already noted by \cite{14, 15} in the hexatic phase close to $\Gamma_1$ (which is not too surprising for dislocations with finite density having an attractive interaction) but this averages out in $G_6$ if the field of view is big enough.
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