Specific heat in two-dimensional melting

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We report the specific heat $C_N$ around the melting transition(s) of micrometer-sized superparamagnetic particles confined in two dimensions, calculated from fluctuations of positions and internal energy, and corresponding Monte Carlo simulations. Since colloidal systems provide single particle resolution, they offer the unique possibility to compare the experimental temperatures of peak position of $C_N(T)$ and symmetry breaking, respectively. While order parameter correlation functions confirm the Kosterlitz-Thouless-Halperin-Nelson-Young melting scenario where translational and orientational order symmetries are broken at different temperatures with an intermediate so called hexatic phase, we observe a single peak of the specific heat within the hexatic phase, with excellent agreement between experiment and simulation. Thus, the peak is not associated with broken symmetries but can be explained with the total defect density, which correlates with the maximum increase of isolated dislocations. The absence of a latent heat strongly supports the continuous character of both transitions.

KTHNY theory, a microscopic melting scenario for two-dimensional solids developed by Kosterlitz, Thouless, Halperin, Nelson, and Young [1–3], motivated extended analytic theories [4–8], numerous experimental studies [9–21] and simulations [22–44] to clarify the detailed melting mechanism and the order of phase transitions in 2D. The KTHNY melting is mediated by the dissociation of two kinds of topological defects, dislocations and disclinations. This scenario predicts two continuous phase transitions, where translational and orientational order is broken at different temperatures by the unbinding of pairs of dislocations and disclinations. In a triangular lattice, a disclination is a five- or seven-fold oriented site and a dislocation consists of oppositely charged disclinations, namely a pair of bound five- and sevenfold sites. Both types of topological defects can be treated as a Coulomb gas obeying a logarithmic interaction potential in two dimensions [45]. For the dislocation unbinding, a vector charge description becomes necessary due to the directional character of the defects, alongside a renormalization analysis accounting for their self-screening whereas a scalar charged gas of defects describes the disclination unbinding. Several experiments [12, 15, 18, 22] and simulations [25–44] clearly show the existence of the hexatic phase, but some studies additionally report first order characteristics [16, 35, 40] versus continuous order [18, 19, 22]. Continuous and first-order characteristics have been observed within the same model, either differently for both KTHNY transitions [11] or preempted by a single first-order transition when the pair potential contains two length scales [12, 43]. It is suggested that the nature and number of transitions in 2D either depends on the dislocation core energy [6, 34] (which might implicitly depend on the particle pair interaction being short- or long-range) or the angular stiffness of the crystal being lower than a critical value [5].

While first-order phase transitions are known to show a discontinuity in the free energy and a $\delta$-like divergence in the specific heat at the transition temperature, the defect free energy and specific heat of the two-dimensional Coulomb gas have only discontinuities and no divergence for both transitions [2, 46, 47]. Thus, this feature can be used to identify the order of the transition. On the experimental side, there have been only calorimetric measurements so far, e.g. on atomic monolayers on graphite which show different results concerning the number of peaks in the specific heat, their position and magnitude [18, 19]. These experiments lack a precise determination of symmetry switching points, leaving the correlation to occurring phase transitions still elusive. Simulations of interacting dislocations show that for small dislocation core energies, the specific heat has a large discontinuity consistent with a first-order transition while for large core energies, a single moderate peak was observed, pointing to a continuous character [34]. Laplacian roughening models [26] which are dual to 2D melting and Lennard-Jones systems [33] display one non-divergent peak along the two-step KTHNY scenario whereas a non-ideal Yukawa system shows two singularities associated with two transitions [53]. However, in contrast to the atomic or molecular systems mentioned above, in colloidal systems, microscopy of individual particles allows a direct comparison between specific heat and symmetry switching points.

In this work, we present a melting study of superparamagnetic colloidal spheres confined in two dimensions and corresponding Monte Carlo simulations. The precise knowledge of the particle pair potential together with high precision single particle resolution and long term stability of the sample allows us to measure an anomaly in the specific heat in a colloidal system and compare it with simulations. Using order parameter correlation
functions, we confirm in the experiments and simulations the two step KTHNY melting scenario from a solid phase through a hexatic fluid to an isotropic fluid, yet we find a single peak in the specific heat. Remarkably, this peak does not coincide with either transition temperature but lies within the hexatic phase. We show that it is connected to a sharp increase of the number of topological defects associated with a progressive unbinding of dislocation pairs on heating above the solid-hexatic transition temperature. Further, we do not find an additional peak correlated to the disclination unbinding which might not be resolvable due to the very small concentration of single disclinations < 5% in the background of a large overall defect density at the hexatic-isotropic transition.

The experimental system consists of an ensemble of spherical superparamagnetic polystyrene beads, with diameter \(d = 4.5 \, \mu m\) and mass density \(1.7 \, kg/dm^3\), dissolved and sterically stabilized with sodium dodecyl sulfate in water. The colloidal suspension is sealed in a millimeter sized glass cell where sedimentation leads to the formation of a monolayer (> \(10^5\) particles) on the bottom glass plate. The whole sample is under steady control and stable for more than 20 months which allows sufficient equilibration times and provides ideal sample conditions, e.g. vanishing density gradients or drifts. The ensemble is kept at room temperature and a highly homogeneous, finely tunable external magnetic field \(H\) perpendicular to the colloidal layer induces a repulsive dipole-dipole interaction between the particles. This is quantified by the inverse system temperature that is defined as the ratio of the mean magnetic energy between two neighboring particles \(E_{\text{mag}}\) and the thermal energy,

\[
\Gamma = \frac{E_{\text{mag}}}{k_B T} = \frac{\mu_0 (\pi n)^{3/2} (\chi H)^2}{4\pi k_B T}
\]

where \(n = 1/a_0^3\) is the 2D particle density with the mean particle distance \(a_0\), and \(\chi\) the magnetic susceptibility of the beads. We assume an error of \(\Gamma \pm 0.5\) due to density and room temperature fluctuations during the measurements. After changing the interaction strength, the system is equilibrated for at least 24 hours before \(\approx 3000\) particles are monitored and tracked by video microscopy. Previous studies of this system have shown excellent agreement with the KTHNY melting scenario [13–15, 18, 22, 23].

In addition, standard Monte Carlo simulations are run in the NVT ensemble, with \(N = 2500\) particles interacting with a dipolar potential: \(\beta V(r) = \Gamma/r^3\), with distances measured in units of \(\pi n)^{-1/2}\). The interactions are cut off at \(R_{\text{cut}} = 9a_0\), which is large enough to avoid effects from the truncation [29]. The system is simulated in a rectangular box with a size ratio \(2 : \sqrt{3}\) and a (hard disc) 2D area fraction \(\phi = 0.07\) to mimic the experimental conditions. Cycles of increasing \(\Gamma\) from the fluid to the crystal, and subsequent decrease to the fluid again were used to confirm that there is no hysteresis within our \(\Gamma\)-resolution.

To determine the respective symmetry breaking temperatures, we analyze the spatial correlation function \(g_6(r) = \langle \psi_6^* (r) \psi_6(0) \rangle\) at different system temperatures \(\Gamma\) for experiment (a) and simulation (b). The data are plotted on a log-log scale in reduced coordinates, where \(a_0 = (n)^{-1/2}\) is the mean particle distance in the respective system. The decay behavior of \(g_6(r)\) has distinct characteristics in the solid (constant), the hexatic liquid (algebraic decay) and in the isotropic liquid (exponential decay). An algebraic exponent of \(-1/4\) marks the hexatic-isotropic transition [2].

FIG. 1. (Color online) Spatial orientational correlation \(g_6(r) = \langle \psi_6^* (r) \psi_6(0) \rangle\) at different system temperatures \(\Gamma\) for experiment (a) and simulation (b). The data are plotted on a log-log scale in reduced coordinates, where \(a_0 = (n)^{-1/2}\) is the mean particle distance in the respective system. The decay behavior of \(g_6(r)\) has distinct characteristics in the solid (constant), the hexatic liquid (algebraic decay) and in the isotropic liquid (exponential decay). An algebraic exponent of \(-1/4\) marks the hexatic-isotropic transition [2].
hexatic transition is more difficult to locate by $g_0(r)$. These values are extracted from Fig. 1. Since the solid-hexatic phase is affected by the system size which might explain the different melting temperatures in experiment and simulation, we present a finite-size analysis of the translational order parameter in the supplemental material confirming these values. It is well known that the width of the hexatic phase is affected by the system size which might explain the different melting temperatures in experiment and simulation.

According to the KTHNY theory, the specific heat at constant pressure $C_p$ behaves as $\xi^{-2}$ for both transitions, with the orientational correlation length $\xi$ from the isotropic fluid to the hexatic phase at $T_i$, and the translational correlation length $\xi_T$ at the transition from the hexatic to the solid phase at $T_m$, respectively [2, 47]. For the unbinding of dislocation pairs e.g. it reads $C_p \sim \exp (-b/|T - T_m|^{\nu})$, where $b$ is a constant and $\nu = 0.36963$ is the critical exponent from renormalization group theory [2, 3]. At the transition points, the specific heat undergoes only an essential singularity and no divergence. However, a system might show a weak peak above $T_m$ (below $\Gamma_M$) caused by a successive unbinding of dislocation pairs while position, width and height of the peak strongly depend on the model [46]. The specific heat $c_N$ per particle and at constant volume can be calculated via the derivative of the internal energy with respect to temperature (inverse $\Gamma$) or from energy fluctuations (see supplemental material),

$$c_N = \frac{1}{N} \frac{\partial \langle E \rangle}{\partial T} = -\frac{k_B \Gamma^2}{N} \frac{d(\langle E \rangle / \Gamma)}{dT} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{N k_B T^2} \quad (2)$$

where $E$ is the total internal energy of the $N$-particle system and the brackets denote a time average [57]. The results are shown in Fig. 2 [4] for the energy summation, the cutoff is set to $15a_0$ for the experiment and $9a_0$ for the simulation (further discussion of the cutoff dependency in the supplemental material). Within the simulations, the calculation of $c_N$ from the derivative of the energy (Fig. 2a) and its fluctuations (Fig. 2b) agree almost quantitatively and show a single peak at $\Gamma_i^{exp} = 69.25$ due to a single change of slope in the energy (inset). In the solid phase we observe a value for $c_N$ in agreement with the Dulong-Petit law that predicts the heat capacity of a two-dimensional monatomic crystal in the harmonic approximation, $C_V = 2Nk_B$ (horizontal line in Fig. 2).

For the experiments, the calculation from the derivative of the energy is too noisy (see supplemental material), and a reliable value can be obtained only from the energy fluctuations (see supplemental material),

$\gamma$-steps, verifying the stability of the orientational quasi-long-range ordered hexatic fluid. For the solid-hexatic transition, we find the (inverse) transition temperatures $\Gamma_i^{exp} \approx 70.3$ and $\Gamma_i^{sim} = 69.25$, for the hexatic-isotropic transition we find $\Gamma_i^{exp} \approx 67.3$ and $\Gamma_i^{sim} = 68.25$ [5-4]. These values are extracted from Fig. 1. Since the solid-hexatic transition is more difficult to locate by $g_0(r)$, we present a finite-size analysis of the translational order parameter in the supplemental material confirming these values. It is well known that the width of the hexatic phase is affected by the system size which might explain the different melting temperatures in experiment and simulation.

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fluctuations (Fig. 2b). We find again a single marginal peak at $\Gamma_N^{exp} \approx 68.4$, very close to the value of the simulations. (Note, however, the different scale for experiment and simulation of $c_N$. As shown in the supplemental material, increased peak height and baseline can be attributed to additional density fluctuations picked up in the experiment which, nevertheless, do not affect the peak position.) The (inverse) temperature $\Gamma_N^{exp}$ of the specific heat peak lies within the hexatic phase below the melting temperature $\Gamma_m$ from solid to hexatic ($\Gamma_N^{exp} < \Gamma_m$ or $T_N^{exp} > T_m$), both in the experiments and simulations. A second peak is not detectable unexpectedly, given the picture of the KTHNY theory which predicts two specific heat discontinuities (eventually marginal) but located at the transition temperatures $\Gamma^c_N$. Already in the 1950's, a shift of the specific heat peak in 2D systems has been reported for quantum fluids like $^4$He films, whose position is found at higher temperatures with respect to the onset of superfluidity ($\Gamma_N^{exp} \approx 0.5$). The authors put this on the increasing importance of surface excitations with reduced film thickness. De Gennes (comment in [59]) pointed out that the temperature onset of superfluidity might be caused by short-range-order effects which become important in one- and two-dimensional salts [60, 61]. Later, Kosterlitz and Thouless considered this effect for the neutral superfluid in 2D [11]. Berker and Nelson gave analytic evidence for a specific heat shift for superfluid films of $^3$He-$^4$He mixtures, and explained this with the gradual unbinding of vortex pairs with increasing temperature while the maximum in the specific heat occurs when the mean separation of vortex pairs is comparable with the vortex core size $\xi_0$. A shift of the specific heat peak to higher temperatures has also been reported in simulations of planar models [63-65] and 2D solids [26, 33, 34].

To explain the shift in the specific heat singularity, we investigate local quantities, in particular, the defect distributions. We analyzed the total number density $\rho$ for all defects (not sixfold coordinated sites, Fig. 2a) as well as the density of isolated dislocations (one dislocation is counted twice, containing two defects) and disclinations, for experiment (Fig. 2b) and simulation (Fig. 2d). We find that in the region of the specific heat peak the overall defect density $\rho$ undergoes a significant increase from $\approx 5\%$ to $\approx 20\%$. Energy costs which become apparent in the specific heat should directly be connected to the creation and dissociation of defects, and should peak when the increase of defects is large which is not necessarily at $\Gamma_m$. This can clearly be seen from the simulations where the sharpest increase of $\rho$ is exactly at the peak position $\Gamma_N^{sim} = 68.5$ ($\Delta \rho \approx 0.1$). With the total defect increase $\Delta N_{def} \approx 220$ at this interaction strength, we can make a rough estimate for the simulation peak height via the dislocation core energy in the hexatic phase $E_c \approx 5.5k_B T$ [60] observing $c_N \approx 30k_B$ (more detailed in the supplemental material). The defect density in the experiment on the other hand, shows a rather broad increase. It must be noted that this includes all kinds of defects, including cluster conformatations which earliest occur in the hexatic phase. Such clustering is beyond KTHNY theory which assumes a dilute gas of defects but is quite natural due to the attractive interaction of the defects. Implicitly, we can extract from the larger specific heat peak height estimated by the total defect increase, compared to the derivative or the fluctuation of the internal energy, that such clustered dislocations have a significantly reduced core energy $E_c < 5.5k_B T$. We checked that such cluster consists only of an equal amount of five- and seven-folded particles in the hexatic phase: clusters are dislocation-cluster (with small core energy) but not dislocation-disclination cluster. The latter, with unequal number of five- and seven-folded particles are only observable quite deep in the isotropic phase (see supplemental material). Thus, we focus on the isolated topological defects that drive the transitions within KTHNY theory: isolated disclinations show their sharpest increase in density below $\Gamma_m$ but very close to the peak position ($\Gamma_N^{exp} \approx 68.2$ for the experiment and $\Gamma_N^{sim} \approx 68.4$ for the simulation). On the other hand, the increase of isolated disclinations is as well shifted in respect to the hexatic-isotropic transition, but only marginally. We do not observe an indication of a second specific heat peak corresponding to this unbinding because this implies an increase of less than $5\%$ in the background of a large overall defect density (see Fig. 2b) and a negligible increase of the energy: a rough estimate of the peak height as above but due to disclination unbinding, disclination core energy ($\approx 5k_B T$) times number of unbinding disclinations, gives $\approx 1k_B$.

Using a colloidal model system and Monte Carlo simulations, we measure the specific heat via fluctuations of the internal energy. We observe a single peak in the specific heat above the solid-hexatic transition ($\Gamma_N > \Gamma_m$), although melting in 2D shows two phase transitions at distinct temperatures. The peak in $c_N$ arises when the change in the defect density is largest, what appears within the hexatic phase and not directly at $\Gamma_m$. Whereas only a few defects are needed to destroy the given order, their cost in energy is small at $\Gamma_m$ (and $T_1$). A second peak in $c_N$ associated to disclination unbinding from dislocations is not detectable since their number density stays small compared to the overall defect density even deep in the isotropic fluid phase. We can further conclude that the absence of a latent heat strongly supports the continuous character of both transitions.

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Specific heat in two-dimensional melting: supplemental material

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The supplemental material contains further criteria for the melting temperature, details about the analysis of the specific heat and a comment about the interaction parameter Γ.

FINITE SIZE ANALYSIS OF THE TRANSLATIONAL ORDER

We have run simulations of the system with different sizes to check for finite size effects (periodic boundary conditions are used in all cases with a rectangular box). The simulations have shown that the transition points are almost unaffected, within the numerical uncertainties, and the peak of the specific heat reduces its height and widens, but does not move in Γ. This can be rationalized considering that long-wavelength fluctuations are absent in smaller systems, reducing the fluctuations. This result confirms the finding from the sub-box analysis of data with a fixed size can be used to obtain the transition points from fluid to hexatic, and from hexatic to crystal phases, independent from the analysis presented in the manuscript. Bagchi et al. proposed to use global order parameters calculated in subsystems with different lengths, \( L \), which scales with different exponents in the isotropic fluid, hexatic fluid and crystal phases [1]. We study the scaling of the translational order parameter in the simulations, \( \Psi_T \), to obtain an estimation of the hexatic-crystal transition, independent from the orientational correlation function, as shown in Fig. 1 of the manuscript. \( \Psi_T \) is defined as

\[
\Psi_T = \langle \frac{1}{N} \sum_k \exp \{i \mathbf{q} r_k \} \rangle^2,
\]

where \( \mathbf{q} \) is the wave-vector that maximizes the value the of \( \Psi_T \) (the same value of \( \mathbf{q} \) is used for all states) and the summation runs over all particles in the system. The scaling of \( \Psi_T \) is presented in Fig. 1 for different states. It is clearly seen in the figure the sharp change from the behaviour of the liquid and hexatic states, with \( \psi_T \sim L^{-2} \), to the crystal, where \( \psi_T \sim L^{-5/3} \), with \( 0 \leq \eta_T \leq 1/3 \), confirming the theoretical expectations, and also the transition point obtained from the analysis in the manuscript.

ENERGY AND SPECIFIC HEAT

The specific heat at constant volume

\[
C_V = \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_V = -k_B \beta^2 \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_V,
\]

(1)

\[
= -k_B \beta^2 \left( \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \right)_V = k_B \beta^2 \left( \frac{\partial^2 (\log Z)}{\partial \beta^2} \right)_V
\]

with the partition function \( Z \) and \( \beta = 1/k_B T \) can be given in terms of the energy fluctuations [2],

\[
\langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2 (\log Z)}{\partial \beta^2}
\]

(2)

leading to

\[
C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}.
\]

(3)

Since we have a purely repulsive system (with a single control parameter Γ) in which pressure and volume can not be changed independently, we subscript the specific heat per particle as

\[
c_{N} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{N k_B T^2}.
\]

(4)

To demonstrate the equivalent energy scale in experiment and simulation, we show the average potential energy per particle and thermal energy

\[
\langle E \rangle / N k_B T
\]

as a function of inverse temperature in Fig. 2. The difference between simulation and experiment is about 5% which we attribute to a demagnetization of particles in experiment due to the dipolar field of the neighboring particles which effectively reduces the outer field.
To be comparable, the cutoff value for the lattice summation is set to $9a_0$ for both experiment and simulation where $a_0$ is the average particle distance. The inset shows that there is only a single change of slope at $\Gamma = 68$ to $\Gamma = 68.5$ which leads to a single peak in the specific heat via the derivative approach (Fig. 3). The derivative of the internal energy (blue straight line in Fig. 3) exactly reproduces the peak in specific heat calculated from energy fluctuations for the simulations (blue dotted line in Fig. 3). The slope of the curves is the same but the data in experiment scatter more compared to simulations. This experimental noise is attributed e.g. to fluctuations since the number of particles is not conserved exactly in the field of view and tiny density fluctuations snap through. Taking the derivative to calculate the specific heat per particle, any peak due to the phase transition(s) is beyond experimental resolution (Fig. 3 filled squares). Here, we would just like to show that the 'baseline' of the noise in $c_N$ from experiment is comparable to the simulation data and agrees in the crystal side with the Dulong-Petit value.

**PEAK AND BASELINE LEVEL IN THE EXPERIMENT**

In a system where a melting occurs due to an attractive interaction potential, energy fluctuations become large around the transition since both phases have typically a significant difference in density. For our two-dimensional system with a repulsive interaction potential, there is no change in density at all between the fluid and the solid phase when particle number is conserved. Just the mean particle distance is larger in the solid due to ordering which minimizes the potential energy. This way the peak in the specific heat is not caused by density fluctuations but by fluctuations in local order and structural rearrangements. In the given soft matter system, any fluctuations due to room temperature or mechanical vibrations lead directly to density fluctuations entering the internal energy beyond $k_BT$. Such perturbations increase the scale of energy fluctuations (right axis of Fig. 2b in the main manuscript) and unlike in simulations and the derivative approach, Dulong-Petit law is not recovered in the crystal. Nevertheless the susceptibility to perturbations is maximized at the phase transition (dislocation unbinding) which affects the peak height in the specific heat but the peak position at $\Gamma_{cN} = 68.5$ is not affected (Fig. 2b of the main manuscript).

**CUTOFF DEPENDENCY**

The energy per particle is calculated up to a cutoff distance. In experiment, where we do not have periodic boundary conditions, this cutoff value reduces the effective field of view for particles where the sum over neighbors can be taken within the same cutoff value. A large cutoff value increases the statistics for every particle whereas a small cutoff value increases the statistics of the number of particles. Fig. 4 shows the specific heat per particle as a function of $\Gamma$ for different cutoff values of $5a_0$, $9a_0$ (as used in simulation), $15a_0$, and $20a_0$. In Fig. 2b of the main manuscript we took a cutoff value of $15a_0$. If the cutoff value is too small, the peak vanishes.

**FIG. 2.** Mean energy $\langle E \rangle / Nk_B T$ (per particle and thermal energy) for the experiment (filled symbols) and the simulation (open symbols). The inset shows a magnification for the simulation in the region of interest.

**FIG. 3.** Specific heat from energy fluctuations (dashed line, simulation) and derivative of internal energy (solid lines, simulation and experiment).
FIG. 4. Experimental specific heat from energy fluctuations, with the energy calculated with different cutoffs, as labeled. Note that the peak decreases with decreasing interaction range.

SPECIFIC HEAT PEAK AND DEFECT CORE ENERGY

The peak height of the specific heat in Fig. 2a of the main manuscript is about $20 k_B$. A rough estimate for the peak height is given by the number of dislocations which dissociate in a small temperature range times the core energy of the dislocations. The core energy of isolated dislocations is approximately $5.5 k_B T$ in the hexatic phase above $T_m$ [3]. We note the change of the overall defect density $\rho$. Between $\Gamma = 68.5$ to $\Gamma = 68$ the change in defect density is $\Delta \rho \approx 0.1$ which corresponds to a change in defect number of $\Delta N_{def} \approx 200$. We then observe

$$c_N \approx \frac{5.5 k_B T}{2 N} \frac{d N_{def}}{d \Gamma} = \frac{5.5 k_B \Gamma}{2 N} \frac{d N_{def}}{d \Gamma} \approx 30 k_B$$

(The factor of $1/2$ comes due to the fact that a dislocation consists of two defects.) This value is already larger than the measured one which implies that the core energy is overestimated.

Fig 5 shows a snapshot for the experimental system at $\Gamma = 68.4$ where the specific heat peaks. Particles with six nearest neighbors are marked with open circles, fivefold coordinated sites with green and sevenfold coordinated sites with orange filled circles. Isolated dislocations which count in the analysis of Fig. 2c,d in the manuscript are illustrated with smaller black dots (isolated dislocations might be cut by the field of view). Most of the defects are arranged in clusters, only 20% appear as isolated dislocations. This is beyond KTHNY theory where a dilute gas of dislocations is assumed for renormalization procedure. If the defect density increases, the clustering is quite natural since the dislocations as well as the disclinations have an attractive interaction [3]. This implicitly means that the fugazity is locally increased in the cluster or equivalently that the core energy is locally reduced $< 5.5 k_B T$. This behavior has already been observed for geometrical defects like interstitials and vacancies where the fugazity of dislocations is increased locally, too [4]. Note, that all cluster consist of the same number of five- and seven-folded particles and may be interpreted as dislocation cluster. Isolated disclinations or cluster of disclinations (with unequal number of five- and seven-folded particles) are not found in the hexatic phase but in the isotropic phase with the isolated disclinations being less than $5\%$ (Fig 2b of the main manuscript).

Since we know implicitly that the core energy of clustered defects is overestimated we restrict to isolated dislocations in the assessment of the specific heat due to defects. In Fig. 2c and Fig. 2d, a tanh is fitted to the defect densities of experiment and simulations to get a smooth derivative. The peak of the derivative (red curve in Fig 2c,d) gives the contribution of the two distinct species of isolated defects. The peak positions of isolated dislocations is already shifted within the hexatic phase, well separated from the melting temperature $\Gamma_m$. Of
course, all defects contribute to the specific heat: adding clustered dislocations and disclinations shifts the peak to even higher temperatures (lower Γ) but it can not be attributed to the onset of disclination unbinding, since the disclination density times disclination core energy is too small: a rough estimate of the disclination core energy (∼5k_BΓ) times the number of unbinding disclinations (∼1% at Γ = 58 ± 1) gives ∼1k_B.

DETERMINATION OF THE MAGNETIC PARTICLE SUSCEPTIBILITY

To determine the exact interaction strength, the magnetic susceptibility χ has to be measured for every colloidal batch. In [5, 6] this was done via a comparison of the pair correlation function g(r) of the experimental system and by computer simulations from J. M. Mendez-Alcatraz in the isotropic fluid phase. With the given χ, melting was found between 69.5 < Γ_m < 62.5 [7]. In [3, 8–10] melting was found at Γ_m = 60.5 ± 0.5 and the second transition at Γ_i = 57 ± 0.5. The susceptibility was further determined with SQUID measurements being consistent with the previous values but with large error bars. In the present manuscript as well as in [13] the experimental melting transition is found to be at Γ_m = 70.2 ± 0.3 if the magnetic susceptibility is again determined via comparison of pair correlation functions g(r) with simulations of a) J. M. Mendez-Alcatraz [5], b) D. Hajnal [11, 12], and c) T. Kruppa [13] and d) A.M. Puertas independently. However, the transitions temperatures are just scaled with a constant factor compared to previous ones and the agreement in the present manuscript with transition temperatures from simulation is excellent. We attribute the changes to the increased resolution of CCD-cameras and digital image processing compared to those a decade ago.

[1] K. Bagchi, H. C. Andersen, Phys. Rev. Lett. 76, 255 (1995)
[2] S. M. Tan, Fundamentals of Statistical Mechanics, Lecture on Statistical Mechanics, University of Auckland.
[3] C. Eisenmann, U. Gasser, P. Keim, G. Maret, H. H. von Grünberg, Phys. Rev. Lett. 95, 185502 (2005).
[4] David Polster, PhD-thesis: http://nbn-resolving.de/urn:nbn:de:bsz:352-268915
[5] K. Zahn, J. M. Mendez-Alcatraz, G. Maret, Phys. Rev. Lett., 79, 175 (1997)
[6] K. Zahn, R. Lenke, G. Maret, Phys. Rev. Lett. 82, 2721 (1999)
[7] K. Zahn, G. Maret, Phys. Rev. Lett. 85, 3656 (2000)
[8] P. Keim, G. Maret, U. Herz, H. H. von Grünberg, Phys. Rev. Lett. 92, 215504 (2004)
[9] H. H. von Grünberg, P. Keim, K. Zahn, G. Maret, Phys. Rev. Lett. 93, 255703 (2004)
[10] P. Keim, G. Maret, and H. H. von Grünberg, Phys. Rev. E 75, 031402 (2007).
[11] D. Hajnal, J. Brader, R. Schilling, Phys. Rev. E, 80, 021503 (2009)
[12] D. Hajnal, M. Oettel, R. Schilling, Jour. of Non-Cryst. Sol. 357, 302 (2011)
[13] S. Deutschländ, T. Kruppa, H. Löwen, G. Maret, and P. Keim, Phys. Rev. Lett. 111, 098301 (2013)