Soft-disk melting: From liquid-hexatic coexistence to continuous transitions

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The phase diagram of two-dimensional soft disks with repulsive power-law pair interactions $\propto r^{-n}$ is determined using Event-Chain Monte Carlo. The recently established melting scenario for hard disks (corresponding to $n = \infty$) is preserved for finite $n$, and first-order liquid-hexatic and continuous hexatic-solid transitions are identified. The density difference between the coexisting hexatic and liquid is non-monotonous as a function of $n$. For smaller $n$, the coexisting liquid shows extremely long orientational correlations, and positional correlations in the hexatic become extremely short. For $n \lesssim 6$, the liquid-hexatic transition is continuous, with correlations consistent with the KTHNY scenario.

Two-dimensional particle systems with short-range interactions may form solids [1], but cannot acquire long-range positional order [2]. Rather, two-dimensional solids are characterized by long-range orientational and quasi-long-range positional order, so that positional correlation functions decay algebraically. In the liquid phase, orientational and positional order are short-ranged, and the corresponding correlation functions decay exponentially. An intermediate hexatic phase may also exist [3]. It is characterized by short-range positional and quasi-long-range orientational order.

Within the Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY) theory of two-dimensional (2D) melting [3], these two symmetry-breaking transitions arise from the subsequent unbinding of topological defects: In the solid, dislocations are bound in pairs, whereas in the hexatic, free dislocations may exist. The dislocations then decompose into free disclinations which break orientational order and yield the isotropic liquid. Both phase transitions are continuous Kosterlitz-Thouless transitions, although a first-order liquid-hexatic transition remains possible within KTHNY theory. Alternative melting theories propose a conventional first-order liquid-solid transition, without the presence of a hexatic phase [4, 5]. These scenarios commonly involve the condensation of defects into grain boundaries and similar aggregates [6, 8].

Over the decades, it has been extremely difficult to decide, from theory, simulation or experiments, which of the above melting scenarios applied to specific two-dimensional models. It was established only very recently that the fundamental hard-disk model has a continuous solid-hexatic transition but a first-order hexatic-liquid transition [9]. This scenario continues to apply for particles that fluctuate in the third dimension, such as hard spheres confined between parallel plates [10]. A similar scenario was shown to apply for Yukawa particles [11].

Experimentally, evidence for liquid-hexatic coexistence was reported both for sterically stabilized uncharged colloids [12] and for charged colloids [13]. In complex plasmas, grain-boundary melting was found [14]. The KTHNY theory was confirmed experimentally for superparamagnetic colloids [15]. Other two-dimensional systems which melt include electrons pinned at a liquid Helium interface [16], and surface-adsorbed atomic layers [17].

In this paper, we present a systematic computational study of melting in two dimensions for a repulsive inverse power-law pair interaction $U(r) = \varepsilon (\sigma/r)^n$. This family of potentials includes hard disks of diameter $\sigma$ in the limit $n \to \infty$, but also the soft interactions typically found in colloidal particles at intermediate $n$, down to long-range interactions such as dipolar ($n = 3$, [15]) and Coulomb forces ($n = 1$, [16]). We will show below that a large part of the parameter space of $n$, the hard-disk melting scenario with a first-order liquid-hexatic transition is preserved. Around $n \simeq 6$, the system crosses over to the conventional KTHNY scenario with two continu-
uous transitions. The hexatic phase is firmly established for all parameters studied.

The soft-disk interaction sets no energy scale, and we may put $\beta \varepsilon = 1$, where $\beta = 1/k_B T$ is the inverse temperature. The phase diagram only depends on the dimensionless interaction strength $\Gamma = \beta \varepsilon (\pi \phi)^{n/2}$, which is related to the dimensionless density $\phi = \sigma^2 N/V$, used in some of the literature. Length scales can be expressed in terms of the interparticle distance $d = (\pi N/V)^{-1/2}$. In these units, the pair interaction is $\Delta U = \Gamma \times (d/r)^n$.

To accommodate the large correlation lengths inherent in 2D melting, we consider systems of $65 \cdot 10^3$ (65 k), 259 k and 1036 k particles. Event-Chain Monte Carlo (ECMC, [9]), recently parallelized [18] and extended to continuous interactions [19], allows us to equilibrate these large systems. The algorithm relies on cooperative continuous particle displacements (see Fig. 1a, b). For efficiency, we truncate the interaction at $r_c = 1.8 \sigma$, the effective interaction is $\tilde{U}(r) = U(\min(r, r_c))$. This approximation neglects at most $2 \cdot 10^{-3}$ of collisions and preserves the phase diagram (Fig. 1d). ECMC yields the pressure as a zero-cost byproduct [19], which we use to construct the equation of state. Truncating the interaction leads to a reduction of pressure by $\approx 0.5\%$ (Fig. 1h).

For each of the $n$ studied, we clearly identify liquid, hexatic, and solid phases (see Fig. 2a–d). In the liquid, both positional correlations and the correlations of the local orientational order parameter $\psi_6$ (with Voronoi weights [22]) are short-ranged; the latter are visualized in Fig. 2e, f. For large $n$, the equation of state displays a clear Mayer-Wood loop [20] (see Fig. 3h) characteristic of a first-order transition (cf. Ref. [9] for a discussion of phase coexistence in the $NVT$ ensemble). At $n = 64$, the liquid-hexatic coexistence interval is wider in density than for hard disks ($n = \infty$), yet qualitatively equivalent: We observe stripe-shaped coexisting phases at first (see Fig. 2f), and a liquid bubble near the transition to the pure hexatic (Fig. 2g). For smaller $n$, the coexistence interval narrows (see Fig. 2h, i) and finally vanishes around $n \approx 6$, where the transition becomes continuous.

The computational cost of long-ranged interactions due to the transition shifting to higher $\phi$ and the necessity of larger cutoffs presently precludes large simulations at $n < 6$.

The phase in coexistence with the liquid is a hexatic. Since correlation functions are ambiguous in the coexistence region, we consider pure hexatics above the transition. Indeed, we find short-ranged positional correlations (Fig. 3h) while orientational correlations are quasi-long-ranged (see Fig. 4h). The positional correlation length $\xi_p$ can be as large as $100 \sigma$, but we can equilibrate systems of sufficient size to reveal the asymptotic exponential decay of the ensemble-averaged pair correlation function $g(r) \propto \exp(-r/\xi_p)$. The positional correlation length strongly decreases with $n$ as the coexistence interval vanishes, in particular at the coexistence density (see Tab. 1). Around $n \approx 6$, at the transition density, the hexatic loses its governing length scale. Single-configuration pair correlations also confirm that positional order drops from $\xi_p \approx 120$ interparticle distances at $n = 64$ to very few neighbors at $n = 6$ (Fig. 3h).

The analysis of the orientational correlations in the transition region is very instructive. We extract the correlation length $\xi_6$ in the liquid from the asymptotic
exponential decay of the respective correlation function $g_6(r) = \langle \psi_6(r_i) \psi_6(r_j) \delta(r - r_{ij}) \rangle$. The orientational correlation length is large but finite in the pure liquid at coexistence. It increases markedly from $n = 64$ to $n = 6, 8$ (see the lower three curves in Fig. 4b).

At $n = 6$, a minute increase in density changes the orientational order from short-range to quasi-long-range behavior, decaying algebraically with an exponent $\sim -\frac{1}{4}$ (Fig. 4b). This agrees with the KTHNY theory which predicts orientational correlations $\propto r^\eta$ in the hexatic, with $\eta = -\frac{1}{4}$ at the transition. Away from the transition point, and for $n > 6$, the orientational correlation function does not display clear power-law behavior. This is also borne out by the finite-size scaling technique of Ref. [21], computing the average orientational order $\Psi_6(L_B) = \langle \psi_6 \rangle_{B}$ in subblocks of linear size $L_B$. Due to finite-size effects, the liquids at coexistence deviate from the ideal short-range behavior (steep bold line of slope $-2$ in Fig. 4b), but they are well beyond the KTHNY stability limit for the hexatic (bold line of slope $-\frac{1}{4}$).

The $n = 64$ and $n = 8$ hexatics at the transition have small slopes (Fig. 4b, $\eta = -0.0026$ and $-0.10$), while for $n = 6$ we find a value close to the stability limit, $\eta = -0.19$. Our data are thus consistent with a continuous Kosterlitz-Thouless transition for $n \lesssim 6$, which is preempted by a first-order transition for larger $n$.

Approaching the hexatic-solid transition, $\xi_6$ increases, and our algorithm ceases to be ergodic. Moreover, the effective lattice constant, reduced by a finite equilibrium concentration of defects, is a priori unknown and the positional order in our samples is usually incommensurate with the periodic boundary conditions, leading to frustration effects. This prevents robust conclusions for the exact density of the hexatic-solid transition point $\phi_{hs}$.

We can, however, give a lower bound for the melting density $\phi_{hs}$, as the highest-density states that could be molten in a $N = 259k$ periodic box (Tab. 1). At the hexatic-solid transition, we find no indications of a discontinuity, in particular, the equation of state shows no anomalies (Fig. 4h).

We have shown in this work that 2D melting in particles with short-range repulsive forces is generically a two-step transition, with a hexatic phase in between the liquid and the solid. We identify two regimes: At large $n$, close to the hard-disk limit, the liquid-hexatic phase transition is clearly first order. In the hexatic, positional correlation lengths are two orders of magnitude larger than the interparticle distance $d$. The density of positional defects is correspondingly small. As $n$ becomes smaller, the nature of the hexatic changes: positional correlation lengths drop to a few $d$ and defects are ubiquitous. The additional entropy due to defects stabilizes the hexatic phase with respect to the liquid state, and the phase-coexistence interval becomes very small. For even smaller $n \lesssim 6$, the liquid-hexatic coexistence turns continuous; our findings are consistent with the complete (twice continuous) KTHNY scenario for softer particles. Owing to the high densities $\phi$ at the transition, and the long-range nature of interactions, this regime is not presently accessible to our simulations.

While the correlation lengths in the hexatic are so vastly different in the two regimes, we observe no qual-
| n  | $\beta P_{\text{coex}} \sigma^2$ | $\phi_{\text{liq}}$ | $\xi_0/d$ | $\phi_{\text{ex}}$ | $\xi_p/d$ | $\phi_{\text{us}}$ |
|----|-------------------------------|----------------|--------|----------------|--------|--------|
| 6  | 38.3                         | 1.506 | 180    | 1.507 | 2.6      | > 1.516 |
| 8  | 23.1                         | 1.193 | 110    | 1.196 | 6.0      | > 1.204 |
| 16 | 12.1                         | 0.937 | 95     | 0.949 | 27       | > 0.960 |
| 64 | 9.27                         | 0.882 | 61     | 0.904 | 96       | > 0.920 |
| 1024 | 9.17                      | 0.889 | 65     | 0.913 | 66       | > 0.924 |
| $\infty$ | 9.18                      | 0.892 | 62     | 0.913 | 51       | > 0.919 |

TABLE I. Phase transitions in $r^{-n}$ soft disks: Coexistence pressures $\beta P_{\text{coex}} \sigma^2$, density $\phi_{\text{liq}}$ and orientational correlation length $\xi_0$ of the liquid at coexistence, density $\phi_{\text{ex}}$ and positional correlation length in the hexatic at coexistence. The last column gives a lower bound for the hexatic-solid transition (melting density) $\phi_{\text{us}}$. The densities can be considered accurate to 0.5%. Pressures are computed in ECMC using the truncated interaction and are thus low by about 0.5%, with an additional statistical error of the same size. The correlation lengths are given in units of the interparticle distance $d = \sigma / \sqrt{\pi \delta}$. They are determined by fitting the exponential tails of the respective correlation functions and are subject to large systematic errors due to the choice of $\phi$ and thus accurate to about ±10%. They are consistent with earlier results for hard disks [3].

The inhomogeneous difference in the structure of the KTHNY topological defects, interpreted as coordination anomalies in the Voronoi diagram [4], even though this is not without problems in a disordered system [22]. The behavior of defects is collective more so than the simple subsequent unbinding picture would suggest. While free dislocations (i.e., isolated pairs of a 5- and a 7-coordinated site) exist and free disclinations are indeed heavily suppressed, the majority of defects are involved in more complex clusters. Most defects form string-like aggregates in which topological charges alternate, and frequently comprise an odd number of bound dislocations. Their classification into grain boundaries, disclinations and dislocations becomes ambiguous. The defect strings circumscribe patches of homogeneous orientational order, and the liquid-hexatic transition can be viewed as the percolation transition of the defect string network. Thus, the liquid-hexatic transition occurs according to a grain-boundary mechanism, similar to proposed direct liquid-solid transitions [6, 7], but starting from a hexatic phase.

We expect that the crossover from first-order to a continuous liquid-hexatic transition should also be observable in experimental systems where the interaction can be tuned between the hard-disk and long-range limits, for example in charged colloids in solution, where the interaction is a Coulomb force with tunable screening length.

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23. Since ECMC, in contrast to standard Monte Carlo acts on the pairwise and not on the total interaction energy, techniques such as Ewald summation are not required even for $n < 6$. The pairwise formulation permits to include long-range interactions outside of the cutoff in a probabilistic way (not required for $n \geq 6$).