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LARGE SCALE SIMULATIONS OF MELTING IN TWO DIMENSIONAL LENNARD-JONES SYSTEMS: EVIDENCE FOR A METASTABLE HEXATIC PHASE

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Large Scale Simulations of Melting in Two Dimensional Lennard-Jones Systems: Evidence for a Metastable Hexatic Phase

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Abstract. Large scale molecular dynamics simulations have been performed for two-dimensional Lennard-Jones systems on massively parallel computers. The calculations were done in the NPT ensemble as recently reformulated by Melchionna *et al.*, avoiding problems associated with mixed phases and artificial treatment of vacancies and interstitials. In the largest systems studied (36864 and 102400 atoms), a metastable hexatic phase was found between solid and liquid, in agreement with the predictions of the theory of melting in two dimensions developed by Kosterlitz and Thouless, Halperin and Nelson, and Young. The hexatic phase was not seen in smaller samples, calling into question the conclusions of many previous simulations performed on smaller systems and shorter time scales.

1. Introduction

In three dimensions (3D), melting is understood only on a macroscopic thermodynamic level; the phase transition is discontinuous, and requires a latent heat. There may be hysteresis, in that it is possible to superheat the solid and undercool the liquid. Empirical rules for 3D melting have been proposed, such as the Lindemann criterion advanced by its namesake 85 years ago and still in use today [1,2]. The Lindemann criterion is that a solid will melt when the root mean square amplitudes of vibrations of the atoms reach some critical value, say 15% of the interatomic spacing. This rather imprecise rule, correlating melting with the disorganized thermal vibrations of all of the atoms in the material, may be contrasted to accepted theories for other phase transitions, e. g., the BCS electron pairing mechanism for superconductivity. At present, there is no credible, fundamental atomistic theory for melting in three dimensions.

The situation is different in two dimensions (2D). A simple and elegant theory of 2D melting mediated by topological defects was developed in a series of papers in the 1970's by Kosterlitz and Thouless [3], Halperin and Nelson [4,5], and Young [6] (KTHNY). A two-

dimensional system may be characterized by two kinds of order, translational and orientational, as will be described in more detail later. A solid exhibits quasi-long-range translational order and true orientational order, while a liquid has neither. As shown in Fig. 1, the KTHNY theory proposed that in certain regions of the phase diagram, a new phase called the hexatic would exist. The hexatic phase has no long-range translational order, but retains quasi-long-range orientational order. The solid transforms into the hexatic, and the hexatic into the liquid, in two continuous phase transitions, the first by the unbinding of dislocation pairs, the second by the unbinding of pairs of disclinations. Note from the figure that the theory does not rule out the possibility of a first-order transition.

In the time since the KTHNY theory was formulated, a large number of experimental and theoretical studies have been done to try to confirm or disprove it, with ambiguous and inconclusive results. A variety of creative experiments have tended to support KTHNY, although not in every case. Murray and Van Winkle [7], for example, found evidence for a two-stage melting process through a hexatic phase in the translational and orientational correlation functions for charged polystyrene-sulphonate submicron spheres confined in water between smooth glass plates. On the other side, Pouligny *et al.*'s experiments on steel spheres confined in a parallel plate capacitor [8] suggested a first-order transition, but their system was small and uncertainties were raised by the presence of in-plane confining walls. Work by Geer *et al.* [9] on free-standing liquid crystal films and by Kusner and coworkers [10] on 2D systems of colloidal particles with dipolar interactions support the KTHNY picture.

A great many computer simulations have been performed for 2D systems with various sizes, statistical ensembles, and potential models in the past 20 or so years. Many, but not all, of these have been equivocal or negative regarding the predictions of KTHNY. For Lennard-Jones systems, Frenkel and McTague [11] did isothermal-isochoric (NVT = constant number of particles N , volume V , and temperature T) simulations for 256 atoms and claimed to find evidence for the hexatic phase. On the other hand, Abraham [12] concluded that the melting transition is first order in an early attempt to do isothermal-isobaric (constant N , pressure P , and T) simulations for 256- and 576-particle systems. NVT simulations by Toxvaerd [13] for as many as 3600 atoms, by Strandburg *et al.* [14] for systems of 1024 particles, and by Bakker *et al.* [15] for 10864 atoms led them to report first-order transitions, but Udink and van der Elsken [16], who applied finite-size scaling to results for a 12480 particle system, supported KTHNY.

For other interatomic potentials, the results are similarly mixed. Weber and coworkers [17 and references therein] have performed a

thorough analysis of melting in systems of up to 16384 hard disks using finite-size scaling and the behavior of the bond-orientational susceptibilities. They provided strong evidence that melting is a first order transition in hard disk systems. At about the same time, Bladon and Frenkel [18] showed that when a short-range attractive interaction is grafted onto hard disks, a crystal becomes unstable to dislocation unbinding and the formation of a hexatic phase near a solid-solid critical point between high- and low-density solid phases.

Earlier this year, we reported [19] on molecular dynamics simulations of large 2D Lennard-Jones systems at long time scales using correct NPT equations of motion. A metastable hexatic phase was observed, but only in the two largest systems studied, providing perhaps the most direct evidence to date for the KTHNY theory of melting in two dimensions. We have since extended these calculations to do more extensive runs for the largest system.

The remainder of the paper is organized as follows: Section 2 provides a brief description of the KTHNY theory as it applies to a 2D Lennard-Jones system. Section 3 provides a few details about the simulations. Results are given in Section 4, and conclusions and future plans are outlined in Section 5.

2. Theory

The Lennard-Jones or 12-6 potential as we use it is cut off at a distance r_c and shifted so that the potential goes to zero at the cutoff,

$$V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] + V_c, \quad r < r_c, \quad (1a)$$

$$= 0, \quad r \geq r_c, \quad (1b)$$

$$V_c = -4\epsilon [(\sigma/r_c)^{12} - (\sigma/r_c)^6] \quad (1c)$$

There is a discontinuity in the forces and higher derivatives of the interatomic potential at the cutoff in this model, but this appears to have little effect on the simulations in runs we have done with this potential and with closely related ones that have no discontinuities in any derivatives at the cutoff. The zero-temperature equilibrium lattice for the Lennard-Jones potential in 2D is a triangular lattice. Each atom has six first nearest neighbors (1nns) at angles spaced by 60° .

The KTHNY theory is based on an elastic continuum Hamiltonian [20]. In 2D, unlike in 3D, dislocation dipoles are thermally activated point defects; to produce finite rather than infinite elastic strain energies,

dislocations must be created in pairs. Each dislocation is in turn comprised of two nearest neighbor disclinations, which are atomic sites with 5- or 7-fold coordination instead of the perfect crystalline solid coordination of 6. In the KTHNY theory, the transition from the solid to the hexatic is accomplished by the unbinding of dislocation pairs, and going from the hexatic to the liquid occurs with the unbinding of pairs of disclinations.

Spatial correlation functions are used to monitor the evolution of the system. The translational correlation function for a reciprocal lattice vectors $\mathbf{G}$ is

$$g_{\mathbf{G}}(\mathbf{r}) = \langle \exp[i\mathbf{G} \cdot (\mathbf{u}(\mathbf{r}) - \mathbf{u}(0))] \rangle, \quad (2a)$$

where $\mathbf{u}(\mathbf{r})$ is the atomic displacement field. For computational reasons, it is more convenient to use the pair correlation function

$$g(\mathbf{r}) = (V/N^2) \langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle. \quad (2b)$$

The orientational correlation function $g_6(\mathbf{r})$ is defined by

$$g_6(\mathbf{r}) = \langle \psi_6(\mathbf{r}) \psi_6^*(0) \rangle, \quad (3a)$$

$$\psi_6(\mathbf{r}_i) = (1/N_{nn}) \sum_{j=1nn} \exp(6i\theta_{ij}), \quad (3b)$$

where the angle θ_{ij} is defined relative to an arbitrary fixed axis. Table 1

Table 1. Behavior of the translational and orientational correlation functions and grouping of dislocations and disclinations in the solid, hexatic and liquid phases in two dimensions.

	Solid	Hexatic	Liquid
$g_{\mathbf{G}}(\mathbf{r})$	$r^{-\eta(T)}$	$e^{-r/\xi(T)}$	$e^{-r/\xi(T)}$
$g_6(\mathbf{r})$	$g_6^{(\infty)} \neq 0$	$r^{-\eta_6(T)}$	$e^{-r/\xi_6(T)}$
Dislocations	pairs	free	free
Disclinations	quartets	pairs	free

shows how the different phases are ordered. In the solid, the long-range translational order decays algebraically, and the orientational order approaches a constant. In the hexatic, the translational correlation function decays exponentially, while the orientational order is quasi-long-range and decays algebraically. The liquid exhibits no long-range order; both correlation functions decay exponentially.

3. Computations

Most previous simulations of 2D melting have been done in an NVT ensemble. This can lead to problems associated with the existence of mixed phase regions, which make it difficult to use the correlation functions as signatures of the different phases. Furthermore, there are questions about how to maintain correct thermal equilibrium concentrations of vacancies [20, 21]. We have therefore performed all of our molecular dynamics (MD) simulations in the NPT ensemble, where such problems do not arise. The first treatment of NPT dynamics allowing variable shape as well as volume for the computational unit cell was introduced by Parrinello and Rahman (PR) [22]. It was subsequently pointed out by Cleveland and others that PR MD is not invariant to cell-basis transformations [23-25]. This was corrected in the recent reformulation of exact NPT equations of motion having the PR form by Melchionna *et al.* [26]. Using these equations allows us to make an unequivocal test of the KTHNY theory.

Simulations were performed for systems of 576, 4096, 16384, 36864, and 102400 atoms confined in parallelograms with varying cell sides as determined from the equations of motion. Periodic boundary conditions were imposed. In most cases, the starting samples were perfect triangular crystals with random velocities assigned to the atoms corresponding to the desired temperature, but in some instances hexatic or liquid starting configurations were used. The equations of motion were integrated by the 5-value Nordsieck-Gear predictor-corrector method. In reduced units in which the potential parameters ϵ and σ , the atomic mass m , and the Boltzmann constant k_B are 1, the time step ranged from 0.0005 to 0.001, which gives a linear drift in the constant of motion of only 2 parts in 10^5 in the course of one million time steps. For the calculations reported here, the cutoff for the potential was $r_c = 4\sigma$.

The simulations were done on the massively parallel ORNL Intel Paragon computers XPS/35 (512 processors) and XPS/150 (2048 processors); the numerical designations correspond to nominal peak G-flops. An atom decomposition scheme was used in the parallel code. Most runs were done with 128 processors. To give a flavor for the CPU

time involved, 5×10^6 time steps for 36864 atoms on 128 processors on the XPS/35 takes approximately 10.5 days of continuous running time, which in the real world translates to about a month. This makes it difficult to pursue every potentially good idea.

4. Results

To search for the existence of the hexatic phase, systematic scans of the P, T phase space were carried out for different system sizes. To monitor the state of the systems, the translational and orientational correlation functions were determined [see Eqs. (2) and (3)] for snapshot configurations. One feature that quickly became manifest was the effect of system size. This is illustrated in Fig. 2, which presents results for the evolution of the density ρ as a function of time for 4096- and 36864-atom periodically repeated unit cells. The 4096-atom sample was run for 10 million time steps of $\Delta t = 0.0005$, the 36864-atom unit cell for 5 million. The ordinate range is the same for the two samples. Note first that the fluctuations are much larger for the smaller sample, which apparently jumps between the liquid and solid phases in a way consistent with a first-order transition. The larger sample exhibits not only much smaller fluctuations in the density, but also a plateau in the evolution of the density from the solid at the beginning to the liquid at the end. This plateau persists for roughly 500000 time steps, and the correlation functions for this metastable state have the signature of the hexatic phase. It is apparent that large system sizes are important for meaningful simulations of 2D melting, and that results of many previous simulations on small samples are suspect.

Fig. 3 shows the behavior of the density as a function of time for the 36864-atom system at $P=20$ and three values of T around the melting temperature. All runs were started from the same perfect crystal lattice structure. At $T=2.15$, the system remains in the solid phase, while at $T=2.17$, it relaxes smoothly to the liquid. At the intermediate temperature $T=2.16$, the system relaxes first into a metastable hexatic state which persists for some time, and then on down to the liquid.

To test the sensitivity of our results to the starting configuration (and to try to stabilize the hexatic phase), runs at $P=20$ and $T=2.154$ were initiated with the perfect crystal structure and with a hexatic configuration obtained at $T=2.16$. The results are shown in Fig. 4. Both runs confirm the existence of a metastable hexatic state, particularly the (shorter) run started with a hexatic configuration, where the metastable hexatic phase persisted for about 1 million time steps. However, neither run succeeded in stabilizing the hexatic phase.

Pair distribution and orientational correlation functions for snapshots taken from the simulations are shown in Fig. 5. At $T=2.15$, the system is a solid; the oscillations in the pair distribution function persist over the entire range of distance, and the orientational correlation function decays to a finite constant value. At $T=2.17$, the system is clearly in the liquid state, as the pair distribution decays rapidly to an average value and $g_6(r)$ decays exponentially. The system at $T=2.154$ displays the signature of the hexatic phase: there is only short-range order in the pair distribution function, but the orientational correlation function decays algebraically. The exponent for the decay is 0.21 ± 0.02 , which is less than the upper limit of $1/4$ predicted by KTHNY. Although a mixed solid-liquid coexistence region is unlikely to occur in an NPT simulation, we have done finite-size scaling analysis of the bond-angular susceptibility in subgrids of the 36864 atom sample. All three phases observed as the temperature changes appear to be homogeneous.

System size is clearly a very important aspect of simulations of (and experiments on) 2D melting. This makes sense in the framework of KTHNY, which is based on an elastic continuum Hamiltonian for interactions between dislocations and disclinations. In the largest system discussed to this point (36864 atoms), nearly 10% of the atoms interact with periodic images of other atoms in the unit cell. We have now done a number of runs for a 320×320 sample of 102400 atoms, and while we have not succeeded in stabilizing the hexatic phase, we have extended its duration as shown in Fig. 6. Simulations for the 102400 systems were started with a hexatic-like configuration, and are compared to results for the 36864-atom sample started from solid and hexatic configurations. The dashed lines are included as guides to indicate the duration of the metastable hexatic state, which persists for three million time steps in the larger system.

5. Conclusions and Future Directions

We have performed extensive simulations of 2D Lennard-Jones systems in a recently reformulated version of NPT dynamics. We believe that our simulations provide the strongest evidence to date for the existence of the hexatic phase predicted by KTHNY, and for their defect-mediated theory of melting in two dimensions. System size and simulation time scales are clearly crucial aspects of the study of the fundamental phenomenon of melting, and present and future computer resources open vistas that may make it possible to provide definitive answers.

At present, we are studying the range of the Lennard-Jones potential, its effect on dislocation core energies and the melting transition.

Subsequent to our work [19], studies of 2D systems with purely repulsive r^{12} interactions have been published that also appear to support the KTHNY theory [27]. A variety of other possibilities have been suggested to us, such as the imposition of external fields to stabilize the hexatic. As previously noted, CPU time requirements make it problematic to follow every potentially fruitful path.

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Figure Captions

Fig. 1. Schematic NPT phase diagram for a 2D system.

Fig. 2. Density ρ vs. time step n at $P=20$ and $T=2.16$ for 4096 atoms (a) and 36864 atoms (b). The time step $\Delta t = 0.0005$ for these runs.

Fig. 3. Density ρ vs. time step n in a 36864-atom sample at three different temperatures near the melting point.

Fig. 4. Density ρ vs. time step n in a 36864-atom sample starting from the solid (top curve) and from a hexatic configuration (bottom curve).

Fig. 5. Pair distribution (a) and orientational correlation (b) functions in a 36864-atom sample at $P=20$ and three temperatures near the melting point. The pair distribution functions for the solid and the metastable hexatic phases have been shifted upward for clarity.

Fig. 6. Evolution of the density with time at $P=20$ and $T=2.154$ for 36864- and 102400-atom systems.

Fig 1

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Fig 2(a)

Fig. 2(b)

Fig 3

Fig 4

Fig 5(a)

Fig 5(b)

Fig 6