Melting in Two-Dimensional Lennard-Jones Systems: Observation of a Metastable Hexatic Phase

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Large scale molecular dynamics simulations of two-dimensional melting have been carried out using a recently revised Parrinello-Rahman scheme on massively parallel supercomputers. A metastable state is observed between the solid and liquid phases in Lennard-Jones systems of 36 864 and 102 400 atoms. This intermediate state shows the characteristics of the hexatic phase predicted by the theory of Kosterlitz, Thouless, Halperin, Nelson, and Young.

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Two-dimensional (2D) melting has been intensively studied for the past two decades, but it remains not well understood to date [1,2]. It has been established that a 2D crystalline system is characterized by two types of order, translational and orientational. In the solid phase the system has quasi-long-range translational order and true long-range orientational order. In the liquid phase there is no long-range order of either kind. A defect-mediated melting theory by Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY) [3–6] predicts that a third phase, called the hexatic, can exist between solid and liquid in a portion of the phase diagram; the system in the hexatic phase has no long-range translational order but does retain quasi-long-range orientational order. Melting can occur via two continuous transitions with the first from solid to hexatic due to dislocation unbinding and the second from hexatic to liquid due to disclination unbinding. However, the theory does not rule out the possibility of a first-order melting transition. Competing theories [7,8], on the other hand, propose that the melting is a single first-order transition from solid to liquid. Over the years a large number of experiments and simulations have been performed to test the KTHNY and other theories; unfortunately, results are sometimes contradictory and fail to provide unambiguous evidence [1,2].

The Lennard-Jones system is one of the most studied in computer simulations of 2D melting. Frenkel and McTague [9] carried out an isothermal-isochoric molecular-dynamics (MD) simulation of a 256-atom system and observed the existence of a hexatic phase in accordance with the KTHNY theory. In contrast, Abraham [10,11] concluded that the melting transition is first order in his isothermal-isobaric Monte Carlo (MC) simulations of 256- and 529-atom systems and in his isothermal-isobaric MD simulations of a 576-atom system. Because of these conflicting results, more simulations were performed on larger systems with longer runs for equilibration. In isothermal-isochoric MC simulations of a 1024-atom system, Tobochnik and Chester [12] found that the nature of the melting transition cannot be unambiguously determined from their data, but later Strandburg, Zollweg, and Chester [13] argued the transition is first order. In isothermal-isochoric MD simulations, a first-order transition was reported by Toxvaerd [14] for systems with up to 3600 atoms and by Bakker, Bruin, and Hilhorst [15] for a system of 10 864 atoms. However, using finite-size scaling to analyze their data on a 12 480-atom system, Udink and van der Elsken [16] found that their results are in reasonably good agreement with the KTHNY theory.

The above-mentioned controversy is not unique to the Lennard-Jones system. Similar results have been found for other systems; among those the hard disk system is an excellent example where most recent computer simulations still give contradictory conclusions [17–19]. Evidently, there are several factors that contribute to the confusion. The first is the size of the system, because finite-size effects blur the distinction between first-order and continuous transitions. Long-wavelength fluctuations play a key role in the KTHNY theory, but they are cut off in a finite system. The second is the time scale of the simulations. It is absolutely necessary to run systems long enough to reach equilibrium, especially if phase transitions are continuous and critical slowing down occurs, and this becomes crucial when system size increases. The third factor is the choice and implementation of the statistical ensemble used. The coexistence region of solid and liquid appearing in isochoric simulations mimics the hexatic phase and it is difficult to distinguish one from the other. Such a region does not occur in isobaric simulations. In addition, there are technical difficulties in equilibrating systems and generating correct ensemble distributions [1,20–23].

The rapid advance of parallel supercomputing technologies has made it possible to push further the limits on system sizes and times. Recently, equations of motion were devised for an exact isothermal-isobaric MD simulation and extended to Parrinello-Rahman (PR) MD [24] by Melchionna, Ciccotti, and Holian [25]. Unlike the original Parrinello-Rahman equations, these new equations are invariant under cell-basis transformation [26–28]. By integrating these equations numerically on a sequence of powerful massively parallel supercomputers, we have performed large scale simulations with millions of time steps on 2D Lennard-Jones systems of up to 102 400 atoms. In comparison with previous studies, this work has two important features: (i) we employ an exact MD scheme to generate a correct isothermal-isobaric statistical ensemble which allows unequivocal testing of the KTHNY theory and (ii) our largest simulations are about one order of magnitude larger in terms of both system size and time. Our studies reveal the existence of a metastable hexatic state in the two largest of the five system sizes simulated.

In our isothermal-isobaric PRMD simulations we used a shifted Lennard-Jones 12-6 potential

$$V(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + V_c\,, & r < r_c\,, \\ 0\,, & r \geq r_c\,, \end{cases} \quad (1)$$

where ϵ and σ are parameters, r is the interatomic distance, r_c is the cutoff radius, and

$$V_c = -4\epsilon[(\sigma/r_c)^{12} - (\sigma/r_c)^6]. \quad (2)$$

Our systems consisted of 576, 4096, 16 384, 36 864, and 102 400 atoms which were confined inside a varying parallelogram with periodic boundary conditions imposed along the edges. In most cases these atoms were initially located at sixfold-coordinated triangular-lattice points and assigned random velocities. The velocities were then properly scaled so that the total linear momentum of the system was zero and the total kinetic energy matched the desired external temperature. Other initial configurations were also used for double-checking the equilibration. Equations of motion [25] were solved via the five-value Nordsieck-Gear predictor-corrector method [29]. A linear shift in the constant of motion was observed and the amount of shift was controlled to about 0.002% every 10^6 steps by using a proper time step. Typically the time step Δt was in the range from 0.0005 to 0.001 with the potential cutoff $r_c = 4$, all in reduced units in which potential parameters ϵ and σ, the Boltzmann constant k_B, and the mass of atom m are equal to 1.

In order to determine phase boundaries and probe the possible hexatic state, we systematically scanned the phase space for different system sizes up to 36 864 atoms. The pair distribution functions and orientational correlation functions were computed directly by definition [1,29] for individual configurations and used to identify different states. For all systems, solid and liquid were the only two apparent equilibrium states found and an abrupt jump in the enthalpy was seen at the transition. These are at first sight consistent with the first-order transition scenario described by Abraham [10,11]. A metastable hexatic state, however, was observed for the first time in the 36 864-atom system. Figure 1 demonstrates the evolution of the enthalpy H in the 36 864-atom system at the external pressure $p = 20$ and three different temperatures. In these particular simulations the initial configurations had the same perfect lattice structure and density but different random velocity distributions and the time steps were all equal to 0.0005. The pair distribution functions and orientational correlation functions for typical equilibrium solid and liquid configurations are given in Fig. 2. At the temperature $T = 2.17$, the system approaches equilibrium directly and stays in the liquid state where the oscillations in the pair distribution function die off rapidly and the orientational correlation function decays exponentially. At $T = 2.15$, the system relaxes quickly and remains in the solid state where the oscillations in the pair distribution function persist over the entire range and the orientational correlation function decays to a constant. In between, at $T = 2.16$, the system enters a seemingly intermediate state in about 0.75×10^6 time steps and remains there for about 0.5×10^6 time steps before it finally settles down in the liquid state.

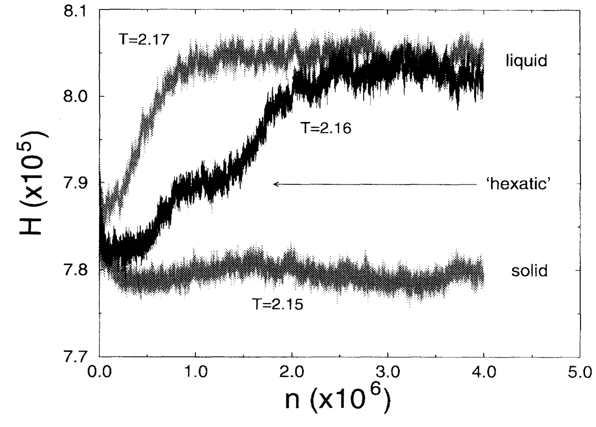

FIG. 1. Evolution of the enthalpy H in Lennard-Jones systems of 36 864 atoms at $p = 20$ and $T = 2.15$, 2.16, and 2.17, where n is the number of time steps with time step $\Delta t = 0.0005$.

Trying to stabilize this intermediate state, we took the configuration of $T = 2.16$ at the one millionth time step and ran it as the initial condition for a slightly lower temperature $T = 2.154$. Figure 3 shows the evolution of the enthalpy. The system is again found to be in a metastable state for about 10^6 time steps, longer than that at $T = 2.16$. The pair distribution functions and orientational correlation functions for a typical configuration in the metastable state are given in Fig. 2. Note that this intermediate state has all the characteristics of the hexatic phase—long-range translational ordering does not exist and the orientational ordering decays algebraically with an exponent of 0.21(2), which is less than $\frac{1}{4}$, the upper limit predicted by the KTHNY theory. The existence of this metastable state is confirmed by a different run starting from the perfect lattice structure as also shown in Fig. 3, although it took more than 5×10^6 time steps for the second run to reach the similar state.

Although an inhomogeneous solid-liquid coexistence region is unlikely to persist in an isobaric simulation, we checked the metastable state for this possibility.

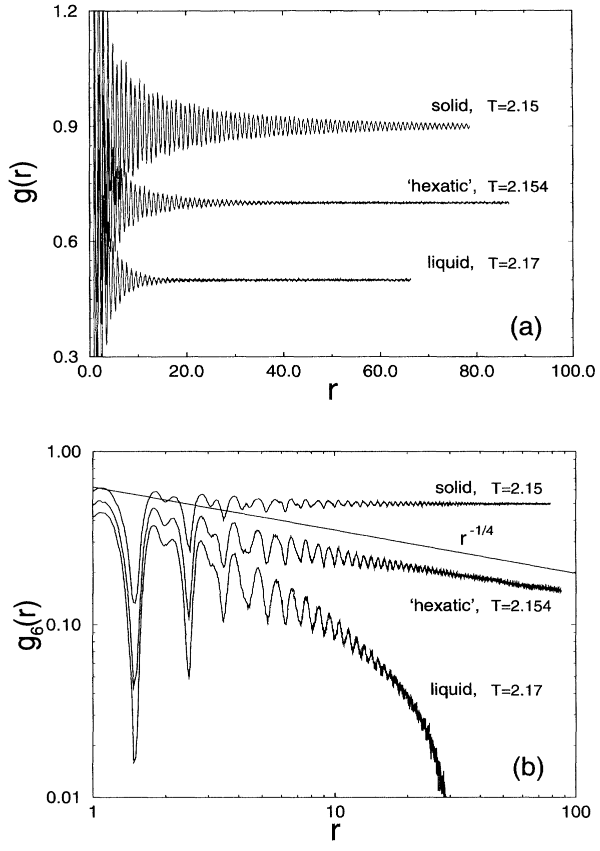

FIG. 2. (a) Pair distribution functions $g(r) = (V/N^2) \times \langle \sum_{i,j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle$ (see Ref. [29]) and (b) orientational correlation functions $g_6(r) = \langle \psi_6(\mathbf{r}) \psi_6^*(\mathbf{0}) \rangle$ with $\psi_6(\mathbf{r}_l) = (1/n_l) \times \sum_j^{n_l} e^{6i\theta_{lj}(\mathbf{r}_l)}$ (see Ref. [1]) for equilibrium solid, liquid, and metastable hexatic configurations in Lennard-Jones systems of 36 864 atoms at $p = 20$ and $T = 2.15$, 2.17, and 2.154. Top two curves in (a) were shifted upward for clarity. The straight line in (b) has a slope of $-\frac{1}{4}$ and is a guide to the eye.

We divided the 36 864-atom system into 36 864, 9216, 2304, and 576 grids and computed the nearest-neighbor bond-angular susceptibility [13] for all subsystems which contain 1, 4, 16, and 64 atoms on the average. For the solid and liquid phases, distributions of the susceptibilities are qualitatively the same as observed by Strandburg, Zollweg, and Chester [13]. The distribution of the susceptibilities for the metastable state, however, shows no qualitative change in its shape with subsystem size, confirming that the state is homogeneous.

Because much longer simulations on systems containing less than 36 864 atoms did not reveal any intermediate states, the system size seems responsible for the metastable state. Fundamentally this may reflect the importance of long-wavelength fluctuations to the existence of the hexatic phase and hence the necessity of larger system size for the stabilization of the state. A single long run of more than 5×10^6 time steps has been made for a 102 400-atom system at $p = 20$ and $T = 2.16$. Results obtained were similar to those of the 36 864-atom system but the equilibration time increased significantly. This suggests that the stabilization of the phase could be very difficult involving simulations of very large systems for very long times.

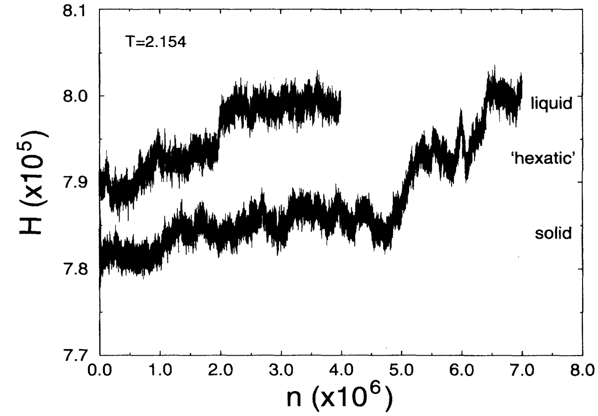

FIG. 3. Evolution of the enthalpy H in Lennard-Jones systems of 36 864 atoms at $p = 20$ and $T = 2.154$ with two different initial conditions, where n is the number of time steps with time step $\Delta t = 0.0005$. The shorter run started from a hexatic configuration obtained at $T = 2.16$ and the longer one from the perfect lattice structure.

A brief comment on the importance of massively parallel supercomputer resources for such simulations is appropriate. The largest simulations were carried out on the Intel Paragon XP/S 35 at the Oak Ridge National Laboratory. This machine has 512 nodes with 32 MB/node and a peak performance of 35 G-flops. A million steps for the 102 400-atom system on 128 nodes takes approximately 150 h.

In summary, a metastable hexatic state between solid and liquid phases was observed for the first time in two-dimensional Lennard-Jones systems of 36 864 and 102 400 atoms in our isothermal-isobaric molecular dynamics simulations. While this result falls short of confirming the complete KTHNY theory, it does provide very strong evidence of the hexatic phase predicted. The suppression of the metastable state in smaller systems makes previous simulations suspect.

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