

Computer Simulation Study of the Melting Transition in Two Dimensions

Ken Bagchi* and Hans C. Andersen†

Department of Chemistry, Stanford University, Stanford, California 94305

William Swope‡

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120

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We have performed computer simulations for a two-dimensional system of classical point particles interacting via an r^{-12} repulsive pair potential to study the melting transition. As the density is increased, the equilibrium system develops hexatic order at pressures lower than the lowest values achievable in an equilibrium crystal. Finite size scaling analysis of the bond orientational order and translational order gives exponents for correlations in the hexatic and solid that are consistent with the Kosterlitz-Thouless-Halperin-Nelson-Young picture.

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The nature of the melting transition in two dimensions has received considerable attention in the past two decades because of the possibility that melting from solid to liquid occurs by two distinct second order transitions separated by an intermediate phase called the hexatic. This fascinating suggestion was first made by Halperin and Nelson (HN) [1], based on the work of Kosterlitz and Thouless (KT) [2]; additional predictions were later added by Young [3]. Several computer simulations have been done to test the theory, but no consensus has been reached [4–18].

The lack of definitive simulation results is understandable since correlation times and correlation lengths can be extremely long near phase transitions. This creates difficulties in equilibration and artifacts due to finite system size, particularly at solid or hexatic densities. Moreover, the simultaneous presence of two distinct long correlation lengths, those for the bond orientational order and the translational order, can confuse a finite size scaling analysis of the data for small systems.

Here we report computer simulation studies of a classical system of point particles in two dimensions interacting via a pairwise additive potential of the form $u(r) = \epsilon(\sigma/r)^{12}$. For all data presented in this Letter, we used reduced units such that $\epsilon = 1$, $\sigma = 1$, $m = 1$, and $k = 1$, where k is Boltzmann's constant. We simulated systems with various reduced densities $\rho^* = (N/V_{2D})\sigma^2$ along the reduced isotherm $T^* = kT/\epsilon = 1$. All results reported here are for densities very close to $\rho^* = 1$, which previous work [9–11] has identified as the approximate boundary between fluid and crystalline states.

The concern about long correlation times led us to use a simulation method of Swope and Andersen [19] based on the bicanonical ensemble (BCE). This method involves a particle insertion-deletion process that alternates the total number of particles between N and $N - 1$ in accordance with an appropriate detailed balance condition. In the present work, we used it in conjunction with molecular

dynamics (MD) and hybrid Monte Carlo (HMC) methods [20]. The deletion of a particle and its subsequent insertion at a different point in the sample greatly enhances the equilibration of defects. It enhances the net migration of holes and interstitials and the climb of dislocations. This method has the added benefit of providing the chemical potential for the simulated state.

The concern about system size effects led us to study and compare the properties of systems of 4096, 16384, and 65536 particles as well as those of subdivisions of the 65536 particle systems.

For fluid states, we performed two separate simulations at each state of interest. For one run, the starting state was chosen to have a random liquidlike configuration. The other was started from a perfect triangular lattice. All runs were done using periodic boundary conditions. Both states were simulated using MD with the velocity Verlet integrator [21] and stochastic collisions [22] to maintain the proper temperature. They were continued until the estimates of the pressure and chemical potential for the two runs agreed within statistical error. This serves as strong proof of our ability to equilibrate. After this point, the simulations were continued, and data were collected over the next 12000τ , where $\tau = (m\sigma^2/\epsilon)^{1/2}$. Each run was then continued using HMC [20]. This method has the advantage of generating configurations consistent with a canonical distribution without any systematic errors due to nonzero time step. These runs consisted of 20000 to 30000 HMC steps, with each step consisting of 1τ of molecular dynamics, with a time step of 0.005τ , to generate the trial configuration. The acceptance rate was roughly 65%.

In addition to recording the pressure and chemical potentials, we calculated the relevant order parameters. The first was the bond orientational order parameter, defined as $\psi_6^2 = |\frac{1}{6N} \sum_l \sum_j \exp(6i\theta_{lj})|^2$, where the sum on l is over all particles, the sum on j is over the nearest neighbors of particle l , and θ_{lj} is the angle between

the line joining particle l and particle j and some fixed reference axis. The second was the translational order parameter, defined as $\psi_l^2 = |\frac{1}{N} \sum_l \exp(i\mathbf{k} \cdot \mathbf{r}_l)|^2$, where \mathbf{r}_l is the position of particle l . The wave vector \mathbf{k} has a magnitude of $2\pi/\sqrt{3}/2\rho$, where the denominator is the average lattice spacing. To allow for the possibility of the crystal tilting, we varied the direction of \mathbf{k} over a 120° range; the \mathbf{k} that produced the maximum value of the sum was used to calculate the order parameter.

At equilibrium, the mean value for the estimates of the pressure, chemical potential, and the two order parameters should not drift with time. For each HMC run, we performed a time series analysis appropriate for time correlated data to verify that each quantity was not drifting, within statistical error [23].

The long-ranged correlations of the order parameters are different in the various phases. For liquids, both types of order decay exponentially. Solids possess truly long-ranged bond orientational order while the translational order decays as a power law, with an exponent $0 < \eta < 1/3$ [24]. Halperin and Nelson [1] suggested that the intermediate hexatic phase would have bond orientational order that decays with a power law exponent $0 < \eta_6 < 1/4$, while the translational order decays exponentially.

We applied a finite-size scaling analysis to the order parameter data obtained from the 65 536 (64K) particle

runs. Each 64K configuration was divided into four equal sub-blocks (which we refer to as 16K sub-blocks since they contain approximately 16 384 particles) and also into 16 equal sub-blocks (which we refer to as 4K sub-blocks). Both order parameters were calculated for the entire system and for all the sub-blocks, and the average results as a function of (sub-)block size were computed. A plot of the logarithm of an average order parameter versus the logarithm of the (sub-)block length provides a diagnostic about the nature of the correlations. For a strictly finite-ranged correlation, the slope of such a plot should be -2 for sizes large compared with the correlation length, but the plot should curve and have a larger, i.e., less negative, slope for sizes that are not large compared with the correlation length. For algebraic decay of correlations, the slope should be the negative of the power law exponent for system sizes in which algebraic decay is realized. Figure 1 contains the results for several densities near the phase boundary.

For a density of 0.9935, the plot indicates that the translational correlations decay exponentially. The bond orientational order plot for this density is barely consistent with a slope of -2 and finite-range correlations. The slope is slightly larger between 4K and 16K, however, suggesting that the correlation length is of the order of the length of the 4K sub-block. The combined behavior leads

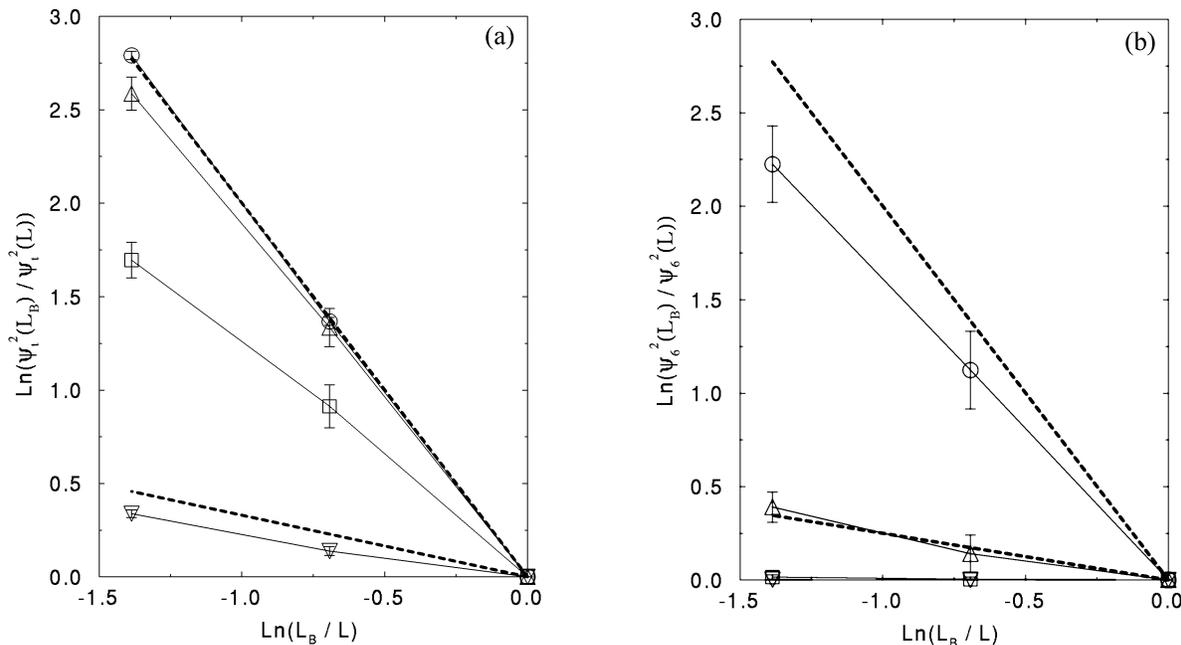


FIG. 1. (a) Plot of the natural logarithm of the ratio $\psi_l^2(L_B)/\psi_l^2(L)$ vs the natural logarithm of L_B/L , where $\psi_l^2(L_B)$ is the average translational order parameter for a (sub-)block of length L_B and L is the length of the total system. Error bars represent single standard deviation error estimates for the ratio. The dark steep dashed line corresponds to a slope of -2 , which indicates a finite correlation length. The dark flatter dashed line has a slope of $-1/3$, corresponding to the curve expected at the KT transition. (b) Plot of the natural logarithm of the ratio $\psi_6^2(L_B)/\psi_6^2(L)$ vs the natural logarithm of (L_B/L) , where $\psi_6^2(L_B)$ is the average bond orientational order. Again, the dark steep dashed line has a slope of -2 , corresponding to a finite correlation length. The dark flatter line has a slope of $-1/4$, which is the expected power law behavior at the HN transition. For both plots, the ○ correspond to a density of $\rho^* = 0.9935$, the △ to a density of $\rho^* = 1.000$, the □ to a density of $\rho^* = 1.007$, and the ▽ to a density of $\rho^* = 1.0108$. The first three are 65 536 particle systems and the last is a 16 384 particle system.

us to conclude that this state corresponds to a high density liquid. At $\rho^* = 1.000$, we see that the translational order is still finite ranged, but the translational correlation length has grown to be on the order of the length of the 4K sub-block. The bond orientational curve, in contrast, is now consistent with a power law decay with an exponent of $\eta_6 \sim 1/4$. Hence we identify this state as being at or near the HN transition. For $\rho^* = 1.007$, the translational plot is approximately straight within statistical error, but the slope is too large in magnitude to correspond to a reasonable exponent for translational correlations in a solid (see above). The slight negative curvature suggests that the correlations may be of finite range but with a correlation length that is much larger than the systems studied here. This agrees well with the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory, which predicts this correlation length to diverge as it approaches the KT transition from below. The power law exponent extracted from the bond orientational data for this density is very close to zero, which is again expected for a high density hexatic. The state with a density of 1.0108 is a solid near the limit of stability of the solid phase (see below). The translational correlations now appear to have a power law decay with an exponent less than $1/3$. Within noise, the power law exponent for the bond orientational correlations is zero; this is consistent with the prediction of true long-range order in the solid.

Figure 2 shows the calculated pressure as a function of density in the transition region. Here, we focus on liquid and hexatic states with a density of 1.007 and less. For the 4K and 16K systems, there is a maximum, suggestive of a van der Waals loop and a first order transition, but the amplitude of the oscillation and the apparent width of the transition decreases as system size increases. For the 64K MD systems, the pressure monotonically increases with density in this range. The 64K HMC data are consistent with a monotonic rise in pressure, when statistical error is taken into account. An analysis of the distributions of both order parameters for all (sub-)block sizes of the 64K system and the distribution of the densities for the 16K sub-blocks showed that they are unimodal, indicating no tendency to phase separation. These results and the trend of the pressure data with system size lead us to conclude that there is no first order phase transition in this density range. If such a transition were to exist in the thermodynamic limit, the trends indicate that the coexisting phases would have a very small density difference (approximately 0.5%), and that both coexisting phases are in the range of densities where the system is hexatic or liquid.

We have also performed 16K particle MD studies of solid phases of this material with various concentrations of net vacancies. (For one state, we also performed 64K MD and 16K HMC simulations and obtained the same results for the thermodynamic properties.) We found

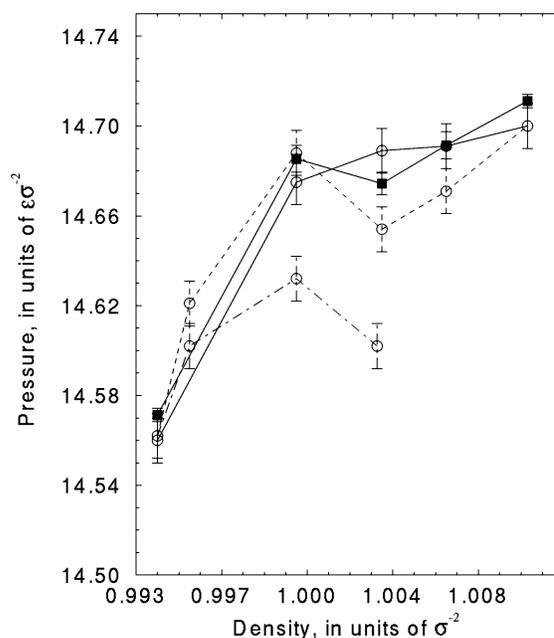


FIG. 2. Plot of the pressure vs density. The dot-dashed, dashed, and solid lines represent data taken from 4K, 16K, and 64K simulations, respectively. The filled squares correspond to HMC data. The open circles represent MD data to which we have applied a nonzero time step correction of -0.06 at all densities [22]. The error bars for the MD data are estimates of the systematic error in this correction. (The statistical error of the data is smaller.) The error bars for the HMC represent single standard deviation estimates of the statistical error.

that crystalline states with a density of about 1.01 or lower are unstable with regard to destruction of their translational order and the formation of a hexatic structure with unbound dislocations. Also, states with more than about 0.1% net vacancies (i.e., one net vacancy for each 1000 lattice sites) are unstable with regard to a clustering of the vacancies to form an inhomogeneous material. Using the method of Swope and Andersen [25], we determined an approximate equation of state for the equilibrium concentration of net vacancies in the solid as a function of density. The state whose data are given in the figures, with a density of 1.0108, is very near the lower limit of stability of the solid with an equilibrium concentration of vacancies. It survived as crystalline for 23 000 HMC steps in a 16K simulation, but there was some evidence for the clustering of vacancies. It survived as crystalline for 8000τ of MD in a 64K simulation, but then became hexatic with unbound dislocations. Thus this state is a lower bound to the density at which the equilibrium solid is stable. The data for the time during which it was crystalline appear in the figures.

Note that the pressure of this state is higher than those of the liquid and hexatic states with densities of 1.007 and less, according to the more accurate HMC data. It follows that the transition out of the solid phase cannot be a first order transition to a liquid with short-ranged

bond orientational order. It is presumably a second order Kosterlitz-Thouless transition, which is consistent with the fact that we observe that the solid has two modes of instability at its lowest density, although we cannot rule out a first order transition to a hexatic with a density higher than 1.007.

The simplest interpretation of these data is that the r^{-12} repulsive potential system in 2D has a Halperin-Nelson second order transition and a Kosterlitz-Thouless second order transition, with an intervening hexatic phase that is stable over a range of densities that is about 1.2% wide. The compressibility of the hexatic is very large, and we cannot rule out a narrow first order transition *within the range of fluid and hexatic states*. We cannot equilibrate hexatic states within a density of about (0.1–0.2)% of the lowest solid density, so we have no direct information about the solid-hexatic transition. The thermodynamic analysis does, however, rule out a first order transition from a crystalline phase to a liquid with finite ranged bond orientational order.

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*Electronic address: ken@rattle.Stanford.EDU

†Author to whom correspondence should be addressed.

Electronic address: fb.hca@forsythe.Stanford.EDU

‡Electronic address: swope@almaden.ibm.COM

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