How the choice of shape and ensemble affect simulations of two-dimensional melting

Juan J. Morales
Departamento de Física, Facultad de Ciencias, Universidad de Extremadura, 06071 Badajoz, Spain

Enrique Velasco
Department of Mathematics, The University, Southampton S09 5NH, England

Søren Toxvaerd
Department of Chemistry, Laboratory III, Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

(Received 20 April 1994)

Nonequilibrium quenching in two-dimensional simulations from a solid or liquid to an interfacial-hexatic regime demonstrates the sensitivity of the final results to the shape of the simulation box (final size effect) and to the molecular dynamics ensemble used (constant density versus constant pressure). Even for a small system of $N=1024$ particles, under no circumstance is stabilization of the structure factor reached before some nanoseconds. This means that the results given by Naidoo *et al.* [Mol. Phys. **80**, 1 (1993)] using hexatic structure boundaries are too small and pose the question of whether all the published work on two-dimensional melting has used systems that are too small and simulation times that are too short.

PACS number(s): 68.10.Jy, 05.70.Fh, 64.70.Kb

I. INTRODUCTION

The Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [1] for two-dimensional (2D) melting systems predicts a second-order (continuous) transition proceeding in two stages: from the solid to the "hexatic" phase (with bond-orientational order) and from the hexatic phase to the isotropic liquid. Alternatively, there is the first-order (discontinuous) transition theory, in which, breaking abruptly its long-range order, the 2D solid melts to the isotropic liquid with no intermediate phase. However, not only has neither theory been good enough to explain categorically 2D melting, but a curious paradox has arisen from the results obtained up to now: while many experimental results seem to confirm the KTHNY theory, most simulation results seem to confirm the first-order transition [2]. The factors that possibly cause this apparent discrepancy could come from different sources such as the specific physical properties of the system under study, the computational technique used to simulate the systems, the size and evolution time of the systems, etc. The influence of some of these factors on the 2D melting behavior has recently been studied [3] for soft-disk systems and long molecular dynamics (MD) simulation runs. The main conclusion was that the final results are strongly dependent on the boundary and initial conditions of the systems being simulated. The same conclusion can be inferred for hard-disk systems [4] and Lennard-Jones (LJ) systems [5], since identical (or closely related) systems have led to very different results.

In the present paper we quench 2D systems from the bulk (liquid and solid) states into the region of phase change and measure the nonequilibrium relaxation times. The growth and disappearance of order are measured by the change in the structure factor $S(k)$, and especially the peak corresponding to the triangular solid ordering is found to be a sensitive measure for phase changes in the systems. The two-dimensional "melting" is known to exhibit hysteresis, a property often associated with a first-order phase transition, but by quenching the system from the bulk phases into the same state point in the "interphase" we obtain a measure of the equilibration times and the sensitivity of the hysteresis to the size and method used (constant pressure or constant temperature, etc.). However, in order to obtain a sufficiently accurate estimate of the nonequilibrium time behavior, it is necessary to perform an ensemble averaging by repeating the experiment many times, quenching from different instantaneous liquid and solid positions. This implies that the investigation would be very time consuming computationally. Furthermore, while this kind of investigation does not answer the question about the equilibrium behavior of 2D material and whether this system exhibits a hexatic phase, it does demonstrate the system's sensitivity to the size of the area and the ensemble in which the nonequilibrium dynamics take place.

II. PROCEDURE AND RESULTS

The state points chosen were liquid (L), melting (M), and two solids (S1,S2), at $\rho r_m^2 = 1.10$, 1.14, and 1.18, and 1.25, respectively, at the isotherm $kT/\varepsilon = 1.0$ for a repulsive LJ potential (Weeks-Chandler-Andersen, WCA, potential [6]), where $r_m = 2^{1/2}\sigma$ is the distance at which the LJ potential has its minimum energy ε and k is the Boltzmann constant. The points of state were chosen because they have already been studied for the microcanonical ensemble [constants energy E, volume V, and number of particles N or MD (EVN)], exhibiting the usual tie line

of the first-order melting behavior [7]. All the systems were started from a box with the usual $\sqrt{3}/2$ ratio between the edges. In the first group of simulations this ratio was maintained at the quenching, while in the second group it was broken into that of a more square shape. The quenching was performed by an instantaneous rescaling of all the positions and the box to the new density. The MD technique used to simulate the systems was the updated version of the Nosé-Hoover (NH) method [8] for the canonical [constant T and ρ, or MD (TVN)] and isothermal-isobaric [constant T and p, or MD (TpN)] ensembles [9].

When the systems are quenched they change their structure, measured by the change in $S(k)$. As already mentioned, we find the time behavior of the main peak in $S(k)$, corresponding to triangular ordering to be the most sensitive measure of the nonequilibrium changes in the system. In the following, we report the ensemble results for the different quenchings.

Figure 1 shows the MD (TVN) results for the mean value of the first peak of $S(k,t)$, averaged over 20 quenched systems. As one can easily see, while the quenching from S1 to M has a quite sluggish decay for $\langle S(k,t)\rangle$, still unfinished by 25 000h, the quenching from S1 to L produces a sharp decay in the structure factor to an almost constant level after the first 5000h. The behavior from L to S1 shows a continuous smooth increase in the structure factor reflecting the building up of the solid structure, while the quenching from L to M seems not to affect the $\langle S(k,t)\rangle$ values. For comparison, the last values at 25 000h appearing in Fig. 1 are about 90, 55, 8, and 7, from top to bottom.

As only the quenchings from S1 to M and from S1 to L seem to follow a definite pattern of decay, we have fitted those values with a best governing equation, finding that

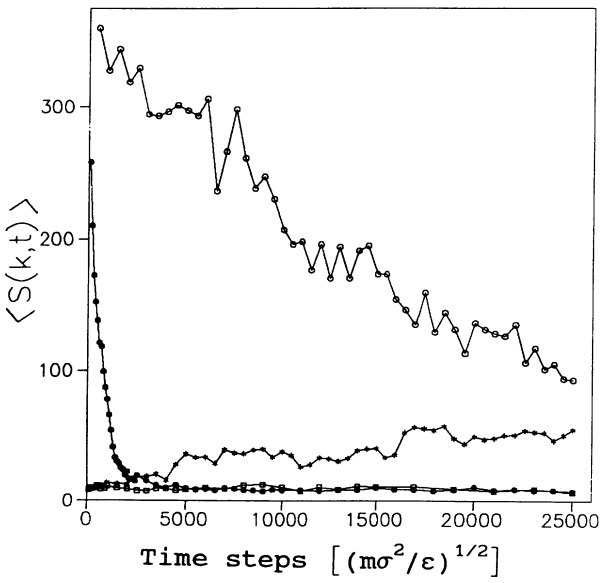

FIG. 1. Structure factor averaged over 20 MD (NVT) configurations from the following quenchings: S1 to M (white circles), S1 to L (black circles), L to M (white squares), and L to S1 (asterisks).

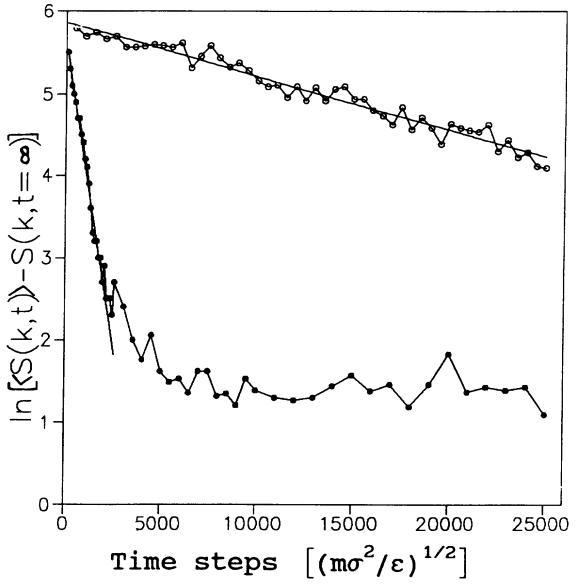

FIG. 2. Logarithmic behavior of the structure factor from S1 to L (black circles) and from S1 to M (white circles), over 20 MD (TVN) configurations.

the minimum value of the sum of the squares of the differences $\mathcal{S}$ between the experimental and theoretical values corresponds to a logarithmic law for melting ($\mathcal{S}=0.48$) and liquid ($\mathcal{S}=0.17$). In the first case the whole set of data up to 25 000h was taken, while for the second case only up to 2000h. This logarithmic behavior permits one to obtain the relaxation time τ of the system from the inverse of the slope in a semilogarthmic plot (Fig. 2), the results being $\tau\cong 650h$ for the liquid and $\tau\cong 15\,500h$ for the melting. The value of $S(k,t=\infty)$ is the structure factor for liquid and melting after a long evolution of the system, when the value is fluctuating around a fixed number. These values were 4.3 and 33 for

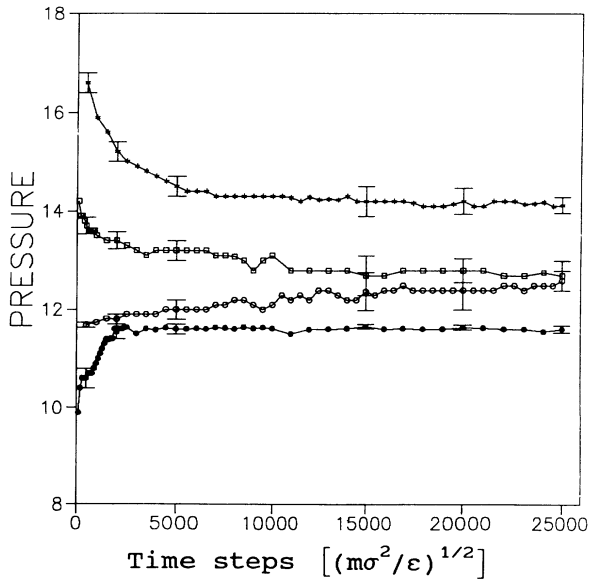

FIG. 3. The same as Fig. 1, but for the pressures.

the liquid and melting, respectively.

The pressures, with their standard deviations, during the above quenchings are shown in Fig. 3. The 25 000h is long enough for pressure stabilization, the first to stabilize being the quenching from S1 to L (after $\cong 2500h$) and the last from S1 to M (after $\cong 17\,000h$). The final results are in agreement, within the statistical errors, with those calculated previously for the same state points in Ref. [7].

As was seen in Fig. 1, for the quenching from S1 to M there was still the same decay behavior after 25 000h, with too high a value for the structure factor. The system was thus allowed to evolve over a longer time until $\langle S(k,t)\rangle$ started to fluctuate around the same mean value. Figure 4 shows this further behavior up to 250 000h, now time averaging $S(k)$ every 20h instead of the instantaneous average peak in $S(k,t)$. It is easy to see the stabilization process in $S(k)$ which, after a sharp decay, seems to fluctuate around a value that was considered to be $S(k,t=\infty)=33$. The pressure remains almost constant with a final mean value $p=12.57\pm0.04$.

The value of $S(k)$ at the "interfacial state" M should, for systems reaching equilibrium, be the same whether the systems are quenched from a liquid state or a solid state. However, as can be seen from Figs. 1 and 3, the two limit values are very different and show no sign of approaching each other even for 250 000h (3 ns). The difference is a consequence of the hysteresis in the (small) 2D system.

The final size effect on the equilibrium is easily demonstrated by changing the shape of the box. A second group of experiments was performed by forcing the triangular shape of the box to change to a quasisquare form by keeping the X length unaltered and scaling the Y length only during the quenching from the higher density. Figure 5 shows the results for the quenching from S2 to L (black triangles) and from S2 to M (white triangles) with the MD (TVN) ensemble, and from S2 to M (black squares) with the MD (TpN) ensemble. The external pressure required as input for the last case was chosen to be $p_{ex}=12.7$, which is the late-time (using only the last, more stable values) mean pressure obtained for the quenching from S1 to M (see Fig. 3). The results are quite different from those obtained in the first group of experiments shown in Fig. 1. It is not possible now to find any characteristic decay for the system, since $\langle S(k,t)\rangle$ falls sharply in the first few hundred steps and then starts to fluctuate with irregular, large amplitudes in

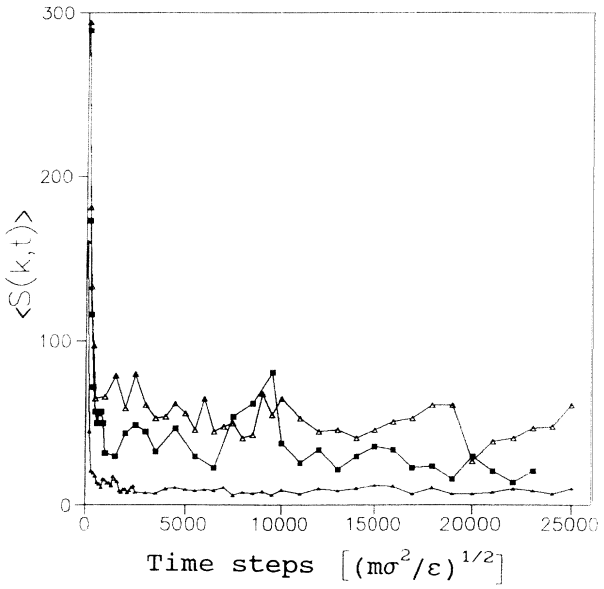

FIG. 5. Structure factor averaged over ten configurations for the following quenchings: MD (TVN) from S2 to M (white triangle), MD (TVN) from S2 to L (black triangles), and MD (TpN) from S2 to M (black squares). All the quenchings were performed by changing the triangular lattice shape of the box to a more likely square shape.

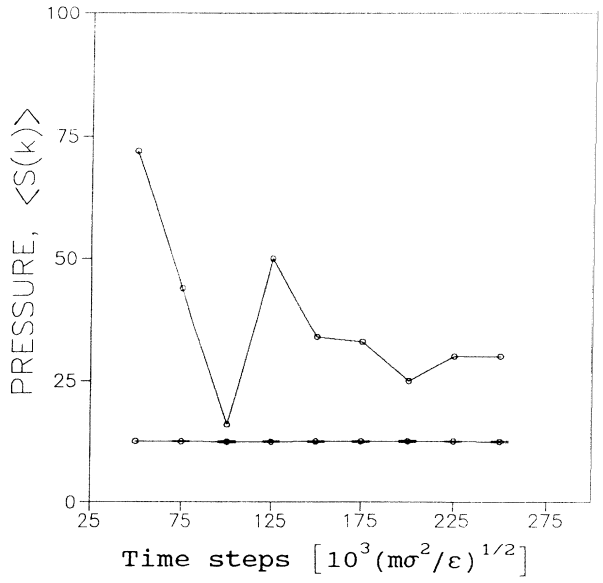

FIG. 4. Late pressure and structure factor behavior from S1 to M, over 20 MD (TVN) configurations.

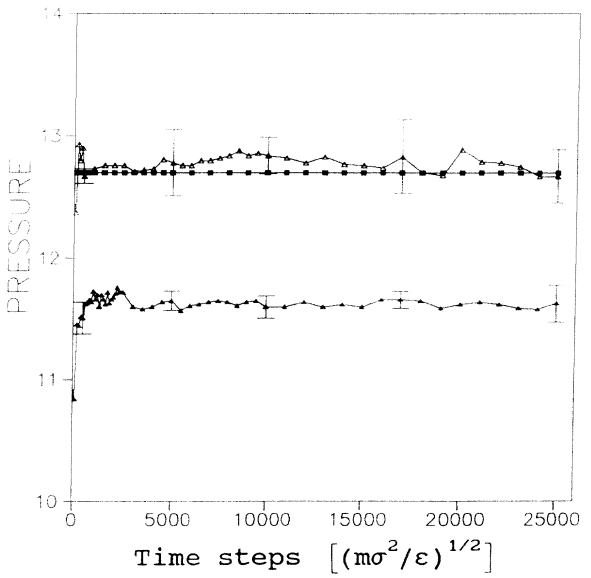

FIG. 6. The same as Fig. 5, but for the pressures.

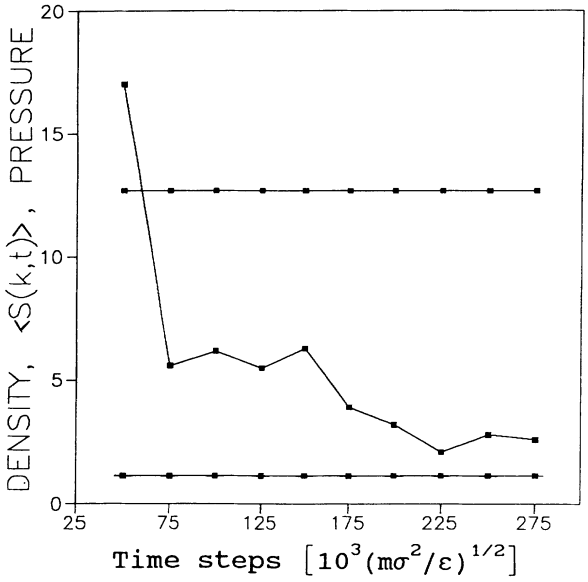

FIG. 7. Late density, structure factor, and pressure behavior from S2 to M over ten MD (*TpN*) configurations.

the melting zone. The mean late-time values for the structure factor as shown in Fig. 5 were 50, 20, and 10, from top to bottom. The pressures, Fig. 6, for the MD (*TVN*) systems show a characteristic behavior similar to their corresponding $\langle S(k,t)\rangle$ values in Fig. 5, while the MD (*TpN*) system shows the constant imposed value of 12.7 from beginning to end. Again the final pressure values coincide with those of Fig. 3 and Ref. [7].

Just as the system quenched from S1 to M in the MD (*TVN*) ensemble, and with the $\sqrt{3}/2$ ratio between the box edges, was allowed to evolve over a longer time, we did the same with the S2 to M quenching in the MD (*TpN*) ensemble with a quasisquare box shape. Figure 7 shows these results. While the behavior is similar to that shown in Fig. 4, the value reached by the structure factor is much smaller and very close to the value obtained for the liquid, $\langle S(k,t=\infty)\rangle = 4.3$. The pressure remains constant, as expected, and the final mean value for the density was $\rho r_m^2 = 1.138 \pm 0.003$.

III. DISCUSSION AND CONCLUSIONS

First the quenching from different phases into the same point of state (T,ρ) in the "interphase" M, shown in Fig. 1, should end up in the same state in the long run, but this was not found to be the case. The 20 MD (*TVN*) quenchings with a $\sqrt{3}/2$ ratio between the axes show, from S1 to M, identical slow behavior with what appears to be a bimodal exponential character, since at 250 000*h* the initial exponential behavior has died away and the mean of the 20 systems gives a slow decline to a final value of $\langle S(k,t)\rangle \cong 30$ (Fig. 4). In contrast, the L to M quenching shows some variation from ensemble member to ensemble member, but the sum is noticeably constant and certainly does not reach the value of 30 under any circumstances. The conclusion is that the systems have not reached equilibrium within 250 000 steps.

Second, for the ten MD (*TVN*) quenchings from S2 to M (Fig. 5) scaling only in the *Y* direction, the early behavior of the system looks the same as before, and the bimodal character seems much more pronounced in this set of quenchings. Nevertheless, and in spite of the initial faster decay towards equilibrium, it is still not in agreement with the L to M results. The conclusions are that the shape of the boundaries affects the system strongly and that the process is very slow, since the mean values still have not settled down after 250 000 steps corresponding to nanosecond times.

The above conclusions were drawn from the results of simulations for $N = 1024$ particles in a constant volume *V*. However, if the melting is first order and associated with a change in density, this (*TVN*) ensemble simulation might not be suitable since it suppresses the density fluctuations necessary for the growth of the subphases. This will result in long equilibration times and strong hysteresis in the small MD system. A constant pressure MD simulation therefore looks more appropriate. But even though this system allows large density fluctuations, the creation of subphases is a slow process and one cannot rescale the volume faster than the system can equilibrate itself [9,10]. So when we perform the MD (*TpN*) quenching from S2 to about $\rho r_m^2 = 1.14$ (Figs. 5 and 7), the structure factor value reached is the same as for the liquid and the equilibrium time is relatively short. Thus the quenched system relaxes to the system (liquid) that has the fastest relaxation time and is therefore pushed into a corner of the phase space, i.e., the liquid. The conclusion is that constant *p* is not good at determining whether this transition is first order.

In summary, we can state that nonequilibrium quenching and ensemble averaging offer a self-consistent test of how big a system should be and for how long it should be followed in order to obtain its equilibrium properties. The liquid-solid transition in 2D is a challenging problem that has been fiercely debated for decades. Computer simulations have played a crucial role in this debate. Many of the simulation results, however, have been for systems of the order of thousands of particles and the nonequilibrium quenching test clearly demonstrates that these systems are much too small to avoid the systems in the transition region being locked into subareas of the phase space. At present, it is beyond computer capability to ensemble average substantially bigger systems and to follow them in nanoseconds, but the strategy is clear: the nonequilibrium systems, when quenched from liquid states and solid states, should end in the same state, and only when this quality is ensured can we trust the simulation results.

ACKNOWLEDGMENTS

The cooperation of the University of Extremadura Computer Center is gratefully acknowledged. This project has been partly supported by Junta of Extremadura (by a grant) and by CICYT (Spain), Project Nos. PB92-0523 and PB91-0090.

[1] K. M. Kosterlitz and J. D. Thouless, J. Phys. C **6**, 1181 (1979); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979); A. P. Young, *ibid.* **19**, 1855 (1979).

[2] For a review see, for example, K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988); *Bond-orientational Order in Condensed Matter Systems* (Springer-Verlag, Berlin, 1992).

[3] K. J. Naidoo, J. Schnitker, and J. D. Weeks, Mol. Phys. **80**, 1 (1993); K. J. Naidoo and J. Schnitker, J. Chem. Phys. **100**, 3114 (1994).

[4] J. A. Zollweg and G. V. Chester, Phys. Rev. B **46**, 11 186 (1992); J. Lee and K. J. Strandburg, *ibid.* **46**, 11 190 (1992).

[5] A. F. Bakker, C. Bruin, and H. J. Hillhorst, Phys. Rev. Lett. **52**, 449 (1984); C. Udink and J. van der Elsken, Phys. Rev. B **35**, 279 (1987).

[6] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[7] S. Toxvaerd, Phys. Rev. Lett. **51**, 1971 (1983).

[8] S. Nosé, Mol. Phys. **52**, 159 (1991); W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[9] S. Toxvaerd, Mol. Phys. **72**, 159 (1991); Phys. Rev. E **47**, 343 (1993).

[10] D. Toxvaerd, Phys. Rev. B **29**, 2821 (1984).