

## Melting transition of near-monolayer xenon films on graphite: A computer simulation study. II.

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Xenon films of greater than one monolayer thickness are simulated using the molecular-dynamics technique. If the total substrate area and coverage are held constant, we find that the first layer of the xenon film melts in an apparent continuous manner over a small temperature interval and is consistent with two-phase, solid-liquid coexistence. The quantitative features of the correlation functions are in excellent agreement with recent x-ray experiments [P. A. Heiney *et al.*, *Phys. Rev. Lett.* **48**, 104 (1982); T. F. Rosenbaum *et al.*, *Phys. Rev. Lett.* **50**, 1791 (1983)]. If the spreading pressure and total coverage are held constant, we find that the melting transition is first order. This is in conflict with the conclusions of Heiney *et al.* based on constant-chemical-potential experiments but is consistent with the constant-area and -coverage simulation. A possible explanation is proposed.

In recent x-ray scattering experiments,<sup>1</sup> Heiney *et al.* examined the melting of the first xenon-monolayer film on the (001) basal plane of pyrolytic graphite at the high-temperature region of the phase diagram, and found results at odds with low-temperature laboratory experiments,<sup>2</sup> and with computer experiments for strictly two-dimensional atomic systems.<sup>3</sup> In particular, they interpreted their results as indicating the melting transition to be continuous, with fluid correlation lengths exceeding 100 atomic spacings. In a very recent experimental study,<sup>4</sup> Rosenbaum *et al.* measured the x-ray diffuse scattering from monolayer xenon on single-crystal substrates of exfoliated graphite, and they concluded that the solid xenon film melts into an orientationally ordered liquid (or hexatic) phase.

In this present study, we extend our earlier investigations<sup>5,6</sup> of the monolayer xenon melting transition at high temperatures and coverages by employing the molecular-dynamics (MD) computer-simulation technique and by specifying constant temperature, total coverage, and spreading pressure (*TpMD*), or constant temperature, total coverage, and substrate area (*TaMD*). The total coverage is approximately 1.1 monolayer, or 10% occupancy in the second adsorption layer. For the *TaMD*-simulation experiments, the first layer of the xenon film melts continuously over a small temperature interval, and this is consistent with two-phase, solid-liquid coexistence. The quantitative features of the correlation functions are in excellent agreement with the experiments.<sup>1,4</sup> For the *TpMD* experiments, this melting transition is found to be first order, in disagreement with the conclusions deduced from laboratory experiment. The possible resolution of this disagreement will be considered.

The details of the computer model and numerical-simulation method for studying xenon on graphite has been presented<sup>5,6</sup> and will not be discussed here. In Ref. 6, the *TaMD*-simulation study used 576 Lennard-Jones xenon atoms and a basal-plane area of  $A^* = 612.5$ , and a continuous melting transition was found, in agreement

with experiment. However, the issue of the "rounding" of a first-order transition because of finite-size effects (e.g., see Ref. 7) needed to be addressed, and this was the primary stimulus for extending the study to a larger system. We have chosen a system four times larger (or 2304 xenon atoms), and have found a "size effect," which does not change the general conclusions of our earlier study.<sup>6</sup> In Ref. 6, we found a small temperature window where the first xenon monolayer melts and freezes continuously in time, and where the two-phase coexistence is prevalent during the temporal excursions. This occurs because of the exchange of atoms between the first and second layer. With our larger system (i.e., 2304 xenon atoms), the temporal density fluctuations of the total monolayer at a given temperature are small in the temperature interval of the melting regime. Therefore, the first-layer phase does not oscillate in time between the density extremes of the solid and liquid phases but remains as a solid-liquid mixture. This is consistent with the picture that small "local" regions of the larger system melt and freeze, as observed in the small-system simulation, but the spatial averaging of these "uncorrelated" density fluctuations over all subregions of the larger system suppresses the extreme temporal variations of the first layer's mean density as observed in our earlier study. In Fig. 1, the mean first-layer density as a function of temperature is presented through the melting regime for both the *TaMD* and *TpMD* experiments. Unless stated otherwise, reduced units for the density and temperature are used<sup>2</sup> and are denoted by  $\rho^*$  and  $T^*$ , respectively. The density-temperature behavior is characteristic of a continuous melting transition for the *TaMD* experiments and of a first-order transition for the *TpMD* experiments. In Fig. 2, the temporal relaxation and fluctuation about equilibrium of the first-layer density in the *TaMD* simulations are presented for several temperatures through the continuous melting regime. A 0.05-ps time step is adopted in the numerical integration. An attempt was made to choose the initializing state of the system ( $t=0$ ) to be significantly away from equilibrium, so that

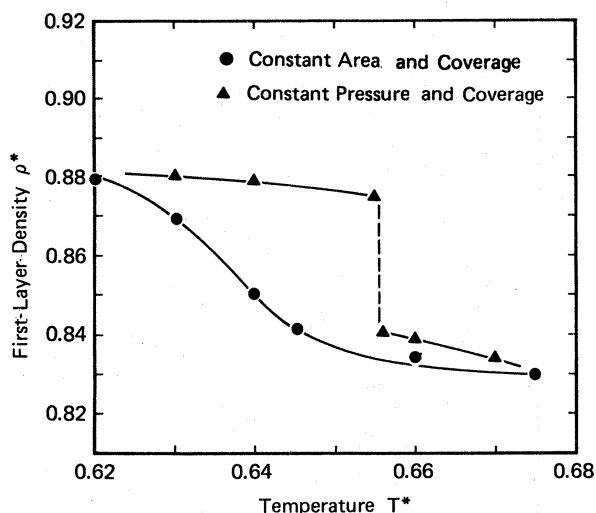


FIG. 1. Mean first-layer density as a function of temperature through the melting regime for both the *TaMD* and *TpMD* simulations.

we may see pronounced temporal relaxation of the system's properties to equilibrium. The results in Fig. 2 are representative of several such experiments. In the case

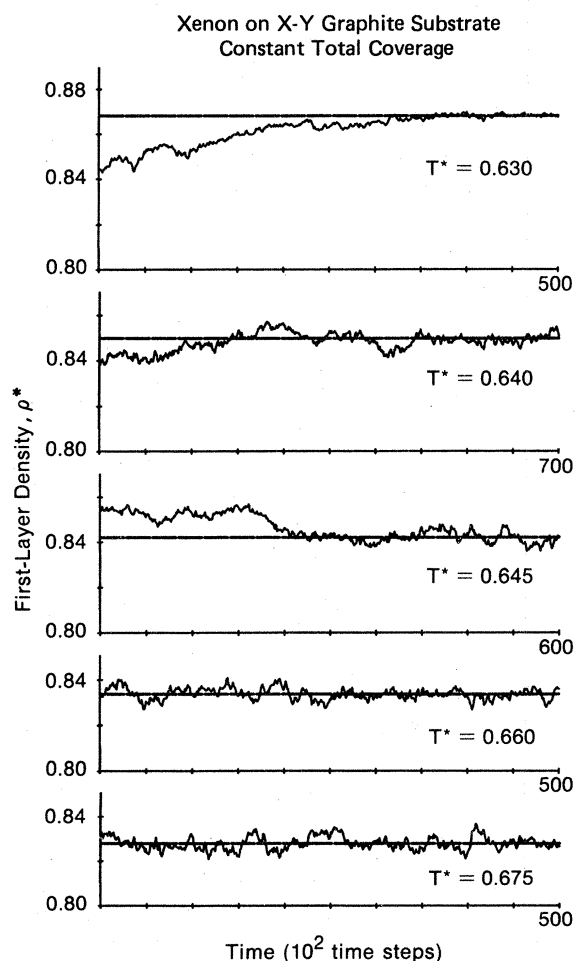


FIG. 2. Temporal relaxation and fluctuation about equilibrium of the first-layer density in the *TaMD* simulations for several temperatures through the continuous melting regime.

of the constant spreading pressure simulations (i.e., *TpMD* experiments), an equilibrium state of a *TaMD* simulation with a density midway between the solid and liquid density was chosen as the initialization state; hence if the system's equilibrium state was solid or liquid, its relaxation to that phase was very apparent with no associated problems ascribed to the establishment of metastable states (i.e., hysteresis). If the intermediate density was representative of the equilibrium state, equilibration would have been rapidly realized by maintaining this intermediate density.

We first discuss the results of the *TaMD* study and their relationship to the laboratory experiments.<sup>1,4</sup> In Fig. 3, the radial distribution function and its corresponding structure factor are shown for selected temperatures, the lowest temperature correlation function being representative of a solid xenon monolayer and the other suggesting a disordered, or "fluid," phase with short-range correlation decreasing from several atomic diameters to a few atomic diameters with increasing temperature. The respective correlation lengths were obtained by fitting the solid

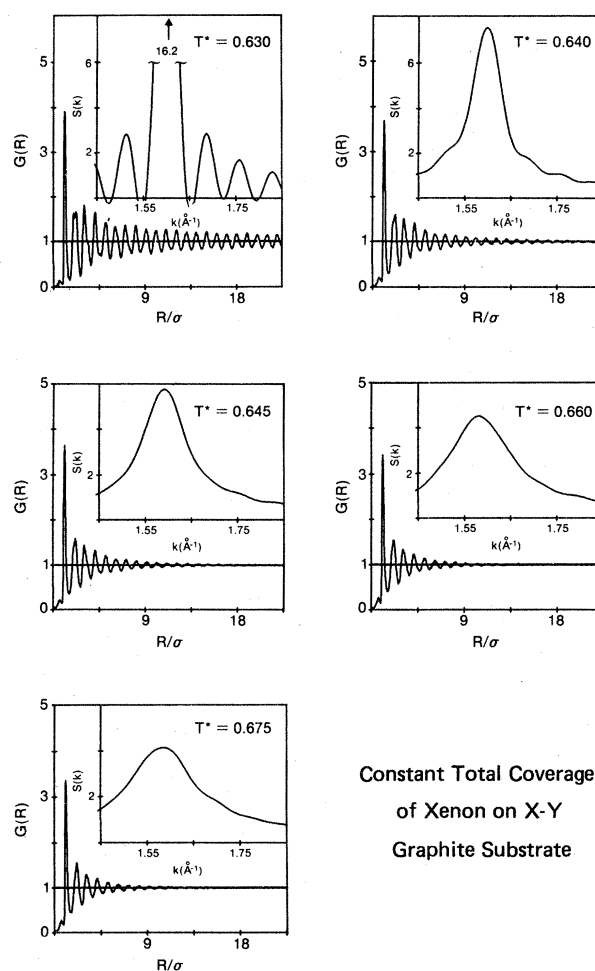


FIG. 3. Radial distribution and its corresponding structure factor for selected temperatures, the lowest-temperature correlation function being representative of a solid xenon monolayer and the others suggesting a disorder phase with short-range correlation.

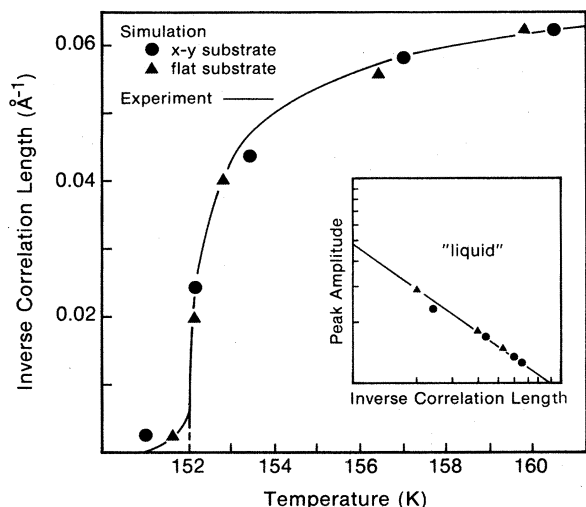


FIG. 4. Inverse correlation length as a function of temperature and the peak amplitude as a function of inverse correlation length, compared with the empirical fits to the laboratory measurements (Ref. 1).

structure factor to a Lorentzian profile and the fluid structure factors to a square root of a Lorentzian profile.<sup>1</sup> The solid correlation length was scaled to the graphite crystallite size in the laboratory experiments at 2000 Å.<sup>8</sup> In Fig. 4, inverse correlation length as a function of temperature and the peak amplitude as a function of inverse correlation length are compared with the empirical fits to the laboratory measurements,<sup>1</sup> where the xenon-xenon Lennard-Jones parameters are renormalized to  $\epsilon/k=237.8$  and  $\sigma=3.95$ . We note the excellent agreement between the computer experiment and the laboratory experiment. In Fig. 5, representative trajectory plots for the first-layer atoms are shown for various temperatures through the melting regime. We note an apparent coexistence of liquidlike and solidlike regions, this being shown by the atomic mobility of the respective regions in the film. With increasing temperature, the dominance of the liquidlike regions increases continuously until the film is entirely liquid. To determine the importance of the  $x$ - $y$  graphite corrugation to the melting phenomena, we did a similar simulation study with an uncorrugated graphite substrate; i.e., the graphite/xenon potential had only a dependence on the normal distance of separation between the adatom and the substrate. In Fig. 4, the comparison between the corrugated and the uncorrugated graphite-substrate experiments is presented, where the xenon-xenon Lennard-Jones parameters for the uncorrugated study are renormalized to  $\epsilon/k=236.9$  and  $\sigma=3.95$ . We concluded that the substrate  $x$ - $y$  structure does not play an important role in the melting phenomenon for this high-temperature-coverage regime.

In a very recent experiment study,<sup>4</sup> Rosenbaum *et al.* measured the x-ray diffuse scattering from monolayer xenon on single-crystal substrates of exfoliated graphite, and they concluded that the solid xenon film melts into an orientationally ordered liquid (or hexatic) phase. We adopt the angular correlation function as defined by Tobochnik and Chester<sup>9</sup> in order to determine whether our

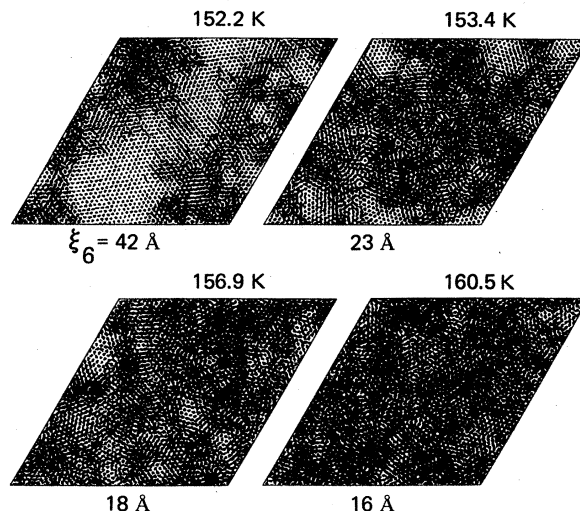


FIG. 5. Representative trajectory plots for the first-layer atoms for various temperatures through the melting regime.

simulated states of the xenon film through the continuous melting regime in the *TaMD* experiments appear as an orientationally ordered "liquid," as measured in the laboratory. The angular correlation function is defined by the equation

$$g_6(r) = \langle \exp[i6\{\theta(r) - \theta(0)\}] \rangle .$$

The angle  $\theta$  is between a vector joining two nearest neighbors and some fixed direction, and  $r$  is the distance between two sets of nearest-neighbor pairs. We analyze the data by assuming an exponential form for the correlation function

$$g_6(r) = \text{const} \times \exp(-r/\xi_6) ,$$

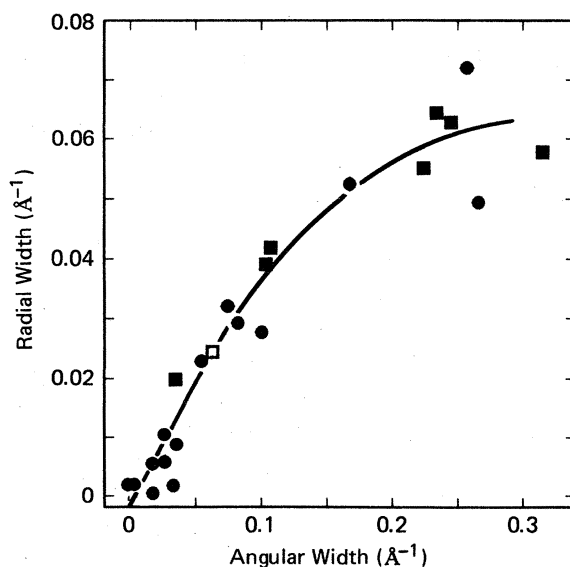


FIG. 6. Experimental results (Ref. 4) for the dependence of the radial spot width on the excess angular spot width, the solid line being a guide to the eye. The square points are the computer-simulated data for  $\xi_6$ , with normalization with respect to the open square.

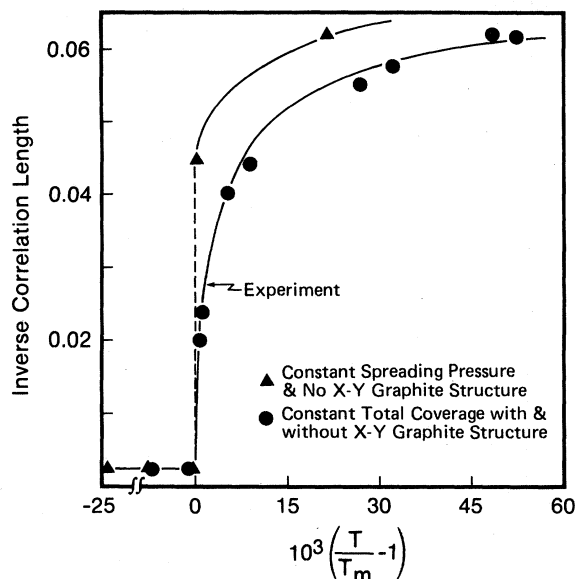


FIG. 7. Comparison of the variation of the inverse radial correlation length as a function of the deviation from the melting temperature  $T_m$  for the  $TaMD$  and  $TpMD$  experiments.

where  $\xi_6$  is the correlation length of orientational order.<sup>9</sup> In Fig. 6, experimental results<sup>4</sup> for the dependence of the radial spot width on the excess angular spot width is shown, the solid line being a guide to the eye. The square points are our computer-simulated data for  $\xi_6$ , with normalization with respect to the open square. We note that the functional behavior of  $\xi_6$  on the inverse correlation length mimics the experimental variation very well. Hence we have learned that for the  $TaMD$ -simulation experiments, the first layer of the xenon film appears to melt continuously over a small temperature interval, the quantitative features of the correlation functions being in excellent agreement with the experiments.<sup>1,4</sup>

A crucial test for the order of the melting transition is to determine its behavior for a constant spreading pressure environment.<sup>10</sup> In Fig. 1, we noted that for constant pressure and total coverage the melting is clearly first order. This is presented in Fig. 7 in a different manner by comparing the variation of the inverse radial correlation length as a function of the deviation from the melting temperature for the  $TaMD$  and  $TpMD$  experiments. There is a discontinuous change of the correlation length in the constant-pressure experiments, in sharp contrast to the continuous variation for the constant-area experiments. We conclude that this melting transition is first order and that we are traversing the two-phase, solid-liquid coexistence region in the  $TaMD$  simulations, thus giving the appearance of a continuous melting transition.

Even though our constant-area and -coverage computer experiments are in very good quantitative agreement with the laboratory findings, our general conclusion that the melting transition is first order is in conflict with the conclusions of Heiney *et al.*<sup>1</sup> based on their constant-

chemical-potential experiments. Two possible explanations immediately come to mind. (1) The excellent agreement between the  $TaMD$  simulations and the laboratory experiments is fortuitous, the simulations mimicking the melting process observed in the laboratory but not truly simulating the intermediate (or hexatic) phase. This would explain our observation of first-order melting in the constant-pressure simulations. (2) In contrast to the computer experiment where the graphite substrate is defect free, the laboratory graphite substrate has imperfections. This is well recognized, but the defects are not well characterized.<sup>11</sup> The probable role of substrate imperfections has been acknowledged: for example, the authors<sup>1</sup> state, "Our data are thus consistent with a continuous transition, with correlations in the fluid phase reaching at least 500 Å before finite-size effects, substrate interactions, or possibly a weak first-order transition play a role." (The authors determined that the average graphite crystallite size is 2000 Å.) In the same paragraph, they state that their Eq. (3) describes the data quite well for the correlation length,  $1/\kappa$ , less than 500 Å. Actually, it appears that the deviation from their Eq. (3) begins at a correlation length of 130 Å. Such substrate imperfections would result in substrate binding-energy heterogeneities. These heterogeneities would give rise to a distribution of melting temperatures approximating the unique melting temperature above a perfect graphite substrate, and two-phase, solid-liquid coexistence would exist although the melting regime over dimensions on the order of the separation between binding-site imperfections; i.e., approximately 130 Å. We understand that these two scenarios are speculation, but until we can better understand the origin of the experimental anomaly ascribed to possible "finite-size effects, substrate interactions, or possibly a weak first-order transition. . .," we feel that we can say little more at this time.

However, we do not share Nelson's recently stated pessimistic view of computer simulation.<sup>12</sup> We quote: "In particular, I doubt that the simulation techniques used by Abraham *et al.* could reproduce the apparently continuous melting transition of incommensurate xenon on graphite observed recently via precision x-ray diffraction by P. A. Heiney *et al.* (Ref. 1). It seems worth noting that second-order melting has also been observed experimentally for incommensurate argon on graphite (Ref. 13). Indeed, the solid-to-liquid transition is always continuous in this case!" From our present study, the status is clear for the high-temperature xenon film on graphite. In another recent molecular-dynamics simulation,<sup>14</sup> we have studied the melting of submonolayer xenon, krypton, and argon films on graphite, this investigation being stimulated by the interesting findings of McTague *et al.*<sup>13</sup> We observed first-order melting of xenon, which mimics the melting of an idealized two-dimensional film, first-order melting of krypton with the existence of an "incipient triple point," and "continuous melting" of argon over a temperature interval of approximately 7 K. The simulation experiments are consistent with the high-resolution x-ray experiment of melting by McTague *et al.*<sup>13</sup> The role of the graphite's lateral substrate structure on the melting of these various rare-gas films is emphasized,<sup>14</sup> particularly

for krypton and argon, and we demonstrate that melting of incommensurate solid argon is not a proper example for the study of two-dimensional melting.

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