

Melting Transition of Near-Monolayer Xenon Films on Graphite: A Computer Simulation Study

Farid F. Abraham

IBM Research Laboratory, San Jose, California 95193

(Received 17 January 1983)

Xenon films on graphite are simulated with a molecular-dynamics technique. Because of exchange of atoms between the first and second layers, there is a very small temperature window where the first layer melts and freezes continuously in time with a period of nanoseconds. Two-phase coexistence is prevalent during the transitions. The first-layer melting transition is first order, but would appear to be continuous if temporally averaged. These features are in quantitative agreement with recent x-ray scattering experiments.

PACS numbers: 68.20.+t, 64.70.Dv, 68.40.-e

In a recent x-ray scattering experiment, Heiney *et al.*¹ examined the melting of xenon on the (001) basal plane of pyrolytic graphite at coverages slightly more than one monolayer and found results which are at odds with lower coverage laboratory experiments² and with computer simulations for strictly two-dimensional atomic systems.³ In particular, they interpreted their results as indicating the melting transition to be continuous, with fluid correlation lengths exceeding 100 atomic spacings for a coverage of 1.1 monolayers. We became very interested in investigating any influence of the *third dimension of freedom* on the *apparent* order of the melting transition for a *quasi* two-dimensional system, especially at these high coverages and temperatures. In an earlier molecular-dynamics simulation study,⁴ we made several simulations in the temperature-pressure regime in question, knowing that the two-dimensional Lennard-Jones phase diagram predicted a first-order, liquid-solid transition, yet anticipating possible new physics associated with *second-layer promotion*. While we reported many interesting features resulting from an intimate interaction between the first and second adsorption layers, we found no evidence for a continuous melting transition.

However, there appeared to be no sound basis for doubting the reliability and validity of these very interesting experimental results, and I felt compelled to examine this problem more closely by computer simulation. My finding was completely unexpected and rather bizarre, but physically reasonable. Since it is currently fashionable, I will clothe the phenomenon in the descriptive phase—a *temporal bifurcation of the condensed-phase state of matter*. What I have found is that there is a very small *temperature window* where the liquid xenon monolayer will freeze by adsorbing atoms from the second layer so that its density is representative of the solid state. How-

ever, this solid state is not constant in time; over a period of nanoseconds, several atoms of the monolayer xenon solid are promoted by fluctuations to the second layer, thereby lowering the first layer's density and driving it back to the liquid phase. This adatom exchange fluctuation mechanism operates on a continuous temporal basis, and the delicate balance between the condensed phase being liquid or solid because of a few percent difference in their densities results in the first layer of xenon atoms melting and freezing continually over a period of nanoseconds. Also, two-phase coexistence is prevalent in the course of the transitions. Because exfoliated graphite is a mosaic of many independent adsorbing substrates and the experimental measurements are averaged over this ensemble of substrates and time, the laboratory experiment sees only an average of the first layer's properties and, hence a *new* phase with properties that are an average of some varying mixture of the quasi two-dimensional solid and liquid states! The magnitude and location of this temperature window and the *continuous* change of the averaged order parameter are in quantitative agreement with the x-ray experiment.

The details of the simulation procedure are given in Refs. 4 and 5 and will be briefly described here. The Lennard-Jones pair potential is chosen to represent the van der Waals interaction between the various atoms of the xenon-graphite system. The xenon-xenon parameters are taken to be $\epsilon/k = 225.3$ K and $\sigma = 4.07$ Å, and the xenon-carbon parameters are taken to be $\epsilon/k = 79.5$ K and $\sigma = 3.74$ Å. Simple pairwise additivity of the atomic interactions is assumed, and the carbon atoms defining the semi-infinite graphite solid are fixed at their lattice sites. In order to reduce computational time in the evaluation of the forces, certain approximations and procedures are implemented. The xenon-xenon

interaction is truncated at 3σ . Also, the chain/link method is employed so that the tests for locating atoms within 3σ of any particular atom need only be performed over a small subset of the total number of the xenon atoms.⁶ The atomic positions of the graphite surface define the basal plane of the computational box, this being a parallelogram compatible with the triangular lattice of a close-packed, two-dimensional crystal. Periodic boundary conditions are imposed at the four faces of the computational cell which pass through the sides of the basal parallelogram at normal incidence to the surface. The basal plane of the computational box must be compatible with the graphite structure, as, otherwise, periodic replication creates unphysical size dependences. A reflecting wall is placed at the top of the computational box at a 9-Å height, but a xenon atom reached this normal extent very infrequently.⁴ Conventional molecular dynamics is employed and consists of numerically integrating Newton's equations of motion to obtain trajectories of the atoms. Using a fifth-degree numerical integration scheme, I adopt a 0.05-ps time step. The atomic velocities are renormalized at every numerical time step so that the mean kinetic energy corresponds to the specified temperature. For equilibrium states, time averaging of the state variables over a sufficiently long interval of the temporal evolution of the system will yield proper equilibrium properties. The xenon density distribution normal to the graphite substrate shows two well-defined peaks separated by a very pronounced minimum region.⁴ This physical separation allows us to define unambiguously the properties associated with the first and second layers. In Ref. 4, both 576- and 5184-atom systems were examined, and no unusual size dependency was observed.

For a strictly two-dimensional atomic system that has a first-order phase transition, it is possible to simulate two-phase coexistence if the density is held fixed and the system is in the appropriate region of the phase diagram.³ In our earlier study,⁴ we concluded that, for sufficiently high temperatures and densities where second-layer population is likely, two-phase coexistence in the first layer is not possible since the second layer acts as an atom reservoir for the first-layer, condensed-phase subsystem. A brief review of this particular finding: The system of 576 Lennard-Jones xenon atoms were equilibrated at a reduced temperature $T^* = kT/\epsilon = 0.7$ for a basal-plane area $A^* = A/\sigma^2 = 612.5$. A fluid phase

was established in the first layer with a density $\rho^* = \rho\sigma^2 = 0.827$. The fluid phase remained as the system's temperature was decreased in increments of 0.01 with accompanying monotonically increasing equilibrium liquid density until, at a temperature of 0.66, the first layer solidified and the density increased discontinuously to that of a solid. Of course, this was accompanied by a discontinuous decrease of the second-layer density because of conservation of the total number of xenon atoms. Thus, in contrast to a two-dimensional system with fixed density, this two-layer system did not support two-phase coexistence as suggested from the two-dimensional phase diagram of a Lennard-Jones system since at this temperature and density the number of xenon atoms in the first layer are not constrained to remain constant. Similarly, I found that the simulated xenon monolayer solidified at a reduced temperature of 0.67. A finer cut of the temperature regime between 0.66 and 0.67 was not made. However, scrutiny of the Heiney *et al.* results made me realize that all of the action occurs over the very short temperature interval of less than 0.004 (in reduced temperature units)! They reported that the xenon monolayer melted at 152 K (reduced temperature of 0.675) with a *liquid* correlation length of 100 to 200 Å and by 153 K (reduced temperature of 0.679) this correlation length dropped to approximately 22 Å. The fact that the temperature regimes for melting from experiment and computer simulation agree very well is gratifying, but it is immediately obvious that we may have *jumped* over the *continuous melting transition* in our computer simulation study.⁴ Therefore, I have performed a series of simulations in the temperature regime bounded by 0.66 and 0.67 and will now discuss my findings.

A series of simulations have been performed at reduced temperatures of 0.664, 0.665, 0.666, and 0.667, and the total simulation time for each temperature needed to be very long. The mean density of the first layer as a function of temperature is presented in Fig. 1. We note that the density decreases *continuously* from the value 0.863 for a solid at a temperature of 0.664 to the value 0.836 for a liquid at the temperature of 0.667, this continuous change occurring over a temperature interval of 0.03! This is in remarkable agreement with the x-ray experiment. A closer examination of the simulation results tells us what is happening. In Fig. 2, the *block-averaged density* of the first layer, averaged over each 1000 time steps, as a function of time is present-

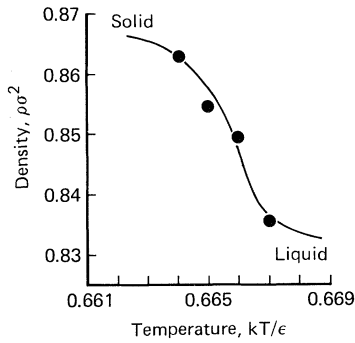


FIG. 1. The equilibrium reduced density $\rho\sigma^2$ of the adsorbed xenon in the first layer as a function of reduced temperature $T^* = kT/\epsilon$.

ed for the various temperatures. We note that at $T^* = 0.664$ the density fluctuates about the mean solid density of 0.863; similarly, at $T^* = 0.667$, the density decays from an initial solid density and fluctuates about the mean liquid density of 0.836. However, for the two intermediate temperatures of 0.665 and 0.666 the first-layer density oscillates between the densities of the solid state and liquid state, the residence time at higher density being significantly longer at the lower temperature. It is apparent why very long total simulation times were required to validate this feature. In Fig. 3, I show a trajectory analysis of the atomic motions in the first layer at specific times in the simulation for $T^* = 0.666$. I note that the first-layer phase is solid at times when its density is high, and it is liquid at times when its density is low. Two-phase coexistence exists at the intermediate densities. Hence, two-phase coexistence in the first-layer takes on a new meaning, where local exchange of xenon atoms between the first and second absorption layers can lead to *temporal freezing or solidification* of the condensed-phase adsorbed layer. Of course, time averaging the first-layer's properties leads to an *apparent continuous transition for the melting of the first layer*.

I conclude that the *effective or apparent* phase diagram for the first xenon layer may be described by the following simple and physically reasonable scenario: For sufficiently low temperatures and low coverages, defined by negligible second-layer occupancy, solid-liquid coexistence for the xenon atoms is possible and the phase boundaries should be accurately given by the two-dimensional Lennard-Jones phase diagram. As the temperature and coverage increase and second-layer population of xenon atoms be-

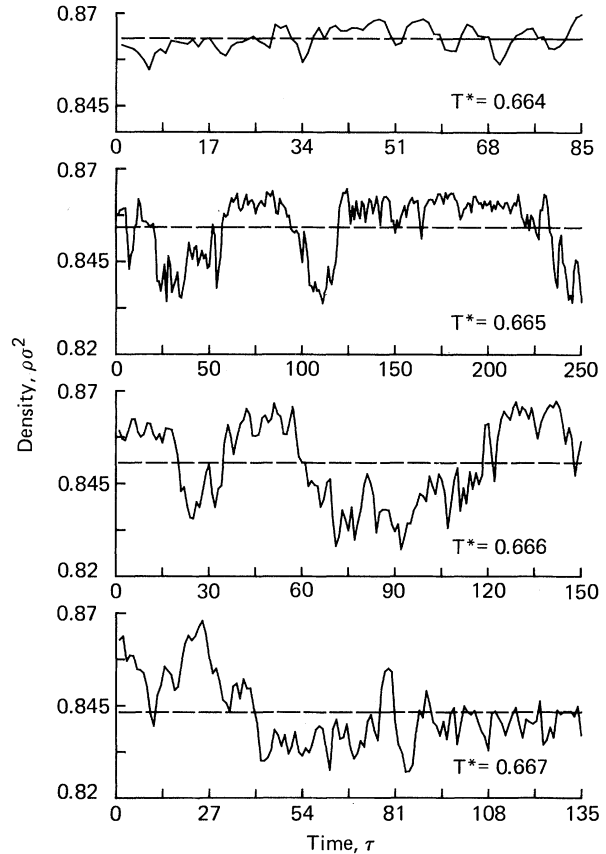


FIG. 2. The block-averaged density of the first xenon layer, averaged over each 1000 time steps, as a function of simulation time τ for various reduced temperatures T^* . The time unit for this figure is 1000 time steps.

comes prevalent, the separation between the solid-liquid coexistence boundaries will shrink in relation to the two-dimensional phase diagram, the shrinkage being directly related to the percentage of second-layer occupancy at the particular temperature. Eventually, the phase boundaries should converge to a common line, because a significant number of second-layer atoms will act as a *quasi-infinite* atom reservoir for the first layer. A simple statistical mechanical calculation incorporating the two-dimensional phase diagram and fluctuation theory may be constructed to predict these features.⁷ Because the interatomic well depths are significantly small for the argon/graphite system [i.e., $\epsilon(\text{Ar-Ar})/\epsilon(\text{Xe-Xe}) \approx 0.5$ and $\epsilon(\text{Ar-C})/\epsilon(\text{Xe-C}) \approx 0.7$], the *apparent continuous melting* of the first-layer argon on graphite would be much more prevalent, and this is observed experimentally.⁸ From my findings, I conclude that it is desirable to study experimen-

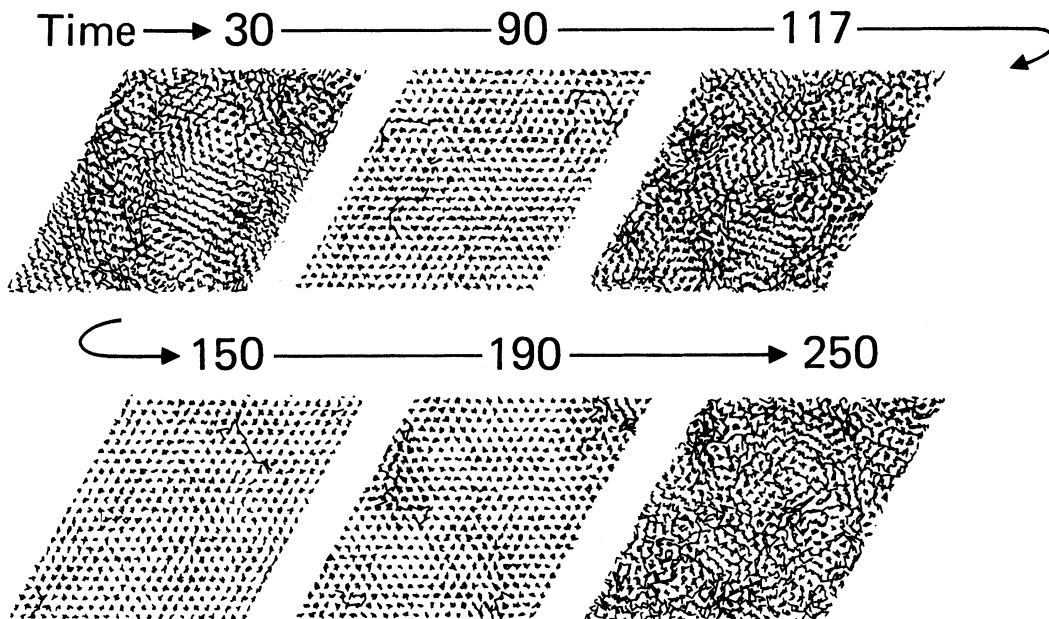


FIG. 3. Trajectory analysis of the atomic motions in the first xenon layer at specific times in the simulation for $T^* = 0.666$. The time unit for this figure is 1000 time steps.

tally the melting of a substrate-free, two-dimensional system. This has recently been achieved^{9,10} for a liquid-crystal, two-layer film where the crystalline phase is found to melt directly into a liquid by a first-order transition.

¹P. A. Heiney, R. J. Birgeneau, G. S. Brown, P. M. Horn, D. E. Moncton, and P. W. Stephens, *Phys. Rev. Lett.* **48**, 104 (1982).

²E. M. Hammonds, P. A. Heiney, P. W. Stephens, R. J. Birgeneau, and P. M. Horn, *J. Phys. C* **13**, L301 (1980).

³F. F. Abraham, *Phys. Rep.* **80**, 339 (1981).

⁴S. Koch and F. F. Abraham, *Phys. Rev. B*, to be published.

⁵F. F. Abraham, S. W. Koch, and W. E. Rudge, *Phys. Rev. Lett.* **49**, 1830 (1982).

⁶R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles* (McGraw-Hill, New York, 1981), Sec. 8-4.

⁷F. F. Abraham, to be published.

⁸J. P. McTague, J. Als-Nielsen, J. Bohr, and M. Nielsen, *Phys. Rev. B* **25**, 7765 (1982).

⁹D. J. Bishop, W. O. Sprenger, R. Pindak, and M. E. Neubert, *Phys. Rev. Lett.* **49**, 1861 (1982).

¹⁰D. E. Moncton, R. Pindak, S. C. Davey, and G. S. Brown, *Phys. Rev. Lett.* **49**, 1865 (1982).