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Molecular Dynamics Simulations of Phase Transitions
in Physisorbed Nobel Gases

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Abstract:

The freezing transition of xenon on graphite and the commensurate-incommensurate transition of krypton on graphite are studied by molecular-dynamics computer simulations. The results are shown to be in good agreement with recent x-ray scattering experiments of these systems. The simulations lead to valuable physical insights into the detailed nature of the investigated phase transitions.

I. Introduction

In the last years many experimentalists and theorists in the physics and chemistry communities became interested in the study of phase transitions of physisorbed systems. Experimental investigations have led to the discovery of a variety of adsorption phenomena at solid surfaces, which have stimulated a great deal of theoretical activity in the study of the phases of quasi two-dimensional systems, such as rare gases on graphite¹. Computer simulations became an important technique for investigations in this field, as evidenced by the great variety of computer experiments which have established the important features of the phase diagram for two-dimensional simple atomic systems².

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Additionally, the phases of quasi two-dimensional systems are investigated with simulation techniques and some first results are reported in Refs. 3, 4.

In the present paper, we summarize the results of recent molecular-dynamics computer simulations for the freezing transition of xenon on graphite ^{5,6} and for the commensurate-in-commensurate transition of krypton on graphite ⁷. In both cases the coverages and temperatures were chosen to correspond to the regions of the respective phase diagrams experimentally studied by Heiney et al. ⁸ and by Moncton et al. ⁹. The results for xenon/graphite and those for krypton/graphite are discussed separately in sections 3 and 4, respectively. In section 2 of this paper we briefly summarize our computer model of the rare-gas/graphite system.

II. The Computer Model

We use the Lennard-Jones 12:6 pair potential

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] , \quad (1)$$

to represent the van der Waals interaction between the various atoms. The parameters ϵ and σ are determined empirically. We take the xenon-xenon parameters $\epsilon/k=225.3$ K and $\sigma=4.07$ Å and the xenon-carbon parameters $\epsilon/k=79.5$ K and $\sigma=3.74$ Å. The krypton-krypton parameters are $\epsilon/k=170$ K and $\sigma=3.6$ Å and the krypton-carbon parameters are taken to be $\epsilon/k=66.6$ K and $\sigma=3.35$ Å. (See Refs. 10,11.) The total potential energy U for a given configuration of N rare gas atoms $\vec{r}(i)$, $i=1, \dots, N$, above a fixed configuration of carbon atoms defining the graphite semi-infinite solid $\vec{R}(j)$, $j=1, \dots, \infty$, has the form

$$U = \sum_{i>j}^N \varphi(|\vec{r}(i) - \vec{r}(j)|) + \sum_{j=1}^N \sum_{\substack{i=1 \\ \{C\}}}^{\infty} \varphi_C(|\vec{r}(i) - \vec{R}(j)|) , \quad (2)$$

where simple pair-wise additivity of the interatomic interactions is assumed.

Our computational cell geometry is such that the graphite surface defines the x-y plane at $z=0$, which is also the basal plane of the computational box. This base is 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. A reflecting wall is placed at the top of the computational box at $z=ZL$.

The molecular-dynamics method used is described in detail in Refs. 5 and 12 and will not be discussed here. In the constant-pressure simulations, we allow the area A of the basal plane to fluctuate in size with the constraint that the height of the computational box remains constant. Therefore, the parallel pressure $P_{||}$, given by

$$P_{||} = kT \left. \frac{\partial}{\partial V} \ln Q \right|_{N,T,ZL} \quad (3)$$

is a constant during a simulation, while the normal pressure P_{\perp} given by

$$P_{\perp} = kT \left. \frac{\partial}{\partial V} \ln Q \right|_{N,T,A} \quad (4)$$

fluctuates about its equilibrium mean value which is governed by the physical situation. In (3) and (4), Q is the canonical partition function.

III. The Freezing Transition of Xenon on Graphite

In a recent x-ray scattering experiment, Heiney et al.⁸ examined the melting of xenon on graphite at coverages slightly more than one monolayer and found results which are at odds with lower-coverage laboratory experiments¹³ and with computer simulations for strictly two-dimensional atomic systems¹¹. 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 influ-

ence 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. Therefore, we made several simulations^{5,6} in the pressure-temperature regime where the two-dimensional Lennard-Jones phase diagram predicts a first-order liquid-solid transition, and where the laboratory experiment suggests that the high-density liquid freezes in a continuous manner.

As a representative example, we discuss our results for a simulation along an isotherm. The temperature has been fixed at $T^* = k_B T / \epsilon = 0.7$, and a series of constant-pressure simulations were performed for pressures ranging from $P_{||}^* = P \sigma^2 / \epsilon = 2.0$ to 4.2, which bound the freezing transition point for this high temperature. The experiments were performed sequentially from the lowest to the highest pressure and vice versa. Careful attention has been given to determine that the system is in "local equilibrium" (stable or metastable) when taking the statistics for the quantities of interest; e.g., the distribution, running mean and "auto-correlation" relation of density, enthalpy and virial pressure were monitored, as well as particle distribution functions and trajectory pictures of the temporal evolution were studied. We found two well defined adsorption layers which were separated by a pronounced minimum region which has a very low population of atoms. This physical separation allows to discuss unambiguously the properties associated with the individual layers. With increasing pressure, we find a monotonic increase of the percentage of atoms in the second layer, this percentage rising from approximately 7% at $P_{||}^* = 2.0$ to 36% at $P_{||}^* = 4.2$. We define the "effective" two-dimensional density for a layer ρ_i^* , $i=1,2$, as the total number of atoms in that layer divided by the mean cross-sectional area.

In Fig.1 we show a series of trajectory pictures of atoms in the first layer for the constant-pressure simulations. The trajectory of the particular atoms is constructed by connecting their x-y positions for a chosen number of time-steps. We note a transition from the liquid state to the solid state by

passing from $P_{||}^* = 2.4$ to $P_{||}^* = 2.6$. This is in contrast to the second layer where we find that the fluid state exists for all pressures because of the low second-layer atomic densities.

Xenon / Graphite, First Layer

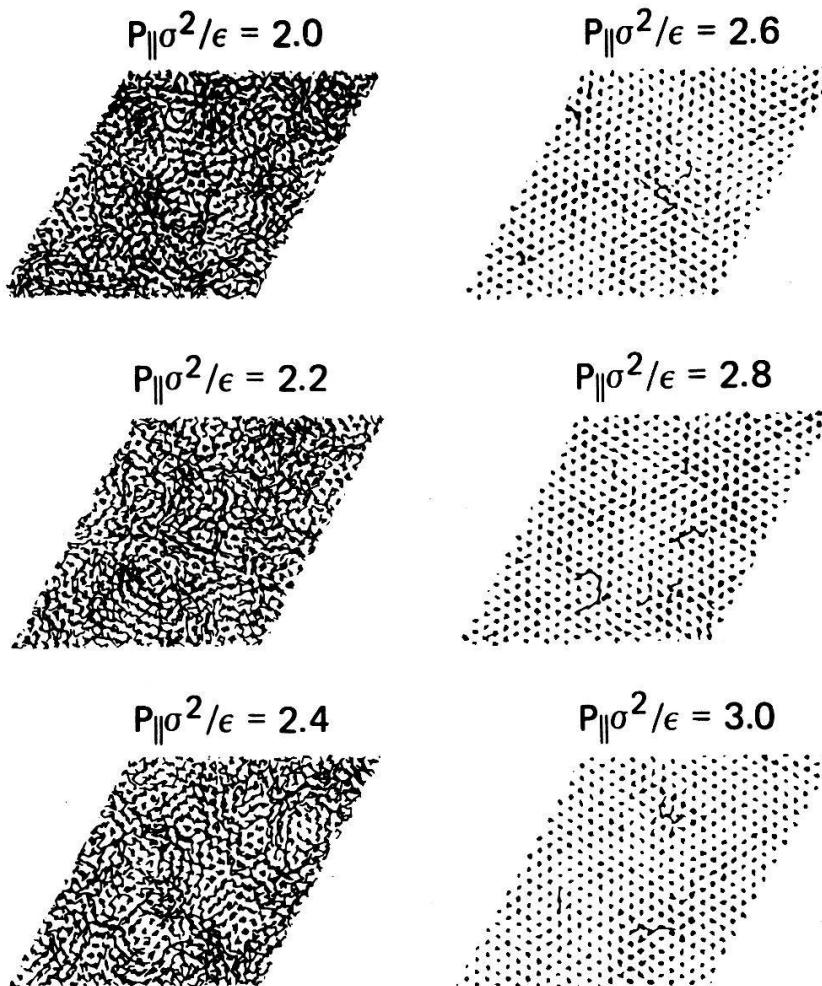


Fig.1

Trajectory pictures of the equilibrium states in the first layer for the constant-pressure simulations at $T^* = 0.7$.

In Fig.2, the effective two-dimensional density ρ_1^* is presented as a function of pressure for the first layer. Starting at pressure $P_{||}^* = 2.0$, the xenon layer equilibrates to the liquid state with a mean density of 0.805.

We observe a discontinuity in density at $P_{||}^* = 2.6$, associated with the first-order freezing transition, and the subsequent solid density increases with increasing pressure. Hyste-

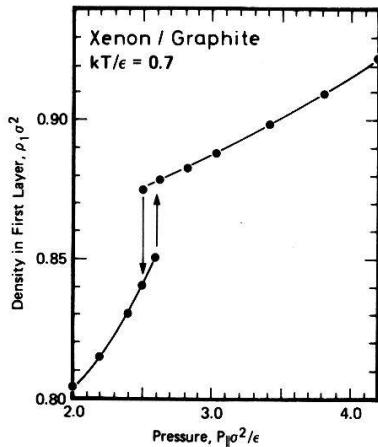


Fig. 2

Effective two-dimensional density in the first layer versus pressure for the constant-pressure simulations.

resis is also demonstrated by sequentially lowering the pressure from an equilibrium solid-state phase, resulting in first-order melting at $P_{||}^* = 2.5$ and a discontinuity in density. Thus, in the constant-pressure simulations we find no evidence for a continuous melting transition.

Very recently a series of constant-density simulations have been performed⁶ 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 results showed that in those simulations the time-average mean density in the first layer decreases continuously from the value for a solid at a temperature of 0.664 to the value for a liquid at a temperature of 0.667, this continuous change occurring over a temperature interval of 0.03. This is in remarkable agreement with the x-ray experiment⁸. The physical reason for this continuous variation is, that in this very small temperature window the liquid-xenon monolayer freezes by adsorbing atoms from the second layer so that its density is representative of the solid state. However, 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 continuously over a period of nanoseconds. Because exfoliated graphite is a mosaic of many independent absorbing 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. As illustration, we show in Fig. 3 a trajectory analysis of the atomic motion in the first layer at specific times in the simulation.

Xenon/Graphite, First Layer

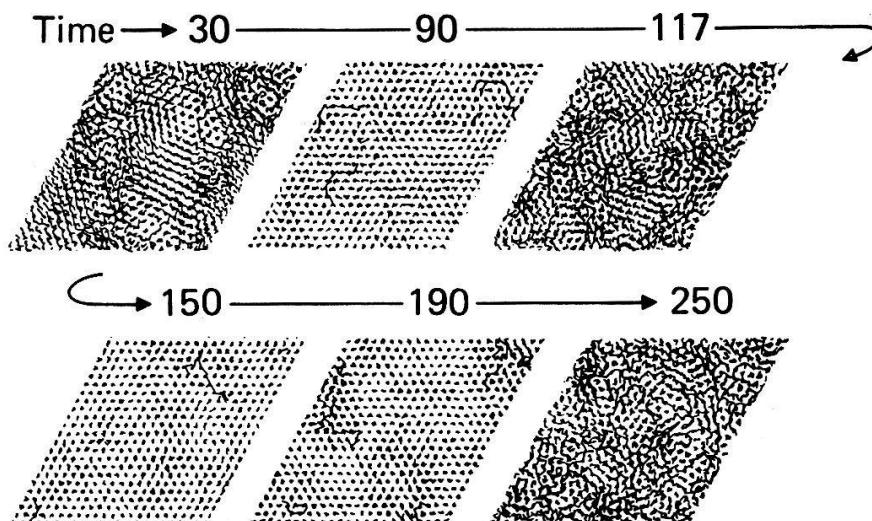


Fig. 3

Trajectory pictures for the atoms in the first layer at specific times in the simulation. (The time unit is 1000 time steps.)

Obviously, the first-layer phase is solid at times when its density is high, and it is liquid at times when its density is low.

Thus, it is clearly demonstrated that the freezing transition of

xenon on graphite is a first-order phase transition.

IV. The Commensurate-Incommensurate Transition of Krypton on Graphite.

In the synchrotron-x-ray study⁹, the authors have found that the experimental diffraction profiles through the incommensurate-commensurate (C-IC) transition of monolayer krypton on graphite behave in an entirely unexpected manner and conclude that, in contrast to expectation, the weakly incommensurate phase arising from this transition is disordered (IC-D). However, Moncton et al.⁹ point out that this disordered phase is unusually well correlated for a liquid, but is clearly not a two-dimensional (2D) solid. The experimental results for the atomic structure factor of the krypton layer are plotted as dashed line in Fig.4.

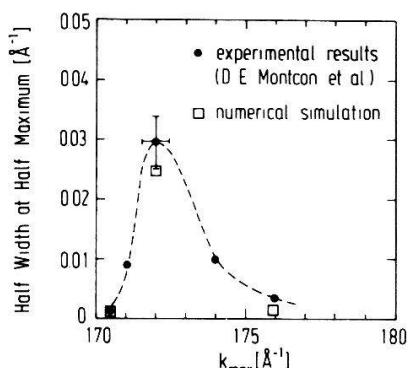


Fig.4

Half width at half maximum (HWHM) of the atomic structure factor versus peak position for krypton on graphite.

We performed a series of molecular-dynamics simulations for this system⁷ to investigate the nature of the weakly incommensurate phase. Because of finite-size effects we were forced to simulate 22'212 atoms. The simulation results are indicated as squares in Fig.4 and are in good agreement with the experimental findings.

In Fig.5 we present a time-sequence of "snapshot pictures" of the incommensurate atoms for the 22'212-atom "disor-

dered phase" (coverage of 1.05). We define a krypton atom as being incommensurate if its position is displaced from a graphite adsorption site by an amount that is greater than two-tenths of a graphite lattice constant. With this definition, approximately 56 % of the krypton atoms are commensurate at this coverage. We note the formation of a rather extensive network of intertwining domain walls defined by the incommensurate atoms. The domain walls are defined and have an approximate thickness of 30 Å. The "typical" dimension of a commensurate island is of the order of 100 Å. The presence of free dislocations, signaled by the misorientation of domain walls relative to each other, characterizes the "disordered" nature of this weakly incommensurate phase.

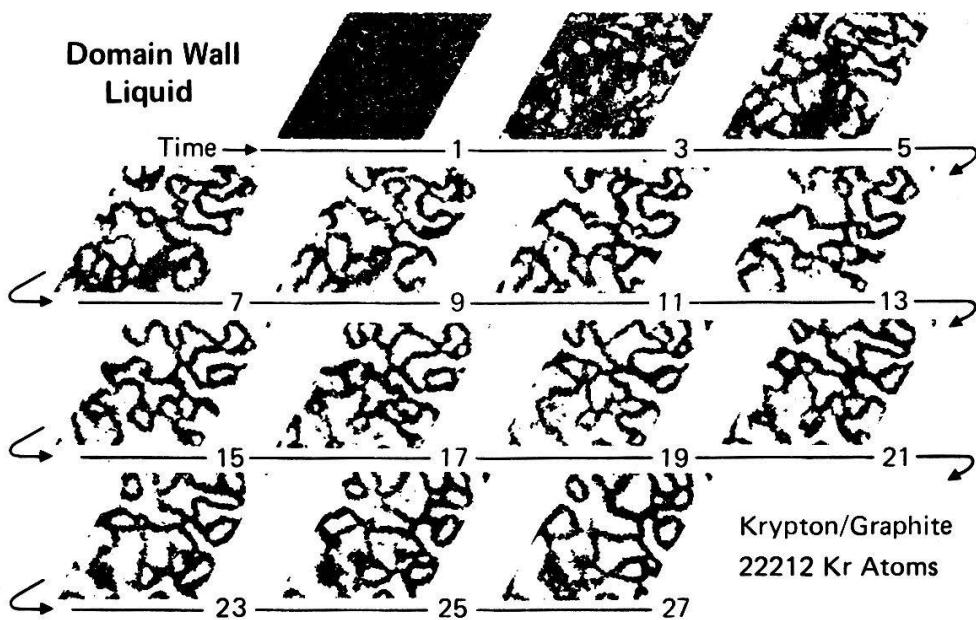


Fig. 5 Time-sequence of trajectory pictures of the incommensurate krypton atoms (<44 %) at a coverage of 1.05 commensurate monolayers, a temperature of 97.5 K and a graphite linear dimension of 620 Å. (The time unit is 1000 time-steps.)

Fig. 5 clearly shows the slow temporal meandering of the domain walls. One may describe this phase as a "domain-wall liquid".

The domain walls have soliton features in the sense of a modified Sine-Gordon theory. The temperature-dependent wall-width has been calculated ¹⁴ and the results show good agreement with the molecular-dynamics simulations.

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