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Orientation of small rafts of xenon atoms physisorbed on Pt(111): A molecular-dynamics study

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A recent experiment using high-resolution He diffraction revealed the existence of incommensurate xenon overlayers of Pt(111). The overlayers were rotated by 30° with respect to the platinum substrate. We present here the results of a molecular-dynamics study of small rafts of xenon atoms on a Pt(111) surface. They reveal a mechanism for the 30° orientation of the incommensurate xenon. The experiments also showed the existence of a $\sqrt{3}\times\sqrt{3}R$ 30° commensurate phase of xenon. In our studies of small rafts at various temperatures, and with a variety of substrate-adatom potentials, we see no existence of this phase.

In a recent experiment using high-resolution He diffraction, Kern, David, Palmer, and Comsa[1] found that xenon adsorbed on Pt(111) exhibited three different structures at coverages $\lesssim$ one monolayer. One structure (C) had domains of dimensions $\sim$500–1000 Å. The xenon atoms were commensurate with those of the underlying platinum and were in the $\sqrt{3}\times\sqrt{3}R$ 30° structure. A second structure (I) was not commensurate with the underlying Pt(111) but was rotated 30° with respect to the substrate. The domains in this case were $\sim$150 Å across. A third structure (R) occurred at the highest coverages and will not be discussed here.

We have been using molecular dynamics to examine the behavior of small rafts of xenon (37 and 49 atoms) on Pt(111). The platinum consists of four layers, each layer containing 324 atoms. This unit of 1296 atoms is then repeated parallel to the surface. The average substrate temperature is 85 K and the average distance between nearest-neighbor platinum atoms is 3.92 Å. The platinum atoms are coupled with a nearest-neighbor central-force model.

The xenon atoms are coupled to platinum atoms in the first platinum layer with a Lennard-Jones potential. They are coupled to the remaining platinum atoms (and, in fact, we simulate a semi-infinite platinum substrate) with a Morse potential which depends on the height of the xenon atoms above the platinum surface. The parameters of these potentials are adjusted to give the correct energy of xenon desorption 6.6 kcal/mol,[2] the correct vibration frequency of xenon atoms perpendicular to the surface 3.25 meV,[3] and a reasonable height of the xenon atoms above the platinum surface of 3.55 Å.[4] This leaves one free parameter. We adjust it to give varying degrees of corrugation to the potential seen by the xenon atoms. At a height of 3.10 Å (our most corrugated potential) the potential varies from 0 K at the hollow site to 28 K at the bridge site and 168 K at the top site.

Finally we have used the Barker X2 potential[5] to treat the direct xenon-xenon interaction. We have used the McLachlan substrate-mediated potential[6] with values of the parameters for xenon on Pt(111) provided by Bruch.[7] We intend to publish the details of our potentials and molecular-dynamics calculations in a larger paper in the future.

We have explored the behavior of rafts of 37 and 49 xenon atoms by starting out with a triangular lattice configuration on our Pt(111) surface. We find that over periods of about 40 psec the rafts maintain their structure even with no corrugation in the Pt-Xe potential. Introducing surface corrugations of various reasonable strengths does not seem to alter the spacing of the xenon atoms which is $\sim$4.60 Å at 70 K. The $\sqrt{3}\times\sqrt{3}R$ 30° spacing would be 4.80 Å. Our results hold for a variety of temperatures, initial configurations, and raft orientations. Thus we do not see the small rafts in the (C) structure observed by Kern *et al.*

On the other hand, we do see evidence of a mechanism which could explain the existence of the (I) structure observed by Kern *et al.* In Figs. 1 and 2 we show the behavior of a raft of 49 particles started with a nearest-neighbor separation of 4.36 Å and with the rafts triangular lattice having the same orientation as the substrate. As can be seen, the raft somehow changes its orientation to 30° with respect to the substrate in 32 psec (the precise method of the rotation is not clear; it is some mix of rotation of the central part of the raft and excursions in which the surface atoms of the raft leave it and then return to it). In Fig. 3 we show the raft for the next 20 psec. Note it is no longer rotating. It maintained the configuration of Fig. 3 for at least 54 psec (after the first 32 psec) at which time we stopped the molecular-dynamics run. The average temperature was 74.1 K and the average atom spacing was 4.61 Å for the period covered in Fig. 3. With the small clusters of adatoms, and the short times involved in our runs, the temperatures of the adsorbate and substrate will not, in general, be the same. We do not believe that the conclusions of our paper would be altered if the two systems had identical average temperatures.

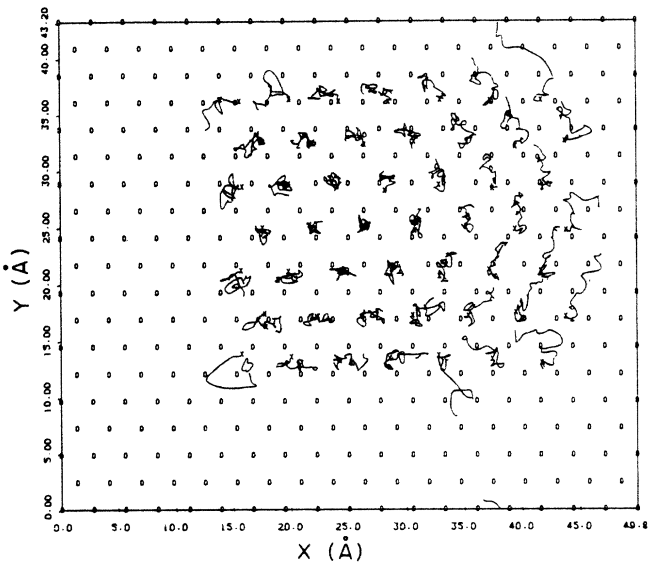

FIG. 1. 49-atom triangular raft 0–16 psec in steps of 4×10^{-15} sec. Points plotted each 0.2 psec. Substrate temperature 85 K. Average temperature parallel to the surface of the adsorbate in the interval 0–32 psec was 68.3 K. Average separation of the xenon adatom in the interval 0–32 psec was 4.61 Å.

The above results suggested the existence of a potential minimum for the raft at 30° even though the xenon atoms were separated by 4.61 Å, not the 4.80 Å they would have in the $\sqrt{3}\times\sqrt{3}R$ 30° overlayer. We have used the computer to explore the existence of such minima with the following simple scheme. We place a rigid raft of xenon atoms above a rigid platinum substrate. We then calculate the average projection of the distance between each xenon atom and the nearest platinum atom on the surface. The potential energy of the xenon atoms is a monotonically decreasing function of the distance parallel to the surface

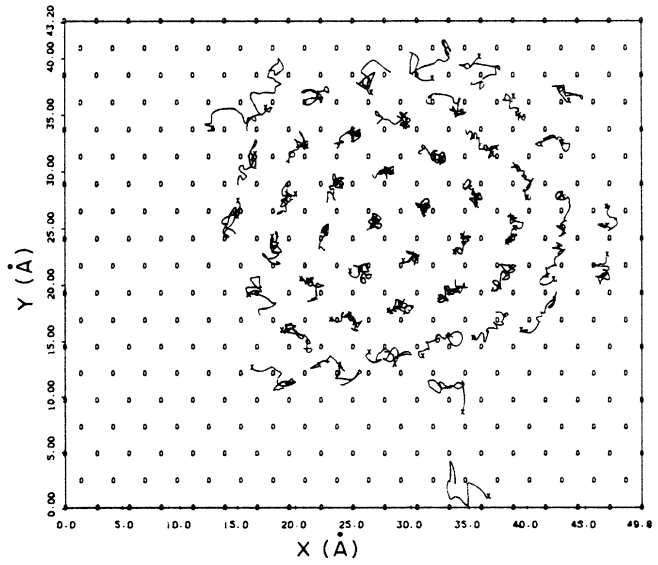

FIG. 2. As for Fig. 1 but 16–32 psec.

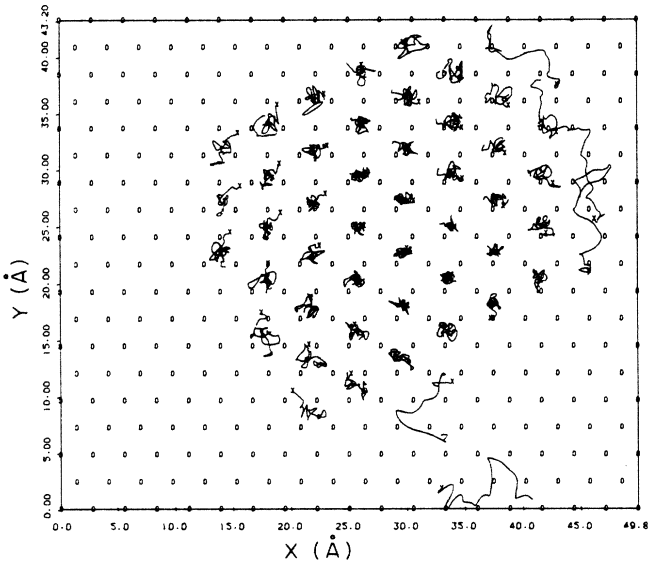

FIG. 3. As for Fig. 1 but 32–52 psec.

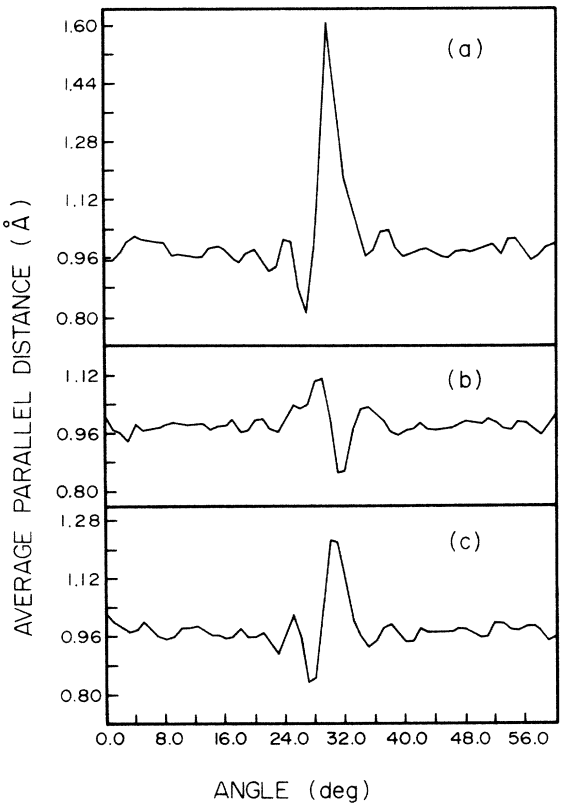

FIG. 4. (a) Dependence of average distance parallel to the surface of the xenon atoms from their nearest platinum atom on raft angle 0.49, atom raft like that of Fig. 1 but with no thermal displacement (i.e., rigid). Central atom at a hollow site, atoms separated by $\sqrt{3}$ times the platinum nearest-neighbor spacing (4.80 Å). (b) As for (a) but with xenon atom spacing of 4.61 Å. (c) As for (a) but with the central atom in the raft at a bridge site, not a hollow site.

from the top site to the hollow site (the largest parallel distance in our scheme). Therefore we can use the behavior of the average distance as a guide to the behavior of the potential energy of the raft. This way we avoid the complexity of a full potential-energy calculation for each atom in the raft and obtain some insight into how the potential energy of the raft depends on its location and orientation with respect to the platinum substrate.

In Fig. 4 we show such average distances obtained when the 49-atom raft (like the one in Fig. 1) is rotated through 60° on a corrugated surface. The top curve is obtained for the centrally located atom at a hollow site and a nearest-neighbor xenon spacing of 4.80 Å ($\sqrt{3}$) times the platinum nearest-neighbor spacing. The middle curve was obtained for an identical rotation, but with a Xe-Xe spacing of 4.61 Å. The same spacing, but with central atom at a bridge site, was used to determine the lower curve. In all three cases potential minima appear for rotation angles near 30°, although the exact value of 30° is achieved only in the last case. These minima with barriers close by could provide a mechanism to lock the raft in the rotated position. We are presently exploring the effects of raft size and starting conditions on rotation using the molecular dynamics programs. In these studies we examine the actual potential energy of the xenon raft rather than the simple average distance given here.

In summary, we see, both from molecular dynamics and a simple scheme based on average parallel distance, that small xenon incommensurate rafts can be stable at orientations of 30° with respect to the substrate. We also see that they can rotate into such 30° orientation even if they begin at another orientation. This sort of behavior can be responsible for the 30° incommensurate (I) structure of domains observed by Kern *et al.* One mechanism would be the formation of small pinned rafts orientated at 30° with respect to the substrate at low coverages and then subsequent nucleation on these.

Our results indicate that some mechanism other than corrugation of the Pt(111) surface must be responsible for the experimentally observed (C) structure. In no case do we see raft atoms take up the 4.8-Å separation needed for this structure.

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