Large Finite-Size Effect on the Critical Temperature of Adsorbed Layers: Xe on Pd [8(100) × (110)]

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The critical temperatures of the first three layers of Xe on a stepped surface of Pd, as well as the roughening temperature, have been recently measured by Miranda *et al.* These temperatures are about half those expected from theory for homogeneous infinite surfaces. Here we propose that this dramatic decrease is due to the finite size of the terraces in the stepped surface and to the existence of preferential adsorption sites along the steps.

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The field of phase transitions in two-dimensional (2D) systems has gained the attention of an increasing number of physicists during the last years due to the richness of novel phenomena owing their existence to the lower dimensionality of the system.[1,2] Theoreticians usually assume a uniform and homogeneous 2D universe in their calculations but unfortunately real surfaces have an unavoidable amount of imperfections. Little is known about the influence of these heterogeneities on the real surface phase transitions, though much theoretical effort[3–5] has been devoted to study finite-size effects. It has been suggested,[5] for instance, that random defects can broaden an otherwise first-order transition but progress in this field has been limited by the lack of a systematic *experimental* set of data on a surface with a well-characterized number and type of defects.

For the first time, experimental results testing the influence of *ordered* imperfections (i.e., steps) in the 2D phase transitions have been reported very recently.[6] In that experiment, a Pd single crystal was intentionally cut at a particular orientation to induce a known terrace width. Low-energy electron diffraction analysis confirmed that a periodic array of terraces eight Pd atoms wide separated by monatomic steps was actually present on the surface. The equilibrium Xe adsorption on that well-defined stepped Pd surface was studied from the submonolayer to the multilayer regime. Multilayer formation takes place via a sequence of first-order layering transitions and, from the experimental isotherms, the value of the critical temperature T_c for each added layer can be obtained. The data show that for Xe on Pd [8(100) × (110)], $T_c = 66.4$ K for the second layer and 67.3 K for the third layer (for the first layer $T_c < 40$ K, the lowest temperature attainable). These experimental values are, however, in large discrepancy with theoretical predictions for an infinite 2D surface. It is firmly established that the critical temperature of the gas-liquid transition for a 2D fluid interacting through Lennard-Jones pair potentials is given[1] by $T_c^{2\mathrm{D}} = 0.533\epsilon/k_\mathrm{B}$, where ϵ is the depth of the potential well. Taking the usual value for Xe, $\epsilon/k_\mathrm{B} = 221$ K, $T_c^{2\mathrm{D}} = 118$ K is obtained. The experimental value is about half of the theoretical estimate. On the other hand, experimental results for Xe adsorbed on large crystallites of graphite[7] are in excellent agreement with the calculated value of the critical temperature. Furthermore, similar agreement exists for Ne,[8] Ar, and Kr[7] adsorbed on graphite.

Here we discuss the possible origin for the apparent discrepancy. We maintain that the finite-size effects produced by the smallness of the terraces in the stepped surface as well as preferential sites for adsorption explain the dramatic decreases of T_c for the two-dimensional liquid-gas transition observed in the experiments.

The argument given in the original work[6] to justify the discrepancy was based on the idea that nearest-neighbor attraction between Xe atoms was strongly reduced because of a variety of substrate-induced effects. Firstly we will show that this is not the case. Several of such effects (adsorption-induced dipole-dipole repulsion, substrate-mediated dispersion forces, elastic distorsion of the adlayer, triple-dipole energy) have been mentioned in this connection. Substrate-induced Xe dipoles were experimentally found to be 0.65 D on the average in the first layer and 0.11 D in the second layer.[9] The static dipole-dipole direct repulsion at a Xe-Xe distance of 4.48 Å gives a repulsive contribution of 16.3 and 0.5 meV to the interaction energies in the first and second layer, respectively.

Substrate-mediated (Sinanoğlu-Pitzer-McLachlan) forces, which represent the interaction between the fluctuating image dipoles of the substrate and those of the adatoms, can be estimated for the Xe on Pd system from the parameters given by Bruch.[10] With a distance of 2 Å from the first layer to the image plane, repulsive energies of 9.5 meV for the first and 0.9 meV for the second layer are obtained. These numbers are to be compared to the $\simeq 75$-meV attraction per atom (van der Waals attraction minus triple-dipole repulsion).

It is known that Pd has by far the strongest (~ 390 meV/atom) adsorption energy for xenon. This suggests the possibility of a certain degree of chemisorption, which could further reduce the nearest-neighbor interactions in the first layer, but it is extremely unlikely that this indirect interaction will have any significant effect on the second or third adsorbed layer.

Thus, we conclude that the interaction energy between Xe atoms in the second layer is *only* reduced by $\lesssim 2\%$ because of the effect of the substrate. The reduction for the third layer will be negligible. This is in agreement with the relation between the experimental critical temperatures in the second and third layers, but cannot explain the reduction by almost a factor of 2 from the theoretical critical temperature for plane surfaces.

We propose that the dramatic decrease of the critical temperature is due to the stepped character of the surface. The steps will have two effects:

(a) Step sites S will be strongly preferred energetically, because of their higher coordination with atoms in the lower layer [see Fig. 1(a)]. These sites along the steps will be occupied first, producing a strong boundary which represents a barrier to correlations between different terraces, while position W is less probably occupied and constitutes a weak boundary.

(b) Since, on one hand, a certain mismatch exists between the terrace width and an integer number of Xe rows, and, on the other hand, weak boundaries locally cause[2] a decrease of the density, two Xe atoms in different terraces will in general be at a distance larger than two atoms in the same terrace. As a result the effective interaction between terraces will decrease, reducing the propagation of correlations across steps.

Speaking in a loose way, we can say that the Xe layer becomes partly one dimensional, and it is well known that these one-dimensional systems have zero critical temperature. Along this line of reasoning, Fisher has shown[3] that the (finite) peak in the heat capacity of a band of Ising spins is shifted to a temperature lower than the critical temperature for the infinite two-dimensional systems.

To study these two effects of the steps on the critical temperature we have used a hexagonal-lattice-gas model with terraces of n rows [see Fig. 1(b)]. To simulate effect (a), the row of sites S in every terrace is given an adsorption energy $-\delta$ with respect to "normal" terrace sites. The row of sites W in the terrace has an adsorption energy $+\delta$. Effect (b) is introduced by reducing the interaction constant ϵ_1 between sites in different terraces with respect to the interaction constant ϵ_0 for two sites in the same terrace (which is set at $\epsilon_0 = 1$).

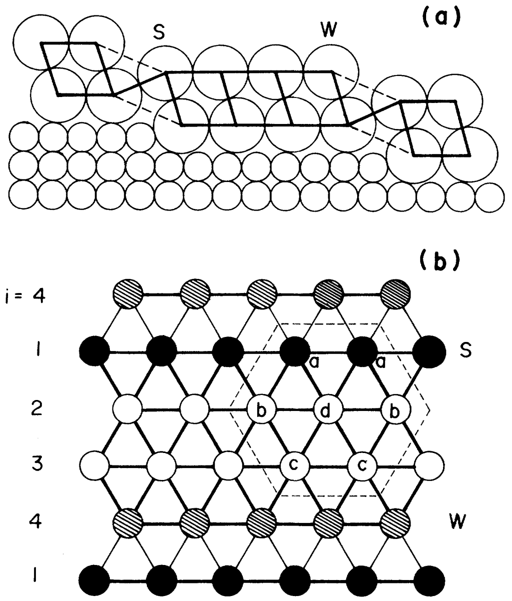

FIG. 1. (a) Schematic lateral view of the stepped Pd surface with two monolayers of Xe adsorbed on it. Xe atoms at sites S have a higher coordination with the lower layer but a reduced interaction with atoms at sites W in a different terrace of the same layer. (b) Top view of the hexagonal lattice model used to simulate step effects. Dark balls represent S sites with a larger ($-\delta$) adsorption energy and hatched balls, W sites with a reduced adsorption energy ($+\delta$). Thick lines mean a normal interaction $\epsilon_0 = 1$, while thin lines hold for a reduced interaction $\epsilon_1 < \epsilon_0$. The notation (a, b, c, d) for the sites within the cell considered in the Bethe-Peierls approximation appears also in the figure.

We solve this model in the Bethe-Peierls approximation: For every row i in a terrace ($i = 1, 2, \ldots, n$) we consider the cell containing a site of that row and all its nearest neighbors. We consider three different fugacities z_a^i, z_b^i, and z_c^i for the sites (other than the central one) in the upper, middle, and lower rows of the cell, respectively [see Fig. 1(b)]. Then we calculate the occupation probabilities p_a^i, p_b^i, p_c^i, and p_d^i for the different cell sites (index d representing the central site). We have then $3n$ equations

$$p_b^i = p_d^i = p_a^{i+1} = p_c^{i-1}, \tag{1}$$

which can be solved by the usual methods for nonlinear equations. In Eq. (1) $i=0$ is equivalent to $i=n$ and $i=n+1$ to $i=1$ because all terraces are equivalent.

Figure 2(a) shows the effect on the critical temperature of the extra adsorption energy δ in the steps for a lattice with terraces of four Xe rows, according to the experimental geometry. For $\delta/\epsilon_0=4$ the critical temperature drops to zero because in the model this energy is sufficient to produce complete occupation of step sites of type S (accordingly, all W sites will be empty) at $T=0$, independently of the state of the rest of the lattice. Thus, the terraces are completely disconnected and correlations cannot propagate at all. However, the drop is very sudden and the effect of δ is rather moderate for $\delta/\epsilon_0 \lesssim 3$.

Figure 2(b) shows the independent effect of reducing the interaction constant ϵ_1 between terraces below the "normal" constant $\epsilon_0=1$. For $\epsilon_1=0$, the Bethe-Peierls approximation does not give zero critical temperature, as it should be found. However, Gómez Santos[11] has calculated the exact critical temperature of the Ising model with terraces ($\epsilon_1 < \epsilon_0$, $\delta=0$, n arbitrary). The exact result for $T_c(\epsilon_1)/T_c(\epsilon_1-\epsilon_0)$ is almost the same as that given by the Bethe-Peierls approximation when $\epsilon_1/\epsilon_0 \gtrsim 0.2$ and only for $\epsilon_1/\epsilon_0 \lesssim 0.1$ is there a sudden drop of the critical temperature to zero in the exact solution which is not reproduced in the Bethe-Peierls approximation.

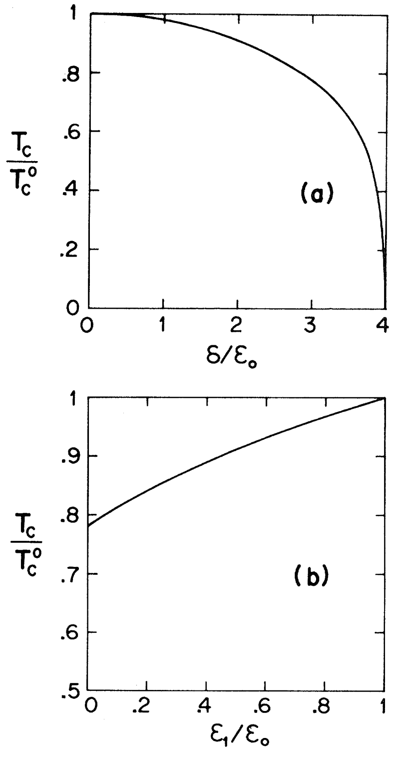

FIG. 2. (a) Effect of the increased adsorption energy δ at step sites on the critical temperature T_c. T_c^0 is the critical temperature of the homogeneous lattice ($\delta=0$). ϵ_0 is the interaction constant between atoms in the same terrace. The terraces have been taken to accomodate four rows of sites. (b) Effect of reducing the interaction constant ϵ_1 between atoms in different terraces.

Figure 3 shows the critical temperature for a lattice with both effects present ($\delta/\epsilon_0=2$, $\epsilon_1/\epsilon_0=0.2$), as a function of the number n of Xe rows which can be accommodated in each terrace. Notice that the effects (a) and (b) above are not merely accumulative. Rather, they reinforce each other, giving a larger reduction in the critical temperature than the sum of them. The value of $\delta/\epsilon_0=2$ corresponds to two extra bonds with the atoms of the lower level in the step, and is quite reasonable for the given experimental geometry. The value $\epsilon_1/\epsilon_0=0.2$ may seem too low if the layer is solid and perfect because, for $n=4$, the mismatch between the Xe lattice constant and the terrace width of Pd is rather small. But at the critical point, the layer is liquid and the "unperturbed" density would be rather different from that imposed by the constraint of the terraces, justifying the chosen value of $\epsilon_1/\epsilon_0=0.2$. For $n=4$ (in Fig. 3) we obtain a reduction of the critical temperature to 59% of that of the homogeneous lattice, which should be compared with 57% observed experimentally.

More interesting, the calculations suggest an extremely weak dependence of T_c on n. This feature of the calculation prompted further experiments on a Pd surface with a smaller density of steps.[12] The chosen Pd [14(100× (110)] surface can accomodate seven rows of Xe on every terrace. The experimental critical temperature for the second layer is shifted in this case to $T_c(7)=74$ K (63% of T_c^0), in

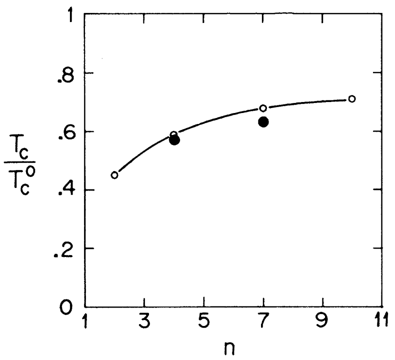

FIG. 3. Dependence of the critical temperature on the terrace width n. The other parameters are fixed, $\delta/\epsilon_0=2$ and $\epsilon_1/\epsilon_0=0.2$. The experimental black points are plotted in the figure (Refs. 6 and 12).

good agreement with calculations (68%).

In summary, we have shown that a regular array of steps on the substrate surface produces a very pronounced decrease in the critical temperatures of 2D first-order phase transitions, as reported for the Xe on Pd system. We firmly believe that with a realistic (e.g., a Lennard-Jones) potential in a Monte Carlo or molecular-dynamics simulation,[13] a more detailed understanding of the system will be obtained, but the relevant factors to explain the experimental results are, we maintain, the finite size of the terraces, the adsorption lines along the steps, and the lack of compactness due to mismatch of the Xe atoms on the terraces.

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[1] For a short, excellent review of 2D phase transitions including noble gases see, e.g., F. F. Abraham, Phys. Rep. **80**, 341 (1981).

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