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Wetting transition behavior of Xe on Cs and Cs/graphite

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Calculations are presented of the adsorption behavior of Xe films on two different surfaces. One is bulk Cs metal; the other is a graphite surface, covered by a monolayer of Cs. With data obtained from grand canonical Monte Carlo simulations, it is found that a Xe wetting transition occurs on the Cs monolayer within the temperature interval 190 to 200 K. On the Cs metal surface, negligible adsorption occurs over the full temperature range of the simulations, which come close to the critical temperature. Experimental testing of these predictions is proposed.

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I. INTRODUCTION

The possible occurrence of a wetting transition is implicit in Young's equation, which expresses the contact angle of an adsorbed film in terms of three interfacial tensions. When the angle θ reaches either 0 or 180 degrees, a transition occurs from the incomplete wetting behavior to either a wetted surface ($\theta=0$) or a dry surface ($\theta=180$ degrees). The *necessary* occurrence of such a transition was postulated some 25 years ago in pioneering work by Cahn and Ebner and Saam.[1,2] During the last decade, such wetting transitions have been found for the cases of a number of gas/surface combinations.[3–27] These transitions are consequences of the very weak adsorption potentials $V(r)$ on these surfaces; the well depth D of the gas-surface interaction is comparable to the well depth ϵ of the adsorbate's interatomic potential.[27] For these systems, the surface is not wet at the triple temperature (T_T); this means that, for pressure P below the saturated vapor pressure P_0, only a thin film adsorbs in equilibrium on the surface. At somewhat higher temperature T_w (somewhere between T_T and the critical temperature T_c), however, there can occur a first-order wetting transition. Over a small range of temperature above T_w, up to the *prewetting* critical temperature (T_{pwc}), this transition, called prewetting, is observed as a discontinuity in the adsorption isotherm at a T-dependent pressure $P_{pw}(T)$. Above this transition pressure, the film thickness diverges at saturation. In the regime of the highest temperatures, $T>T_{pwc}$, continuous wetting behavior is observed and the coverage diverges as P approaches P_0.

Such intriguing transitions have been observed thus far for He, Ne, and H_2 on bulk alkali metal surfaces and Hg on W and sapphire; similar behavior has been predicted for heavier inert gases on alkali metals[27,31] and for water on graphite and other surfaces.[32] This weak-adsorption, wetting transition behavior stands in contrast with the wetting behavior of physisorbed inert gases and H_2 on graphite, a consequence of the very strong attraction provided by that surface.[33] Typically, the well depth D of the adsorption potential of the inert gases on Cs, for example, is of order the well depth ϵ of the interatomic potential of the adsorbate. On graphite, instead, the D values for these gases are a factor of 5 to 10 larger than ϵ, depending on the specific gas.

Two other kinds of behavior can occur, in principle, for fluids that do not wet solid surfaces at T_T. One is a critical wetting transition, which has been seen on liquid surfaces, but not yet on solid surfaces.[34] The other kind of behavior is the complete absence of a wetting transition, as found for Ne/Cs.[17]

In this paper, we evaluate the wetting behavior of Xe on two surfaces. One is a bulk Cs surface. The ratio D/ϵ is about 1.5 in this case,[27] suggesting that the surface is not wet at the triple point.[38] In fact, we find nonwetting behavior for all simulated temperatures, up to nearly T_c; similar behavior was found in experiments and theoretical studies of Ne/Cs, for which $D/\epsilon=0.7$. In addition, we investigate the Xe adsorption on a graphite surface coated with a monolayer of Cs. This problem has been studied experimentally, using He-atom scattering and LEED.[35] When Xe was dosed onto a monolayer of Cs at temperatures between 40 K and 100 K at a Xe flux corresponding to a pressure at the surface of 10^{-9} mbar to 10^{-4} mbar, no evidence was seen for Xe adsorption with either LEED or He-atom scattering.[35]

An analogous question of how wetting behavior varies with alkali film thickness has been examined for the case of He and H_2 interacting with alkali metal films on Au surfaces.[36,37] In those cases, it was found that the wetting temperature was measurably different from that of the pure alkali value for films as thick as 2 nm. In the present study, the wetting temperature of Xe on the Cs monolayer is found to be 190 K, somewhat above the experimental triple temperature of Xe, $T_T=161.4$ K. This is quite different from the extreme nonwetting on the bulk Cs surface and the strong wetting behavior on graphite.

In the next section we treat adsorption on bulk Cs. In Sec. III we address the problem of Xe on Cs/graphite. In Sec. IV we summarize our results.

II. SIMULATED ADSORPTION OF Xe ON Cs

We have computed the coverage N as a function of pressure P using the Grand Canonical Monte Carlo method, abbreviated GCMC. In this ensemble, T and the chemical potential or pressure are specified, and coverage $N(P,T)$

evaluated. The results of such simulations, carried out in sufficiently large sample volumes and including extensive Monte Carlo sampling, are accurate, if the assumed potentials are accurate. The simulation method is identical to that employed in our previous papers concerning wetting transitions.[38–40] Summarizing briefly, we establish a unit cell which is a rectangular solid of dimensions L_x, L_y, and L_z. We take the values $L_x=L_y=10\sigma$, where $\sigma=0.41$ nm is the Lennard-Jones (LJ) diameter of the Xe atoms. The height of the computational cell, perpendicular to the Cs surface, L_z is set equal to 24.4σ. This value must be large in order to determine the "true" behavior close to the transition, as was established in the previous simulation studies.

The Xe-Xe interaction is taken to have the commonly assumed (but approximate) LJ form (without cut-off), with parameters $\epsilon=221$ K and $\sigma=0.41$ nm. What is particularly important in determining the wetting behavior is the adsorption potential.

The Xe-Cs interaction $V(z)$ used here is that computed from first principles by Chizmeshya, Cole, and Zaremba (CCZ).[27] This potential has repulsive kinetic energy contributions from both the electron-adsorbate interactions and the electrostatic interaction between the adatom and the ionic charge density. The attraction is derived from a damped van der Waals interaction, with an *ab initio* dispersion coefficient. The resulting potentials and the derived predictions of wetting behavior[27] have been tested with a fairly large number of systems. The CCZ potential has the following functional form:

$$V_{CCZ}(z) = V_0(1+\alpha z)e^{-\alpha z} - f_2(\beta(z-z_{vdW})(z-z_{vdW}))\frac{C_{vdW}}{(z-z_{vdW})^3}.$$

The first term in this expression is the Hartree-Fock repulsive energy, while the second term is the attractive van der Waals contribution to the interaction. C_{vdW} and z_{vdW} are the strength and reference plane position of the vdW potential, respectively.[27–29] The damping function, $f_2(x)=1-e^{-x}(1+x+x^2/2)$, accounts for the effect of atom-substrate wave function overlap on the vdW correlation energy. The second damping function, $\beta(z)=\alpha^2 z/(1+\alpha z)$, overcomes the unphysical divergence at $z=z_{vdW}$.[27,30] The CCZ parameters for the Xe-Cs interaction are $V_0=0.544$ (eV), $\alpha=0.893$ (a_0^{-1}, $a_0=0.529$ Å), $C_{vdW}=9.249$ (eV$\cdot a_0^3$), and $z_{vdW}=0.440$ (a_0).[27]

Predictions based on the CCZ potential were found to be consistent with experimental wetting data for He/Cs; for the case of He/Rb, instead, there is some indication that the potential is too shallow (by 5 to 10%), but there is a significant disagreement between various groups' measured wetting properties in that case.[41,42] For Ne/Cs, there is some ambiguity about the accuracy of V because of computational uncertainty in the simulations near T_c; in contrast, the calculations agree with measurements for Ne/Rb.[17,43] Recently, for H_2 on Rb and Cs we found that the computed potentials are about 20% too shallow, based on a comparison with experimental wetting data on those surfaces.[16,44]

For Xe/Cs, the ratio of adsorption well depth to gas-gas well depth is 328 K/221 K ~ 1.5, a relatively small value, so an extended temperature regime of nonwetting is expected.[27] Results of the simulations on Cs are shown in Fig. 1. The plotted results are the total density of atoms, N/A (including vapor atoms), except for one curve, which shows the surface excess adsorption, N_x/A. The surface excess adsorption is defined as the difference between the actual coverage (computed or measured) and the nominal coverage present if the density near the substrate were that of a gas phase. In Fig. 1, the surface excess adsorption is negligibly small (less than a monolayer; density about 6 atoms per nm^2) even at the highest temperature explored ($T=286$ K). This extreme nonwetting behavior is found over the complete range of T and P, which extends quite close to the bulk critical temperature, $T_c=289.7$ K (experimental). The simulation results are not presented for the critical region, $T>286$ K, in which the correlation length exceeds the lateral dimension of the unit cell.

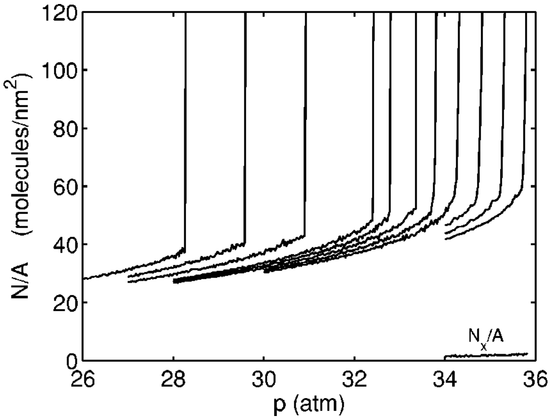

FIG. 1. The two-dimensional density, N/A, of Xe atoms adsorbed on Cs substrate at temperatures approaching the critical temperature. From left to right, $T=270$, 273, 276, 279, 280, 281, 282, 283, 284, 285, 286 K. The surface excess adsorption, N_x/A, is negligible in all cases, as exemplified in the curve at lower right corner, for 286 K.

Our finding of nonwetting below saturation is consistent with our limited experimental data[35] for Xe/Cs/graphite (a more attractive substrate), which explored just the very low P region, finding negligible adsorption at all T over the interval 170 K $\leq T \leq$ 286 K. The absence of a wetting transition contradicts calculations based on the so-called "simple model," which predicted a wetting temperature $T_w=235$ K based on the CCZ potential.[27] Previous experience has found a similar discrepancy for the very weakest adsorption potentials.[38]

The "simple model" evaluates the free energy of a hypothetical film in terms of the gas-surface interaction and the bulk fluid's macroscopic properties at a given temperature. In so doing, it employs a highly oversimplified description of the relative energies of wetting vs nonwetting films. In particular, it neglects the presence of any film at temperature less than the wetting temperature and uses the bulk liquid-vapor surface tension to characterize the cost of forming the film. For these reasons, and perhaps others, it is not surprising that the model fails to describe the transition behavior in very weakly attractive situations. Indeed, the curious and fortunate situation is that the model works rather well in predicting wetting in the case of more attractive potentials than Xe/Cs.[38]

III. ADSORPTION AND WETTING TRANSITION ON Cs MONOLAYER

The Xe adsorption potential $V(z)$, assumed to depend only on z, the coordinate normal to the surface, is obtained by adding separate contributions from the Cs monolayer and the graphite substrate:

$$V(z) = V_{Cs}(z) + V_{gr}(z). \tag{1}$$

We are neglecting both corrugation of the potential and three-body interactions involving the Xe and all Cs atoms and the graphite. The former approximation is plausible on alkali metal surfaces because the adsorption occurs so far above the outer plane of substrate atoms. The latter approximation has been explored previously in a similar context and found to change the well-depth of order 10%.[45] The graphite potential is the semiempirical potential of Carlos and Cole, fit to experimental scattering and thermodynamic data from Penn State and Caltech, respectively.[46–49] The contribution to the Xe potential contributed by the Cs monolayer, with the structure derived from LEED measurements of the $p(2\times 2)$ overlayer, with spacing 0.492 nm between Cs atoms, about 10% smaller than the bulk crystal spacing:[50]

$$V_{Cs}(z) = \frac{A_{10}}{z^{10}} - \frac{A_4}{z^4}. \tag{2}$$

Here, the coefficient values are $A_{10}=2.5\times 10^9$ KÅ^{10} and $A_4=4.69\times 10^5$ KÅ^4. These values are based on integration of the LJ type of Xe-Cs interactions computed by Patil.[51] The Cs layer lies 0.28 nm above the surface of graphite, according to LEED data and an analysis by Hu *et al.*[52] Note that the attractive well provided by the single Cs layer is about 50% deeper than that provided by the bulk Cs crystal. This exemplifies a breakdown of the pairwise sum approach to modeling adsorption potentials, which is not surprising for a nearly free electron gas at the Cs surface.

Figure 2 shows the resulting potential and its various components, the contribution from the Cs layer, the top layer of C and the more distant C layers. It is seen that the well depth ($\sim$680 K) of the total potential in this case is more than a factor of two greater than that ($D=328$ K) on the bare Cs surface. Thus, much greater adsorption is expected in this case than was found above.

Figure 3 shows the resulting adsorption isotherms, which confirm this expectation. Below 192 K, less than a monolayer film is present below saturation (the point at which the coverage diverges). This is a nonwetting regime.[54] In contrast, the results exhibit a coverage jump associated with a prewetting transition within the interval 192 K$<T<$206 K. The transition behavior is seen very clearly in density profiles, shown for $T=194$ K and 200 K in Figs. 4 and 5. These exhibit density discontinuities at relative (to saturation) pressure $P^*=P/P_0=0.97$ at 194 K and $P^*=0.95$ at 200 K, respectively. At these transition pressures, the surface excess density jumps by a factor of $\sim$7 and $\sim$3.5, respectively.

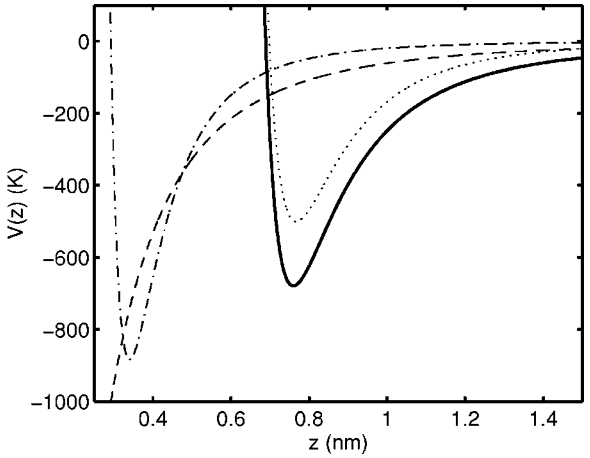

FIG. 2. Contributions to the total adsorption potential (full curve) of a Xe atom above Cs-covered graphite. The dotted curve is a contribution from the Cs layer. The dash-dotted curve is the potential due to the top layer of C atoms, while the contribution of the remaining C layers is dashed.

For $T>206$ K, a continuous growth of a wetting film is observed. These results for the prewetting transition phenomenon are qualitatively the same as those found in previous simulation studies of this transition.[18,38–40]

IV. DISCUSSION

The simulation results indicate that Xe adsorption on the Cs monolayer is very different from that on bulk Cs, a logical consequence of the significantly deeper well in the former case. For bulk Cs, negligible adsorption is found at all T below T_c; similar behavior was found to be the case for Ne/Cs in both calculations and experiments.[17,43] As mentioned above, the reduced ratio $D^*=D/\epsilon$ in the Xe/Cs case is about 1.5, while $D^*=0.7$ for Ne/Cs. The value $D^*=1.5$ is similar to that found for H$_2$/Rb, in fact, which is a system exhibiting a wetting transition at a reduced temperature

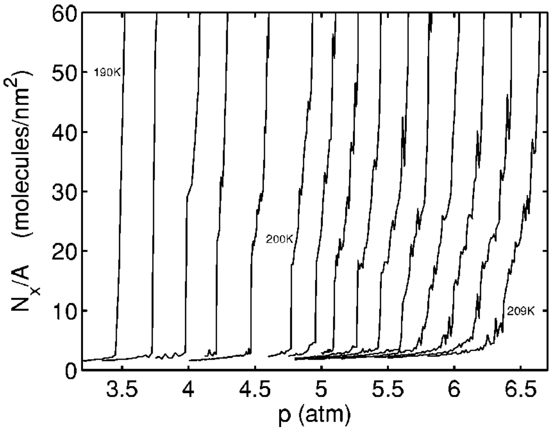

FIG. 3. Surface excess adsorption isotherms, N_x/A, of Xe above Cs/graphite at temperatures (from left to right) $T=190$, 192, 194, 196, 198, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209 K.

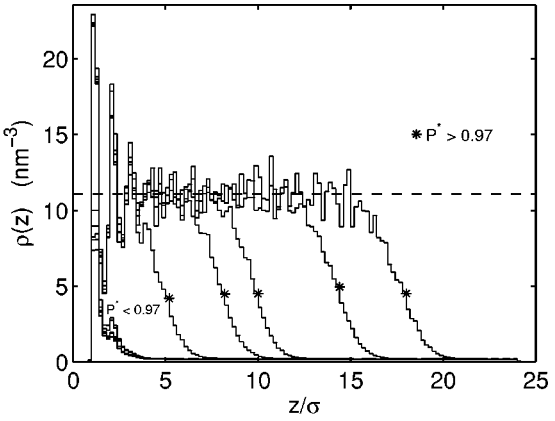

FIG. 4. Density profiles of Xe at $T=194$ K, as a function of the reduced distance above the Cs/graphite substrate, for various ratios $P^* \equiv P/P_0$ of the pressure to saturated vapor pressure. The curves with and without asterisks correspond to reduced pressures above and below the prewetting pressure $P^* \sim 0.97$, respectively. The data indicated as $P^* < 0.97$, just below the prewetting transition, show coverage of less than one layer. The five curves above the transition (indicated by asterisks) correspond to reduced pressures $P^* > 0.97$ (from left to right: $P^* \sim 0.973, 0.979, 0.985, 0.991, 0.996$). The dashed line is the bulk liquid density.

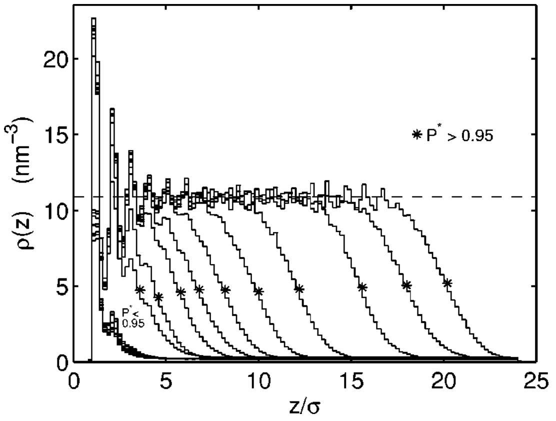

FIG. 5. Density profiles of Xe at $T=200$ K, as a function of the reduced distance above the Cs/graphite substrate, for various ratios $P^* \equiv P/P_0$ of the pressure to saturated vapor pressure. The curves with and without asterisks corresponds to reduced pressures above and below the prewetting pressure $P^* \sim 0.95$, respectively. Below $P^* = 0.95$, less than a monolayer adsorbs. The ten curves above the prewetting transition line (indicated by asterisks) correspond to $P^* > 0.95$ (from left to right: $P^* \sim 0.955$, 0.960, 0.966, 0.972, 0.975, 0.980, 0.985, 0.992, 0.995, 0.997). The dashed line is the bulk liquid density.

$T^* = T/T_c = 0.58$.[12–14,16,44] One might then ask why a wetting transition occurs in the latter case, but not for Xe/Cs. We explain the difference qualitatively with the "simple model," which expresses the wetting temperature in terms of the surface free energy of the film at the transition. The relatively lower wetting temperature of H_2, we believe, is a consequence of quantum effects that reduce the surface tension, facilitating the wetting. This trend was discussed previously in terms of "nonuniversal" predictions of the simple model.[53] One should bear in mind that, as discussed above, this model does not work quantitatively for such ultra-weak adsorption systems as Ne and Xe on Cs.

The simulations indicate that a wetting transition occurs at $T^* = T/T_c = 0.66$ for the case of a Cs monolayer on graphite (for Xe $T_c = 289.7$ K). It would be worthwhile to explore this phenomenon experimentally since it is a relatively convenient system experimentally. If feasible, the variation of the wetting behavior with Cs thickness should be explored. Such an experimental study was carried out for the case of He wetting on Cs-plated Au. The result was a significant shift of T_w for Cs films greater than 2 nm, showing the sensitivity of adsorption to quite weak long range interactions.[36,37] In future simulation work, we intend to explore Xe adsorption on both that surface and multilayer Cs films on graphite.

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