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Model adsorption potentials of rare gases on boron nitride

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Calculations are presented for the interaction of rare-gas atoms (Ar, Kr, Xe) on the (0001) surface of boron nitride. The interaction potential is constructed with use of a damped dipole and a quadrupole attractive part and a repulsive part derived from the effective-medium theory. Only one free parameter has been used to fit the constructed potential to experimental data available. We checked our procedure by calculating the second virial coefficient of the adsorbed atoms interacting with the surface of BN and the interaction potential for the same rare gases on graphite (0001). In both cases we find good agreement with experiments. Finally, we comment on the similarities between rare gases interacting with BN and with graphite and on how our model potential can be applied to other systems.

I. INTRODUCTION

In the last few years there has been considerable activity in calculating the interaction of an atom with a surface. While there has been some success in *ab initio* calculations of the interaction of helium and hydrogen atoms with metal surfaces,[1] only recently has such an approach been used to treat helium interacting with surfaces of semimetals[2] or insulators.[3] These theoretical studies have been motivated, in part, by the detailed data from atom beam scattering experiments[4] as well as by the increased amount of data coming from adsorption isotherm measurements on powders of insulators and lamellar halides.[5,6] Among the various systems, the interaction of rare gases with the surface of boron nitride presents a few interesting and challenging aspects. BN has a structure similar to graphite with hexagons of atoms tightly bound in a plane and with weak-coupling forces between planes. The lattice constants of the two substances differ a few percent from each other. Adsorption experiments on BN (Refs. 6–8) have given results qualitatively similar to corresponding experiments on graphite, yet important differences emerged. For example, the onset of triplet point and the commensurate-incommensurate phase transition at monolayer coverage which take place on graphite do not appear on boron nitride, and the phase diagram for Kr adsorbed on BN differs from the Kr-graphite phase diagram.[6–8] While it is recognized that the surface of BN powders is more heterogeneous than the corresponding surface of graphite, this seems not to be the determining factor in the dissimilarities observed.[6–8]

Our motivation for this calculation is twofold: first, to produce reliable rare-gas–BN potentials that can be used for statistical mechanics or structural calculations and second, to put forward a model potential to be used for other gas-atom–insulator interactions.

II. CALCULATIONS

The potential between an atom and a solid can be written as[9–13]

$$V(r)=V_A(r)+V_R(r)\ , \tag{1}$$

where $V_R(r)$ is the repulsive part and $V_A(r)$ is the attractive one. Attraction between rare-gas atoms and surfaces of solids arises because of the interaction between the fluctuating multipole moments of the incoming atom and the solid. In particular we have taken the attraction to be given by the superposition of damped dipole and quadrupole interactions between the gas atom and atoms of the solid; in this respect we have followed the work of Celli *et al.*[3]

$$V_A(r)=\sum_i [U_d(\,|\,x_i\,|\,)+U_q(\,|\,x_i\,|\,)]\ , \tag{2}$$

$$U_d(\,|\,x_i\,|\,)=\frac{-3a_S d C_3}{\pi x_i^6}[1-f_6(x_i)]\ , \tag{3}$$

$$U_q(\,|\,x_i\,|\,)=\frac{-15C_5}{\pi\rho_c x_i^8}\ , \tag{4}$$

where ρ_c is the number density of the atoms of the surface, C_5 is the quadrupole coefficient (see below), a_S is the area of the surface unit cell, d is the interlayer spacing, $f_6(x_i)$ is a damping function,[11,14] and x_i is the vector connecting the adatom to the ith atom on the surface. The damping has the function of "turning off" the attractive interaction at short distances where the electronic charge distributions of the adatom and the solid start to overlap. As a functional form for this damping we have taken the result of Tang and Toennies[14] calculations based on observations of atom-atom collisions. We have limited the damping contribution to the dipole-dipole term; the complete expression, when averaged over the surface, reads[3,10,11,13,15]

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$$V_A(Z)=\frac{-3C_3}{d^3}\xi(4,Z/d)-\frac{10C_5}{\rho_c a_S d^6}\xi(6,Z/d)+12\,dC_3\left[\sum_{k=0}^{5}\frac{\gamma^k E_{5-k}(\gamma Z)}{k!Z^{4-k}}+\frac{\gamma^4}{6!}(1+\gamma Z)\exp(-\gamma Z)\right], \qquad (5)$$

where $\xi(n,x)$ is a Riemann ζ function,[16] $E_n(x)$ is the exponential integral,[16] z is the vertical distance from the adsorbate to the surface, $a_S=5.43$ Å^2 is the area of the unit cell, and γ is the softness parameter in the charge density of the surface. The repulsive part is evaluated using the effective medium theory[17,18] which assumes a proportionality between V_R and the weighted average charge density of the solid. This model has been successful in predicting the repulsive part for many He-H_2/metal systems.[2,18–21] We refer to the numerous papers on the subject for a discussion on the method and its applicability. Following Refs. 11, 22, and 23, we have

$$V_R(\mathbf{r})=\alpha_{\text{eff}}\bar{\rho}(\mathbf{r}) \qquad (6a)$$

$$\alpha_{\text{eff}}=\alpha_0-\alpha_{\text{at}}\ , \qquad (6b)$$

$$\alpha_{\text{at}}=\int_\Omega \phi_\alpha(\mathbf{r}'-\mathbf{r})d\mathbf{r}'\ , \qquad (6c)$$

$$\bar{\rho}(\mathbf{r})=\frac{1}{\alpha_{\text{at}}}\int_\Omega \phi_\alpha(\mathbf{r}'-\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}'\ , \qquad (6d)$$

where Ω is the volume of a sphere with a large radius R_c. The weighting function is the electrostatic potential ϕ_α of the isolated atom. If the charge density is, in first approximation, translationally invariant[19] and decays exponentially going away from the surface, then

$$\alpha_{\text{eff}}=\alpha_0-\frac{8\pi k e Z_a}{\beta^3}\ , \qquad (7)$$

$$\bar{\rho}_0(Z)=\frac{1}{2}\frac{\beta^2\alpha(-\gamma^2+2\beta^2)}{(\beta^2-\gamma^2)^2}e^{-\gamma Z}\ , \qquad (8)$$

where Z_a is the atomic number of the adsorbate atom, $k=9\times10^9$ N m^2/c^2, $\alpha\exp(-\gamma Z)$ is the charge density of the surface, β is the softness parameter in the charge density of the adsorbate, here represented by a simple exponential

$$\rho_{\text{at}}=\frac{Z_a\beta^3}{8\pi}e^{-\beta r}\ . \qquad (9)$$

The parameter β is determined from the magnetic susceptibility data according to Ref. 24. From Freeman's charge density contours,[25] we have evaluated the contributions due to nitrogen and boron atoms. We have then used Steele's formula[9] to evaluate the total charge density due to the contributions of all atoms and then we averaged it over the surface to obtain

$$\rho_0(Z)=\frac{\alpha_1 4\pi(1+\gamma_1 Z)}{a_S\gamma_1^2}e^{-\gamma_1 z}+\frac{\alpha_2 4\pi(1+\gamma_2 Z)}{a_S\gamma_2^2}e^{-\gamma_2 Z}\ , \qquad (10)$$

where $\alpha_1=38.4$ Å^{-3}, $\gamma_1=4.78$ Å^{-1} for boron, and $\alpha_2=1.94$ Å^{-3}, $\gamma_2=2.57$ Å^{-1} for nitrogen. At large distance Eq. (10) can be approximated by $\alpha\exp(-\gamma Z)$, where $\alpha=2.62$ Å^{-3}, $\gamma=5.13$ Å^{-1}.

In the calculation of the repulsive part there is only one free parameter α_0; in the case of He on metals this parameter can be calculated using various methods.[17,18,24] Such calculations cannot be repeated in the present case, since we are dealing with more complex atoms than helium and we are considering an insulator BN. However, we expect the proportionality of repulsion with charge density to be a plausible description of

TABLE I. Comparison between experimental measurements (Refs. 8, 29–31) of $\langle z\rangle$, B_{2S}, $|E_0|$ with the calculations of this paper. C_3 is in meV Å^3 and C_5 is in meV Å^5.

Systems	α_0 (meV Å^3)	$\langle z\rangle$ (Å)	$\lvert D\rvert$ (meV)	B_{2S}[a] (cm^3/g)	C_3	C_5	$\lvert E_0\rvert$ (meV)[e]	$\lvert E_1\rvert$ (meV)
Ar-BN	2.04×10^6	2.95	93.24	1.9×10^{-2} (1.5×10^{-2})[b]	707	1115	89.4	74.7
Kr-BN	2.56×10^6	3.08	112.59	4.0×10^{-2} (4.8×10^{-2})[b]	997	1724	109.4	103.6
Xe-BN	4.65×10^7	3.17	155.82	2.0×10^{-1} (2.5×10^{-1})[b]	1487	2775	147.3	136.8
Ar-graphite	7.83×10^4	3.08 (3.2)[d]	104.97	7.8×10^{-2} (6.0×10^{-2})[c]	1208	1751	95.8	79.1
Kr-graphite	1.63×10^5	3.16 (3.3)[d]	139.10	2.6×10^{-2} (1.7×10^{-2})[c]	1730	2712	126.0	104.2
Xe-graphite	3.21×10^5	3.31	164.85	7.7×10^{-1} (7.9×10^{-1})[c]	2430	4373	158.6	131.4

[a] B_{2S} is calculated at $T=273$ K.

[b] Values in the parentheses are the experimental measurements of Ref. 8.

[c] Values in the parentheses are the experimental measurements of Ref. 29.

[d] Values in the parentheses are the experimental measurements of Refs. 30 and 31.

[e] $|E_0|$ are the experimental measurements Refs. 6–9.

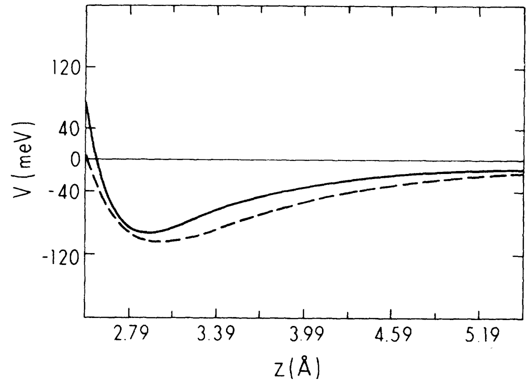

FIG. 1. Laterally averaged potentials of Ar-BN (solid line) and Ar-graphite (dashed line).

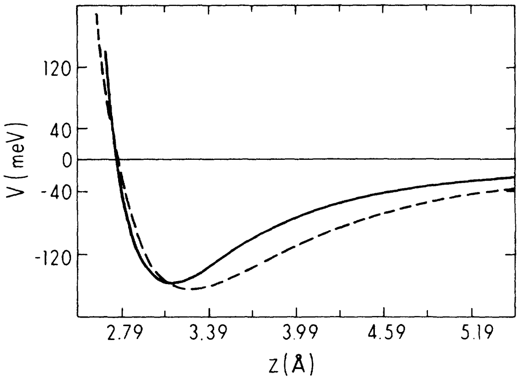

FIG. 3. Laterally averaged potentials of Xe-BN (solid line) and Xe-graphite (dashed line).

the interaction (see also Cole and Toigo, Ref. 24). Such an approach has also been followed for interactions of He atoms with semimetal and semiconductor surfaces.[2,12] The laterally averaged potential is found using Eqs. (1), (5), and (6).

Finally we comment on the calculation of the quadrupole term C_5. We have followed the simple formula developed by Cole *et al.*[15]

$$C_5=\frac{g_0\gamma_0E_qE_S}{8(E_q+E_S)}\ , \tag{11}$$

where the parameter g_0, γ_0, E_q, and E_s are easily found from the literature for most systems.[15,26] This formula is expected to give semiquantitative results. Yet, it is important to include such an estimate because it has a non-negligible effect on the potential (see Sec. III). Formally we have not included damping since for $Z \gtrsim 2.5$ Å it has a negligible effect on the total potential. Of course for $Z \ll 2$ Å it becomes a very important contribution.

III. RESULTS AND DISCUSSION

In Table I we report the parameters used in our calculations and the most significant results. α_0 is the only free parameter. It has been adjusted so as to reproduce the ground state of each system as known from adsorption isotherm data.[6–9,27,28] $\langle z\rangle$ is the expectation value of finding the atom at a distance z from the plane of the nuclei of the surface atoms

$$\langle z\rangle=\int\psi_0^*(Z)Z\psi_0(Z)dZ\ . \tag{12}$$

We have also calculated the second virial coefficient of the adsorbed atoms

$$B_{2S}=A\int dZ(e^{-V_0(Z)/(k_BT)}-1)\ , \tag{13}$$

where $V_0(Z)$ is the gas-surface interaction potential, k_B is the Boltzmann's constant, and A is the specific area [$A=6$ m^2/g for BN (Ref. 6) and $A=12$ m^2/g for graphite[29]].

We have compared our B_{2S} coefficients with the values obtained by Levy *et al.*[8] based on the analysis of the adsorption data. Our values for Ar, Kr, and Xe are 1.9×10^{-2} cm^3/g, 4×10^{-2} cm^3/g, and 2×10^{-1} cm^3/g and thus are in good agreement with their values of 1.5×10^{-2} cm^3/g, 4.8×10^{-2} cm^3/g, and 2.5×10^{-1} cm^3/g, respectively. A similar comparison is made for rare gases on graphite in Table I.

In Figs. 1–3 we have plotted the potentials for Ar, Kr, and Xe interacting with BN. For comparison we have also plotted the potentials for the same rare gases interacting with the surface of graphite. In the latter case the potential was constructed similarly as for BN. The rare-gas–graphite potential is in good agreement with existing potentials[29] and with experimental data. We therefore are confident that our method is reliable.

We next compare our $\langle z\rangle$ values for rare gases on graphite with the values obtained from Refs. 30 and 31 based on the analysis of LEED and EXASFS data; for Ar and Kr we obtain 3.08 and 3.16 Å in good agreement with 3.2 and 3.3 Å of Refs. 30 and 31. There are no data for rare gases on BN; however our values are consistent with the calculations of Ref. 8: for Ar, Kr, and Xe Ref. 8 obtains 2.83, 2.96, and 3.17 Å, respectively.

From Figs. 1–3 we find that the well depth of the potentials for rare gases on BN is about 10% smaller than for the same atoms on graphite. However, C_3 coefficients are typically 30 to 40% lower for BN than graphite.[26] While the trend is consistent,[32] a simple scal-

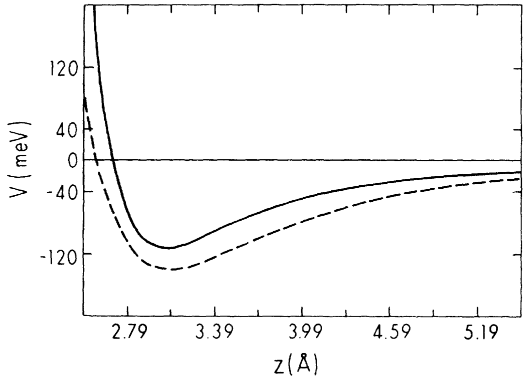

FIG. 2. Laterally averaged potentials of Kr-BN (solid line) and Kr-graphite (dashed line).

ing of C_3 and D (well depth) would fail. Our calculations suggest that quadrupole terms are important (16% of D) at the equilibrium distance,[15] while damping has little effect (1% of D) at that distance but rises quickly for lower distances.

In conclusion we have built a potential for rare gases interacting with BN that has only one free parameter. This procedure uses available information about the surface (charge density, dielectric function) or the atom (polarizability); it therefore can be extended to other gas-atom–insulator systems.

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