Lateral variation of the physisorption potential for noble gases on graphite

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The adsorption potential of noble gases on graphite is calculated. The method used is the summation of two-body anisotropic interactions between the adatom and each carbon atom, which takes into account the graphite anisotropy. The lateral variation which results depends on the uncertain role of anisotropy in the repulsive part of the interaction. In any case, the computed variation is of the order of twice the value computed by Steele [Surf. Sci. 36, 317 (1973)] and is widely used. Our conclusion is consistent with thermodynamic data.

I. INTRODUCTION

Physical adsorption on the graphite basal plane is a problem of wide interest.[1,2] Because of the anisotropic covalent bonding of graphite, homogeneous surfaces are relatively easy to obtain, even when the graphite is exfoliated. Moreover, the small intralayer spacing between carbon atoms means[3] that the simplifying assumption of a continuous smooth substrate is usually adequate[4-7] for treating incommensurate adsorbed phases. On the other hand, the very existence and properties of commensurate phases are sensitive[8-12] to the laterally varying part of the adsorption potential,

$$V(\vec{r}) = V_0(z) + \sum_{\vec{G} \neq 0} V_G(z) e^{i \vec{G} \cdot \vec{R}} . \tag{1}$$

Here the adatom position $\vec{r} = (z, \vec{R})$, where $\hat{z}$ is the surface normal and $\vec{R}$ is a two-dimensional vector in the x-y plane. $\vec{G}$ is a reciprocal-lattice vector appropriate to the graphite symmetry. For graphite, there are six equivalent vectors of magnitude $G = 2.95$ Å^{-1} whose contributions dominate the second term in Eq. (1). It is the corresponding corrugation in $V(\vec{r})$ which we study in this paper.

Measurements of He scattering from graphite[13,14] indicated that the conventional adsorption potentials[3] were inadequate in this case. The same conclusion was suggested by the low-coverage specific-heat data.[15] Both types of experiment indicated that the laterally varying component, i.e., V_G, was about a factor of 2 larger than expected. Carlos and Cole[16] proposed that this was due partly to anisotropy of the carbon atoms in graphite.[17] Their quantitative model was found to be consistent with both the scattering and thermodynamic data for He.[18] Further support for this approach was provided by calculations of Crowell and Brown, which describe the role of anisotropy for the graphite itself[19] and in H$_2$ adsorption.[20] The latter results were qualitatively consistent with scattering data of Mattera *et al.*[21]

This paper applies the method of Carlos and Cole[16] (CC) to calculate adsorption potentials of noble gases on graphite. Overall, our results are consistent with those found in recent attempts to deduce the corrugation empirically by comparing experiments with statistical mechanical theories.[8-10]

II. CALCULATIONS

Following CC,[16] we write the potential energy as a sum of anisotropic two-body interactions $U(\vec{x}_i)$, where $\vec{x}_i = \vec{r} - \vec{R}_i$ is the separation between the adatom at $\vec{r}$ and the carbon atom at lattice site $\vec{R}_i$:

$$V(\vec{r}) = \sum_i U(\vec{r} - \vec{R}_i) , \tag{2a}$$

$$U(\vec{x}) = 4\epsilon((\sigma/x)^{12}[1 + \gamma_R(1 - \tfrac{6}{5}\cos^2\theta)]$$
$$- (\sigma/x)^6 [1 + \gamma_A(1 - \tfrac{3}{2}\cos^2\theta)]) . \tag{2b}$$

Here $x = |\vec{x}|$ and θ is the angle between $\vec{x}$ and the surface normal. The coefficients γ_A and γ_R are associated with the anisotropy of the attractive and repulsive parts of the interaction, respectively. The factors $\tfrac{6}{5}$ and $\tfrac{3}{2}$ were chosen[16] so that the laterally averaged potential $V_0(z)$ assumes the usual form,[3] independent of γ_R and γ_A:

$$V_0(z) = (4\pi\epsilon\sigma^6/a_s d^4)[\tfrac{2}{5}(\sigma/d)^6 \zeta(10, z/d) - \zeta(4, z/d)] , \tag{3}$$

$$\zeta(n,x) = \sum_{j=0}^{\infty} (j + x)^{-n} , \tag{4}$$

where $a_s = 5.24$ Å^2 is the area of the basal-plane unit cell and $d = 3.37$ Å is the interlayer spacing. The Fourier components satisfy expressions given in Ref. 16. For completeness, we note the form of Eq. (1) if only the smallest G components are nonzero,

$$V(\vec{r}) = V_0(z) + 2V_G(z)\{\cos(2\pi s_1) + \cos(2\pi s_2)$$
$$+ \cos[2\pi(s_1 + s_2)]\} , \tag{5}$$

where $as_1 = 2x/\sqrt{3}$ and $as_2 = y - x\sqrt{3}$. Here $a = 2.46$ Å is the spacing between hexagons, and the x axis originates

at the center of a hexagon and points toward a neighboring carbon atom. Thus a simple two-dimensional theory would require one input parameter V_G.

The justification for the functional form in Eq. (2) is discussed by CC. The angular dependence on $\cos^2\theta$ is the simplest assumption consistent with the polar symmetry of the carbon atom in graphite; we omit the azimuthal dependence associated with the hexagonal symmetry within the basal plane. The model incorporates the principal anisotropy of graphite by calculating γ_A from the dielectric properties, as follows. One describes the adatom with an isotropic oscillator model,[22] with characteristic energy E_a. The anisotropic carbon atom in graphite has, in principle, two such energies, $E_{c\|}$ and $E_{c\perp}$ and two polarizabilities, $P_\|$ and $P_\perp$; the orientation is relative to the graphite c axis. The resulting anisotropic dispersion coefficient is[16]

$$\gamma_A = -\tfrac{2}{3}(1-b)/(1+b) \ , \tag{6}$$

$$b = \frac{P_\perp(1+E_a/E_{c\|})}{P_\|(1+E_a/E_{c\perp})} \ . \tag{7}$$

It was argued by CC that the optical properties of graphite correspond to $P_\perp/P_\| \simeq 3.5$ and $E_{c\perp} \simeq E_{c\|} \simeq 12$ eV; this implies that $\gamma_a \simeq 0.4$, independent of adatom species. The positive sign of γ_A means that the adatom is less strongly attracted to the C atom when the adatom is above the C atom than when the adatom lies at some finite angle. For example, the ratio of the attractive force at $\theta=0$ to that at $\theta=45°$ is about 0.7 [see Eq. (2)].

The anisotropy of the repulsive part of the two-body potential arises from the spheroidal charge distribution about each C atom. The value $\gamma_R = -0.54$ was derived[16] by fitting the He scattering data.[13,14] The sign indicates a more repulsive interaction when the adatom is above a C atom. This augments, in effect, the anisotropy of the attractive force. We have no quantitative basis for choosing the value of γ_R for gases other than He, but expect that the sign will remain negative because of the same effect of the carbon atoms' charge configuration.

We have calculated the interaction using values of ϵ and σ chosen recently.[23,24] These input parameters yield

potentials that are consistent with neutron scattering, low-energy electron diffraction, and surface extended x-ray absorption fine structure determinations of equilibrium positions, and thermal measurements.[25–28] Three alternative assumptions were made about the values of the anisotropy parameters: (i) no anisotropy (NA) ($\gamma_A = \gamma_R = 0$), (ii) attractive anisotropy (AA) ($\gamma_R = 0$, $\gamma_A = 0.4$), (iii) anisotropy in both attraction and repulsion (AR) ($\gamma_R = -0.54$, $\gamma_A = 0.4$).

The results of these calculations are summarized in Table I. First of all, one sees that the absolute corrugation energy increases with the size of the adatom; however, the corrugation *decreases relative* to ϵ. This familiar conclusion[3] follows because a larger adatom "sees" a smoother surface, all other things being equal. What is new are the actual values of the variation across the surface. These are seen to increase with the addition of anisotropy to both the attractive and repulsive components of the force. This follows from the observations above that the γ values increase the attraction and decrease the repulsion for $\theta \neq 0$ as compared with $\theta = 0$. Thus they increase the binding at the hexagon center (S) position relative to the atop (AT) and the saddle point (SP).

The results in Table I include a comparison with previous results obtained[3] with isotropic $U(\vec{x})$ and more traditional value of σ and ϵ. The corrugation is substantially larger for the new potentials. The cause, besides the anisotropy, is that the values of σ used previously were larger, corresponding to effectively larger adatoms.

Finally, we may compare our results with recent statistical mechanical studies of adsorbed phases. Sander and Hautman[8] found that the Kr data[29,30] were consistent with an enhancement of the corrugation by 44–100 % relative to that obtained by Steele. In particular, they find $V_G/\epsilon_a = 0.05 \pm 0.01$, where ϵ_a is the Lennard-Jones parameter for the adatoms. Recent work[31] on this interaction strength, including substrate screening, gives $\epsilon_{Kr} = 150$ K. Thus $V_G = 7.4 \pm 1.5$ K. Since $V_{AT} - V_S = 9V_G$ in a two-dimensional model,[32] the semiempirical result is $V_{AT} - V_S \simeq 67.5 \pm 14$ K. This seems incompatible with the potential AR in Table I. Similarly for Xe, the potential of Refs. 10 and 11 gives $V_{AT} - V_S \simeq 76$ K. This seems to rule out the AR potential in this case. On the other hand, the Steele potential[3] is insufficiently corrugat-

TABLE I. Results of potential-energy calculations for gases above graphite; energy units are kelvin. Input parameters are ϵ and σ. $V_0(Z_0)$ is the minimum of the laterally averaged potential, $V_0(z)$, which occurs at z_0. The potentials V_{AT}, V_{SP}, and V_S are each the minimum, as a function of z, of $V(\vec{r})$ at fixed x,y. The positions S, SP, and AT are the adsorption site (hexagon center), saddle point (bridge site) and atop the C atom, respectively. Alternative models used are discussed in the text: NA (no anisotropy), AA (anisotropic attraction), and AR (anisotropic attraction and repulsion). The last column is from Ref. 3.

Atom	ϵ[a]	σ (Å)[b]	z_0 (Å)	$\|V_0(z_0)\|$	$V_{SP}-V_S$ NA	AA	AR	$V_{AT}-V_S$ NA	AA	AR	$V_{AT}-V_S$ (Steele)
He	16.2	2.74	2.73	191	22	27	38	24	30	43	
Ne	30.7	2.80	2.79	378	38	49	67	43	54	73	
Ar	71.6	3.10	3.09	1100	65	79	109	72	88	120	
Kr	85.6	3.21	3.19	1430	68	83	114	76	91	126	42
Xe	104	3.36	3.34	1910	69	83	115	77	91	127	36

[a]From Ref. 16 (He) or Ref. 24 (others).
[b]From Ref. 23.

ed to be consistent with any of these recent analyses or with the He scattering data.[18]

We believe that it is premature to draw definitive conclusions about these potentials. A more extensive study of the thermodynamic consequences of any given assumption is needed. In parallel, work is needed on *ab initio* derivations of the repulsive part of the interaction. We are currently attempting this second line of investigation.

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