RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Model adsorption potentials for He and Ne on graphite

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(Received 8 July 1985)

Calculations are presented concerning the adsorption of the atoms He and Ne on graphite. The ingredients of the potential are a repulsion obtained from the effective-medium theory, an anisotropic van der Waals dipolar attraction between atoms, and a quadrupole dispersion interaction. It is shown that alternative plausible models are compatible with experimental data obtained with atom and neutron scattering and adsorption isotherms.

Considerable attention has been attracted recently to the theory of the physisorption interaction.[1-8] The adsorption potential $V(\mathbf{r})$ is usually assumed to arise from the addition of an attractive dispersion energy to a repulsive overlap interaction,

$$V(\mathbf{r}) = V_A(\mathbf{r}) + V_R(\mathbf{r}) \quad . \tag{1}$$

Discussion centers on the form of each of these terms. For example, the attraction is known to behave as $V_A \sim -C_3 z^{-3}$ at large distance z, but this should be modified at small z to include damping and other multipolar dispersion contributions.[5,6] As to the repulsion, there exists a consensus regarding the case of He on metal surfaces to the effect that $V_R(\mathbf{r})$ is approximately proportional to the unperturbed charge density at the adatom's position. There is not yet, however, agreement on the value of the proportionality coefficient.[2-4,7-10]

This paper addresses the problems of He and Ne interacting with a graphite surface. Our interest arises partly from the desire to assess the applicability of the ideas previously applied to He interacting with metals. In addition, we would like to understand a body of relevant experimental information[11-13] and several recent calculations.[2,14-19]

Our work considers several alternative models, the predictions of which we evaluate and discuss below. The attraction is taken to be a superposition of dipole and quadrupole interactions between the adatom and the carbon atoms,

$$V_A(\mathbf{r}) = \sum_i \left[U_d(\mathbf{r}-\mathbf{R}_i) + U_q(|\mathbf{r}-\mathbf{R}_i|) \right] \quad . \tag{2}$$

The dipole term is anisotropic,[15-17]

$$U_d(\mathbf{x}) = \frac{-3a_s d C_3}{\pi x^6}\left[1+\gamma_A\left(1-\tfrac{3}{2}\cos^2\theta\right)\right] \quad . \tag{3}$$

Here a_s is the area of a surface unit cell (containing two atoms), d is the interlayer spacing, $\gamma_A = 0.4$ is calculated[15] from the dielectric anisotropy, and θ is the angle between $\mathbf{x}$ and the surface normal. This *ab initio* model has found empirical support in analyses of He and H_2 scattering as well as N_2 thermodynamic data.[15,16,20] The γ_A term contributes only to the periodic, lateral variation of the potential. The C_3 values computed theoretically are 180 meV Å^3 for He and 346 meV Å^3 for Ne.[21,22]

In Eq. (2) we have taken the quadrupole term to be isotropic for simplicity,

$$-U_q(x) = q C_8 x^{-8} \quad , \tag{4}$$

where q is a parameter adjusted to include ($q = 1$) or suppress ($q = 0$) this contribution. The value $C_8 = 15C_5/\rho_c\pi$ expresses the two-body coefficient in terms of the carbon number density ρ_c and the theoretical quadrupole coefficient C_5 (97 meV Å^5 for He and 268 meV Å^5 for Ne). As discussed elsewhere, this term contributes 20% of the well depth.[6]

We have evaluated two models of the repulsion. The first, denoted model I, assumes a simple proportionality between V_R and the local electron density,

$$V_R(\mathbf{r}) = \alpha\rho(\mathbf{r}) \quad . \tag{5}$$

If the charge density were translationally invariant, this would correspond to the result of Takada and Kohn,[4] which gives a value $\alpha = 450$ eV a_0^3 for He/graphite. Model II is based on the effective-medium theory,[7] the application of which is reviewed by Batra.[3] This relates the repulsion to a weighted average of the density within a spherical volume Ω centered on $\mathbf{r}$:

$$V_R(\mathbf{r}) = \alpha_{\text{eff}}\bar{\rho}(\mathbf{r}) \quad , \tag{6}$$

$$\alpha_{\text{eff}} = \alpha_0 - \alpha_{\text{at}} \quad , \tag{7a}$$

$$\alpha_{\text{at}} = \int_\Omega \phi_a(\mathbf{r}'-\mathbf{r})\,d\mathbf{r}' \quad , \tag{7b}$$

$$\bar{\rho}(\mathbf{r}) = \frac{1}{\alpha_{\text{at}}}\int_\Omega \rho(\mathbf{r}')\phi_a(\mathbf{r}'-\mathbf{r})\,d\mathbf{r}' \quad . \tag{8}$$

We have taken the sphere's radius $R_c = 2.5$ Å, a conventional choice.[7] $\phi_a(x)$ is the electrostatic potential of the isolated atom, supplemented by the potential due to a uniform charge within R_c of net magnitude equal to the atomic charge outside R_c. The coefficient α_0 (appropriate to uniform jellium) is estimated to be 340 ± 35 eV a_0^3.[3,7,9,10] Our graphite charge density is that of Weinert, Wimmer, and Freeman,[23] previously employed by Harris, Liebsch, and Weinert (HLW) to treat He/graphite.[2] The latter work differs from ours in most other respects.

For He, we have evaluated several properties of experi-

TABLE I. Comparison between experimental measurements (Refs. 11–13) of the ^{4}He matrix element (V_G^{00}), energy levels E_n, and mean distance, with calculation of this paper and Ref. 2 (HLW). Energies are in meV. The cases shown are illustrative examples of models capable of yielding satisfactory agreement with the value E_0 (see Fig. 1). The parameters α_0, C_3, and q are defined in Eqs. (3) and (5)–(7). Model I uses Eq. (5), while model II uses Eq. (6). Both E_n and V_G^{00} values have an uncertainty ±0.01 meV. Other matrix-element values are discussed in the text, as are ^{3}He energy levels.

Source	α or α_0 (eV a_0^3)[a]	C_3 (meV Å^3)	q	V_G^{00}	$\langle z \rangle$ (Å)	E_0	E_1	E_2	E_3	E_4
Expt.				0.28	2.85[b]	12.06	6.36	2.85	1.01	0.17
Model I	500	173	1	0.38	3.17	12.02	6.46	3.07	1.26	
	480	187	0	0.36	3.19	12.06	6.57	3.20	1.36	0.48
	460	167	1	0.39	3.15	11.99	6.41	3.03	1.22	
	480	170	1	0.38	3.16	12.00	6.43	3.05	1.24	0.41
	420	178	0	0.37	3.14	12.01	6.50	3.13	1.31	0.45
	420	161	1	0.40	3.11	12.02	6.40	3.00	1.20	0.39
	400	170	0	0.37	3.13	12.02	6.49	3.12	1.29	
Model II	320	143	1	0.34	3.02	11.99	6.30	2.88	1.10	0.33
	320	162	0	0.31	3.05	12.10	6.49	3.07	1.25	0.41
	380	161	1	0.31	3.11	12.06	6.42	3.01	1.20	0.39
	380	178	0	0.28	3.14	12.05	6.52	3.14	1.31	0.45
HLW[c]	· · ·	185[c]	0	0.44	3.25	12.00	6.30	2.90	1.15	0.35

[a] In the case of model I, the parameter shown is α. In the case of model II, it is α_0.

[b] Carneiro *et al.* (Ref. 11) with uncertainty ±0.05 Å.

[c] The treatment of Ref. 2 uses an attraction $C_3(z-z_0)^{-3}$ with $z_0 = 1.22$ Å.

mental relevance. Each hypothetical potential has been used to calculate eigenvalues E_n of the Schrödinger equation involving the laterally averaged potential. The eigenfunctions ψ_n have been used to calculate matrix elements,

$$V_G^{mn} = \int \psi_m(z)\, V_G(z) \psi_n(z)\, dz \quad , \tag{9}$$

where $V_G(z)$ is the Fourier amplitude of the periodic potential for the smallest nonzero reciprocal-lattice vector **G**.

For specificity, we limit our discussion to those models which are consistent with the experimental value $E_0 = -12.06 \pm 0.1$ meV of Derry *et al.*[13] for ^{4}He. Table I shows results for selected models and parameter choices and compares these with both experimental data[11–13] and calculations of HLW (Ref. 2) (see also Fig. 1). The first observation is that there is, overall, semiquantitative agreement between our calculations, theoretical expectation, and experiment. One would like to go beyond this general statement and resolve the ambiguity evident in Table I. First, we note the principal differences between models I and II. The latter has a reduced corrugation (evident in the matrix elements) and yields a smaller value α_0 than the parameter α; both are due to the averaging in Eq. (8). The latter relation is explained by the fact that $\bar{\rho}/\rho \simeq 1.7$ near the potential minimum. In comparing the models, note that

$$\alpha_0 = \alpha_{\mathrm{at}} + V_R/\bar{\rho} \quad ,$$
$$\alpha_0 = \alpha_{\mathrm{at}} + \alpha\rho/\bar{\rho} \quad . \tag{10}$$

With $\alpha_{\mathrm{at}} = 125$ eV a_0^3, this gives $\alpha_0 = 390$ eV a_0^3 for a typical value $\alpha = 450$ eV a_0^3. With respect to the corrugation difference, we are inclinded to reject model I because it predicts higher values of the matrix element than is consistent with experiment.[12]

We note, in this connection, that the *mn* dependence of matrix elements not displayed in Table I is in good agreement with experiment.[12] For example, the theoretical (experimental) values are 0.28 (0.28), 0.20 (0.20), 0.20 (0.19), 0.13 (0.13), 0.15 (0.16), 0.12 (0.12), 0.09 (0.09), 0.10 (0.10), 0.09 (0.11), and 0.06 (0.08) meV for the sequence $mn = 00$, 10, 11, 20, 21, 22, 30, 31, 32, and 33 (using the fourth example of model II).

We next consider the value of $\langle z \rangle_{\mathrm{He}}$. The experimental result of Carneiro, Passell, Thomlinson, and Taub[11] lies below all theoretical values in Table I. Indeed, HLW considered possible reasons for which the experimental result is uncertain. To assess the point further, we consider mea-

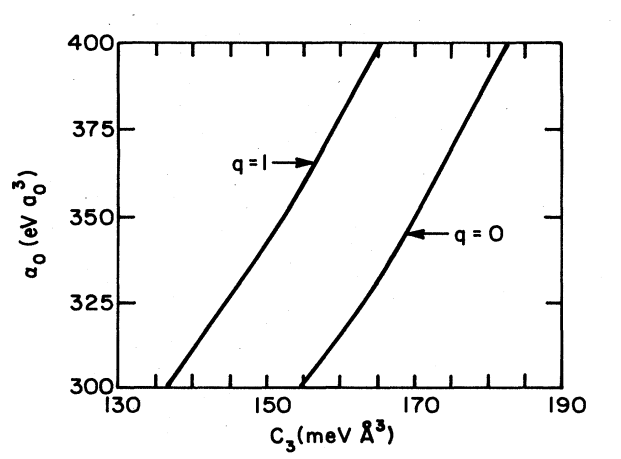

FIG. 1. Correlation obtained empirically between acceptable values of the coefficients α_0, C_3, and q for He. As discussed in the text, the criterion imposed is compatibility with the measured ^{4}He ground-state level E_0.

sured values of $\langle z \rangle$ for other gases on graphite. Low-energy electron diffraction and surface extended x-ray absorption fine-structure data yield $\langle z \rangle = 3.2 \pm 0.1$ Å and 3.3 ± 0.1 Å for Ar and Kr, respectively.[24,25] We may estimate $\langle z \rangle - \langle z \rangle_{\mathrm{He}}$ using combining rules for the distance parameter in the gas-surface interaction.[26,27] The result is $\langle z \rangle - \langle z \rangle_{\mathrm{He}} = -0.05$, 0.24, and 0.32 Å for the gases Ne, Ar, and Kr, respectively. This leads to the estimate $\langle z \rangle_{\mathrm{He}} \sim 3.0$ Å, intermediate between the experimental result and the lower values predicted by model II; see below for a discussion of Ne.

The eigenvalues predicted by model II potentials are seen in Table I to be satisfactory, apart from the shallowest level. This latter discrepancy is a property of all potentials proposed since the experiment.[13] At first sight one might inquire into the possibility of experimental error, since small $|E_n|$ values come from the difference between two nearly equal quantities. However, we note that the same discrepancy exists for the highest observed ^{3}He level; Derry *et al.*[13] report $|E_n| = 11.62$, 5.38, and 1.78 meV, while the fourth potential of model II predicts 11.53, 5.56, and 2.28 meV. We are left, it seems, without an explanation. We note also (Fig. 1) that potentials with the quadrupole term are compatible with C_3 values smaller than the theory predicts.[22] One possible explanation is the role of damping in the dispersion interaction; in the case of interatomic forces[5,27,28] this is written

$$V(r) = -\sum_{n=3}^{\infty} C_{2n} f_{2n}(br) r^{-2n} \ , \tag{11}$$

$$f_6(x) = 1 - e^{-x} \sum_{k=0}^{6} x^k/k! \ . \tag{12}$$

Here the parameter b^{-1} should be the length (0.28 Å for graphite[29]) characteristic of the spatial variation of the charge density. Equation (12) yields a damping factor 0.9 at He-C separation ~ 3 Å relevant to the energy levels. In our treatment, this effect would then lead to an "effective" $C_3 \sim 160$ meV Å^3. This value is seen in Table I to be compatible with the presence of the quadrupole term and the value $\alpha_0 = 380$ eV a_0^3 (or, indeed, with its absence if α_0 is 15% smaller).

We turn next to the case of Ne on graphite. The relevant experimental data are limited to low coverage adsorption isotherms, from which a well depth $D \sim 33$ meV may be estimated.[30] We take this as a starting point for distinguishing between the various potentials, which give results shown in Fig. 2. The other input to our assessment is the use of a 10% damping of the theoretical C_3, giving an effective value $C_3 \sim 300$ meV Å^3. From Fig. 2 we conclude that compatibility with these criteria yields a value $\alpha_0 \sim 900$ eV a_0^3 if the quadrupole term is included, and $\alpha_0 \sim 775$ eV a_0^3 if it is not. Either estimate is higher than the theoretical value ~ 670 eV a_0^3.[3,10] Note, however, that the value of Ref. 10 would increase to 720–750 eV a_0^3 if the theoretical value of the diamagnetic susceptibility of Ne is substituted for the experimental value, as suggested recently by Perdew and Zunger, Levy and Perdew, and Vosko and Wilk.[31,32]

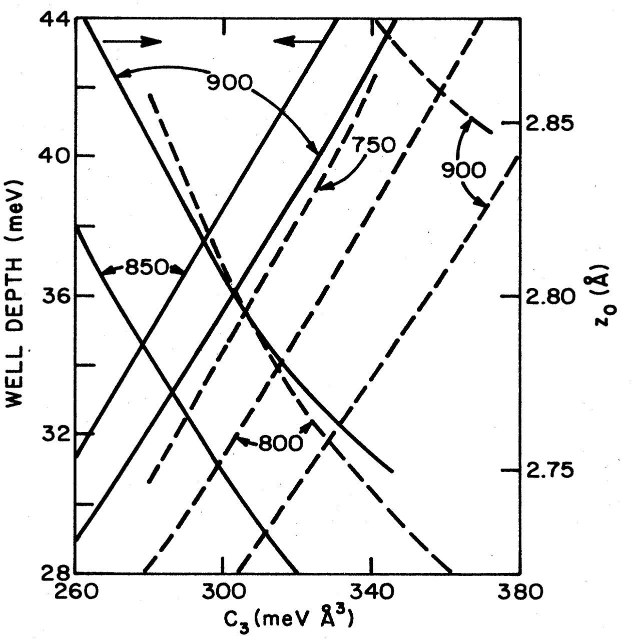

FIG. 2. Calculated values of the well depth (positive slope curves) and equilibrium position (negative slope) of Ne on graphite as a function of C_3, α_0, and q. Full (dashed) curves are calculated with (without) the quadrupole term Eq. (4). Labels refer to the values assumed for α_0, expressed in eV a_0^3. The z_0 values for $q = 0$, $\alpha_0 = 750$ eV a_0^3 nearly coincide with those for $q = 1$, $\alpha_0 = 850$ eV a_0^3 and are therefore not shown.

We return to the question of equilibrium position. The potentials discussed above yield equilibrium positions 2.78 ± 0.03 Å; the inclusion of zero-point motion gives $\langle z \rangle_{\mathrm{Ne}} \simeq 2.85$ Å, reasonably consistent with the experimental values and discussion cited above concerning the other gases.

We summarize our results as follows. The effective-medium theory,[7] tested previously for metals,[3] provides a quantitative description of He and Ne adsorption on graphite. In the He case, energies, mean distance, and corrugation of the potential are in satisfactory agreement with experiment, except for the shallowest energy levels. We find that averaging of the density [Eq. (6)] is necessary for this consistency. Some evidence is presented to the effect that the dipole contribution ($\sim C_3$) should be damped in the vicinity of the equilibrium position, in accord with expectation based on noble-gas interatomic potentials. Finally, the Ne analysis suggests that a somewhat higher value of α_0 is appropriate there than theory provides. The discrepancy is ~ 25% if the quadrupole term is included, but < 10% if it is not.

This work has benefited from discussion with A. Baldereschi and M. Posternak, who provided the charge density used herein.[23] It has been supported in part by National Science Foundation Grants No. DMR-8419261 and No. Int.-8219606, as well as NATO Grant 616/83, and Consiglio Nazionale delle Ricerche and Ministero Pubblica Istruzione.

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