

Three-body contribution to the adsorption potential of atoms on graphite

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Calculations are presented of the three-body, triple-dipole (DDD) potential energy $V^{(3)}(\mathbf{r})$ of a noble-gas atom on a graphite surface. $V^{(3)}(\mathbf{r})$ is constructed from a sum over pairs of anisotropic C atoms at \mathbf{R}_i and \mathbf{R}_j of the DDD interaction $u_3(\mathbf{r}, \mathbf{R}_i, \mathbf{R}_j)$. The result for $V^{(3)}$ is positive near the equilibrium position and of order 20% of the empirical well depth D . This term tends to reduce the corrugation of the equipotential surfaces. When incorporated in some model potentials (for He and Ne), the effect of the new term is qualitatively consistent with experimental data.

I. INTRODUCTION

It is intriguing that "simple" inert gases adsorbed on graphite exhibit quite diverse kinds of behavior in the submonolayer regime. While some systems (e.g., Ar) can be interpreted in terms of idealized two-dimensional (2D) models, others display phases (commensurate, domain wall, striped, incipient triple point) which manifest the presence of the substrate.¹⁻⁵ This diversity arises from the variety of competitions between the two relevant potential-energy functions: the gas-surface interaction $V(\mathbf{r})$ and the gas-gas interaction. Explanation of the data requires accurate knowledge of $V(\mathbf{r})$ because of the delicacy of this energy balance.

Numerous calculations of $V(\mathbf{r})$ exist for the many gases studied.⁶ Most are semiempirical, based on the assumption of additivity of interactions $u_2(\mathbf{x})$ between the adatom and individual C atoms:

$$V^{(2)}(\mathbf{r}) = \sum_i u_2(\mathbf{r} - \mathbf{R}_i), \quad (1)$$

where the sum is over all C sites at \mathbf{R}_i and the 2 denotes a pairwise sum. The potential $u_2(\mathbf{x})$ is typically a parametrized function which can be usefully adapted to include anisotropy of the graphite.⁷⁻¹¹ An alternative, less empirical, approach to constructing $V(\mathbf{r})$ is derived from the delocalized character of the graphite electrons and the nature of their overlap with the adatom's electrons. Several such calculations exist for the gases He and Ne.¹²⁻¹⁴ Among these many calculations, none includes three-body (triple dipole) dispersion forces, the subject of this paper.¹⁵ Specifically, we evaluate and assess the effect of a term¹⁶

$$V^{(3)}(\mathbf{r}) = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} u_3(\mathbf{r}, \mathbf{R}_i, \mathbf{R}_j), \quad (2)$$

where u_3 is the nonadditive dispersion energy¹⁷ arising in third-order perturbation theory from the interactions of fluctuating dipole moments on the adatom and two C atoms. An analogous triple-dipole (DDD) interaction for spherical atoms has been shown^{18,19} empirically to provide an accurate correction to Eq. (1) for the case of 3D inert gas systems; there the pair potentials are sufficiently well

known to provide a test of the presence of the correction term. Scattering and thermodynamic data have also been found to be consistent with the presence of such a $V^{(3)}$ term in the case of He near noble-gas-plated surfaces.²⁰⁻²² Some indication of the importance of this term for bare graphite can be obtained from the adsorption potential expansion of Nijboer and Renne.²³ They showed that the expansion parameter is of order twice the product $n_C \alpha_C$ of the C atom's density and static polarizability $\alpha_C = \frac{1}{3} \text{Tr} \alpha$; this exceeds 0.2 for graphite.^{24,25}

II. CALCULATIONS

Our model of graphite follows that of Ref. 8, in which the C-atom polarizability tensor is diagonal, with matrix elements $\alpha_{11} = \alpha_{22} = b\alpha_{33}$; the z axis is perpendicular to the basal plane. The anisotropy ratio b was estimated to be of order 3.5 on the basis of dielectric data.⁸ Then the DDD interaction¹⁷ can be manipulated to yield

$$u_3 = \frac{3\nu_{ACC}}{(2b+1)^2} (b^2T + bS + W)(r_{AB}r_{AC}r_{BC})^{-3}, \quad (3)$$

$$\nu_{ACC} = \frac{3\alpha_A \alpha_C^2 E_C E_A (E_A + 2E_C)}{4(E_A + E_C)^2}, \quad (4)$$

$$T \equiv B_{11} + B_{21} + B_{12} + B_{22}, \quad (5)$$

$$S \equiv B_{31} + B_{32} + B_{13} + B_{23}, \quad (6)$$

$$W \equiv B_{33}, \quad (7)$$

$$B_{\alpha\beta} \equiv \sum_{i=1}^3 C_{AB}^{i\alpha} C_{BC}^{\alpha\beta} C_{CA}^{\beta i}, \quad (8)$$

$$C_{AB}^{ij} \equiv \delta_{ij} - 3\hat{\mathbf{r}}_{AB}^i \hat{\mathbf{r}}_{AB}^j.$$

Here the adatom is at \mathbf{r}_A and the C atoms are at \mathbf{r}_B and \mathbf{r}_C . The energies E_A and E_C are characteristic energies of the adatom and C atom, respectively; α_A is the static polarizability of the adatom.²⁷

To provide generally useful results, we scale out of Eq. (2) the factor dependent on the adsorbate, ν_{ACC} , leaving a dimensionless DDD potential,

$$\Gamma_{\mathbf{R}}(z) \equiv a^9 V^{(3)}(\mathbf{r}) / \nu_{ACC}, \quad (9a)$$

TABLE I. Parameters of adsorption on graphite. D and z_{eq} are the well depth and equilibrium position; v_{ACC} is the triple-dipole interaction coefficient. $V_0^{(3)}$ is the laterally averaged DDD potential and ΔV_C is the change in corrugation [defined by Eq. (10)], both evaluated at z_{eq} . The superscript 3 refers to the direct DDD contribution, while r refers to the change due to modifying C_{12} in Eq. (12); see Eq. (14).

	D^a (meV)	v_{ACC}/a^{9b} (meV)	z_{eq}^a (Å)	$V_0^{(3)}/D$	$-\Delta V_C^{(3)}$ (meV)	$-\Delta V_C^{(r)}$ (meV)
He	16.4	111	2.57	0.59	0.42	3.0
Ne	33	221	2.79	0.32	0.50	2.3
Ar	95	810	3.09	0.20	0.91	2.2
Kr	123	1180	3.19	0.17	0.96	1.6
Xe	165	1810	3.34	0.13	0.90	1.2

^a Values from Table II of Ref. 26, except He value from Ref. 8, using the anisotropic 6-12 potential.

^b Computed from Eq. (4) with E_A parameters from Ref. 27.

$$\Gamma_{\mathbf{R}}(z) = \sum_{\mathbf{G}} \Gamma_{\mathbf{G}}(z) \exp(i\mathbf{G} \cdot \mathbf{R}). \quad (9b)$$

The function Γ is thus Fourier expanded, with the reciprocal-lattice vectors \mathbf{G} reflecting the 2D periodicity in $\mathbf{R}=(x,y)$. The quantity $a=1.42$ Å is the C-C spacing. Figure 1 presents the terms Γ_0 and Γ_1 , for $G=0$ and $G_1=2.95$ Å⁻¹, respectively. Other terms' net contribution is smaller by more than an order of magnitude. In this case, the difference between potentials above surface positions A and S satisfies

$$V_C \equiv V_A - V_S \simeq -9V_1; \quad (10)$$

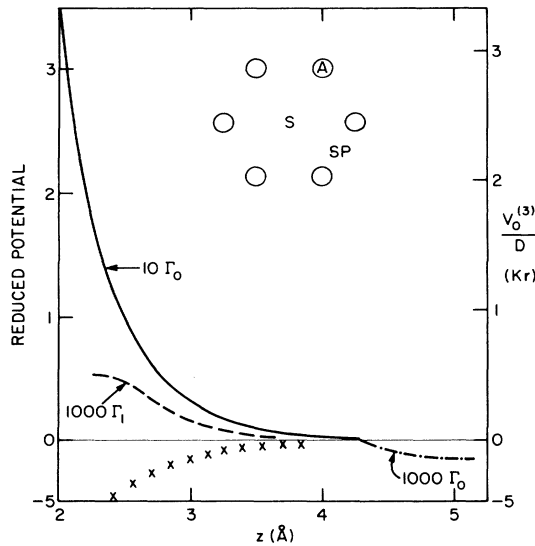


FIG. 1. Fourier components of the reduced DDD potential, defined by Eq. (10). Note the different ordinate scales for positive and negative values as well as the distinct multiplicative factors. The right ordinate (referring to the solid curve) is the ratio of this potential to the well depth $D=123$ meV for the case of Kr (Ref. 26). The crosses represent the ratio of the two lowest Fourier components of the repulsion based on Eq. (12), multiplied by 100. The upper right geometry indicates the notation used for basal plane positions.

we call this difference the corrugation. Since $V_0^{(3)}$ is proportional to $\Gamma_1 > 0$, the DDD contribution $\Delta V_C^{(3)}$ tends to reduce the corrugation.²⁸

We observe in Fig. 1 that while $V_0^{(3)}$ is attractive at large z , it is repulsive near typical adatom positions. This is consistent with the result of Nicholson.¹⁵ As seen in Fig. 2, this means that the distance dependence differs from that of the two-body term,⁸

$$V^{(2)}(\mathbf{r}) = - \sum_i \frac{B [1 + \gamma_A (1 - \frac{3}{2} \cos^2 \theta)]}{|\mathbf{r} - \mathbf{R}_i|^6}, \quad (11a)$$

$$B = \frac{3\alpha_A \alpha_{33} E_C (1+b)}{4(1+E_C/E_A)}. \quad (11b)$$

Here θ is the angle between $\mathbf{r} - \mathbf{R}_i$ and \hat{z} ; $\gamma_A \simeq 0.4$ is the anisotropy parameter.⁸ This difference means that the net dispersion potential cannot be written simply as a two-body $|\mathbf{r} - \mathbf{R}_i|^{-6}$ sum with a modified coefficient. Figure 1 and Table I indicate that the DDD term at the equilibrium position z_{eq} is of order 20% of the experimental well depth D for gases on graphite. The decrease of this ratio with increasing atomic size reflects the fact that this term's growth with size is smaller than that of D . The re-

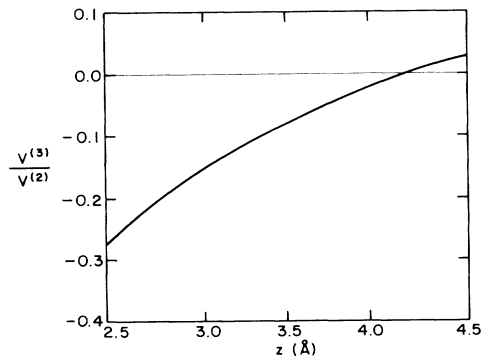


FIG. 2. Ratio of the three-body dispersion term to the two-body dispersion term. Case shown is for $Q \equiv E_C/E_A = 1$; the general case is proportional to $(2Q+1)/(Q+1)$.

sult for He is anomalously large, but this is not especially meaningful due to the zero-point motion's outward displacement by about 0.3 Å of $\langle z \rangle$ relative to z_{eq} .

Our first conclusion, then, is that the DDD term is sufficiently large as to necessitate its inclusion in the construction of $V(\mathbf{r})$. Let us now estimate the implications for the various models described above. We suppose that one has previously developed such a model, which is now to be modified by inclusion of the new term. Consider first an empirical potential of the form of Eq. (1), with a repulsive part based on a power law

$$V_{\text{rep}}^{(2)} = \sum_i C_{12} |\mathbf{r} - \mathbf{R}_i|^{-12}. \quad (12)$$

Let us choose to adjust the coefficient C_{12} so as to keep the value at z_{eq} of the lateral average of the net potential, after $V^{(3)}$ is added, equal to the original value, without the $V^{(3)}$ term; in an obvious notation,

$$0 = \delta V_{\text{rep},0}^{(2)}(z_{\text{eq}}) + V_0^{(3)}(z_{\text{eq}}), \quad (13)$$

$$\frac{\delta C_{12}}{C_{12}} \equiv - \left[\frac{V_0^{(3)}}{V_{\text{rep},0}^{(2)}} \right]_{z_{\text{eq}}}.$$

It is interesting to determine the consequences for the corrugation; this changes by an amount

$$\Delta V_C^{(r)} = \frac{\delta C_{12}}{C_{12}} (V_A - V_S)_{\text{rep}}^{(0)}$$

$$\simeq (V_1/V_0)_{\text{rep}}^{(0)} \theta V_0^{(3)}, \quad (14)$$

where the superscript zero denotes the unperturbed value.

The resulting changes for various systems are presented in Table I. They are seen to be of the same sign ($-$) as $\Delta V_C^{(3)}$, but of larger magnitude; this is evident from Fig. 1 where the ratio of Fourier coefficients in the repulsive case is observed to be roughly a factor of 2 larger in magnitude than the DDD ratio. Thus the principal effect on such an empirical potential is to reduce the empirical repulsion (r^{-12} term); including $\Delta V_C^{(3)}$ yields a net reduction of the corrugation by 2–3 meV.

We now consider briefly the adsorption potential calculations based on “first principles.” The He-graphite potential of Freeman,¹² derived with the Gordon-Kim method,²⁹ has a severely inadequate well. If the asymptotic dispersion attraction,

$$V \sim -C_3 z^{-3}, \quad (15)$$

is naively added to the Freeman result, however, a reasonably satisfactory potential is obtained;³⁰ the deepest calculated bound state is then only 10% smaller in magnitude than the experimental value.³¹ More recently, an alternative *ab-initio* method for treating the He repulsion has been evaluated by Liebsch, Harris, and Weinert,¹³ when combined with Eq. (15), a satisfactory net potential was obtained. Both these results and those of Toigo and Cole¹⁴ (TC henceforth) need to be reexamined in light of the presence of the $V^{(3)}$ term postulated here. For illustration, we consider the implications for the TC potentials of He and Ne. These were constructed from an effective

medium theory of the repulsion and one or more dispersion terms. The model-II potentials of TC involve a parameter α_0 ; this coefficient relates the immersion energy of an atom into uniform jellium to the jellium density. Figure 3 shows what happens, for example, to the fourth version of that potential; similar qualitative conclusions apply to the others. The revised potential of Fig. 3 has been obtained from the earlier version by (a) reducing α_0 from 380 to 305 eV a_0^3 and (b) adding the $V^{(3)}$ term. The result is seen to be somewhat shallower and have a softer repulsive wall than the original potential. It is to be noted that these α_0 values fall at opposite extremes of the range of theoretical estimates;^{32–36} we consider the “new” value to be as reasonable as the old one.

The revised potential will differ in one *major* respect from the earlier version: it is substantially less corrugated. To quantify this, we estimate the matrix element of the corrugation function,

$$\int dz V_1(z) \psi_0^2(z), \quad (16)$$

using the unperturbed wave function ψ_0 . Its magnitude decreases from 0.28 meV to 0.18 meV. Indeed a value near 0.2 meV has recently been asserted by Jonsson and Weare³⁷ to be compatible with scattering data. The principal reason for this change is that the repulsive part of the TC potential has been reduced by our procedure. This finding is completely analogous to that described above in the case of the empirical power-law potentials. As discussed by TC, uncertainty concerning several aspects of the theory (α_0 , damping of the dispersion terms, and presence of higher-order multipoles) leads to ambiguity in its predictive capability. The DDD term adds a new ingredient to this discussion. In the case of Ne-graphite, the new term may resolve a puzzling feature of their analysis. TC found that compatibility with experimental data³² led to a model-dependent choice $\alpha_0 \simeq 775$ (900) eV a_0^3 , instead of the theoretical^{33,36} value ~ 670 eV a_0^3 . The effect of this discrepancy is substantial because what enters the potential calculation directly is the parameter

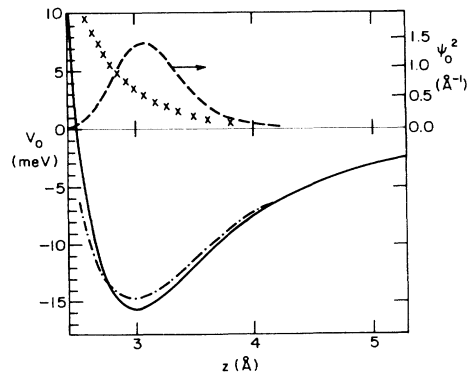


FIG. 3. Original TC potential for He/graphite (solid curve) and its associated probability density (dashed curve, right scale). The crosses denote present results for the DDD potential $V^{(3)}$. The dashed-dotted potential is obtained by including this term and reducing the α_0 parameter in the TC theory, as described in the text.

$$\alpha_{\text{eff}} = \alpha_0 - \alpha_{at}, \quad (17)$$

where³⁶ $\alpha_{at} \approx 485 \text{ eV } a_0^3$. It is α_{eff} which multiplies the average electron density near the atom. Thus the empirical value was $\alpha_{\text{eff}} \approx 290 (415) \text{ eV } a_0^3$, much larger than the theoretical value $\alpha_{\text{eff}} = 185 \text{ eV } a_0^3$. We may now resolve this difficulty tentatively by invoking the role of the $V^{(3)}$ term. Since this gives nearly 11 meV for Ne near the equilibrium position (Table I), the term provides about 60% of the TC repulsion, so that α_{eff} need not be so large as the previously inferred value. Incorporating $V^{(3)}$ as described above, we revise α_{eff} to the values $\sim 120 (170) \text{ eV } a_0^3$. From Eq. (17) we arrive at new semiempirical values $\alpha_0 \approx 605 (655) \text{ eV } a_0^3$. These are within 10% of theoretical predictions.^{33,36}

We address briefly the value of the C_3 coefficient in Eq. (15). Equation (11a) gives an asymptotic dependence of this form, with a two-body coefficient

$$C_3^{(2)} = \frac{\pi B n C}{6}. \quad (18)$$

Using the graphite parameters of Ref. 25 and the atomic parameters of Ref. 26, we obtain $C_3^{(2)}$ values of order 10–15% smaller than the many-body values calculated in Ref. 6. This is consistent with the *additive* role of $C_3^{(3)}$ implicit in the large z behavior of Fig. 2 and in calcula-

tions of Nicholson, at substantially larger z .^{15,38}

We summarize our results. The triple-dipole interaction energy is found to be substantial, of order 20% of the well depth at the equilibrium position. The computed corrugation is opposite to that of both the anisotropic two-body dispersion and repulsive potentials. Some supportive evidence is adduced tentatively for the presence of this term in the cases of He and Ne. No definite conclusion is possible because of uncertainties about several aspects of the theory. What is clear is that the distance dependences of $V^{(3)}$ and $V^{(2)}$ are quite distinct, so that no simple empirical expression embodies both. We emphasize that the present model of $V^{(3)}$ is as justified as analogous calculations for inert gas systems. The relative contribution in that case is well established, although relatively smaller in magnitude. An interesting question is whether the “fortuitous” cancellation¹⁹ of (nondispersive) exchange terms for those systems will also occur in adsorption,³⁹ leaving only dispersive contributions to the many-body energy.

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