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Van der Waals interaction between an atom and a solid surface*

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This paper contributes to the theory of the long-range attractive polarization force between a neutral atom and a crystalline solid surface in the nonrelativistic limit. The first two terms in the asymptotic expansion of the polarization energy are used to define an atom-solid potential of the form $V_{\text{pol}} = -C(Z-Z_0)^{-3}$. The constant C appearing in this expression is known from the earlier work of E. M. Lifshitz. The present paper gives a theory of the position of the "reference plane," Z_0, which is important in applications to physisorption. An explicit expression for Z_0 is first derived for atoms interacting with a jellium metal and with an insulating crystal consisting of atoms which interact via dipole-dipole forces. These model calculations are then incorporated into a computation of the polarization energies of rare-gas atoms physisorbed on noble-metal surfaces. The computed energies are found to be consistent with observed adsorption energies.

I. INTRODUCTION

A physisorbed atom can be considered as being bound to a solid surface under the combined action of two potentials: the long-ranged attractive polarization potential which, in the nonrelativistic limit, has the asymptotic form

$$V_{\text{pol}} \sim -C/Z^3 , \qquad (1.1)$$

where Z is the distance from the surface; and a short-ranged repulsive potential arising from the overlap of the electronic clouds of the atom and of the surface.[1] The present paper deals exclusively with the polarization potential.

In a classic paper,[2] Lifshitz has given a macroscopic formulation of the attractive Van der Waals forces between two bodies characterized by spatially nondispersive, frequency-dependent dielectric functions. This formulation[2-5] implicitly contains an exact expression for the constant C appearing in (1.1). Thus, the extreme asymptotic behavior of V_{pol} can be regarded as known. However, in applications to physisorption, the separation Z is typically of the order of 10^{-8} cm, a distance which is not large on the scale of the thickness of the "surface" itself. In this situation, it becomes important to know the reference plane with respect to which Z is to be measured. Because of the rapid variation of V_{pol} with Z, it is clear that a knowledge of the reference-plane position is crucial in obtaining a reliable estimate of the contribution of the polarization energy to the heat of adsorption.

A precise definition of this reference plane can be obtained from the second term in the asymptotic expansion of the polarization energy

$$V_{\text{pol}} \sim -C/Z^3 - D/Z^4 + \cdots . \qquad (1.2)$$

Equivalently, we can write

$$V_{\text{pol}} \sim -C/(Z-Z_0)^3 , \qquad (1.3)$$

thereby defining the reference-plane position, Z_0. This procedure is clearly analogous to the one followed previously[6] in defining the correct reference plane for the image potential. Our main objective in this paper is to develop a similar theory of the reference-plane position for the atom-surface polarization potential. Although the need for defining the reference-plane position has been indicated before,[7] the precise relationship between Z_0 and the microscopic details of the solid surface has not previously been given.

In Sec. II we derive a general expression for the atom-solid polarization energy using second-order perturbation theory. This expression is then shown to be equivalent asymptotically to the usual Lifshitz formula.[2,4] By continuing the asymptotic expansion of the energy in inverse powers of the atom-surface separation, the reference-plane position Z_0 is defined. This derivation shows that the reference-plane position is determined by the spatial nonlocality of the electronic density response function of the solid. Although a number of extensions of the Lifshitz theory to include a spatially nonlocal dielectric function have appeared,[8-10] these have all made simplifying assumptions which precluded a realistic description of the solid surface. The advantage of the present approach is that the microscopic details of the surface are accounted for completely.

The expression for the reference-plane position given in Sec. II and Appendix A is a general but formal result. In Sec. III we consider various systems for which either an explicit or an approximate estimate of the reference-plane position can be made. In particular, we first consider a simple metal represented by jellium and evaluate the appropriate quantities which enter for the physisorption of He on such a metal. We then consider a model of a simple-cubic dielectric solid in which the atoms are spherically symmetric and interact

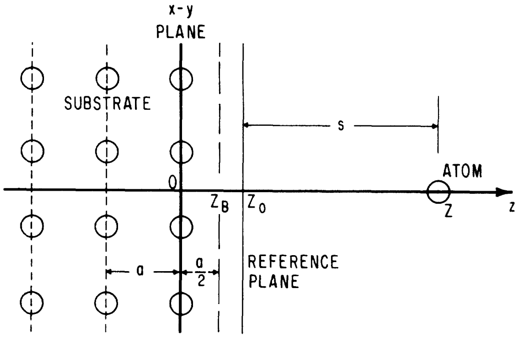

FIG. 1. Geometry of the atom–substrate system. The origin of coordinates has been chosen arbitrarily to lie in the plane of surface atoms.

via the dipole-dipole interaction. For the specific case of small local-field corrections, an explicit expression for the reference-plane position can be found. Finally, we consider the adsorption of rare-gas atoms on noble-metal surfaces. The results for this example are obtained using a simple interpolation of the expressions found for jellium and the insulating solid. Quantitative estimates of the polarization energy for Xe physisorbed on the noble metals are made and are shown to be consistent with experimentally determined binding energies. Section IV concludes the paper with a brief discussion of the results.

II. POLARIZATION ENERGY

A. Derivation

To derive the interaction between a semi-infinite crystalline solid and a neutral atom we shall adopt a method which is analogous to the one used in obtaining the Van der Waals interaction between two atoms.[11,12] The geometrical arrangement that we are considering is illustrated in Fig. 1. Since we are interested in the polarization contribution to the interaction, we can assume that there is no appreciable overlap of the electronic wave functions of the atom and solid. In this situation, exchange of electrons between the two subsystems does not occur and it is possible to consider the electrons of the solid as being distinguishable from those in the atom. Furthermore, we neglect relativistic effects which become important for separations much larger than those of interest in physisorption. We therefore use the following Hamiltonian in describing the system,

$$H = H_a + H_s + V_{as} \,. \tag{2.1}$$

Here, H_a and H_s are the Hamiltonians for the isolated atom and solid, respectively, and V_{as} is the Coulomb interaction between the two subsystems given explicitly by

$$V_{as} = \int d\vec{r}\, d\vec{r}\,' \frac{\hat{\rho}^s(\vec{r})\hat{\rho}^a(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \,, \tag{2.2}$$

with

$$\hat{\rho}^{s,a}(\vec{r}) = n_+^{s,a}(\vec{r}) - \hat{n}^{s,a}(\vec{r}) \,. \tag{2.3}$$

The charge densities of the nuclei are represented by $n_+^{s,a}(\vec{r})$; the electron density operators for the solid and the atom are denoted by $\hat{n}^s(\vec{r})$ and $\hat{n}^a(\vec{r})$, respectively. We use atomic units throughout ($|e| = m = \hbar = 1$).

Since the atom and solid are weakly coupled for large separations, the interaction energy can be calculated perturbationally. The first-order contribution is given by

$$E^{(1)} = \langle \Psi_0^a \Psi_0^s | V_{as} | \Psi_0^a \Psi_0^s \rangle = \int d\vec{r}\, \rho_0^a(\vec{r}) \varphi_0^s(\vec{r}) \,. \tag{2.4}$$

Here, $|\Psi_0^{a,s}\rangle$ denote the unperturbed ground-state wave functions of the respective subsystems. The corresponding unperturbed atomic density is denoted by $\rho_0^a(\vec{r})$; $\varphi_0^s(\vec{r})$ is the electrostatic potential of the undisturbed solid and exhibits the same periodicity in planes parallel to the surface as the surface itself. We can therefore write

$$\varphi_0^s(\vec{r}) = \sum_h e^{i\vec{Q}_h \cdot \vec{r}} \, \tilde{\varphi}_0^s(z, \vec{Q}_h) \,, \tag{2.5}$$

where $\vec{Q}_h = (Q_{hx}, Q_{hy}, 0)$ is a reciprocal-lattice vector in the plane of the surface. The average potential $\tilde{\varphi}_0^s(z, \vec{Q}_h = 0)$ is determined by the charge density of the solid averaged over the surface area. Since we have assumed that the charge density of the solid does not overlap the atomic charge density, $\tilde{\varphi}_0^s(z, \vec{Q}_h = 0)$ is constant over the region of the atom and the $\vec{Q}_h = 0$ component of (2.5) does not contribute to Eq. (2.4). The remaining terms give contributions to (2.4) which decay exponentially away from the surface and can therefore be neglected in comparison to those contributions to the energy which have a power-law dependence. The exponentially decreasing terms will of course be important near the surface, particularly since they exhibit variations in directions parallel to the surface.

The second-order contribution in the perturbation expansion of the energy is

$$E^{(2)} = \sum_{\substack{\alpha \neq 0 \\ \beta \neq 0}} \frac{|\langle \Psi_0^a \Psi_0^s | V_{as}' | \Psi_\alpha^a \Psi_\beta^s |^2}{(E_0^a - E_\alpha^a) + (E_0^s - E_\beta^s)} \,. \tag{2.6}$$

Here V_{as}' is that part of the interaction in (2.2) which contains the combination $\hat{n}^s(\vec{r})\hat{n}^a(\vec{r}\,')$. The unperturbed atom and solid electronic eigenfunctions and eigenenergies are denoted by $|\Psi_\alpha^{a,s}\rangle$ and $E_\alpha^{a,s}$, respectively. This contribution is clearly negative, corresponding to an attractive interaction.

Making use of the identity

$$\frac{1}{A+B}=\frac{2}{\pi}\int_0^\infty du\frac{A}{A^2+u^2}\,\frac{B}{B^2+u^2}\,,\quad A,B>0\,, \tag{2.7}$$

and the time-reversal symmetry of the matrix elements in (2.6), one can express Eq. (2.6) in terms of retarded response functions as follows:

$$E^{(2)}=-\int d\vec{r}\int d\vec{r}\,'\int d\vec{x}\int d\vec{x}\,'\,v(\vec{R}+\vec{x}-\vec{r})v(\vec{R}+\vec{x}\,'-\vec{r}\,')\times\int_0^\infty\frac{du}{2\pi}\chi_a(\vec{x},\vec{x}\,';iu)\chi_s(\vec{r},\vec{r}\,';iu)\,. \tag{2.8}$$

The imaginary frequency transforms of the response functions are defined as

$$\chi_{a,s}(\vec{r},\vec{r}\,';iu)\equiv i\int_0^\infty dt\,e^{-ut}\langle[\hat{n}^{a,s}(\vec{r},t),\hat{n}^{a,s}(\vec{r}\,',0)]\rangle_{a,s}\,, \tag{2.9}$$

where as usual, the bracketed quantity on the right-hand side is the ground-state expectation value of the indicated commutator. In (2.8) we have introduced the position $\vec{R}=(X,Y,Z)$ of the atomic nucleus with respect to which the positions of the atomic electrons are measured.

To proceed with the evaluation of (2.8) it is convenient to introduce the two-dimensional Fourier transform of the Coulomb potential,

$$v(\vec{r}-\vec{r}\,')=\frac{1}{L^2}\sum_{\vec{q}}\left(\frac{2\pi}{q}\right)e^{i\vec{q}\cdot(\vec{\rho}-\vec{\rho}\,')}\,e^{-q|z-z'|};\quad[\vec{r}=(\vec{\rho},z)]\,, \tag{2.10}$$

where L^2 is the surface area of the solid and $\vec{q}=(q_x,q_y,0)$ is a two-dimensional wave vector in the plane of the surface. Inserting this into (2.8), we find

$$E^{(2)}=-\int_0^\infty\frac{du}{2\pi}\frac{1}{L^4}\sum_{\vec{q},\vec{q}\,'}\left(\frac{2\pi}{q}\right)\left(\frac{2\pi}{q'}\right)e^{-Z(q+q')}\,e^{i\vec{R}\cdot(\vec{q}-\vec{q}\,')}\times\int d\vec{x}\int d\vec{x}\,'\,e^{i\vec{\kappa}\cdot\vec{x}}\,e^{-i\vec{\kappa}\,'^{*}\cdot\vec{x}\,'}\,\chi_a(\vec{x},\vec{x}\,';iu)\int d\vec{r}\int d\vec{r}\,'\,e^{-i\vec{\kappa}\cdot\vec{r}}\,e^{i\vec{\kappa}\,'^{*}\cdot\vec{r}\,'}\,\chi_s(\vec{r},\vec{r}\,';iu)\,, \tag{2.11}$$

where we have introduced the complex wave vector

$$\vec{\kappa}=\vec{q}+iq\hat{z}\,. \tag{2.12}$$

For the assumed periodicity of the surface, the $\vec{q}\,'$ summation is restricted to

$$\vec{q}\,'=\vec{q}+\vec{Q}_h\,. \tag{2.13}$$

With these values of $\vec{q}\,'$, we note that $e^{-Z(q+q')}\lesssim e^{-ZQ_h/\sqrt{2}}$ over the whole range of the $\vec{q}$ summation. Thus, all the terms with $Q_h\neq 0$ decay exponentially away from the surface as in the case of the electrostatic potential. Only the $\vec{Q}_h=0$ term gives rise to a power-law dependence of the interaction energy and corresponds to the conventional Van der Waals interaction.

Retaining only the $\vec{Q}_h=0$ term, a factor $\exp(-2qZ)$ appears in (2.11) which cuts off the q sum for values of $q\gtrsim 1/Z$. If Z is much larger than the size of the atom, the exponentials in the integral over the atomic coordinates can therefore be expanded as

$$\int d\vec{x}\int d\vec{x}\,'\,e^{i\vec{\kappa}\cdot\vec{x}}\,e^{-i\vec{\kappa}^{*}\cdot\vec{x}\,'}\,\chi_a(\vec{x},\vec{x}\,';iu)=\kappa_\mu\kappa_\nu^{*}\int d\vec{x}\int d\vec{x}\,'\,x_\mu\chi_a(\vec{x},\vec{x}\,';iu)x_\nu'+\cdots=2q^2\alpha(iu)+O(q^4)\,. \tag{2.14}$$

Here $\alpha(iu)$ is the frequency-dependent atomic polarizability evaluated at the imaginary frequency $\omega=iu$. The first term in this expansion, when substituted into (2.11), represents that contribution to the polarization energy from the interaction of the instantaneous dipole on the atom with its image in the solid. It should be noted that the higher-order multipole interactions give rise to terms in the expansion which are at least of order q^4.

Inserting (2.14) into (2.11) and again retaining only the $\vec{Q}_h=0$ term, we finally obtain

$$E^{(2)}=-\frac{2}{\pi}\int_0^\infty du\,\alpha(iu)\,F(iu,Z)\,, \tag{2.15}$$

where

$$F(iu,Z)\equiv\frac{2\pi^2}{L^2}\sum_{\vec{q}}e^{-2qZ}\int dz\int dz'\,e^{qz}\,e^{qz'}\times\chi_s(z,z',\vec{q},\vec{q};iu) \tag{2.16}$$

and

$$\chi_s(z,z',\vec{q},\vec{q}+\vec{Q}_h;iu)\equiv\frac{1}{L^2}\int d\vec{\rho}\int d\vec{\rho}\,'\,e^{-i\vec{q}\cdot\vec{\rho}}\,e^{i(\vec{q}+\vec{Q}_h)\cdot\vec{\rho}\,'}\times\chi_s(\vec{r},\vec{r}\,';iu)\,. \tag{2.17}$$

Equations (2.15), (2.16), and (2.17) constitute a slight generalization of the usual Lifshitz formula in that both the lattice periodicity and the spatial nonlocality of the solid electronic response function are fully included.

B. Asymptotic form of the interaction and reference plane position

As already noted, the factor $\exp(-2qZ)$ cuts off the $\vec{q}$ summation and it is therefore sufficient to determine only the small-q behavior of the function

$$f(q,iu)\equiv\int dz\int dz'\,e^{qz}\,e^{qz'}\,\chi_s(z,z',\vec{q},\vec{q};iu)\;. \tag{2.18}$$

Physically, this corresponds to the fact that the density fluctuation (averaged over a unit cell in the surface plane) induced by the instantaneous dipole on the atom is spread out along the surface when Z is large. Thus, only the long-wavelength behavior of the response function is important.

By expanding $f(q,iu)$ in powers of q, $F(iu,Z)$ can itself be expanded in inverse powers of Z. Such an expansion is facilitated by first noting the physical significance of $f(q,iu)$. Consider the response of the solid to the external time-dependent charge distribution

$$\rho_{\text{ext}}(\vec{r},t)\equiv\delta(z-Z)\,e^{i\vec{q}\cdot\vec{\rho}}\,e^{ut}\;. \tag{2.19}$$

The induced electron density in the solid will then have the form

$$\delta n(\vec{r},t)=\delta\tilde{n}(\vec{r},\vec{q},iu)\,e^{i\vec{q}\cdot\vec{\rho}}\,e^{-qZ}\,e^{ut}\;, \tag{2.20}$$

where

$$\begin{aligned}\delta\tilde{n}(\vec{r},\vec{q},iu)&\equiv\sum_h e^{i\vec{Q}_h\cdot\vec{\rho}}\left(\frac{2\pi}{q}\right)\\&\quad\times\int dz'\,\chi_s(z,z',\vec{q}+\vec{Q}_h,\vec{q};iu)\,e^{qz'}\\&\equiv\sum_h e^{i\vec{Q}_h\cdot\vec{\rho}}\,\delta\tilde{n}_{\vec{Q}_h}(z,\vec{q},iu)\;.\end{aligned} \tag{2.21}$$

Averaging (2.21) over the surface of the solid, we find that $f(q,iu)$ can be expressed as

$$f(q,iu)=\frac{q}{2\pi}\int dz\,e^{qz}\,\delta\tilde{n}_0(z,q,iu)\;. \tag{2.22}$$

This equation relating $f(q,iu)$ to a quantity having a simple physical interpretation is especially useful in the following.

Since our objective is to obtain an expansion of $f(q,iu)$ in powers of q, it would appear that a straightforward expansion of e^{qz} and $\delta\tilde{n}_0(z,q,iu)$ in (2.22) could be undertaken. In the work of Lang and Kohn,[6] this approach was possible since for the static response of the jellium model, $\delta\tilde{n}(\vec{r},\vec{q},0)$ is localized near the surface. In the more general situation of a crystalline solid at nonzero frequencies this is no longer the case and an immediate expansion of (2.22) leads to indeterminate expressions. For example, in the high-frequency limit $\delta\tilde{n}_0(z,q,iu)$ is proportional to $dn_{\text{eq}}(z)/dz$ (see Appendix A), where $n_{\text{eq}}(z)$ is the equilibrium electron density in the solid. Since this quantity oscillates about a zero mean value deep within the solid, the immediate expansion of (2.22) in powers of q is not possible.

A simple device which obviates this difficulty is to consider an appropriate average of $\delta\tilde{n}_0(z,q,iu)$ which eliminates the periodic part of this function. We are therefore led to consider the following quantity

$$\delta\bar{n}(z,q,iu)\equiv\frac{1}{a}\int_{z-a/2}^{z+a/2}dz'\,\delta\tilde{n}_0(z',q,iu)\;. \tag{2.23}$$

Here a is the spacing between lattice planes in a direction perpendicular to the surface. The use of this averaged density offers a number of formal as well as practical advantages. First we note that

$$\int dz\,e^{qz}\,\delta\tilde{n}_0(z,q,iu)=\int dz\,e^{qz}\,\delta\bar{n}(z,q,iu)+O(q^2)\;, \tag{2.24}$$

which can be verified by interchanging the order of integration on the right-hand side. Since we ultimately require the integral on the left-hand side of (2.24) only to first order in q, it is clear that $\delta\bar{n}(z,q,iu)$ and $\delta\tilde{n}_0(z,q,iu)$ are interchangeable to this order. For the example of jellium, a can be chosen to be zero and $\delta\bar{n}$ is then equal to $\delta\tilde{n}_0$.

Having eliminated the periodic part of $\delta\tilde{n}_0(z,q,iu)$, $\delta\bar{n}(z,q,iu)$ is expected to be localized near the surface so that a straightforward expansion of $f(q,iu)$ is now possible. Introducing the expansion

$$\delta\bar{n}(z,q,iu)=\delta\bar{n}_0(z,iu)+q\,\delta\bar{n}_1(z,iu)+\cdots\;, \tag{2.25}$$

into (2.22) with $\delta\tilde{n}_0(z,q,iu)$ replaced by $\delta\bar{n}(z,q,iu)$, we obtain

$$\begin{aligned}f(q,iu)&=\frac{q}{2\pi}\int dz\,\{\delta\bar{n}_0(z,iu)+q[z\,\delta\bar{n}_0(z,iu)\\&\quad+\delta\bar{n}_1(z,iu)]+O(q^2)\}\end{aligned} \tag{2.26}$$

$$=\frac{q}{2\pi}\int dz\,\delta\bar{n}_0(z,iu)[1+2q\bar{z}(iu)+O(q^2)], \tag{2.27}$$

with the definition

$$\begin{aligned}\bar{z}(iu)&\equiv\frac{\int dz\,z\,\delta\bar{n}_0(z,iu)}{\int dz\,\delta\bar{n}_0(z,iu)}\\&\quad+\frac{1}{2}\,\frac{\int dz\,[\delta\bar{n}_1(z,iu)-z\,\delta\bar{n}_0(z,iu)]}{\int dz\,\delta\bar{n}_0(z,iu)}\;.\end{aligned} \tag{2.28}$$

The quantity $\delta\bar{n}_0(z,iu)$ is proportional to the averaged electron density induced by a uniform external electric field applied in the direction of the inward normal to the surface and which increases in magnitude at the rate e^{ut}. This induced density is highly localized at the surface of the solid and its integrated amplitude $\int dz\,\delta\bar{n}_0(z,iu)$ represents the total surface screening charge. As will be shown shortly, this screening charge can be expressed in terms of quantities which are characteristic of the bulk.

The function $\bar{z}(iu)$ is introduced in analogy with the quantity appearing in the theory of the static image potential in the jellium model.[6] Because of the formal identity (2.24), $\bar{z}(iu)$ as defined by (2.28) in terms of $\delta\bar{n}(z,q,iu)$ is the same as the analogous quantity defined in terms of $\delta\tilde{n}_0(z,q,iu)$. The first term in (2.28) is simply the centroid of the induced density $\delta\bar{n}_0(z, iu)$. The second term, including $\delta\bar{n}_1(z, iu)$, has no simple physical interpretation. However, it is known that the second term vanishes in the static limit $u=0$ for the jellium model and in this case $\bar{z}(0)$ as defined in (2.28) is just the centroid of the induced surface charge. Furthermore, it can be shown that the second term also vanishes in the high-frequency limit (See Appendix A). Unfortunately, we have not been able to determine whether or not the second term in (2.28) vanishes for arbitrary frequencies u. Thus the identification of $\bar{z}(iu)$ as the centroid of the induced surface charge $\delta\bar{n}_0(z, iu)$ is not possible in general. Of course, to the extent that the term of order q^2 in (2.27) can be calculated directly, as in the model of a dielectric solid considered in Sec. III B, the above identification is not necessary. Nonetheless, the limiting behavior of $\bar{z}(iu)$ at zero frequency in the jellium model and at high frequencies in general suggests that the second term in (2.28) could be neglected as a reasonable approximation in those cases for which $\bar{z}(iu)$ cannot otherwise be directly determined. In Appendix A this question is considered in more detail, and an alternative formal expression for $\bar{z}(iu)$ is derived on the basis of charge conservation.

We now return to the explicit determination of $\delta\bar{n}_0(z, iu)$, thereby relating Eq. (2.15) to the Lifshitz formula. The easiest way to establish this relationship is to make use of the continuity equation

$$\frac{\partial}{\partial t} n(r, t) + \nabla \cdot \vec{j}(r, t) = 0 \ . \tag{2.29}$$

Using the explicit time dependence given in (2.20), and averaging Eq. (2.29) over both the surface area and according to (2.23), we obtain in the $\vec{q}=0$ limit

$$u\, \delta\bar{n}_0(z, iu) + \frac{\partial}{\partial z} \bar{j}_z(z, iu) = 0 \tag{2.30}$$

or

$$\bar{j}_z(-\infty, iu) = u \int_{-\infty}^{\infty} dz\, \delta\bar{n}_0(z, iu) \ . \tag{2.31}$$

Alternatively, $\bar{j}_z(-\infty, iu)$ is determined by the mean electric field deep in the interior. This field arises from the external charge distribution which is screened by the induced surface charge. Using Gauss' law, the mean electric field deep in the metal is $\vec{E} = -E_0 e^{ut} \hat{z}$ with

$$E_0 = 2\pi\left(1 - \int_{-\infty}^{\infty} dz\, \delta\bar{n}_0(z, iu)\right) \ . \tag{2.32}$$

Thus, the amplitude of the current induced in the bulk by the total field $\vec{E}$ is

$$\bar{j}_z(-\infty, iu) = \sigma(iu) E_0 \ , \tag{2.33}$$

where $\sigma(iu)$ is the bulk conductivity. Combining (2.31), (2.32) and (2.33) we find

$$\int_{-\infty}^{\infty} dz\, \delta\bar{n}_0(z, iu) = \frac{2\pi\,\sigma(iu)/u}{1 + 2\pi\,\sigma(iu)/u} = \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1} \ , \tag{2.34}$$

where we have introduced the bulk dielectric function which is related to the conductivity by $\epsilon(iu) = 1 + 4\pi\,\sigma(iu)/u$.

Using the term of order q in (2.27) together with the expression for the integrated density (2.34), we find that Eq. (2.15) yields

$$E^{(2)} = -C/Z^3 + O(Z^{-4}) \tag{2.35}$$

with

$$C = \frac{1}{4\pi} \int_0^{\infty} du\, \alpha(iu) \left(\frac{\epsilon(iu) - 1}{\epsilon(iu) + 1}\right) \ . \tag{2.36}$$

In this form, the asymptotic expression for the polarization force is clearly identical to the result obtained by Lifshitz[2,4] in a different way.

Although (2.35) gives the leading-order contribution to the polarization energy, it cannot be applied directly to the problem of physisorption since the origin of coordinates has not been specified. To obtain a unique reference plane with respect to which the position of the atom should be measured, we require the next term in the asymptotic expansion. This term is of order Z^{-4} and its value is determined by the coefficient of q^2 in Eq. (2.27). As we mentioned following (2.14), the next term in the expansion of the atomic response function is of order q^4 and leads to a correction in the energy of order Z^{-5}. Furthermore, it is known[12] that the contribution of the term of third order in the perturbation expansion of the interaction energy between two atoms varies as R^{-11}. The analogous term for the solid-atom interaction is expected to vary as Z^{-8}. (See Appendix C for a discussion of a restricted class of higher-order corrections in the perturbation expansion). Thus, the term of order Z^{-4} that we now consider is indeed the dominant correction.

Including both terms in (2.27), Eq. (2.15) becomes

$$E^{(2)} = -(C/Z^3)[1 + 3Z_0/Z + O(Z^{-2})] \ , \tag{2.37}$$

where

$$Z_0 \equiv \left[\frac{1}{4\pi} \int_0^{\infty} du\, \alpha(iu) \left(\frac{\epsilon(iu) - 1}{\epsilon(iu) + 1}\right) \bar{z}(iu)\right] \times \left[\frac{1}{4\pi} \int_0^{\infty} du\, \alpha(iu) \left(\frac{\epsilon(iu) - 1}{\epsilon(iu) + 1}\right)\right]^{-1} \ . \tag{2.38}$$

Z_0 represents the reference plane position for the Van der Waals interaction; this position is simply an appropriately weighted average of $\bar{z}(iu)$. As shown by the above derivation, the spatial dispersion in the solid density response function is important in determining the reference plane position Z_0.

If distances are reckoned from the position of the reference plane Z_0, a correction of order Z^{-4} will not appear explicitly in the expansion of $E^{(2)}$. Reverting to an arbitrary coordinate system, we can write

$$V_{\mathrm{pol}} \equiv E^{(2)} \simeq -C/(Z-Z_0)^3 + O(Z^{-5}) \; . \qquad (2.39)$$

Such a representation of the interaction will break down sufficiently close to Z_0. However, for the separations $(Z_{\mathrm{eq}} - Z_0)$ typically encountered in physisorption (~4–7 a.u.), Eq. (2.39) should be applicable. Of course, this assertion can only be checked by explicitly evaluating $E^{(2)}$ without resorting to the asymptotic expansion. Within the so-called semiclassical infinite barrier model, the metallic response function can be obtained analytically[13,14] and used to evaluate Eq. (2.15) directly. Such a calculation[15] revealed that (2.39) gave an accurate representation of the position dependence of the interaction down to within about one atomic unit of the infinite barrier. While many of the features of this model are unrealistic, this calculation suggests that (2.39) does in fact provide a reasonable representation of the interaction for the separations of interest in physisorption.

In Sec. III we evaluate C and Z_0 for two simplified model systems and use these results to estimate the polarization contribution to the binding energy of rare-gas atoms physisorbed on noble-metal surfaces.

III. APPLICATIONS

A. Jellium

We begin with an application of the results of Sec. II to the case of a simple metal for which the jellium model is a reasonable approximation. In particular, we consider the adsorption of He on such metals and evaluate the Van der Waals coefficient C and the reference-plane position Z_0.

In order to obtain a quantitative estimate of the reference-plane position, we require an expression for $\bar{z}(iu)$. An approximate expression can be obtained by considering the limiting behavior of $f(q, iu)$ at high and low frequencies and then making a simple interpolation between these limits.

The zero-frequency limit is known from the work of Lang and Kohn[6]

$$f(q, iu=0) \equiv f_0(q) = (q/2\pi)(1 + 2q Z_c + \cdots) \; . \qquad (3.1)$$

Here Z_c is the centroid of the surface charge in the jellium model for a static external field. Similarly, as shown in Appendix A, the high-frequency limit is given by

$$\begin{aligned} f(q, iu) &\sim \frac{f_\infty(q)}{u^2} + O(u^{-4}) \\ &= -\frac{q}{u^2}\int dz\, e^{2qz}\frac{dn_{\mathrm{eq}}(z)}{dz} + O(u^{-4}) \; , \end{aligned} \qquad (3.2)$$

where $n_{\mathrm{eq}}(z)$ is the equilibrium electronic density profile. For the jellium model with a step-function positive background, $f_\infty(q)$ reduces to

$$f_\infty(q) = n_B q(1 + 2q Z_B + \cdots) \; , \qquad (3.3)$$

where n_B is the electron density in the bulk of the metal and Z_B is the position of the edge of the positive background. [According to (2.27) it is also the position of the centroid in the high-frequency limit.] We now introduce a simple interpolation for $f(q, iu)$ to be used for arbitrary q and which is consistent with the known zero- and high-frequency limits given in (3.1) and (3.2). Since $f(q, iu)$ is an even, monotonically decreasing function of u, it can be approximated by the Padé approximant

$$f(q, iu) = f_0(q) f_\infty(q)/[f_\infty(q) + f_0(q) u^2] \; . \qquad (3.4)$$

Expanding this function in powers of q, using (3.1) and (3.3) and comparing the result with (2.27) we find

$$\int dz\, \delta\bar{n}_0(z, iu) = \frac{\omega_{\mathrm{sp}}^2}{u^2 + \omega_{\mathrm{sp}}^2} \qquad (3.5)$$

and

$$\bar{z}(iu) = (\omega_{\mathrm{sp}}^2 Z_c + u^2 Z_B)/(u^2 + \omega_{\mathrm{sp}}^2) \; , \qquad (3.6)$$

where $\omega_{\mathrm{sp}} = \omega_p/\sqrt{2}$ is the surface-plasmon frequency. Equation (3.5) is the same as the result obtained using a free-electron-like (or random-phase approximation) dielectric function $\epsilon(iu) \simeq 1 + \omega_p^2/u^2$ in (2.34). To the extent that ω_p is the only characteristic frequency of jellium, the interpolations given in (3.5) and (3.6) should be accurate.

To complete the evaluation of Z_0 we require the atomic polarizability which is expressible as

$$\alpha(iu) = \sum_n \frac{f_{0n}}{u^2 + \omega_{0n}^2} \; . \qquad (3.7)$$

Here f_{0n} is the oscillator strength for transitions from the ground to the nth excited state and ω_{0n} is the corresponding energy difference. Using (3.5)–(3.7) in (2.36) and (2.38), we find

$$C = \frac{1}{8}\sum_n \frac{f_{0n}\omega_{\mathrm{sp}}}{\omega_{0n}(\omega_{0n} + \omega_{\mathrm{sp}})} \qquad (3.8)$$

and

$$Z_0 - Z_B = \frac{1}{16C}\sum_n \frac{f_{0n}\omega_{\mathrm{sp}}}{\omega_{0n}(\omega_{0n} + \omega_{\mathrm{sp}})}\,\frac{\omega_{0n} + 2\omega_{\mathrm{sp}}}{\omega_{0n} + \omega_{\mathrm{sp}}}(Z_c - Z_B) \; . \qquad (3.9)$$

This latter equation locates the reference plane with respect to the edge of the positive background.

Equations (3.8) and (3.9) were evaluated for He as a function of the electron density parameter, r_s; the results are plotted in Fig. 2. The values for Z_c were obtained by interpolating the results of Lang and Kohn[6] as a function of the density parameter r_s. The parameters defining the He polariz-

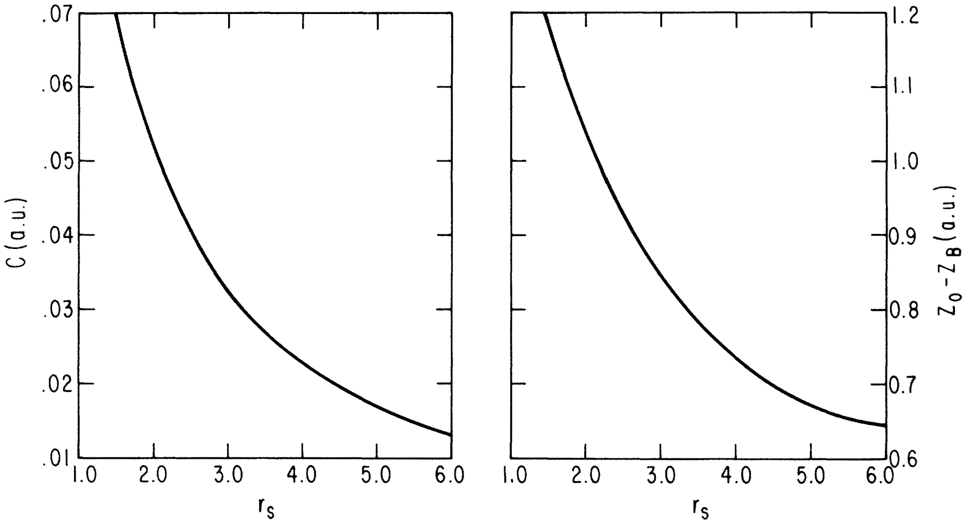

FIG. 2. Van der Waals coefficient C and the reference-plane position Z_0 for the He-jellium system as a function of the density parameter r_s. C in atomic units is equivalent to 4.03 eV Å^3 and the separation $Z_0 - Z_B$ is given in Bohr radii (0.53 Å).

ability were obtained from the variational calculation of Victor and Dalgarno.[16] These latter parameters were found to give a good value for the Van der Waals constant for the He-He interaction.

Since the static centroid Z_c lies outside the edge of the positive background, the reference-plane position Z_0, as obtained using (3.9), does so as well. The significance of this result is that the Van der Waals potential V_{pol} can be considerably stronger than results obtained by arbitrarily measuring the adatom position from either the location of the plane of surface atoms or from the edge of the jellium background.[7] For example, for a value of r_s equal to 2 corresponding to Al, $Z_0 - Z_B$ is 1.04 a.u. Assuming that $Z_{\text{eq}} - Z_B$ for He on Al is 7.0 a.u. as given in the work of Kleinman and Landman,[7] the Van der Waals energy obtained from (2.39) is approximately 60% larger than the value obtained assuming that $Z_0 \simeq Z_B$.

B. Dielectric solid

As our second example, we consider an insulating crystal consisting of nonoverlapping, spherically symmetric atoms. For simplicity, we shall restrict our discussion to a simple cubic crystal bounded by a (100) face, however the generalization of the following analysis to other crystal structures or surface planes is not difficult.

Our objective is again the expansion of $f(q, iu)$ given in (2.18) in powers of q. Because of our assumption of nonoverlapping atoms, it is possible to consider the response of each atom to the total potential rather than the response of the solid to the external potential. Thus introducing the atomic-density response function $\chi_d(\vec{r}, \vec{r}'; iu)$ for the atoms in the solid, we have

$$f(q, iu) = e^{qZ}\left(\frac{q}{2\pi}\right)\frac{1}{L^2}\int d\vec{r}\int d\vec{r}'$$

$$\times e^{-i\vec{\kappa}\cdot\vec{r}}\sum_{\vec{l}}\chi_d(\vec{r}-\vec{l}, \vec{r}'-\vec{l}; iu)\varphi_T(\vec{r}', iu) . \tag{3.10}$$

Here $\vec{l}$ is the position vector of the lattice sites and $\varphi_T(\vec{r}'; iu)$ is the total potential which arises from the external charge distribution (2.19) and the induced charges on each of the atoms. The complex wave vector $\vec{\kappa}$ is defined in (2.12). Since $\chi_d(\vec{r}-\vec{l}, \vec{r}'-\vec{l}; iu)$ is a function localized about the position $\vec{l}$, we can expand the factors $e^{-i\vec{\kappa}\cdot\vec{r}}$ and $\varphi_T(\vec{r}'; iu)$ in (3.10) about each of the lattice sites l. Retaining only the lowest-order term in this expansion corresponds to treating the interactions between the atoms in the solid in the dipole approximation. Within this approximation, we find

$$f(q, iu) = e^{qZ}\left(\frac{q}{2\pi}\right)\frac{1}{L^2}\sum_{\vec{l}} e^{-i\vec{\kappa}\cdot\vec{l}}\, i\vec{\kappa}\cdot\vec{p}(\vec{l}) , \tag{3.11}$$

where $\vec{p}(\vec{l})$ is the dipole moment on site $\vec{l}$,

$$\vec{p}(\vec{l}) = \alpha_d\vec{E}_T(\vec{l}) \tag{3.12}$$

$$= \alpha_d[\vec{E}^{\text{ext}}(\vec{l}) + \vec{E}^{\text{ind}}(\vec{l})] . \tag{3.13}$$

α_d is the atomic polarizability [see Eq. (2.14)] and $\vec{E}_T(\vec{l})$ is the total electric field at $\vec{l}$. The external field $\vec{E}^{\text{ext}}(\vec{l})$ due to the external charge distribution (2.19) is

$$\begin{aligned}\vec{E}^{\text{ext}}(\vec{l}) &= -\nabla\varphi_{\text{ext}}(\vec{r})\big|_{\vec{r}=\vec{l}} \\ &= -(2\pi/q)\, e^{-qZ}\, i\vec{\kappa}^*\, e^{i\vec{\kappa}^*\cdot\vec{l}} .\end{aligned} \tag{3.14}$$

The induced electric field at $\vec{l}$, $\vec{E}^{\text{ind}}(\vec{l})$, is the field due to the dipoles on all other sites $\vec{l}' \neq \vec{l}$, i.e.,

$$E_\mu^{\text{ind}}(\vec{l}) = \sum_{\vec{l}'}{}' D_{\mu\nu}(\vec{l}-\vec{l}')p_\nu(\vec{l}') , \tag{3.15}$$

where $D_{\mu\nu}(\vec{l}-\vec{l}')$ is the dipolar field

$$D_{\mu\nu}(\vec{l}-\vec{l}') \equiv \nabla_\mu\nabla_\nu\frac{1}{|\vec{r}-\vec{l}'|}\bigg|_{\vec{r}=\vec{l}}$$

$$= \frac{3(\vec{l}-\vec{l}')_\mu(\vec{l}-\vec{l}')_\nu}{|\vec{l}-\vec{l}'|^5} - \frac{\delta_{\mu\nu}}{|\vec{l}-\vec{l}'|^3} . \qquad (3.16)$$

The prime on the summation sign in (3.15) indicates that the term $\vec{l}'=\vec{l}$ is to be omitted. The Greek letter subscripts indicate Cartesian components and a repeated index summation convention is used.

Equation (3.13) together with (3.14) and (3.15) give a system of linear equations in the unknowns $\vec{p}(\vec{l})$. It is now convenient to define reduced dipole moments parallel and perpendicular to the surface

$$\vec{p}(\vec{l}) \equiv -2\pi i\, e^{-qz} e^{i\vec{\kappa}^*\cdot\vec{l}}\,[p_\parallel(\vec{l})\hat{q} - ip_\perp(\vec{l})\hat{z}] . \qquad (3.17)$$

In terms of the variables $p_\parallel(\vec{l})$ and $p_\perp(\vec{l})$ we obtain the coupled linear equations

$$p_\parallel(\vec{l}) = \alpha_d\Big(1 + {\sum_{\vec{l}'}}' e^{i\vec{\kappa}^*\cdot(\vec{l}'-\vec{l})}[D_{\parallel,\parallel}(\vec{l}-\vec{l}')p_\parallel(\vec{l}') - iD_{\parallel,\perp}(\vec{l}-\vec{l}')p_\perp(\vec{l}')]\Big) , \qquad (3.18a)$$

$$p_\perp(\vec{l}) = \alpha_d\Big(1 + {\sum_{\vec{l}'}}' e^{i\vec{\kappa}^*\cdot(\vec{l}'-\vec{l})}[iD_{\perp,\parallel}(\vec{l}-\vec{l}')p_\parallel(\vec{l}') + D_{\perp,\perp}(\vec{l}-\vec{l}')p_\perp(\vec{l}')]\Big) . \qquad (3.18b)$$

The notation $D_{\parallel,\perp}$, for example, signifies $\hat{q}_\mu D_{\mu\nu}\hat{z}_\nu$. We note that due to the translational symmetry along the surface, the solutions $p_\parallel(\vec{l})$ and $p_\perp(\vec{l})$ will only be a function of the plane index l_z where

$$\vec{l} = \vec{l}_\parallel + l_z\hat{z} . \qquad (3.19)$$

In terms of the definition (3.17), Eq. (3.11) simplifies to

$$f(q,iu) = q^2\frac{1}{L^2}\sum_{\vec{l}} e^{2ql_z}[p_\parallel(\vec{l}) + p_\perp(\vec{l})]$$

$$= n_s q^2\sum_{l_z} e^{2ql_z}[p_\parallel(l_z) + p_\perp(l_z)] . \qquad (3.20)$$

Here n_s is the number of atoms per unit area in planes parallel to the surface.

The explicit solution of Eqs. (3.18a) and (3.18b) for a bounded solid is of course not trivial. The dependence of the dipole moments on the plane index l_z arises from the fact that the local fields acting on the atoms in the surface region are different from those deep in the interior. The degree to which the surface dipole moments differ from those in the interior depends on the magnitude of the parameter $(n\alpha_d)$, where n is the number of atoms per unit volume. If this parameter is small, an expansion of Eqs. (3.18) in terms of it is possible and the lowest-order correction due to the internal fields can be obtained explicitly. The leading order term is simply α_d which represents the dipole moment induced by the external field in the absence of the internal fields. The influence of the internal fields appears on including the next lowest-order correction in this expansion.

To obtain the required expansions, we first sum Eqs. (3.18) over the parallel component $\vec{l}_\parallel$ of the lattice vector and define the quantities

$$d_{ij}(l_z - l_z') \equiv {\sum_{\vec{l}_\parallel'}}' e^{i\vec{\kappa}^*\cdot(\vec{l}'-\vec{l})} D_{ij}(\vec{l}_\parallel - \vec{l}_\parallel', \vec{l}_z - \vec{l}_z') ,$$

$$(i,j = \parallel, \perp) . \qquad (3.21)$$

If $l_z' = l_z$, the term $\vec{l}_\parallel' = \vec{l}_\parallel$ is to be omitted from the summation. In addition, we define the new variables

$$p_+(l_z) = \tfrac{1}{2}[p_\parallel(l_z) + p_\perp(l_z)] \qquad (3.22a)$$

and

$$p_-(l_z) = \tfrac{1}{2}[p_\parallel(l_z) - p_\perp(l_z)] . \qquad (3.22b)$$

In terms of these quantities Eqs. (3.18) become

$$p_+(l_z) = \alpha_d\Big(1 + \frac{1}{2}\sum_{l_z'}[d_{++}(l_z - l_z')p_+(l_z') + d_{+-}(l_z - l_z')p_-(l_z')]\Big) , \qquad (3.23a)$$

$$p_-(l_z) = \tfrac{1}{2}\alpha_d\sum_{l_z'}[d_{-+}(l_z - l_z')p_+(l_z') + d_{--}(l_z - l_z')p_-(l_z')] , \qquad (3.23b)$$

where

$$d_{++}(l_z - l_z') = d_{\parallel,\parallel}(l_z - l_z') + d_{\perp,\perp}(l_z - l_z') , \qquad (3.24a)$$

$$d_{+-}(l_z - l_z') = d_{\parallel,\parallel}(l_z - l_z') + 2id_{\perp,\parallel}(l_z - l_z') - d_{\perp,\perp}(l_z - l_z') , \qquad (3.24b)$$

$$d_{-+}(l_z - l_z') = d_{\parallel,\parallel}(l_z - l_z') - 2id_{\parallel,\perp}(l_z - l_z') - d_{\perp,\perp}(l_z - l_z') , \qquad (3.24c)$$

$$d_{--}(l_z - l_z') = d_{++}(l_z - l_z') . \qquad (3.24d)$$

The expansion of Eqs. (3.23) to order α_d^2 can now easily be obtained. Since $p_-(l_z)$ is of order α_d^2 to lowest order, $p_+(l_z)$ is found to be

$$p_+(l_z) \simeq \alpha_d + \tfrac{1}{2}\alpha_d^2\sum_{l_z'} d_{++}(l_z - l_z') + O(\alpha_d^3) . \qquad (3.25)$$

We therefore find that (3.20) becomes

$$f(q,iu) = 2n_s q^2\sum_{l_z} e^{2ql_z}p_+(l_z)$$

$$= \frac{2n_s q^2\alpha_d}{1 - e^{-2qa}} + n_s q^2\alpha_d^2$$

$$\times\sum_{l_z}\sum_{l_z'} e^{2ql_z} d_{++}(l_z - l_z') + O(\alpha_d^3) . \qquad (3.26)$$

Here a is the interplanar spacing and we have assumed that $l_z = -na$ with $n = 0, 1, \ldots$. To complete the evaluation of $f(q,iu)$ to this order in the atomic polarizabilities, we require the quantity $d_{++}(l_z - l_z')$ which is to be determined from (3.24a) and (3.21).

This function is evaluated in Appendix B; substituting the result found there into the summation in (3.26) we find to zeroth order in q that

$$\sum_{l_z}\sum_{l_z'} e^{2ql_z} d_{++}(l_z - l_z') = -\frac{1}{qa}\frac{2\pi n}{3}(1+qa) - \gamma\pi n\,, \tag{3.27}$$

where γ is a numerical constant given in (B16) whose value for a simple cubic lattice with a (100) face is 0.052 295.

Substituting (3.27) into (3.26) and comparing the latter order by order with (2.27) we find that

$$\int dz\, \delta\bar{n}_0(z, iu) = 2\pi n\alpha_d(iu)\left(1 - \frac{2\pi n\alpha_d(iu)}{3} + O((n\alpha_d)^2)\right) \tag{3.28}$$

and

$$\bar{z}(iu) = \tfrac{1}{2}a[1 - \gamma\pi n\alpha_d(iu) + O((n\alpha_d)^2)]\,. \tag{3.29}$$

We can now verify that Eq. (3.28) agrees with Eq. (2.34). We note that the bulk dielectric function of the solid is related to the atomic polarizability within the dipole approximation by[17]

$$\epsilon(iu) = [1 + \tfrac{8}{3}\pi n\alpha_d(iu)]/[1 - \tfrac{4}{3}\pi n\alpha_d(iu)]\,. \tag{3.30}$$

Using this in (2.34) and expanding to second order in $n\alpha_d$ yields (3.28).

Although the constant γ depends on the crystal structure and the surface plane, a number of rather general observations can be made concerning the quantity $\bar{z}(iu)$. In the absence of local-field effects, $\bar{z}(iu)$ is equal to $a/2$ where a is the interplanar spacing. It should be recalled that the origin in this section was chosen to coincide with the plane of surface atoms. Thus this position is analogous to the location of the edge of an effective neutralizing positive background as in the case of the jellium model. The correction to this position when the internal fields are taken into account is seen to be small because of the small value of γ. The smallness of γ is related to the fact that the value of the dipole moments near the surface do not differ greatly from those in the bulk. If $p_+(l_z)$ were strictly independent of l_z, $\bar{z}(iu)$ would be identically equal to $\frac{1}{2}a$. The actual values of $p_+(l_z)$ are somewhat smaller near the surface and therefore lead to a decrease in $\bar{z}(iu)$. [Note that the value of $\bar{z}(iu)$ would decrease by a if the dipoles in the surface layer were zero.] The reason that the magnitude of the dipole moments is essentially constant right to the surface is that the function $d_{++}(l_z - l_z')$ is considerably larger when $l_z = l_z'$ than for $l_z \neq l_z'$. One would therefore expect $\bar{z}(iu)$ to be close to $\frac{1}{2}a$ even for the exact solution of Eqs. (3.23). In other words, even relatively large local-field corrections in $\epsilon(iu)$ result in rather small shifts of the reference-plane position.

In the zero-frequency limit $u=0$, Eq. (3.29) gives the reference-plane position for the image potential of an external point charge adjacent to a dielectric solid. It should again be emphasized that this result is correct only to order $[n\alpha_d(0)]$. However it does demonstrate that the reference plane is shifted to a position which is closer to the surface plane of atoms as compared to the case in which internal fields are neglected entirely.

In the high-frequency limit $n\alpha_d(iu)$ is indeed small so that (3.29) is seen to be consistent with the general high-frequency result found previously.

The Van der Waals reference plane is obtained from (2.38) with $\bar{z}(iu)$ given by (3.29). In the limit that $n\alpha_d(iu) \to 0$, Z_0 is equal to $\frac{1}{2}a$. Deviations from this position again occur because of local-field effects. However, since (2.38) is a weighted average of $\bar{z}(iu)$ over all frequencies, the displacement of Z_0 from $\frac{1}{2}a$ will be smaller than the corresponding displacement of the image-potential reference plane given by $\bar{z}(0)$. It therefore seems that placing the reference-plane position at Z_B should be a good approximation when considering physisorption of atoms on insulating crystals. Within this approximation, one can *equivalently* think of the solid as a uniform dielectric characterized by a local dielectric function of the form $\epsilon(iu)\,\theta(\frac{1}{2}a - z)$.

In passing, it is of interest to note that the reference-plane position Z_0 is exactly $\frac{1}{2}a$ if the interaction between the adatom and the solid atoms is taken to be a Van der Waals potential varying as $1/R^6$. The magnitude of the local-field effects gives a measure of the importance of three-body forces, etc., in determining the interaction potential between the atom and the solid.

C. Adsorption of rare-gas atoms on noble metals

As our final application we consider the physisorption of rare-gas atoms on noble-metal surfaces. The main reason for choosing to study these systems is that their physisorption characteristics have been investigated extensively for certain metal-atom combinations.[18-22] In addition, the electronic properties of both the atoms[23] and the noble metals[24] are known quite accurately so that a quantitative evaluation of C and Z_0 becomes feasible. Furthermore, although a complete metal-atom potential has not been derived, the previous analysis does provide an explicit expression for the polarization contribution. If the actual equilibrium position of the atom can be obtained or estimated independently, the attractive polarization energy can be calculated using (2.39) and compared with the total observed adsorption energy.

In order to evaluate the coefficient C we require the atomic polarizabilities and the dielectric functions of the noble metals. The latter were determined from available optical data.[24] In particular, $\epsilon(iu)$ is given by

$$\epsilon(iu) = 1 + \frac{2}{\pi}\int_0^\infty d\omega\, \frac{\omega\, \epsilon_2(\omega)}{\omega^2 + u^2}\ , \tag{3.31}$$

where $\epsilon_2(\omega)$ is the imaginary part of the observed dielectric function and gives the distribution of oscillator strengths for the electronic excitations. Empirically, it is found that $\epsilon_2(\omega)$ can be divided into two parts

$$\epsilon_2(\omega) \equiv \epsilon_2^f(\omega) + \epsilon_2^b(\omega)\ ; \tag{3.32}$$

here, ϵ_2^f and ϵ_2^b are respectively the contributions from "free" and "bound" electrons. $\epsilon_2^f(\omega)$ is simply taken to be $\omega_{pf}^2/[\omega\,\tau(\omega^2 + \tau^{-2})]$, where ω_{pf}^2 and τ^{-1} are experimentally determined parameters. (Lifetime effects can be neglected numerically when performing the frequency integrals along the imaginary frequency axis.) Equation (3.32) then defines $\epsilon_2^b(\omega)$ as the remainder; it represents the contribution from interband (primarily d electron) transitions. Using the definition (3.32), we can also define

$$\epsilon(iu) \equiv 1 + \epsilon_f(iu) + \epsilon_b(iu)\ . \tag{3.33}$$

While this division of $\epsilon(iu)$ is not necessary for evaluating C, it turns out to be convenient to do so when determining Z_0.

The frequency-dependent atomic polarizabilities were approximated by functions of the form (3.7) consisting of only a few terms (four in the case of He and two for the other rare-gas atoms). The effective oscillator strengths and excitation frequencies to be used in these expressions were obtained from Ref. 23. These effective polarizabilities give accurate Van der Waals coefficients for the rare-gas atom-atom interactions and should therefore be satisfactory in determining the metal-atom polarization energy.

With this input the constants C were evaluated using Eq. (2.36) for the various rare-gas-atom-noble-metal systems. The results are listed in Table I. The value of C was found to vary by about an order of magnitude on going from He through to Xe for all the metals studied. This variation essentially reflects the larger polarizabilities of the heavier rare-gas atoms.

The reference-plane position Z_0 was determined in the following way. The division of the dielectric function into free- and bound-electron parts [see (3.33)] suggests that a noble metal can be considered as a two component system. The free-electron component dominates the low-frequency response of the metal, that is for frequencies less than ω_{pf}, while the bound-electron component dominates at frequencies $u > \omega_{pf}$. As a simple model of the metal, we shall therefore consider the free-electron component as being represented by jellium with $r_s = (3/\omega_{pf}^2)^{1/3}$. In addition, the system of ion cores will be considered as an insulator with conductivity $\sigma_b(iu)$. This latter idealization corresponds to the model studied in Sec. III B.

The surface screening charge density $\delta\bar{n}_0(z, iu)$ for this combined system is then the sum of the jellium screening charge and surface polarization charge of the dielectric. As can be seen from (2.31), the magnitude of the jellium and dielectric screening charges is proportional to the respective conductivities of the two components. Furthermore, for the purpose of this discussion, we approximate $\bar{z}(iu)$ by the centroid of the total screening charge [see discussion following (2.28)]. With this interpretation, $\bar{z}(iu)$ is simply a weighted average of the centroids for each of the components, with weights proportional to the respective conductivities. We therefore have

$$\bar{z}(iu) \simeq \frac{\epsilon_f(iu)\,\bar{z}_f(iu) + \epsilon_b(iu)\,\bar{z}_b(iu)}{\epsilon_f(iu) + \epsilon_b(iu)}\ . \tag{3.34}$$

For the free-electron centroid $\bar{z}_f(iu)$ we shall take the jellium result (3.6). Similarly, we assume that $\bar{z}_b(iu)$ is given by an expression of the form (3.29); for the noble metals, it is sufficient to assume that $\bar{z}_b(iu) \simeq Z_B$ for all frequencies since $n\alpha_d$ is small.[25] These choices are of course approximations to the correct $\bar{z}_f(iu)$ and $\bar{z}_b(iu)$; the presence of a polarizable dielectric will in fact modify the centroid of the jellium component as compared to the result obtained in its absence. Nevertheless, these choices should be reasonable interpolations. For example, the low-frequency limit of (3.34) is Z_c, the centroid of the jellium surface charge in the presence of a static external field. This result is essentially correct, since the field at the position of the ion cores is almost completely screened by the jellium component. Thus, the polarizability of the ions can only have a small effect at $u = 0$. Similarly, for $u \gtrsim \omega_{pf}$, $\bar{z}(iu)$ reduces to Z_B, the appropriate centroid for a dielectric solid.

Substituting (3.34) into (2.38), the reference-plane position was evaluated for all the rare-gas atom-noble metal combinations. The values of Z_0 relative to Z_B are listed in Table I. Considering the large variation in the atomic polarizabilities, it is clear that Z_0 is relatively insensitive to variations in this quantity. However, there is a more pronounced variation of Z_0 with the dielectric function of the metal. Since the bound-electron dielectric function increases from Cu to Ag to Au, (3.34) shows that the value Z_B receives an increasingly larger weight, leading to a reduction in Z_0. This variation is clearly evident in Table I. Although the values of Z_0 appear rather small, they nonetheless can have an important effect. Since the equilibrium atom-metal separation is expected to decrease with decreasing atomic weight for the series Ne-Xe (based on the equilibrium separa-

TABLE I. The Van der Waals coefficient C and reference-plane position Z_0 measured relative to the positive background edge for various rare-gas atoms on the (111) surface of the noble metals. All values are given in atomic units.

	He		Ne		Ar		Kr		Xe	
	C	Z_0	C	Z_0	C	Z_0	C	Z_0	C	Z_0
Cu	0.0558	0.4174	0.1120	0.4044	0.3723	0.4889	0.5232	0.5178	0.7650	0.5584
Ag	0.0617	0.3714	0.1244	0.3582	0.4025	0.4459	0.5613	0.4765	0.8127	0.5196
Au	0.0679	0.2942	0.1374	0.2826	0.4384	0.3577	0.6088	0.3843	0.8762	0.4224

tions in the rare gas solids), it is clear that it is relatively more important to accurately determine the reference-plane position for the lighter atoms when evaluating the polarization energy from (2.39).

To complete the estimate of the polarization contribution to the binding energy we require the equilibrium position of the atom on the surface relative to the reference-plane position Z_0. For the case of Xe on the (111) face of Ag the equilibrium position relative to the plane of surface atoms (denoted as s in Fig. 1) has been measured to be 6.81 a.u.[22] This separation is very close to the sum of the covalent radii of the Xe and Ag atoms (6.84 a.u.). Since the covalent radii of Ag and Au atoms are very similar ($r_{\mathrm{Ag}} = 2.89$ a.u.; $r_{\mathrm{Au}} = 2.84$ a.u.) and since the lattice spacings of the metals are nearly equal ($d_{\mathrm{Ag}} = 7.72$ a.u.; $d_{\mathrm{Au}} = 7.71$ a.u.), it is reasonable to assume that the corresponding separation of Xe on Au is also ~6.81 a.u. For lack of an unambiguous procedure for estimating the equilibrium position in terms of either the covalent radii or the lattice spacing, we have also used 6.81 a.u. as the equilibrium position of Xe on Cu. Since the covalent radius of Cu is smaller than that of Ag, the actual equilibrium separation is probably somewhat smaller. In this case, the estimate of the polarization energy for Xe on Cu should be a lower bound. Since the equilibrium separation for the other rare-gas atoms on the metals cannot be estimated with the same confidence, we shall restrict our discussion of the polarization energy to the example of Xe. Similar experimental determinations of the equilibrium separations for the other atoms would clearly be of value in establishing trends in the polarization energy.

Using these estimated equilibrium positions of Xe on the (111) face of the noble metals, the polarization energies were calculated and are listed in Table II. These values are rather similar for all the noble metals, being close to 0.3 eV. If the reference-plane position had arbitrarily been chosen to coincide with the background edge Z_B, the values of the polarization energy would typically have been 30% smaller.

If the polarization force were the only attractive component of the metal-atom interaction, the polarization energies in Table II would provide an upper bound on the binding energy (or heat of adsorption). The fact that the calculated values of $|V_{\mathrm{pol}}|$ are larger than the experimentally determined binding energies is consistent with the fact that the total interaction also includes a repulsive part. Work on the theory of the repulsive energy is currently in progress.

Before closing this section we would like to emphasize a number of points related to making a comparison between the theoretical and experimental values of the energy in Table II. The theoretical value is the polarization contribution to the total binding energy for a single atom interacting with a perfect (111) face of a noble metal. Experimentally it is known that the heat of adsorption depends to a certain extent on both the surface structure of the metal[21] and the degree of coverage of the adsorbed species.[21,26] Thus, it is clearly important that a well-characterized surface be used in adsorption studies and that the zero-coverage limit of the binding energy be determined. The value of E_{BE} for Ag quoted in Table II is that for a monolayer coverage; strictly speaking it should not be used as a basis of comparison. Similarly, the binding energies of Xe on Cu and Au were obtained without specifying the surface structure and therefore the assumption of a (111) face introduces additional uncertainties. Further experimental studies, for which these parameters are well defined, would clearly be of value.

IV. CONCLUDING REMARKS

In this paper we have defined and approximately calculated the reference-plane position Z_0 from

TABLE II. The polarization energy, V_{pol}, for Xe physisorbed on the (111) surface of the noble metals.

	C (a.u.)	$(Z_{\mathrm{eq}} - Z_0)$ (a.u.)	$-V_{\mathrm{pol}}$ (eV)	E_{BE} (eV)
Cu	0.765	~4.28	≥ 0.27	0.23[a]
Ag	0.813	4.10	0.32	0.3[b]
Au	0.876	4.14	~ 0.34	0.2[a]

[a] Reference 21.

[b] Reference 22.

which the Lifshitz polarization force exerted by a solid on an atom is to be reckoned. Although this answers one important question in the theory of physisorption, a number of equally important issues require further work. These include a more satisfactory theory of the repulsive forces[7]; a good treatment of the spatial variation of the interaction potential along the surface, which establishes the actual equilibrium position of the adatom on the surface; and finally, a unified treatment of the entire interaction energy which does not make the separation into distinct attractive and repulsive components.

We mention also two minor corrections. In the calculation of the polarization interaction between two semi-infinite solids, it is known that second-order perturbation theory fails and it is necessary to treat the interaction self-consistently.[2,3,27,28] For the surface-atom systems under consideration in this paper, the self-consistency corrections are found to be less than 10% (Appendix C). Another well-known correction is for relativistic effects.[2,3] At the short distances considered in the present context, these also are negligible.

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APPENDIX A

In this appendix we investigate the implications of the conservation of charge on the question raised in Sec. II concerning the expansion of $f(q, iu)$ in powers of q. This conservation law provides a relation between the density-density response function and the current-current response function, namely,

$$u^2\chi(\vec{r}, \vec{r}\,'; iu) = \nabla_\mu \nabla'_\nu[\delta_{\mu\nu} n_{eq}(\vec{r})\delta(\vec{r} - \vec{r}\,') - \chi_{\mu\nu}(\vec{r}, \vec{r}\,'; iu)] , \tag{A1}$$

where $n_{eq}(r)$ is the equilibrium electron density of the solid and the current-current response function is defined as

$$\chi_{\mu\nu}(\vec{r}, \vec{r}\,'; iu) = i \int_0^\infty dt\, e^{-ut}\langle[j_\mu(\vec{r}, t), j_\nu(\vec{r}\,', 0)]\rangle . \tag{A2}$$

The induced density $\delta\tilde{n}_0(z, q, iu)$ can be obtained from (A1) using (2.21). The first term on the right-hand side of (A1) gives a contribution to be denoted as $\delta\tilde{n}_0^{(1)}(z, q, iu)$ which comes from the leading order term in a high-frequency expansion of $\chi(\vec{r}, \vec{r}\,'; iu)$. We find

$$\delta\tilde{n}_0^{(1)}(z, q, iu) = -\frac{2\pi}{u^2} e^{qz} \frac{\partial n_{eq}(z)}{\partial z} , \tag{A3}$$

where

$$n_{eq}(z) = \frac{1}{L^2}\int d\vec{\rho}\, n_{eq}(\vec{r}) \tag{A4}$$

is the equilibrium density averaged over the surface area. To obtain $\delta\bar{n}^{(1)}(z, q, iu)$ we must apply the averaging procedure defined in (2.23) to (A3); the resulting quantity can then be expanded in powers of q. However, since we only require $f(q, iu)$ to second order in q, we can evaluate $f(q, iu)$ by simply averaging $dn_{eq}(z)/dz$ [see Eq. (2.24)]. Doing so, we find that

$$f^{(1)}(q, iu) = (n_B q/u^2)[1 + 2q Z_B + O(q^2)] , \tag{A5}$$

where n_B is the mean *total* electron density in the bulk of the solid and Z_B is defined as that position for which

$$\int_{-\infty}^{\infty} dz\, [\bar{n}_{eq}(z) - n_B\, \theta(Z_B - z)] = 0 . \tag{A6}$$

It is clear that Z_B is the edge of the uniform positive background required to neutralize the total electron density. Equation (A5) is applied in Sec. III to the example of the jellium model, although the above derivation shows that it is a general result applicable to any semi-infinite solid.

The second term in (A1) gives the contribution

$$f^{(2)}(q, iu) = -\frac{1}{u^2}\int dz \int dz'\, e^{qz} e^{qz'} \times \kappa_\mu \kappa_\nu^* \chi_{\mu\nu}(z, z', \vec{q}, \vec{q}; iu) . \tag{A7}$$

Here, the Fourier components $\chi_{\mu\nu}(z, z', \vec{q}, \vec{q}; iu)$ are defined as in (2.17). In the following it is convenient to abreviate this quantity to $\chi_{\mu\nu}(z, z', \vec{q})$. Following the discussion in Sec. II we note that

$$\int dz \int dz'\, e^{qz} e^{qz'} \chi_{\mu\nu}(z, z', \vec{q}) = \int dz \int dz'\, e^{qz} e^{qz'} \bar{\chi}_{\mu\nu}(z, z', \vec{q}) + O(q^2) , \tag{A8}$$

where

$$\bar{\chi}_{\mu\nu}(z, z', \vec{q}) \equiv \frac{1}{a}\int_{z-a/2}^{z+a/2} d\bar{z}\, \frac{1}{a}\int_{z'-a/2}^{z'+a/2} d\bar{z}'\, \chi_{\mu\nu}(\bar{z}, \bar{z}', \vec{q}) . \tag{A9}$$

The use of $\bar{\chi}_{\mu\nu}$ in the following again avoids difficulties with the use of the actual microscopic response.

We now define

$$\Psi(z, z', \vec{q}) \equiv \kappa_\mu \kappa_\nu^* \bar{\chi}_{\mu\nu}(z, z', \vec{q}) \tag{A10}$$

$$\begin{aligned} &= q_x^2 \bar{\chi}_{xx}(z, z', \vec{q}) + q_y^2 \bar{\chi}_{yy}(z, z', \vec{q}) + q^2 \bar{\chi}_{zz}(z, z', \vec{q}) \\ &\quad + q_x q_y[\bar{\chi}_{xy}(z, z', \vec{q}) + \bar{\chi}_{yx}(z, z', \vec{q})] \\ &\quad + i q q_x[\bar{\chi}_{xz}(z, z', \vec{q}) - \bar{\chi}_{zx}(z, z', \vec{q})] \\ &\quad + i q q_y[\bar{\chi}_{yz}(z, z', \vec{q}) - \bar{\chi}_{zy}(z, z', \vec{q})] . \end{aligned} \tag{A11}$$

Assuming that the system is invariant under reflection in the $x - z$ and $y - z$ planes, the diagonal components of $\bar{\chi}_{\mu\nu}(z, z', \vec{q})$ are even functions of q_x and q_y, i.e.,

$$\begin{aligned}\bar{\chi}_{xx}(z,z',q_x,q_y) &= \bar{\chi}_{xx}(z,z',-q_x,q_y)\\ &= \bar{\chi}_{xx}(z,z',q_x,-q_y),\ \text{etc.} \end{aligned} \tag{A12}$$

Similarly, $\bar{\chi}_{xy}(z,z',\vec{q})$ is an odd function of both q_x and q_y,

$$\begin{aligned}\bar{\chi}_{xy}(z,z',q_x,q_y) &= -\bar{\chi}_{xy}(z,z',-q_x,q_y)\\ &= -\bar{\chi}_{xy}(z,z',q_x,-q_y)\ ,\end{aligned} \tag{A13}$$

as is also $\bar{\chi}_{yx}(z,z',q_x,q_y)$. Finally, we note that

$$\begin{aligned}\bar{\chi}_{xz}(z,z',q_x,q_y) &= -\bar{\chi}_{xz}(z,z',-q_x,q_y)\\ &= \bar{\chi}_{xz}(z,z',q_x,-q_y)\ ,\end{aligned} \tag{A14}$$

with similar relations holding for $\bar{\chi}_{yz}(z,z',q_x,q_y)$. Thus, on expanding $\bar{\chi}_{\mu\nu}(z,z',q)$ in powers of q (assuming such an expansion to exist) and using the above results, we see that the diagonal terms in (A11) involve powers of q^2, q^4, etc.; the fourth term begins with a term of order q^4 and the last two terms begin with terms explicitly of order q^3. Furthermore, we make use of the facts that the following integral of a diagonal component

$$\int dz'\bar{\chi}_{\mu\mu}(z,z',\vec{q}) \tag{A15}$$

tends to a constant as $z\to-\infty$, while the integral

$$\int dz'\bar{\chi}_{xz}(z,z',\vec{q})\ , \tag{A16}$$

for example, tends to zero. Thus, on expanding $\int dz \int dz' e^{qz} e^{qz'} \Psi(z,z',\vec{q})$ to order q^2, only the diagonal components of $\bar{\chi}_{\mu\nu}(z,z',\vec{q})$ are required. In particular, we find that

$$\begin{aligned} q^2\int dz\int dz' e^{qz}e^{qz'}\bar{\chi}_{zz}(z,z',\vec{q}) &= -\frac{q}{2}\int dz\int dz' e^{qz}e^{qz'}\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\bar{\chi}_{zz}(z,z',\vec{q})\\ &= -\frac{q}{2}\int dz\int dz'\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\bar{\chi}_{zz}(z,z',0)-\frac{q^2}{2}\\ &\quad\times\int dz\int dz'(z+z')\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\bar{\chi}_{zz}(z,z',0)+O(q^3)\ . \end{aligned} \tag{A17}$$

Noting that time-reversal symmetry implies

$$\bar{\chi}_{zz}(z,z',0)=\bar{\chi}_{zz}(z',z,0)\ , \tag{A18}$$

we see that

$$\begin{aligned} q^2\int dz\int dz' e^{qz}e^{qz'}\bar{\chi}_{zz}(z,z',\vec{q}) &= -\frac{q}{2}\left[\int dz\int dz'\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\bar{\chi}_{zz}(z,z',0)\right.\\ &\quad\left.+2q\int dz\, z\int dz'\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\bar{\chi}_{zz}(z,z',0)+O(q^2)\right]\ . \end{aligned} \tag{A19}$$

Similar results are obtained for the terms involving $\bar{\chi}_{xx}(z,z',\vec{q})$ and $\bar{\chi}_{yy}(z,z',\vec{q})$. Thus we find that

$$f^{(2)}(q,iu)=\frac{n_B q}{u^2}\left(\int dz\, g(z,iu)+2q\times\int dz\, z g(z,iu)+O(q^2)\right)\ , \tag{A20}$$

where

$$g(z,iu)\equiv\frac{1}{2n_B}\int dz'\left(\frac{\partial}{\partial z}+\frac{\partial}{\partial z'}\right)\times[\bar{\chi}_{\parallel}(z,z',iu)+\bar{\chi}_{\perp}(z,z',iu)]\ . \tag{A21}$$

Here

$$\bar{\chi}_{\perp}(z,z',iu)\equiv\bar{\chi}_{zz}(z,z',0) \tag{A22}$$

and

$$\bar{\chi}_{\parallel}(z,z',iu)\equiv\bar{\chi}_{xx}(z,z',0)=\bar{\chi}_{yy}(z,z',0)\ , \tag{A23}$$

with explicit dependence on the frequency restored. We have also assumed that the x and y directions are equivalent. Using the definitions in (2.27), we see that

$$\int dz\ \delta\bar{n}_0(z,iu)=\frac{\omega_{sp}^2}{u^2}\left(1+\int dz\, g(z,iu)\right) \tag{A24}$$

and

$$\bar{z}(iu)=\left(Z_B+\int dz\, z g(z,iu)\right)\Big/\left(1+\int dz\, g(z,iu)\right)\ . \tag{A25}$$

Equating the quantity on the right-hand side of (A24) to (2.34), we can write

$$\bar{z}(iu)-Z_B=\frac{u^2}{\omega_{sp}^2}\left(\frac{\epsilon(iu)+1}{\epsilon(iu)-1}\right)\int dz\ (z-Z_B)g(z,iu)\ . \tag{A26}$$

This of course is only a formal definition of $\bar{z}(iu)$ in that the quantity $g(z,iu)$ is in general unknown. However, this expression may prove to be a practical method by which to calculate $\bar{z}(iu)$.

Having realized that only the diagonal elements of $\bar{\chi}_{\mu\nu}(z,z',\vec{q})$ are needed to the required order in q, we can also evaluate $\delta\tilde{n}_0^{(2)}(z,q,iu)$ using (2.21) and (A1). In particular, we find

$$\delta\bar{n}^{(2)}(z,q,iu)=\frac{2\pi}{u^2}\left[\int dz'\left(\frac{\partial}{\partial z'}\bar{\chi}_{\parallel}(z,z',iu)+\frac{\partial}{\partial z}\bar{\chi}_{\perp}(z,z',iu)\right)+q\int dz'\, z'\left(\frac{\partial}{\partial z'}\bar{\chi}_{\parallel}(z,z',iu)+\frac{\partial}{\partial z}\chi_{\perp}(z,z',iu)\right)+\cdots\right]\ . \tag{A27}$$

Comparing this with (2.25), we have

$$\delta\overline{n}_0^{(2)}(z,iu) \equiv \frac{2\pi}{u^2}\int dz'\left(\frac{\partial}{\partial z'}\overline{\chi}_{\parallel}(z,z',iu) + \frac{\partial}{\partial z}\chi_{\perp}(z,z',iu)\right) \tag{A28a}$$

and

$$\delta\overline{n}_1^{(2)}(z,iu) \equiv \frac{2\pi}{u^2}\int dz'\,z'\left(\frac{\partial}{\partial z'}\overline{\chi}_{\parallel}(z,z',iu) + \frac{\partial}{\partial z}\overline{\chi}_{\perp}(z,z',iu)\right) . \tag{A28b}$$

Using these expressions, the condition that the identity

$$\int dz\, z\,\delta\overline{n}_0^{(2)}(z,iu) \overset{(?)}{=} \int dz\; \delta\overline{n}_1^{(2)}(z,iu)$$

be satisfied and therefore that $\overline{z}(iu)$ be the centroid of the surface screening charge is

$$\frac{\partial}{\partial z}\overline{\chi}_{\parallel(\perp)}(z,z',iu) \overset{(?)}{=} \frac{\partial}{\partial z'}\overline{\chi}_{\parallel(\perp)}(z,z',iu) .$$

Since we have not been able to determine whether or not this relation is satisfied, the identification of $\overline{z}(iu)$ with the centroid has not been possible.

APPENDIX B

Here we give the evaluation of the sums required in (3.21), that is,

$$d_{\mu\nu}(l_z - l_z') = e^{q(l_z'-l_z)}\sum_{\vec{l}_{\parallel}'}{}' e^{i\vec{q}\cdot(\vec{l}_{\parallel}'-\vec{l}_{\parallel})}\, D_{\mu\nu}(\vec{l}_{\parallel} - \vec{l}_{\parallel}', l_z - l_z') \tag{B1}$$

$$\equiv e^{q(l_z'-l_z)}\, S_{\mu\nu}(l_z - l_z') . \tag{B2}$$

Case i: $l_z \neq l_z'$

Defining $\vec{r} = \vec{\rho} + z\,\hat{z}$ with $z \neq l_z'$, we have

$$\begin{aligned} S_{\mu\nu}(l_z - l_z') &= \sum_{\vec{l}_{\parallel}'} e^{iq\cdot(\vec{l}_{\parallel}'-\vec{\rho})}\,\nabla_\mu\nabla_\nu \frac{1}{|\vec{r} - \vec{l}'|}\bigg|_{\vec{r}=\vec{l}} \\ &= e^{-i\vec{q}\cdot\vec{\rho}}\,\nabla_\mu\nabla_\nu \int d\vec{\rho}'\,\frac{e^{i\vec{q}\cdot\vec{\rho}'}}{[(\vec{\rho}-\vec{\rho}')^2 + (z - l_z')^2]^{1/2}} \sum_{\vec{l}_{\parallel}'}\delta(\vec{\rho}' - \vec{l}_{\parallel}')\bigg|_{\vec{r}=\vec{l}} \\ &= e^{-i\vec{q}\cdot\vec{\rho}}\,\nabla_\mu\nabla_\nu \int d\rho'\,\frac{e^{i\vec{q}\cdot\vec{\rho}'}}{[(\vec{\rho}-\vec{\rho}')^2 + (z - l_z')^2]^{1/2}}\, n_s \sum_h e^{i\vec{Q}_h\cdot\vec{\rho}'}\bigg|_{\vec{r}=\vec{l}} \\ &= \begin{cases} -2\pi n_s \displaystyle\sum_h \frac{k_\mu k_\nu}{K} e^{-K(l_z - l_z')} , & l_z > l_z' \\ -2\pi n_s \displaystyle\sum_h \frac{k_\mu^* k_\nu^*}{K} e^{-K(l_z' - l_z)} , & l_z < l_z' \end{cases} , \end{aligned} \tag{B3}$$

where we have defined the quantities

$$\vec{K} = \vec{q} + \vec{Q}_h\ ; \quad \vec{Q}_h = Q_{h\parallel}\hat{q} + Q_{h\perp}(\hat{z}\times\hat{q}) \tag{B4}$$

and

$$\vec{k} = \vec{K} + iK\hat{z}\ , \quad K = |\vec{q} + \vec{Q}_h| . \tag{B5}$$

The specific quantity required in Sec. III is $d_{++}(l_z - l_z')$:

$$\begin{aligned} d_{++}(l_z - l_z') &= d_{\parallel,\parallel}(l_z - l_z') + d_{\perp,\perp}(l_z - l_z') \\ &= n_s \sum_{h\neq 0} \frac{2\pi}{K} Q_{h\perp}^2\, e^{-K|l_z - l_z'|}\, e^{q(l_z' - l_z)} . \end{aligned} \tag{B6}$$

Case ii: $l_z = l_z'$

It was found that the value of $S_{\mu\nu}(0)$ could not be obtained from the results of case (i) by simply subtracting the divergent contribution coming from $\vec{l}_{\parallel} = \vec{l}_{\parallel}'$. However, $S_{\mu\nu}(0)$ could be obtained using Ewald's method in the following way. Define

$$T_{\mu\nu} \equiv \sum_{\vec{l}'}{}' e^{i\vec{q}\cdot(\vec{l}'-\vec{l})}\, D_{\mu\nu}(\vec{l} - \vec{l}') , \tag{B7}$$

where the summation extends over an *infinite* lattice with the point $\vec{l} = \vec{l}'$ excluded. Then we see that

$$S_{\mu\nu}(0) = T_{\mu\nu} - \sum_{l_z' \neq l_z} S_{\mu\nu}(l_z - l_z') . \tag{B8}$$

The sum in (B7) was evaluated using Ewald's method[29] with the result

$$\begin{aligned} T_{\mu\nu} = &-4\pi n \sum_{\vec{G}\neq 0} \frac{(\vec{q}+\vec{G})_\mu(\vec{q}+\vec{G})_\nu}{|\vec{q}+\vec{G}|^2} e^{-|\vec{q}+\vec{G}|^2/4R^2} - 4\pi n \frac{q_\mu q_\nu}{q^2} e^{-q^2/4R^2} \\ &+ \frac{4}{3\sqrt{\pi}} R^3\,\delta_{\mu\nu} + R^3 \sum_{\vec{l}\neq 0} e^{i\vec{q}\cdot\vec{l}} \left[\frac{l_\mu l_\nu}{l^2}\left(H(Rl) - \frac{1}{l}H'(Rl)\right) + \delta_{\mu\nu}\frac{1}{l}H'(Rl)\right]. \end{aligned} \tag{B9}$$

Here $\vec{G}$ is a three-dimensional reciprocal-lattice vector and

$$H(x)=\frac{2}{\sqrt{\pi}}\frac{1}{x}\int_x^\infty dy\, e^{-y^2}\ . \tag{B10}$$

$H'(x)$ and $H''(x)$ are the first and second derivatives of $H(x)$, respectively, and R is an arbitrary number. Expanding $T_{\mu\nu}$ in powers of q we find

$$T_{\mu\nu}=\left(\frac{4\pi n}{3}\delta_{\mu\nu}-4\pi n\frac{q_\mu q_\nu}{q^2}\right)+O(q^2)\ , \tag{B11}$$

where we have noted that

$$\frac{4}{3\sqrt{\pi}}R^3+\frac{R^3}{3}\sum_{\vec{1}\neq 0}\left[H''(Rl)+\frac{2}{l}H'(Rl)\right] -\frac{4\pi n}{3}\sum_{\vec{G}\neq 0}e^{-G^2/4R^2}=\frac{4\pi n}{3}\ . \tag{B12}$$

Furthermore the sum in (B8) can be evaluated using (B3) with the result

$$\sum_{l_z'\neq l_z}S_{\mu\nu}(l_z-l_z')=-2\pi n_s\sum_h\frac{k_\mu k_\nu+k_\mu^* k_\nu^*}{K}\,\frac{1}{e^{Ka}-1}\ . \tag{B13}$$

Using (B11) and (B13) to evaluate $d_{++}(0)=S_{++}(0)$, we find

$$d_{++}(0)=-\frac{4\pi n}{3}-2\pi n\sum_h\frac{aQ_h}{e^{aQ_h}-1}+O(q)\ . \tag{B14}$$

With the results (B6) and (B14), we can now evaluate the sum appearing in (3.26) to zeroth order in q. Specifically, we find that

$$\begin{aligned}
\sum_{l_z}\sum_{l_z'}e^{2ql_z}d_{++}(l_z-l_z')
&=\sum_{l_z}\sum_{l_z'}e^{q(l_z+l_z')}S_{++}(l_z-l_z')\\
&=\sum_{l_z}e^{2ql_z}S_{++}(0)+\sum_{\substack{l_z\ \ l_z'\\ l_z\neq l_z'}}\sum e^{q(l_z+l_z')}\,2\pi n_s\\
&\quad\times\sum_{h\neq 0}\frac{Q_{h\perp}^2}{K}e^{-K|l_z-l_z'|}\\
&=\frac{1}{2qa}(1+qa+\ldots)\left(-\frac{4\pi n}{3}-2\pi n\sum_{h\neq 0}\frac{aQ_h}{e^{aQ_h}-1}+\cdots\right)\\
&\quad+\frac{\pi n}{qa}\left(\sum_{h\neq 0}\frac{aQ_h}{e^{aQ_h}-1}-qa\sum_{h\neq 0}\frac{aQ_h}{(e^{aQ_h}-1)^2}+\cdots\right)\\
&=-\frac{1}{qa}\frac{2\pi n}{3}(1+qa+\cdots)-\gamma\pi n+O(q)\ ,
\end{aligned} \tag{B15}$$

where

$$\gamma=\sum_{h\neq 0}\frac{aQ_h}{(e^{aQ_h}-1)(1-e^{-aQ_h})}\ . \tag{B16}$$

For the example being considered of the simple cubic crystal with a (100) face, the sum in (B16) is equal to 0.052 295.

APPENDIX C

Here we present a somewhat more general formulation of the solid-atom polarization interaction with the purpose of determining the importance of treating this interaction self-consistently.

We begin with the Hamiltonian (2.1) with a coupling constant λ;

$$H_\lambda=H_a+H_s+\lambda V_{as}\ . \tag{C1}$$

The interaction energy between the atom and solid is

$$\Delta E_\lambda=E_\lambda(Z)-E_\lambda(Z=\infty)\ , \tag{C2}$$

where $E_\lambda(Z)$ is the ground-state energy of Hamiltonian (C1) at a separation Z. Since $E_\lambda(Z=\infty)=E_0(Z)$, the Feynman-Hellman theorem gives

$$\Delta E_1=\int_0^1 d\lambda\,\langle\Psi_\lambda|V_{as}|\Psi_\lambda\rangle\ , \tag{C3}$$

where $|\Psi_\lambda\rangle$ is the ground state of the Hamiltonian (C1). Neglecting the electrostatic part of the interaction in (C3), the polarization energy is given by

$$V_{\text{pol}}\equiv\int_0^1 d\lambda\int d\vec{r}\int d\vec{r}\,'\,v(\vec{r}-\vec{r}\,')\langle\Psi_\lambda|\,\delta\hat{n}^s(\vec{r})\,\delta\hat{n}^a(\vec{r}\,')\,|\Psi_\lambda\rangle \tag{C4}$$

$$=\int_0^1 d\lambda\int d\vec{r}\int d\vec{r}\,'\,v(\vec{r}-\vec{r}\,')\int_0^\infty\frac{du}{\pi}\chi_{sa}^\lambda(\vec{r},\vec{r}\,';iu)\ . \tag{C5}$$

In Eq. (C4), the density fluctuation operators are defined as

$$\delta\hat{n}^{s,a}(r)\equiv\hat{n}^{s,a}(r)-\langle\Psi_\lambda|\hat{n}^{s,a}(r)|\Psi_\lambda\rangle\ . \tag{C6}$$

The response function appearing in (C5) is again defined analogously to the one appearing in (2.9), that is,

$$\chi_{sa}^\lambda(\vec{r},\vec{r}\,';iu)=i\int_0^\infty dt\,e^{-ut}\langle\Psi_\lambda|[\hat{n}^s(\vec{r},t),\hat{n}^a(\vec{r}\,')]|\Psi_\lambda\rangle\ . \tag{C7}$$

The evaluation of the polarization energy is thus reduced to the calculation of the response function $\chi_{sa}^\lambda(\vec{r},\vec{r}\,';iu)$. This quantity can be calculated within a self-consistent field approximation. Schematically, this approximation implies that χ_{sa} satisfies the integral equation

$$\chi_{sa}=\chi_s+\chi_a(1+v\,\chi_{sa})\ , \tag{C8}$$

where χ_s and χ_a are the response functions of the solid and atom, respectively, evaluated when $\lambda=0$, and v is the Coulomb potential. The solution to (C8) can be obtained in the dipole approximation. Substituting this solution into Eq. (C5), one obtains, after some algebra, the result

$$V_{\text{pol}}=\int_0^\infty\frac{du}{2\pi}\ln\{[1-\alpha(iu)F(iu,Z)]^2\times[1-2\alpha(iu)F(iu,Z)]\}\ . \tag{C9}$$

Here $\alpha(iu)$ and $F(iu, Z)$ have been defined previously in Sec. II. If the product $\alpha(iu)\,F(iu, Z)$ is small, this result clearly reduces to (2.15). Since $\alpha(iu)$ and $F(iu, Z)$ achieve their maximum values at $u=0$, it is sufficient to consider this particular value of the frequency. Evaluating $2\alpha(0)\,F(0, Z)$ for Xe on a metal surface at a value of $Z=4$ a.u. gives 0.1. Thus corrections to (2.15) from self-consistency are indeed small for the systems of interest in this paper.

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[1] Although this separation is not exact when the charge distributions of the atom and surface overlap, we shall in this paper accept it as the basis of our discussion.

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