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†Work supported in part by the National Science Foundation via the Laboratory for Research on the Structure of Matter and Grant No. GH-42283.

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¹³Our data are all consistent with Wrighton's results (Ref. 12), of which we became aware only recently. He reports ϵ_1 and ϵ_2 spectra at 16, 85, and 300 K, and thus did not observe the discontinuous behavior near 42 K.

Effect of Spatial Dispersion upon Physisorption Energies: He on Metals

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(Received 24 April 1974)

Microscopic calculations of noble-gas adsorption on metals which include the effect of metallic nonlocal dielectric response are presented for two models of electronic boundary conditions at the metal surface. Spatial dispersion causes the Van der Waals interaction to decrease slower than the conventional d^{-3} law indicates. Systematics of the physisorption indicate that interaction energies, but not equilibrium positions, are very sensitive to nonlocality. The results are relatively insensitive to the details of the electronic boundary conditions.

Because of the fundamental nature of chemical reactions at surfaces and their important role in such practical problems as catalysis¹ and oxidation, the understanding of these reactions is recognized as one of the major goals of surface science. Essential to this objective is the complete description of the adsorption process, i.e., an understanding of *both* chemical and physical adsorption. These adsorption processes have been historically distinguished by the order of magnitude of their binding energies (i.e., electron volts for chemisorption and hundredths of electron volts for physisorption). Recently, we have presented a new theory^{2,3} which indicates that the repulsive contribution to physical adsorption on metals can be determined from *ab initio*

considerations which are consistent with modern ideas of surface physics, in contrast to some earlier work.⁴⁻⁸ Treatment of the attractive (or Van der Waals) part of the physical adsorption interaction, however, has followed²⁻⁸ the traditional method^{9,10} of describing the coupling between the electromagnetic field and the solid media by means of a spatially local dielectric constant.

The question of the influence of dispersion in the metal upon the Van der Waals interaction was raised by Lifschitz in his pioneering paper,⁹ and these effects have not been studied systematically since then. The object of this paper is the determination, for the first time, of the effects of dispersion and of varying surface electronic

boundary conditions upon physical adsorption of a gas on a metal. The Van der Waals contribution, E_{VW} , to the interaction energy between an atom in vacuum and a metal surface is given by^{3, 11, 12}

$$E_{VW}(d) = \lim_{N \rightarrow 0} \frac{k_B T}{\pi} \sum_{n=0}^{\infty} \left(\frac{\xi_n}{c} \right)^3 \int_1^{\infty} \frac{p^2 dp}{N} (F_1^{-1} + F_2^{-1}), \quad (1a)$$

$$\xi_n \equiv 2\pi n k_B T, \quad c k_{\parallel} \equiv \xi_n (p^2 - 1)^{1/2}, \quad (1b)$$

where d is the distance separating the atom and metal plane and c the velocity of light in vacuum. The summation in Eq. (1a) is over integer values of n , where the $n=0$ term is given half weight, k_B is Boltzmann's constant, T is absolute temperature, N is the gas density, and k_{\parallel} is the component of wave vector in the plane of the surface (atomic units are used exclusively here). The dispersion relations for the normal surface modes (TM and TE) of the electromagnetic field (i.e., surface plasmons) are represented by F_1 and F_2 [specified in Eqs. (5) below]. Equation (1a) is derived by summing the free energies of the normal electromagnetic modes,^{11,12} which is equivalent to Lifschitz's approach.⁹ Calculation of E_{VW} , therefore, reduces to a solution of Maxwell's equations.

In the presence of metallic spatial dispersion the relationship in the metal between the Fourier components of the electric displacement, \vec{D} , and the electric field, \vec{E} , can be written as

$$\vec{D}(z, \vec{k}_{\parallel}, \omega) = \int_{-\infty}^0 dz' \epsilon(z, z', \vec{k}_{\parallel}, \omega) \times \vec{E}(z', \vec{k}_{\parallel}, \omega), \quad z < 0, \quad (2)$$

in which ω is the frequency and the metal fills the negative- z half space. Maxwell's equation with the insertion of Eq. (2) cannot be solved generally, and we utilize a model which corresponds to the bulk metallic hydrodynamic constant¹³

$$\epsilon_M(\vec{k}, \omega) = 1 - \omega_p^2 [\omega(\omega + i/\tau) - (\alpha k)^2]^{-1}, \quad (3)$$

where ω_p is the plasma frequency (i.e., $\omega_p^2 = 4\pi n_+$, where n_+ is the electron density for free-electron metals), τ is a damping lifetime, and α^2 is set equal to $0.6V_F^2$ (V_F is the Fermi velocity) in order to recover the bulk-plasmon dispersion relation from the hydrodynamic equation.¹³⁻¹⁶ In relating Eqs. (2) and (3), we employ two solvable models of the surface electronic boundary conditions: specular reflection¹⁷ and diffuse reflection.¹⁸ Specular reflection is equivalent to assum-

ing that the field components parallel (perpendicular) to the surface plane are even (odd) under inversion about the surface plane; the exact solution of Maxwell's equations for this case are well known.¹⁹ The diffuse-reflection boundary condition corresponds to assuming that

$$\epsilon(z, z', \vec{k}_{\parallel}) = \int_{-\infty}^{\infty} (dk_z/2\pi) \exp[ik_z(z - z')] \epsilon_M(\vec{k}) \equiv \epsilon_M(z - z', \vec{k}_{\parallel}), \quad (4)$$

where we have suppressed the ω argument. This boundary condition, therefore, corresponds to the same contribution from each volume element of dielectric as in the bulk constitutive relation. Exact solutions of Maxwell's equations for diffuse reflection have been found independently by several workers.²⁰⁻²²

The influence of spatial dispersion upon the Van der Waals interaction can be clarified by simple physical arguments, without resort to the calculational details of the exact solutions with retardation, which are quite complicated and will be reported elsewhere.²³ The general form of the dispersion relations of TM (F_1) and TE (F_2) surface modes in Eqs. (1) are evaluated on the imaginary frequency axis $\omega = i\xi$:

$$F_j(i\xi, p) \equiv D_j(i\xi, p) \exp(2p\xi d/c) - 1, \quad (j=1, 2), \quad (5a)$$

$$D_1(i\xi, p) = [(S_A + p\epsilon_A)/(S_A - p\epsilon_A)] C_{1M}, \quad (5b)$$

$$D_2(i\xi, p) = [(S_A + p)/(S_A - p)] C_{2M}, \quad (5c)$$

$$S_A = (\epsilon_A - 1 + p^2)^{1/2}. \quad (5d)$$

The quantity ϵ_A is the dynamic dielectric function of the atom. The dispersion relation of the modes of the isolated metal are specified by $C_{jM}^{-1}(k_{\parallel}, \omega) = 0$; the surface plasmons correspond to C_{1M} .

Because of the exponential in Eq. (5a), the major contribution to E_{VW} comes from terms for which $p\xi \approx c/2d$. For the small d with which we are concerned, the important limit is $p \rightarrow \infty$, since $\epsilon_A \rightarrow 1$ as $\xi \rightarrow \infty$. In the case of a local metallic dielectric function, $C_{1M}(p \rightarrow \infty, \xi)$ is a finite function of ξ alone [$C_{2M}(p \rightarrow \infty, \xi) \rightarrow \infty$]. The finiteness of C_{1M} in this limit reflects the fact that the surface-plasmon frequency $\omega_s \rightarrow \omega_p/\sqrt{2}$ as $k_{\parallel} \rightarrow \infty$ for a local metallic dielectric function [i.e., see Eq. (1b)]. A simple transformation of variables^{9,10} in Eq. (1) yields the result that $E_{VW} \sim d^{-3}$. This reasoning is the justification for the conventional⁴⁻¹⁰ inverse-cube law of the Van der Waals force.

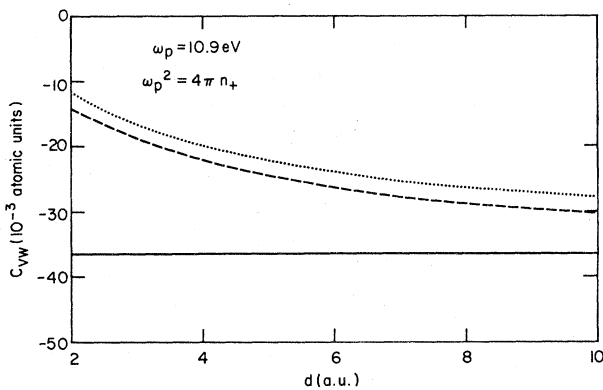


FIG. 1. Van der Waals constant (i.e., $C_{VW} \equiv d^3 E_{VW}$) for He adsorbed on Mg (i.e., $\alpha = 0.56$ a.u.). Results are shown for spatial dispersion with specular reflection (dashed line) and diffuse reflection boundary (dotted line) conditions and for the local dielectric function model (solid line). Infinite lifetime τ is assumed here.

In the case of the model nonlocal dielectric functions we are considering, however, both C_{1M} and $C_{2M} \rightarrow \infty$ as $p \rightarrow \infty$. This has the consequence that there is negligible contribution to the integral in Eq. (1a) from terms with large p . The d dependence of E_{VW} cannot be deduced from a transformation of variables and is more complicated than the inverse-cube law. This result follows from the fact that, for both of our models, the surface mode is admixed with volume modes¹⁹; the admixture increases with increasing k_{\parallel} , so that $\omega_s \rightarrow \infty$ as $k_{\parallel} \rightarrow \infty$.^{19,21,23,24} The negligible contribution from terms with large k_{\parallel} exists also in the random-phase approximation solved with specular-reflection boundary conditions.¹⁹ Another consequence of the admixture is that the contribution to E_{VW} of modes localized at the surface (i.e., d -dependent modes) decreases relative to their contribution in the local-dielectric-function case (i.e., $\alpha = 0$). We expect, therefore, that E_{VW} will be weaker with spatial nonlocality than without.

These results are illustrated in Fig. 1, in which we plot $C_{VW} \equiv d^3 E_{VW}$ as a function of d for He on a typical free-electron metal, Mg. The polarizability of He includes both discrete and continuum contributions.^{2,3} The salient points are that E_{VW} varies more slowly than the inverse-cube law in the spatial dispersion models and that the Van der Waals interaction is weaker in these cases than in the case of the corresponding local dielectric function (i.e., $\alpha = 0$), in accord with the previous discussion. Another important feature of Fig. 1 is that the effect of spatial dispersion on E_{VW} is much more significant

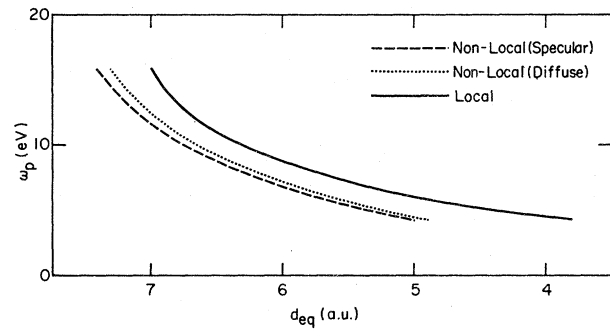


FIG. 2. Equilibrium position d_{eq} of physisorbed He atoms on free-electron metals (i.e., $\omega_p^2 = 4\pi n_+$) for our three models. The relative insensitivity of d_{eq} to the degree of dispersion and different electronic boundary conditions is illustrated. Infinite lifetime τ is assumed here.

than that of the different boundary conditions.

In order to study the effects of nonlocality upon He physical adsorption, we add the repulsive portion, E_R , of the interaction energy, which has been studied in detail elsewhere^{2,3}:

$$E_R(d) = \int d^3r n_M \left(\frac{\delta T[n_M + n_A]}{\delta n} - \frac{\delta T[n_M]}{\delta n} \right), \quad (6a)$$

$$n_M = \frac{1}{2} n_+ \{1 - (z/|z|)[1 - \exp(-\beta|z|)]\}, \quad (6b)$$

where n_+ is the electron density and β is a variational parameter. The isolated atomic and metallic electron densities are labeled by n_A and n_M , respectively. The quantity $T[n]$ is the kinetic energy functional of the electronic density.²⁵ In performing the calculation of E_R ,^{2,3} we use the extended Thomas-Fermi version of the density-functional formalism²⁵ expanded to first order in the gradient operator. We represent n_A ²⁶ and n_M ²⁷ by variational solutions which describe the isolated systems adequately.^{2,3,26,27}

Equilibrium positions, d_{eq} , obtained from the position of the minimum in the total interaction energy, $U \equiv E_R + E_{VW}$, are displayed in Fig. 2 for He on a variety of free-electron metals (i.e., $\omega_p^2 \equiv 4\pi n_+$). Note that the values of d_{eq} for the three models are within 1 a.u. of one another and the changes in electronic boundary conditions produce small changes in d_{eq} . The equilibrium position, therefore, is relatively insensitive to the model used to describe the metal.

The monotonic increase in the physisorption interaction energy [i.e., $-U(d_{eq})$] of He on metals with increasing electron density for the two nonlocal models is exhibited in Fig. 3. This monotonic behavior is to be contrasted with the peak in $-U(d_{eq})$ for local coupling. Comparison of the surface-plasmon solutions of the hydrodynamic

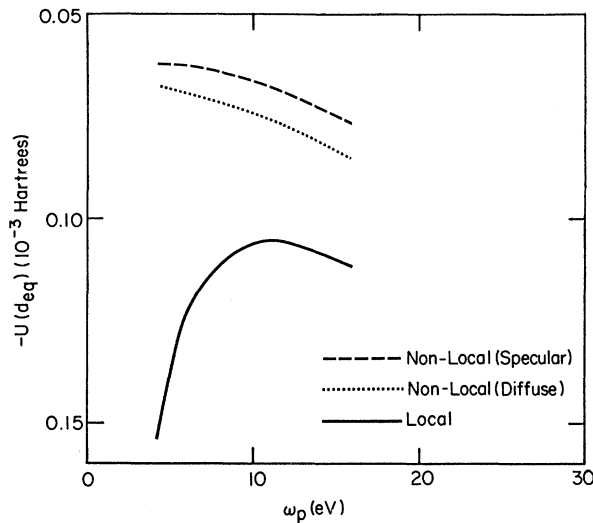


FIG. 3. Physisorption energies for He adsorbed on free-electron metals for the three models of electromagnetic coupling. The monotonic increase in $-U(d_{eq})$ with plasmon frequency for nonlocal couplings illustrates a distinction from the case of local coupling. Infinite lifetime τ is assumed here.

and Boltzmann equations¹⁵ indicate that $\frac{1}{3} < \alpha^2 / v_F^2 < 0.6$ for $\omega < \omega_p$; this corresponds to small ξ values which make the major contribution to E_{vw} . Such a reduction in α brings the magnitudes of the binding energies for the nonlocal models into closer agreement with those for the local model. From the results of our calculations we observe that within the errors in the currently available experimental data the degree of agreement achieved between the calculated and experimental values is not changed upon the inclusion of spatial dispersion.²⁸ We would like to remark here that caution should be exercised in applying model calculations to comparisons with experimental data because of substantial discrepancies in the present experimental situation. Therefore, the need for additional well-controlled experiments on physisorption systems and further theoretical studies is indicated. Detailed results of our studies will be discussed in a forthcoming publication.²³

The above results illustrate for the first time the systematic effects of nonlocal electromagnetic coupling upon physical adsorption interaction. The main conclusions of our studies can be summarized as follows: (1) Van der Waals interaction calculated via nonlocal coupling schemes varies with distance *more slowly* than the inverse-cube law obtained from local approximations, (2) the interaction is *weaker* in the non-

local models, (3) equilibrium distances are *relatively insensitive* to nonlocal corrections, and (4) different boundary conditions at the metal surface (diffuse and specular) introduce *minor* changes to the above results.

The authors are indebted to Mrs. Carol Troy for her continuous assistance in the preparation of the manuscript.

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