

Local and nonlocal effects in the theory of physisorption

Uzi Landman

Xerox Corporation, Webster Research Center, Webster, New York 14580

George G. Kleinman

Research Laboratories, General Motors Corporation, Warren, Michigan 48090

(Received 5 September 1974)

A review of our microscopic theory of physisorption is presented. The effects of spatial dispersion in the metal for two boundary conditions at the metal surface are discussed and compared with results of the local-dielectric-response theory. It is shown that in the presence of spatial dispersion the Van der Waals interaction decreases more rapidly than the d^{-3} law of the local theory. In both cases, an adequate determination of the attractive energy requires an accurate description of the dynamic polarizability of the incident atom. Repulsive contributions to the interaction energy are included via the density-functional formalism, resulting in a complete description of the interaction energy curve. The equilibrium distances of the atom are a monotonically increasing function of the metallic-electron density and are not affected significantly by nonlocality in the metal.

I. INTRODUCTION

Understanding of the fundamental interactions between atoms and molecules and solid surfaces is a basic essential for a consistent theoretical analysis of adsorption studies and surface reaction mechanisms.^{1,2} Customarily in the literature^{1,3} a distinction is drawn between the *physical* and *chemical* states of adsorption, on the basis of binding energy magnitudes (of the order of 10^{-2} eV and several eV, respectively). Physical adsorption is the state of weak coupling between the substrate and the incident particle. The physisorption interaction is considered to result from the presence of Van der Waals forces with no transfer of charge or sharing of electrons between the components of the system. It is believed to serve as a precursor to the chemisorption state which enhances the transition to this state.² Moreover, the reduction of motional degrees of freedom of the physisorbed molecule may be of importance in the evaluation of adsorption and reaction mechanisms. In addition, a complete description of the variation in the interaction energy as a function of the distance between the incident particle and the surface is of major significance in the interpretation gas surface scattering experiments.⁴

Considerable effort has been applied to the problem of understanding the nature of the physisorption interaction, and a number of semiempirical, semiclassical, and quantum-mechanical formulations have been suggested in the literature, and have been reviewed by several authors.^{1-3,5} However, detailed studies on a microscopic level of the interaction mechanism, systematics of the interaction as a function of the physical parameters describing the interacting atom or molecule, and the surface and actual computations of the interaction energies have not been usually performed. In a

series of recent publications⁵⁻⁸ we have presented a microscopic theory of the physisorption interaction where both the attraction and repulsion between the atoms and the surface are included. Furthermore, the effect of nonlocality (dispersion) and varying surface electronic boundary conditions have been systematically studied.^{7,8} In this paper we present a brief review of our theory and give additional results for He adsorption on metals. In particular, the effects of nonlocality in the metal and dynamical frequency response of the atomic species are demonstrated.

II. VAN DER WAALS INTERACTION

The total Hamiltonian H for the combined metal-atom system is represented by⁹

$$H = H_M + H_A + H_{em} + H_{SR} + H_{VW}, \quad [1]$$

where H_{em} is the Hamiltonian of the vacuum-quantized electromagnetic field, H_M and H_A are the Hamiltonians of the isolated atom and metallic systems, H_{SR} describes the short-range interactions between the atom and metal, and H_{VW} corresponds to the interaction between all the particles of the system and the quantized long-wavelength electromagnetic field (i.e., the Van der Waals interaction). The ground-state energy of the system is derived from the Schrödinger equation⁵

$$H|G,d\rangle = E|G,d\rangle, \quad [2]$$

where $|G,d\rangle$ is the ground-state for separation d between the metal and atom. Since at large separations the contributions from H_{SR} are negligible, it can be shown that at $T=0^\circ$ K the interaction energy can be written as

$$E_{VW} = \langle G,d|H_{VW}|G,d\rangle, \quad [3]$$

where E_{VW} is the Van der Waals energy. It should be

noted that the exchange correlation and electrostatic interaction energies calculated at short distances approach the Van der Waals interaction at large separation. Thus, the Van der Waals is the *whole* energy of attraction containing the exchange correlation and electrostatic contributions.⁵ H_{VW} describes the coupling of the vector potential \mathbf{A} with the particle current density⁹

$$H_{\text{VW}} = - \int d^3r \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r}). \quad [4]$$

Lifshitz *et al.* have considered the Van der Waals interaction as originating from the random fluctuations of the electromagnetic field in the solid which extends beyond its boundaries and induce spontaneous transitions in the atoms.^{10,11} In the above derivation a local description of the solid is adopted, restricting the validity of the theory to relatively large distances d . Other methods of calculating Van der Waals forces have been proposed.¹² According to Van Kampen *et al.*,¹³ the interaction originates from the change in zero-point energies of surface collective modes introduced upon bringing the components of the interacting system from infinity to the distance d . Furthermore, it has been shown that for a local description of the solid, this approach is equivalent to Lifshitz's result. This formulation can be conveniently generalized to include the effects of dispersion and varying electronic boundary conditions at the surface, as we have previously shown.^{7,8} Consequently, the Van der Waals contribution, E_{VW} , to the interaction energy between an atom in vacuum and a metal surface separated by a distance d is given (in atomic units) by⁷

$$E_{\text{VW}}(d) = \lim_{N_0 \rightarrow 0} \frac{k_B T}{\pi} \sum_{n=0}^{\infty} \left(\frac{\xi_n}{c}\right)^3 \int_1^{\infty} \frac{p^2 dp}{N_0} (F_1^{-1} + F_2^{-1}), \quad [5]$$

$$\xi_n \equiv 2\pi n k_B T, \quad ck_{||} \equiv \xi_n (p^2 - 1)^{\frac{1}{2}}, \quad [6]$$

where T is the absolute temperature, k_B is the Boltzmann constant, c is the velocity of light in vacuum, N_0 is the gas density, and $k_{||}$ is the component of the wave vector in the surface plane. The summation is carried over integral values of n , with the $n=0$ term given half-weight.

The dispersion relation for the normal surface modes of the electromagnetic field (i.e., surface plasmons) are represented by $F_1(TM)$ and $F_2(TE)$ evaluated on the imaginary frequency axis $\omega = i\xi$:

$$F_j(i\xi, p) = D_j(i\xi, p) \exp\left(\frac{2p\xi d}{c}\right) - 1, \quad (j=1, 2), \quad [7a]$$

$$D_1(i\xi, p) = \frac{(S_A + p\epsilon_A)}{(S_A - p\epsilon_A)} C_{1M}, \quad [7b]$$

$$D_2(i\xi, p) = \frac{(S_A + p)}{(S_A - p)} C_{2M}, \quad [7c]$$

$$S_A = (\epsilon_A - 1 + p^2)^{\frac{1}{2}}. \quad [7d]$$

The dispersion relation of the modes of the isolated metal are specified by $C_{jM}^{-1}(k_{||}, \omega) = 0$; the surface plasmons correspond to C_{1M} . In the presence of metallic spatial dispersion, we use a model which corresponds to the bulk metallic hydrodynamic dielectric constant¹⁴

$$\epsilon_M(\mathbf{k}, \omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau) - (\alpha k)^2}, \quad [8]$$

where $\omega_p = (4\pi n_+)^{\frac{1}{2}}$ (n_+ is the electron density for free electron metals, τ is a damping lifetime, and α^2 is set equal to $0.6 V_F^2$, where V_F is the Fermi velocity, in order to recover the bulk plasmon dispersion relation from the hydrodynamic equation.⁷ In the local case the metallic dielectric function is given by Eq. (8) with $\tau \rightarrow \infty$ and $\alpha = 0$.

The relationship, in the metal, between the Fourier components of the electric displacement, \mathbf{D} , and the electric field \mathbf{E} can be written⁷ as

$$\mathbf{D}(z, \mathbf{k}_{||}, \omega) = \int_{-\infty}^0 dz' \epsilon(z, z', \mathbf{k}_{||}, \omega) \mathbf{E}(z', k_{||}, \omega), \quad z < 0, \quad [9]$$

where ω is the frequency. In relating Eqs. (8) and (9), two soluble models of the surface electronic boundary conditions are used: specular¹⁵ and diffuse¹⁶ reflection.

Finally, the rarefied gas atoms are characterized by the dielectric function

$$\epsilon_A(\omega) = 1 + 4\pi N_0 \alpha_A(\omega) \quad [10]$$

in which α_A is the dynamic polarizability of the atom,¹⁷ which when considered a function of the imaginary frequency is given in atomic units by

$$\alpha_A(i\xi) = \sum_{j=1}^{\infty} \frac{f_j}{\xi^2 + \omega_j^2} + \int_{E_{\text{IP}}}^{\infty} dE \frac{f_c(E)}{\xi^2 + E^2}, \quad [11]$$

where f_j and ω_j are the discrete oscillator strengths and transition frequencies, respectively, and $f_c(E)$ and E_{IP} represent the continuum oscillator strength and ionization potential, respectively.

Examination of the expression for E_{VW} [Eq. (5)] reveals that the Van der Waals interaction is highly dynamic deriving contributions from the whole frequency range as expressed by the integration over all imaginary frequencies. In particular, He has a very strong continuum over all imaginary frequencies. In particular, He has a very strong continuum polarizability¹⁸ so that contributions from frequencies which are much larger than energies characteristic to the metal (e.g., the plasma and Fermi energies) are important. First, we demonstrate the importance of the inclusion of the complete excitation spectrum of the atomic species in both the local and nonlocal theories of physisorption.¹⁹ (To facilitate a comparison between the two modes of description we have introduced the function $C_{\text{VW}} \equiv d^3 E_{\text{VW}}$.) In Fig. 1 calculated C_{VW} 's for He adsorption on Al ($\hbar\omega_p = 15.8$ eV) are shown for the local case (dash-dot curve) and for the two boundary

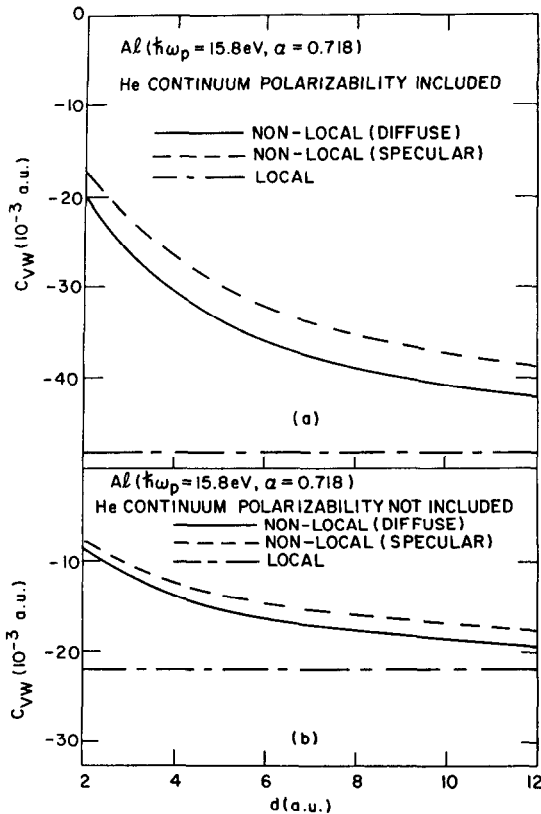


FIG. 1. (a) Van der Waals constant (i.e., $C_{VW} = d^3 E_{VW}$), for He adsorption on Al. Results are shown for the local case (dash-dotted) and nonlocal model for specular (dashed) and diffuse (solid) electronic boundary condition at the surface. The complete excitation spectrum of He including the continuum polarizability has been used in the calculation; (b) Same as in (a) with the first atomic twelve transitions of He used in the calculation. Infinite lifetime, τ , is assumed.

conditions of the nonlocal model. Comparison of the results shown in Fig. 1(a) where the complete excitation spectrum of He was used, with those shown in Fig. 1(b) where the first 12 excitation only were employed, demonstrates the importance of an adequate description of the frequency response of the atomic species in calculations of the Van der Waals interaction. Furthermore, examination of the dependence of C_{VW} on the distance d reveals a d^{-3} dependence in the local case and a more rapid variation than the inverse-cube-law, for the nonlocal models. The difference in the force laws which are derived from local and nonlocal descriptions of the Van der Waals interaction has been discussed by us in a previous paper.⁷

In the case of the model nonlocal dielectric functions we are considering, 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. (5) from terms with large p . This result follows from the fact that, for both electronic boundary conditions, the surface mode is admixed with volume modes;²⁰ the admixture increases with increasing $k_{||}$, so that $\omega_s \rightarrow \infty$ as $k_{||} \rightarrow \infty$.^{20,21} The negligible contribution from terms with large $k_{||}$ exists also in the random phase approximation solved with specular reflection boundary conditions.²⁰ 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., $\alpha=0$). Consequently, E_{VW} will be weaker with spatial nonlocality than without. Another important result demonstrated in Fig. 1 is that the effect of spatial dispersion is much more significant than that of the different boundary conditions.

The different distance dependencies of the Van der Waals interaction energy in the local and nonlocal descriptions are further illustrated in Fig. 2, for He adsorption on three metals (Na, Mg, and Al). In this figure the difference $\Delta C_{VW} = C_{VW}(\text{nonlocal}) - C_{VW}(\text{local})$, is plotted as a function of distance, d , for "diffuse" electronic boundary conditions. [Values of $C_{VW}(\text{local})$ for He adsorption on these metals are given in Fig. 1 of Ref. 5.] The systematic increase in the attraction and in ΔC_{VW} , correlated with the increase in plasma frequency characterizing the substrate is evident from the figure.

III. REPULSIVE INTERACTION

Since a detailed study of the repulsive interaction has been given by us in previous publications,^{5,6} we restrict ourselves to presentation of the basic formulae. The repulsion is a consequence of the Heisenberg uncertainty principle, since assemblage restricts the electrons to a smaller volume with a consequent increase in the electronic kinetic energy, ΔT

$$\Delta T[n_e] = T_d[n_e] - T_\infty[n_A, n_M], \quad (12)$$

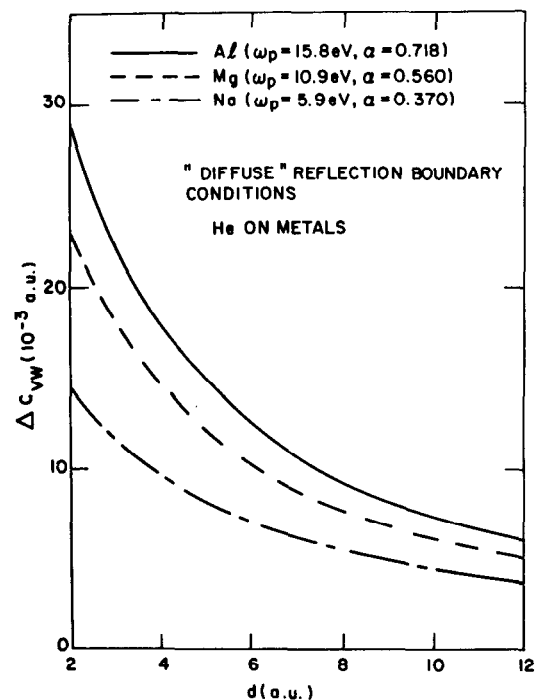


FIG. 2. Deviation of the Van der Waals constant caused by spatial dispersion, $\Delta C_{VW} \equiv C_{VW}(\text{nonlocal}) - C_{VW}(\text{local})$. Results are shown for the adsorption of He on Al (solid), Mg (dashed), and Na (dash-dotted). "Diffuse" reflection boundary condition is used. Infinite lifetime, τ , is assumed.

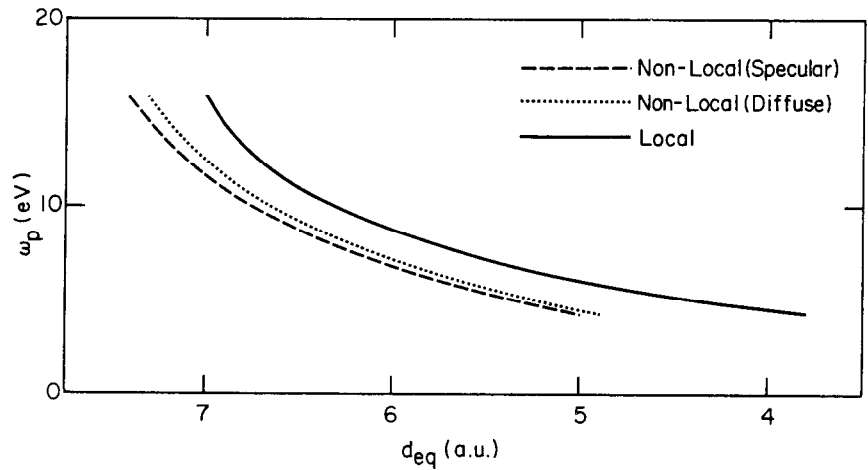


FIG. 3. Equilibrium position, d_{eq} , of physisorbed He atoms on free-electron metals (i.e., $\omega_p^2 = 4\pi n_+$) for the local case and for two boundary conditions in the nonlocal model. The relative insensitivity of d_{eq} to the degree of dispersion and different electronic boundary conditions is illustrated. Infinite lifetime, τ , is assumed.

where T_d and T_∞ are the kinetic energies of the atom and metal electron at a distance d and at infinite separation respectively, n_e , n_A , and n_M are the electron number densities of the combined atom-surface system, isolated atom, and metal, respectively. Using the Thomas-Fermi version of the density-functional²² formalism expanded to first-order in the gradient operator it can be shown⁵ that the zeroth-order change in kinetic energy can be determined approximately without resorting to self-consistent calculation, i.e.,

$$\Delta T[n_e] \equiv E_R(d)$$

$$= \int d^3r n_M \left(\frac{\delta T}{\delta n} [n_M + n_A] - \frac{\delta T}{\delta n} [n_M] \right). \quad [12a]$$

$$n_M = \frac{n_+}{2} \{ 1 - (z/|z|) [1 - \exp(-\beta|z|)] \}, \quad [12b]$$

where n_+ is the positive jellium charge density and β a variational parameter.²³ $T[n]$ is the kinetic energy functional of the electronic density.

IV. EQUILIBRIUM DISTANCES

The total energy of interaction $U(d)$ is given by the sum of the attractive and repulsive interactions

$$U(d) = -E_{VW}(d) + E_R(d). \quad [13]$$

The resulting interaction energy curve exhibits a minimum at the equilibrium distance d_{eq} .

Equilibrium positions, d_{eq} , obtained from the position of the minimum in the total interaction energy are displayed in Fig. 3 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, i.e., local and two boundary conditions for the nonlocal model are within 1 a.u. of one another and that 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 d_{eq} with increasing plasma frequency is also demonstrated. Finally, it is important to note^{5,6} that the values of the equilibrium positions are larger than the value obtained from the sum of covalent radii of the metallic and He atoms.

¹G. C. Bond, *Catalysis by Metals* (Academic, New York, 1962).

²A. Clark, *The Theory of Adsorption and Catalysis* (Academic, New York, 1970).

³D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths, London, 1962).

⁴W. H. Weinberg and R. P. Merrill, *Surf. Sci.* **33**, 493 (1972).

⁵G. G. Kleiman and U. Landman, *Phys. Rev. B* **8**, 5484 (1973).

⁶G. G. Kleiman and U. Landman, *Phys. Rev. Lett.* **31**, 707 (1973).

⁷G. G. Kleiman and U. Landman, *Phys. Rev. Lett.* **33**, 524 (1974).

⁸G. G. Kelman and U. Landman, *Phys. Rev. B* (to be published).

⁹A. A. Abrikosov, L. P. Gor'kov, and L. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, New Jersey, 1963), Sec. 30.

¹⁰E. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **29**, 94 (1955) [*Sov. Phys. JETP* **2**, 73 (1956)].

¹¹I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, *Adv. Phys.* **10**, 165 (1961).

¹²See Refs. 26-35 and 48-52 cited in Ref. 5. A recent method not mentioned in the above was proposed by V. Peuckert [*Z. Physik* **241**, 191 (1971)] and developed by R. A. Craig [*J. Chem. Phys.* **58**, 2988 (1973)]. In this method a generalized expression for the correlation energy of an inhomogeneous electron gas is utilized.

¹³N. G. Van Kampen, B. R. A. Nijboer, and K. Schram, *Phys. Lett. A* **26**, 307 (1968).

¹⁴R. H. Ritchie, *Prog. Theoret. Phys. (Kyoto)* **29**, 607 (1963).

¹⁵G. E. H. Reuter and E. H. Sondheimer, *Proc. Roy. Soc. A* **195**, 336 (1948).

¹⁶J. Heinricks, *Solid State Comm.* **12**, 167 (1973).

¹⁷P. W. Langhoff and M. Karplus, *J. Chem. Phys.* **52**, 1435 (1970).

¹⁸S. S. Huang, *Astrophys. J.* **108**, 354 (1948).

¹⁹For details of the calculation see Ref. 5, Sec. 2.

²⁰R. Fuchs and K. L. Kliewer, *Phys. Rev. B* **3**, 2270 (1971).

²¹A. A. Maradudin and D. L. Mills, *Phys. Rev. B* **7**, 2784 (1973).

²²P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

²³J. R. Smith, *Phys. Rev.* **181**, 522 (1969).