

Reponses Of A Metallic Bubble: A Self-Consistent Calculation Including Correlation And Exchange Effects

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The Van der Waals energy of molecules interacting with metallic bubbles is determined from spherical-tensor theory by using the response field susceptibility of the spherical bubble. The correlation and exchange effects of the electron response inside the metal are included by using the local density approximation (LDA). The dependence of the Van der Waals energy on the first Euler angle is manifestation of the anisotropy of the interaction. In order to illustrate the non-locality and the correlation and exchange effects as well as the importance of the spherical bubble curvature and anisotropy of the interaction on the potential magnitudes, we present numerical results for typical systems (HF,HCl) molecules on (Ag,Al) surfaces.

Keywords: metallic bubble, Van der Waals energy, correlation and exchange effect.

1. INTRODUCTION

It has been shown, both theoretically [1-3] and experimentally [4-6], that the vicinity of the surface strongly modifies the dynamical properties of the atomic or molecular system, giving rise to a wide variety of 'surface effects', such as Van der Waals interaction, desorption energy, alteration radiative properties, etc.

In this paper, we present by taking into account correlation and exchange effects of the electron response inside the metal a formulation of the Van der Waals energy of a molecule placed inside or outside a metallic bubble. The theoretical approach is based on formalism which uses generalized susceptibilities [7] or electric-field propagators

$\epsilon_1 \underline{S}^{\epsilon_2}(\vec{r}, \vec{r}', \omega)$, connecting two points \vec{r} , \vec{r}' inside or outside the metallic bubble. In this formalism, the estimation of the Van der Waals energy requires the knowledge of the dynamic polarizabilities of adatoms and the dynamic response functions of the substrate. However, the alterations of atomic or molecular properties at the vicinity of special importance when the surface presents a positive or negative radius of curvature at an μm or nm scale. For such systems as atoms confined in microcavities [8,9], atomic diffraction by atomic mirrors [10], molecule in porous materials [11] or carbon nanotubes [12] or at the tip of a near-field microscope, spectroscopic properties are dramatically changed. Nevertheless, the validity of the present model is limited to intermediate distances between the microsystem and the surface, in the following sense: (i) the distance is small enough to make negligible any retardation effect (which forbids applying the model to account for radiation and excitation of resonant modes in the

solid); (ii) the distance is large enough to ignore the short-range repulsive forces due to the overlap of the electronic orbitals of the two partners and to consider the solid as a continuous medium. In the case of a curved surface the radius of curvature is also involved and to be considered when examining the validity of the treatment at the short distance. This point will be examined further in our case for a spherical bubble.

The paper is organized as follows. Section 2, is devoted to the response of the metal with correlation and exchange effects. A general formulation of the molecule-bubble dispersion and induction energy is developed in section 3. In section 4, we investigate numerically the variations of the dipolar contribution to the van der Waals energy with the orientation of the molecule, the distance of approach, the radius of the metallic bubble and the mean electronic density of the metal, for molecules HF and HCl adsorbed on metals (Ag, Al). Moreover, to describe the dynamical properties of adatoms, we use the Drude oscillator model.

II. THE RESPONSE OF THE METAL

The molecule is described as a sum of fluctuating electric moments. In the following for sake of simplicity we shall restrict to a dipolar moment but the method can be easily extended to higher orders by using proper expansions of the source potential. The validity of the method is restricted to the intermediate distance range for the following reasons : (i) because of the quasistatic approximation, it does not take into account retardation effects which become significant at large distances ($\geq 100 \text{ au}$) ; (ii) at distances of a few au, electronic orbitals of the atom and the solid

overlap, giving rise to a repulsive interaction; (iii) at such short distances the description of the solid as a continuous medium becomes questionable.

Indeed, the fluctuating dipole located at point \vec{r}_ℓ inside or outside the metallic bubble (cf. Fig 1), induces in the metal a fluctuation of the charge density $\delta\rho(\vec{r},\omega)$ for a specific frequency. Let $\Phi_1(\vec{r},\omega)$ be the potential, created by the dipole and by $\delta\rho$, at a point \vec{r} in the medium. In the quasi-static approximation, Φ_1 obeys the Poisson equation :

$$\Delta\Phi_1(\vec{r},\omega) = -4\pi\delta\rho(\vec{r},\omega). \quad (1)$$

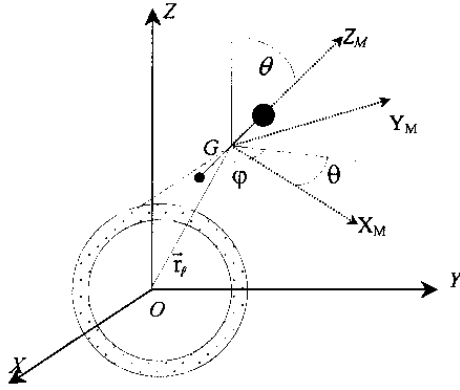


Figure 1 : Interaction between a molecule and a spherical bubble of radii a, b , centred at point O . (O, X, Y, Z) : absolute frame. (G, X_M, Y_M, Z_M) : molecular frame.

2.1 Response potential with correlation and exchange effects

After introduction of correlation and exchange effects, the electric potential in the metal can be seen as the sum of two terms [13,14] :

$$\phi_1(\vec{r},\omega) = \tilde{\phi}_1(\vec{r},\omega) + \phi_{xc}(\vec{r},\omega) \quad (2)$$

where $\tilde{\phi}_1(\vec{r},\omega)$ is the Coulomb potential of existed charges:

$$\tilde{\phi}_1(\vec{r},\omega) = \sum_{\ell} \frac{(-1)^{\ell}}{\ell!} \underline{M}^{(\ell)}(\omega) [\ell] \underline{N}_{\vec{r}}^{(\ell)} \frac{1}{|\vec{r} - \vec{r}_\ell|} \quad (3)$$

and $\phi_{xc}(\vec{r},\omega)$ is the correlation and exchange potential given in the local density approximation (LDA) by [15,16]

$$\phi_{xc}(\vec{r},\omega) = \frac{\partial V_{xc}}{\partial \rho} \delta\rho(\vec{r},\omega). \quad (4)$$

The symbol $[\ell]$ means a contracted tensorial product of order ℓ . In LDA approximation,

the correlation and exchange factor $\left(\frac{\partial V_{xc}}{\partial \rho}\right)$ is

supposed independent on \vec{r} .

In the random phase approximation (RPA), by taking into account the correlation and exchange effects, we can write the induced charge density, in the (k, ω) representation, under the form :

$$\delta\rho_{n,m}(k, \omega) = \sum_{k'}^{\ell} \chi_n^{\ell}(k, k', \omega) \phi_{1n,m}(k', \omega), \quad (5)$$

where $\chi_n^{\ell}(k, k', \omega)$ is the electron gas susceptibility of the metal.

Using Eqs (2) and (4), $\delta\rho_{n,m}$ becomes

$$\delta\rho_{n,m}(k, \omega) = \sum_{k'}^{\ell} \chi_n^{\ell}(k, k', \omega) \left[\tilde{\phi}_{1n,m}(k', \omega) + \frac{\partial V_{xc}}{\partial \rho} \delta\rho_{n,m}(k', \omega) \right]. \quad (6)$$

By use of the matrix

$$P_n(k, k', \omega) = \delta_{k,k'} - \frac{\partial V_{xc}}{\partial \rho} \chi_n^{\ell}(k, k', \omega) \quad (7)$$

the equation (6) can be written as

$$\sum_{k'} P_n(k, k', \omega) \delta\rho_{n,m}(k', \omega) = \sum_{k'}^{\ell} \chi_n^{\ell}(k, k', \omega) \tilde{\phi}_{1n,m}(k', \omega). \quad (8)$$

Then, one gets the following relationship

$$\delta\rho_{n,m}(k, \omega) = \sum_{k'}^{\ell} \tilde{\chi}_n^{\ell}(k, k', \omega) \tilde{\phi}_{1n,m}(k', \omega), \quad (9)$$

where $\tilde{\chi}_n^{\ell}(k, k', \omega)$ is defined by

$$\tilde{\chi}_n^{\ell}(k, k', \omega) = \sum_{k''} P_n^{-1}(k, k'', \omega) \chi_n^{\ell}(k'', k', \omega). \quad (10)$$

We notice that the matrix $\tilde{\chi}_n^{\ell}(k, k', \omega)$ is symmetric. Consequently, the matrix $P_n(k, k', \omega)$ expressed by the relationship (7) is also symmetric and commutes with $\tilde{\chi}_n^{\ell}(k, k', \omega)$. We can then show that the matrix product $\tilde{\chi}_n^{\ell}(k, k', \omega)$ (cf. Eq (10)) is symmetric. Then, $P_n^{-1}(k, k', \omega)$ can be written under the form :

$$P_n^{-1}(k, k', \omega) = \underline{I} + \frac{\partial V_{xc}}{\partial \rho} \tilde{\chi}_n^{\ell}(k, k', \omega) \quad (11)$$

Where \underline{I} is the matrix unity.

Using the Green's identity, a self-consistent equation of the Coulomb potential can be written as [17,18]

$$\sum_{k'} \tilde{E}_n(k, k', \omega) \tilde{\phi}_{1n,m}(k', \omega) = C_{k,n} (b^2 f_n(kb) \tilde{\phi}_{1n,m}'(b, \omega) - a^2 f_n(ka) \tilde{\phi}_{1n,m}'(a, \omega)), \quad (12)$$

where

$$\bar{E}_n(k, k', \omega) = k^2 \delta_{k, k'} - 4\pi \chi_n^\ell(k, k', \omega) - 4\pi \frac{\partial V_{xc}}{\partial \rho} \left(\chi_n^\ell(k, k', \omega) \right)^2 \quad (13)$$

$$\tilde{\phi}'_{1n,m}(r_c, \omega) = \left[\int d\Omega Y_n^{*m}(\Omega) \frac{\partial \tilde{\phi}_1(\vec{r}, \omega)}{\partial r} \right]_{r=r_c}, \quad r_c = a, b. \quad (14)$$

$f_n(kr)$ is a linear combination of regular and irregular spherical Bessel functions j_n and y_n and $C_{k,n}$ is normalization constant defined by

$$\frac{1}{C_{k,n}^2} = \int_a^b r^2 dr [f_n(kr)]^2. \quad (15)$$

The quantity $k^{-2} \bar{E}_n(k, k', \omega)$ can define the dielectric constant of the metallic bubble. The off-diagonal elements ($k \neq k'$) represent the surface effect. By neglecting these elements, we can define a new constant composed of the Lindhard's constant $\varepsilon_{RPA}(k, \omega)$ and another constant making intervene the correlation and exchange effects :

$$\bar{E}_n(k, \omega) = k^2 \left[\varepsilon_{RPA}(k, \omega) - \frac{4\pi V_{xc}}{\partial \rho} \left(\chi_n^\ell(k, \omega) \right)^2 \right] = k^2 \bar{\varepsilon}(k, \omega) \quad (16)$$

with

$$\varepsilon_{RPA}(K, \omega) = 1 - \frac{4\pi}{k^2} \chi_n^\ell(k, \omega) \quad (17)$$

Using an expansion over the spherical harmonics, the Coulomb potential modified by correlation and exchange effects can be written, in (r, ω) representation, as

$$\tilde{\phi}_1(\vec{r}, \omega) = \sum_{n,m} (\bar{F}_n(r, \omega) \tilde{\phi}'_{1n,m}(b, \omega) - \bar{G}_n(r, \omega) \tilde{\phi}'_{1n,m}(a, \omega)) Y_n^m(\Omega) \quad (18)$$

with

$$\bar{F}_n(r, \omega) = b^2 \sum_{k,k'} C_{k,n} C_{k',n} f_n(kr) f_n(k'b) \bar{E}_n^{-1}(k, k', \omega) \quad (19)$$

$$\bar{G}_n(r, \omega) = a^2 \sum_{k,k'} C_{k,n} C_{k',n} f_n(kr) f_n(k'a) \bar{E}_n^{-1}(k, k', \omega) \quad (20)$$

Using the continuity of the potential and its derivative at the vicinity of the inner and the outer surface, the response potential can be respectively written as [16,17]

$$\phi_r(\vec{r}, \omega) = \sum_{n,m} \bar{\Delta}'_n(a, b, \omega) \frac{r^n}{a^{2n+1}} A_{n,m}(\omega) Y_n^m(\Omega) \quad (21)$$

$$\phi_r(\vec{r}, \omega) = \sum_{n,m} \bar{\Delta}'_n(a, b, \omega) \frac{b^{2n+1}}{r^{n+1}} A_{n,m}(\omega) Y_n^m(\Omega) \quad (22)$$

The factors $A_{n,m}(\omega)$ are readily derived from the Cartesian components of the fluctuating multipolar moments $\underline{M}^{(\ell)}(\omega)$, which describe the molecule, by

$$A_{n,m} = T_{n,m}^{(\ell)}[\ell] \underline{M}^{(\ell)}(\omega) \quad (23)$$

The analytical expressions of first Tank tensors $T_{n,m}^{(1)}$, related to the fluctuating dipole located at point \vec{r}_ℓ inside or outside the metallic bubble, are given for $\vec{r}_\ell = (0, 0, R)$, in the Cartesian basis, by

$$\begin{cases} (T_{n,m}^{(1)}(\vec{r}_\ell))_x = \left(\frac{n(n+1)}{2n+1} \pi \right)^{1/2} \frac{(\delta_{m,-1} - \delta_{m,1})}{R^{1-n}} \\ (T_{n,m}^{(1)}(\vec{r}_\ell))_y = i \left(\frac{n(n+1)}{2n+1} \pi \right)^{1/2} \frac{(\delta_{m,-1} + \delta_{m,1})}{R^{1-n}} \\ (T_{n,m}^{(1)}(\vec{r}_\ell))_z = -2n \left(\frac{\pi}{2n+1} \right)^{1/2} \frac{\delta_{m,0}}{R^{1-n}} \end{cases} \quad (24)$$

$$\begin{cases} (T_{n,m}^{(1)}(\vec{r}_\ell))_x^0 = \left(\frac{n(n+1)}{2n+1} \pi \right)^{1/2} \frac{(\delta_{m,-1} - \delta_{m,1})}{R^{1+2}} \\ (T_{n,m}^{(1)}(\vec{r}_\ell))_y^0 = i \left(\frac{n(n+1)}{2n+1} \pi \right)^{1/2} \frac{(\delta_{m,-1} + \delta_{m,1})}{R^{n+2}} \\ (T_{n,m}^{(1)}(\vec{r}_\ell))_z^0 = -2n(n+1) \left(\frac{\pi}{2n+1} \right)^{1/2} \frac{\delta_{m,0}}{R^{n+2}} \end{cases} \quad (25)$$

The reflection factors of order n : $\Delta_n(a, b, \omega)$, which take into account the nonlocality and the correlation and exchange effects of metallic bubble electrons, are given respectively for the inner and the outer surface of the bubble by

$$\bar{\Delta}'_n(a, b, \omega) = \frac{(n+1)^2 \bar{F}_n(a, \omega) \bar{G}_n(b, \omega) + [b + (n+1) \bar{F}_n(b, \omega)] [a - (n+1) \bar{G}_n(a, \omega)]}{n(n+1) \bar{F}_n(a, \omega) \bar{G}_n(b, \omega) - [b + (n+1) \bar{F}_n(b, \omega)] [a + n \bar{G}_n(a, \omega)]} \quad (26)$$

$$\bar{\Delta}_n^0(a, b, \omega) = \frac{n^2 \bar{F}_n(a, \omega) \bar{G}_n(b, \omega) + [a + n \bar{G}_n(a, \omega)] [b - n \bar{F}_n(b, \omega)]}{n(n+1) \bar{F}_n(a, \omega) \bar{G}_n(b, \omega) - [a + n \bar{G}_n(a, \omega)] [b + (n+1) \bar{F}_n(b, \omega)]} \quad (27)$$

2.2. Multipolar propagators

Assuming a linear response of the bubble to fluctuating external sources, the tensors ${}^\ell \underline{S}^\ell(\vec{r}, \vec{r}_\ell, \omega)$ relate the multipolar momentum $\underline{M}^{(\ell)}(\omega)$ to the gradients of the response field in the form [18]:

$$\underline{E}^{(\ell)}(\vec{r}, \omega) = {}^\ell \underline{S}^{\ell'}(\vec{r}, \vec{r}_\ell, \omega) [{}^{\ell'} \underline{M}^{(\ell')}] \quad (28)$$

These propagators can be derived from the

response field gradients:

$$\underline{E}^{(\ell)}(\vec{r}, \omega) = -\underline{\nabla}_{\vec{r}}^{(\ell)} \phi_r(\vec{r}, \omega), \quad (29)$$

where $\Phi_r(\vec{r}, \omega)$ is the response potential of the bubble surface.

By use of the transformation matrix from spherical to Cartesian coordinates, one gets the expression of the multipolar propagators, respectively, at the vicinity of the inner and the outer surface, in the Cartesian basis, set:

$$\underline{S}^{(\ell)}(\vec{r}, \vec{r}', \omega) = -\sum_{n,m} \frac{\Delta_n^l(a, b, \omega)}{a^{2n+1}} \underline{\nabla}_{\vec{r}}^{(\ell)} \{ \mathbf{T}^n \mathbf{Y}_n^m(\Omega) \} \underline{T}_{n,m}^{(\ell)}(\vec{r}') \quad (30)$$

$$\underline{S}^{(\ell)}(\vec{r}, \vec{r}', \omega) = -\sum_{n,m} b^{2n+1} \Delta_n^0(a, b, \omega) \underline{\nabla}_{\vec{r}}^{(\ell)} \left\{ \frac{\mathbf{Y}_n^m(\Omega)}{r^{n+1}} \right\} \underline{T}_{n,m}^{(\ell)}(\vec{r}') \quad (31)$$

where $\underline{\nabla}_{\vec{r}}^{(\ell)}$ is the gradient operator of order ℓ in the Cartesian basis. Note that the propagators $\underline{S}^{(\ell)}(\vec{r}, \vec{r}', \omega)$, also called 'Electric-field susceptibility', take into account only the intrinsic properties of the surface.

III. APPLICATION TO THE VAN DER WAALS ENERGY OF A MOLECULE

The van der Waals energy $V(\vec{R})$ of a molecule, whose centre of mass G is located at point $\vec{r}_r = \vec{R}$ with respect to the centre O of the spherical bubble (see. Fig 1), is a sum of inductive ($V_i(\vec{R})$) and dispersive ($V_d(\vec{R})$) contributions [19]:

$$V(\vec{R}) = V_i(\vec{R}) + V_d(\vec{R}) \quad (32)$$

where

$$V_i(\vec{R}) = -\frac{1}{2} \underline{\mu} \cdot \underline{S}^1(\vec{R}, \vec{R}, 0) \cdot \underline{\mu} + \frac{1}{3} \underline{\mu} \cdot \underline{S}^2(\vec{R}, \vec{R}, 0) \cdot \underline{\mu} + \dots \quad (33)$$

$$V_d(\vec{R}) = \frac{\hbar}{2\pi} \sum_{\ell_1, \ell_2} \frac{1}{(2\ell_1 - 1)!!} \times \int_0^\infty d\xi \xi^{\ell_1} \underline{\alpha}^{\ell_2}(\xi) [\ell_1 + \ell_2] \xi^{\ell_2} \underline{S}^{\ell_2}(\vec{R}, \vec{R}, i\xi) \quad (34)$$

$\underline{\chi}^{\ell_1 \ell_2}(\xi)$ is the molecular polarizability tensor in the absolute frame (O, X, Y, Z) tied to the spherical bubble. The symbol $[\ell_1 + \ell_2]$ means a contracted tensorial product of order $\ell_1 + \ell_2$ is an imaginary frequency. In the inductive contribution, $\underline{\mu}$, and $\underline{\Theta}$ denote the permanent dipole and quadrupole moments of the molecule.

From Eqs (33) and (34) it is seen that the dipolar contribution of the van der Waals energy can be written as

$$V^{(1)}(\vec{R}) = V_i^{(1)}(\vec{R}) + V_d^{(1)}(\vec{R}) \quad (35)$$

with

$$V_i^{(1)}(\vec{R}) = -\frac{1}{2} \underline{\mu} \cdot \underline{S}^1(\vec{R}, \vec{R}, 0) \cdot \underline{\mu}, \quad (36)$$

$$V_d^{(1)}(\vec{R}) = \frac{\hbar}{2\pi} \int_0^\infty d\xi \xi^1 \underline{\alpha}^1(i\xi) [2] \underline{S}^1(\vec{R}, \vec{R}, i\xi) + \frac{\hbar}{6\pi} \int_0^\infty d\xi \xi^2 \underline{\alpha}^1(i\xi) [3] \underline{S}^1(\vec{R}, \vec{R}, i\xi). \quad (37)$$

Using Eqs (30) and (31) together with Eqs (24) and (25), one can write the dipolar contributions of the van der Waals energy $V_i^{(1)}(\vec{R})$ and $V_d^{(1)}(\vec{R})$, for $\vec{R} = (0, 0, R)$, as

(i) a molecule inside a bubble

$$V_i^{(1)}(R) = \frac{\mu^2}{2R^3} \sum_n \Delta_n^1(a, b, 0) \left(\frac{R}{a} \right)^{2n+1} \times \left(\frac{n(n+1)}{2} \sin^2 \theta + n^2 \cos^2 \theta \right), \quad (38)$$

$$V_d^{(1)}(R) = -\frac{\hbar}{2\pi R^3} \sum_n n \left(\frac{R}{a} \right)^{2n+1} \int_0^\infty d\xi \Delta_n^1(a, b, i\xi) \times \left\{ \begin{aligned} & \times \left[\alpha_{//}^1(i\xi) \left(\frac{n+1}{2} \sin^2 \theta + n \cos^2 \theta \right) + \alpha_{\perp}^1(i\xi) \left(\frac{n+2}{2} (1 + \cos^2 \theta) + n \sin^2 \theta \right) \right. \\ & \left. + \frac{n-1}{3R} \cos \theta \left[\alpha_{//}^2(i\xi) \left(\frac{n+2}{2} \sin^2 \theta + n \cos^2 \theta \right) + \alpha_{\perp}^2(i\xi) \left(\frac{n+2}{2} (3 \cos^2 \theta - 1) + 3n \sin^2 \theta \right) \right] \right] \end{aligned} \right\} \quad (39)$$

(ii) a molecule outside a bubble

$$V_i^{(1)}(R) = \frac{\mu^2}{2R^3} \sum_n \Delta_n^0(a, b, 0) \left(\frac{b}{R} \right)^{2n+1} \times \left(\frac{n(n+1)}{2} \sin^2 \theta + (n+1)^2 \cos^2 \theta \right), \quad (40)$$

$$V_d^{(1)}(R) = -\frac{\hbar}{2\pi R^3} \sum_n (n+1) \left(\frac{b}{R} \right)^{2n+1} \int_0^\infty d\xi \Delta_n^0(a, b, i\xi) \times \left\{ \begin{aligned} & \times \left[\alpha_{//}^1(i\xi) \left(\frac{n}{2} \sin^2 \theta + (n+1) \cos^2 \theta \right) + \alpha_{\perp}^1(i\xi) \left(\frac{n}{2} (1 + \cos^2 \theta) + (n+1) \sin^2 \theta \right) \right. \\ & \left. - \frac{n+2}{3R} \cos \theta \left[\alpha_{//}^2(i\xi) \left(\frac{n-1}{2} \sin^2 \theta + (n+1) \cos^2 \theta \right) + \alpha_{\perp}^2(i\xi) \left(\frac{n-1}{2} (3 \cos^2 \theta - 1) + 3(n+1) \sin^2 \theta \right) \right] \right] \end{aligned} \right\} \quad (41)$$

The molecule is referred to the absolute frame (O, X, Y, Z) by its Euler angles θ and φ (cf. Fig1). Trough the above procedure, φ disappears in the final expression implying a cylindrical symmetry of the molecule-bubble system.

IV. NUMERICAL CALCULATIONS

4.1 Modelization of the interacting partners

The parallel and perpendicular polarizabilities of the molecule, $\alpha_{//}^1(i\xi)$, $\alpha_{\perp}^1(i\xi)$, $\alpha_{//}^2(i\xi)$ and $\alpha_{\perp}^2(i\xi)$ can be evaluated from the three-dimensional anisotropic oscillator model [20]

$${}^1\alpha_{//\perp}^1(\omega) = \frac{{}^1\alpha_{//\perp}^1(0)\omega_{//\perp}^2}{\omega_{//\perp}^2 + \xi^2}, \quad (42)$$

$${}^2\alpha_{//\perp}^1(\omega) = \frac{{}^2\alpha_{//\perp}^1(0)\omega_{//\perp}^2}{\omega_{//\perp}^2 + \xi^2}. \quad (43)$$

Numerical values of the static polarizabilities ${}^1\alpha_{//}^1(0)$, ${}^1\alpha_{\perp}^1(0)$, ${}^2\alpha_{//}^1(0)$ and ${}^2\alpha_{\perp}^1(0)$ together with the corresponding frequencies $\omega_{//}$ and ω_{\perp} are given in Table 1.

The functions $\bar{F}_n(r, i\xi)$ and $\bar{G}_n(r, i\xi)$, which are involved in the expression of the reflection factors (Eqs (26) and (27)), can be determined in principle within the framework of RPA and LDA approximations, by inverting the dielectric constant matrix $\bar{E}_n(k, k', i\xi)$. Nevertheless, neglecting the off-diagonal terms, one gets a simple relationship between the diagonal terms and the dielectric constant taking into account the correlation and exchange effects,

$$\bar{E}_n(k, k', i\xi) = k^2 \bar{\epsilon}(k, i\xi) \delta_{k, k'} \quad (44)$$

By use of the hydrodynamical model [16,21,22] for the spatial dispersion, one gets from Eqs (16) and (17) the following expression for $\bar{\epsilon}(k, i\xi)$:

$$\bar{\epsilon}(k, i\xi) = 1 + \frac{\omega_p^2 - k^2 \delta_{xc}^2(i\xi)}{\xi^2 + k^2 \delta^2}, \quad (45)$$

with

$$\delta_{xc}^2(i\xi) = \frac{\xi^2 + 2\omega_p^2}{4\pi} \frac{\partial V_{xc}}{\partial \rho} = \frac{2\omega_p^2 + \xi^2}{9} \left[1.222\alpha_s^2 + \frac{0.75924\alpha_s^3}{\epsilon + 1.4} \right] \quad (46)$$

ω_p is the free-electron plasma frequency ; δ is a parameter related to the Fermi velocity :

$$\delta \approx \sqrt{3/5} v_F \text{ and } r_s = [3/4\pi\rho]^{1/3} \text{ is the mean electronic density of the metal [14].}$$

This model, describing the non-local behaviour and the correlation and exchange effects of the electrons within the metal, requires numerical parameters ω_p , δ and r_s (see. Table 2). By replacing the discrete sum in Eqs (19) and (20) by an integral over k , one gets analytical expressions for $\bar{\Delta}_n^i(a, b, i\xi)$ and $\bar{\Delta}_n^0(a, b, i\xi)$:

$$\bar{\Delta}_n^i(a, b, i\xi) = (b^{2n+1} - a^{2n+1}) X \left[\frac{n^2 \bar{g}_n(a, i\xi) + 1}{n(n+1) \bar{g}_n(a, i\xi) - 1} b^{2n+1} - \frac{n(n+1) \bar{g}_n(a, i\xi) - 1}{(n+1)^2 \bar{g}_n(a, i\xi) + 1} a^{2n+1} \right]^{-1}, \quad (47)$$

$$\bar{\Delta}_n^0(a, b, \omega) = (b^{2n+1} - a^{2n+1}) X \left[\frac{(n+1)^2 \bar{g}_n(b, \omega) + 1}{n(n+1) \bar{g}_n(b, \omega) - 1} b^{2n+1} - \frac{n(n+1) \bar{g}_n(b, \omega) - 1}{n^2 \bar{g}_n(b, \omega) + 1} a^{2n+1} \right]^{-1} \quad (48)$$

where

$$\bar{g}_n(r, i\xi) = \frac{1}{n(n+1)} \left[\frac{1}{\epsilon_m(i\xi)} + \bar{f}_n(r, i\xi) \right] \quad (49)$$

with

$$\bar{f}_n(r, i\xi) = \frac{2n+1}{\delta^2 - \delta_{xc}^2(i\xi)} \left(\left(\frac{r\omega_p}{\bar{u}(r, i\xi)} \right)^2 + \delta_{xc}^2(i\xi) \right) I_{n+1/2}(\bar{u}) K_{n+1/2}(\bar{u}) \quad (50)$$

$$\bar{u}(r, i\xi) = r \sqrt{\frac{\omega_p^2 + \xi^2}{\delta^2 - \delta_{xc}^2(i\xi)}} \quad (51)$$

and

$$\epsilon_m(i\xi) = 1 + \frac{\omega_p^2}{\xi^2}. \quad (52)$$

$I_{n+1/2}$ and $K_{n+1/2}$ are modified Bessel functions.

In absence of correlation and exchange effects ($\partial V_{xc}/\partial \rho = 0$) :

$$\bar{f}_n(r, i\xi) \equiv f_n(r, i\xi) = (2n+1) \left(\frac{r\omega_p}{\delta u(r, i\xi)} \right)^2 I_{n+1/2}(u) K_{n+1/2}(u), \quad (53)$$

with

$$u(r, \omega) = \frac{r}{\delta} \sqrt{\omega_p^2 + \xi^2} \quad (54)$$

Note that the local limit can be readily obtained by making $I_{n+1/2}(\bar{u}) K_{n+1/2}(\bar{u}) = 0$; then g_n becomes independent on r ,

$$g_n(r, i\xi) \equiv g_n(i\xi) = \frac{1}{n(n+1)\epsilon_m(i\xi)}. \quad (55)$$

	$\mu(D)$	$\omega_p(a.u.)$	$\omega_{\perp}(a.u.)$	$\alpha_{//}(a.u.)$	$\alpha_{\perp}(a.u.)$	${}^1\alpha_{\perp}^2(a.u.)$	${}^1\alpha_{\perp}^2(a.u.)$
HF	1.736	1.561	0.375	5.2	3.84	2.193	0.319
HCl	1.08	0.737	0.898	14.08	4.27	12.408	2.015

Table 1: Molecular parameters, from Ref.[20]

	$\omega_p^a(a.u.)$	$\delta^a(a.u.)$	$r_s^b(a.u.)$
Al	0.562	0.697	2.07
Ag	0.845	1.031	

Table2: Metallic parameters, from Refs.^a[23], ^b[24]

4.2 Results

The van der Waals energies are calculated using Eqs (38)-(55) together with the numerical data of Tables 1 and 2, for (HF,HCl) molecules adsorbed in (Al,Ag) spherical bubbles.

(i) Figs 2a and b illustrate the influence of the orientation of the molecule on $V^{(1)}$ as well as the difference between the local and no local response

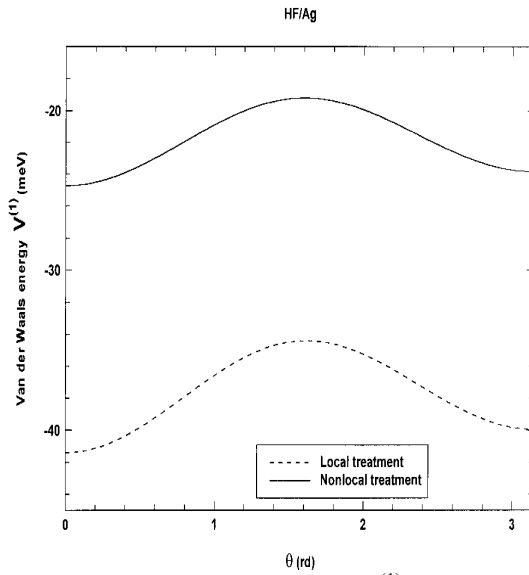


Figure 2a: Van der Waals energy $V^{(1)}$ as functions of the Euler angle θ in the case of HF molecule at a distance $R=a-6$ au from the center O of an Ag bubble of radii $a=30$ au and $b=40$ au.

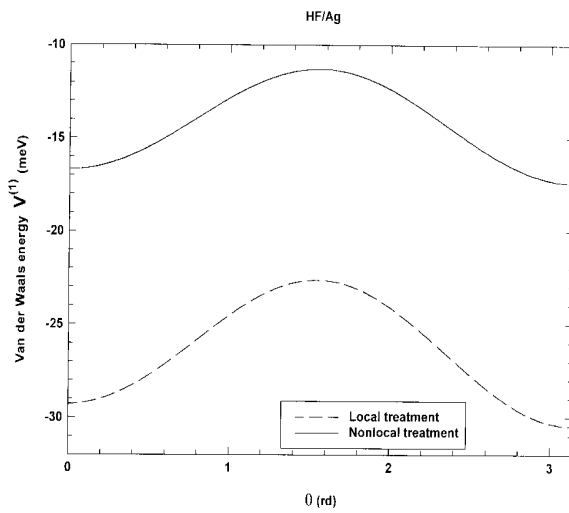


Figure 2b: Van der Waals energy $V^{(1)}$ as functions of the Euler angle θ in the case of HF molecule at a distance $R=b+6$ au from the center O of an Ag bubble of radii $a=30$ au and $b=40$ au.

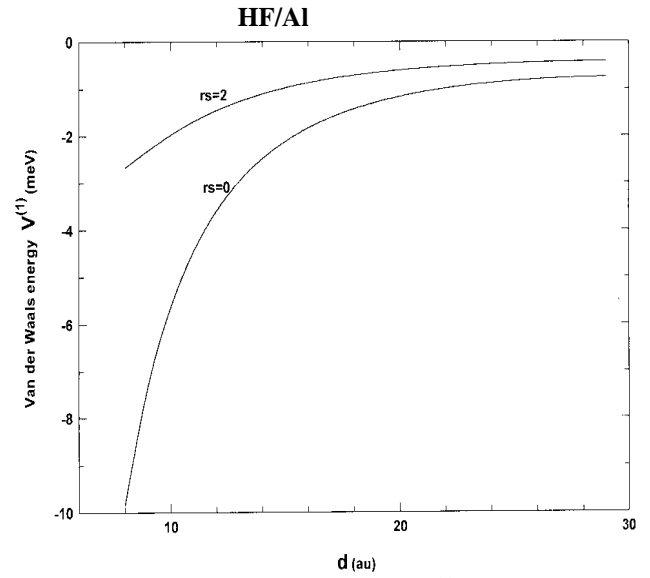


Figure 3a: Van der Waals energy $V^{(1)}$ for HF molecule inside an Al bubble ($a=30$ au and $b=40$ au) as function of the distance d to the inner sphere.

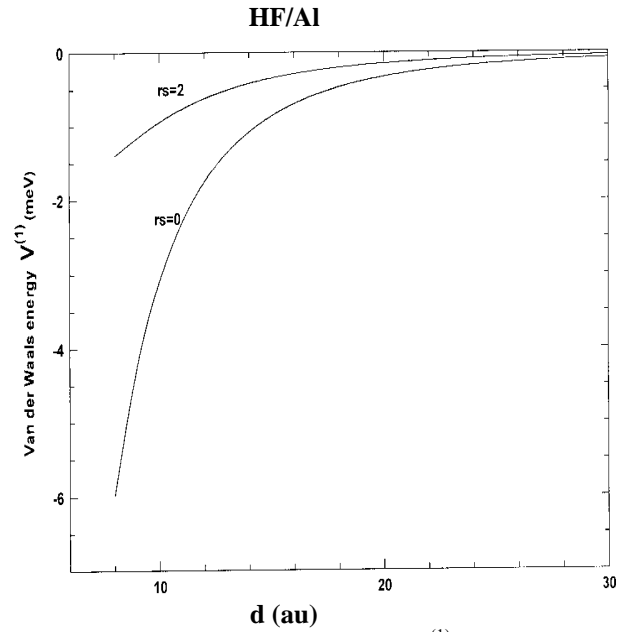


Figure 3b: Van der Waals energy $V^{(1)}$ for HF molecule outside an Al bubble ($a=30$ au and $b=40$ au) as function of the distance d to the outer sphere.

of the metal electrons. However, the anisotropy of the interaction introduces a dependence of the van der Waals energies $V^{(1)}$ on the first Euler angle θ .

One sees from Figs 2a and b that $|V^{(1)}|$ is maximum when $\theta=0$ and $\theta=\pi$, obtained in other investigations [16,22,25]; in this calculation, the configurations $\theta=0$ and $\theta=\pi$, are not equivalent. This slight difference between the two configurations comes owing to the fact that in our calculation we held account also the third rank polarizability tensors: α^2 .

(ii) In Figs 3a and b, $V^{(1)}$ is plotted, in the case of $\theta=0$, as a function of d , the distance from the dipole source to the inner or outer spheres of an Al bubble ($a=30$ au, $b=40$ au), for a HF molecule. In this calculation, we have introduced the correlation and exchange effects of the electron response inside the metal. Figs 3a and b show that the correlation and exchange effects significantly reduce the Van der Waals energies. Here, at a distance of approach $d=10$ au and for radii ($a=30$ au, $b=40$ au), a reduction by a factor of about 3 is observed. Neglecting the correlation and exchange effects may then results into a strong overestimate of van der Waals energies.

(iii) Finally, in Figs 4a and b, the HCl-Ag systems are respectively studied for fixed values ($a=30$ au, $R=a+6$ au) and ($b=40$ au, $R=b+6$ au). In Figs 4a, the energy is plotted as a function of b ($b \geq a$). It is seen that $V^{(1)}$ approaches its limiting value, i.e. the energy corresponding to a spherical cavity in an infinite medium at relatively low values of b , which shows that the effect induced by the source in the solid is actually restricted to a rather thin spherical sheet. In Figs 4b, the energy is plotted as a function of a (a is varied from 0 to b). For $a=0$, one recovers the value of $V^{(1)}$ of a molecule outside a filled spheroid. On the other hand, as expected, $V^{(1)}=0$ for $a=b$.

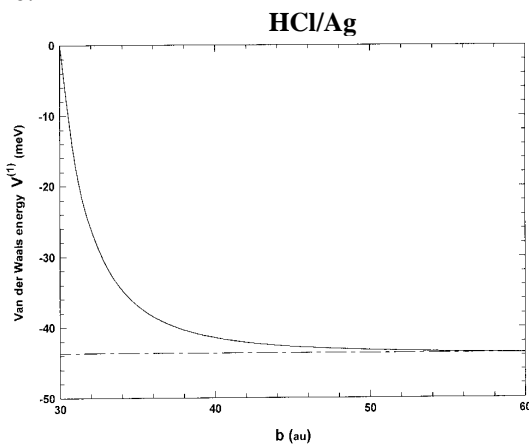


Figure 4a: $V^{(1)}$ as a function of the outer radius b ; $a=30$ au; $R=24$ au. The asymptotic value at large b corresponds to a molecule inside a spherical cavity in an infinite medium (broken line).

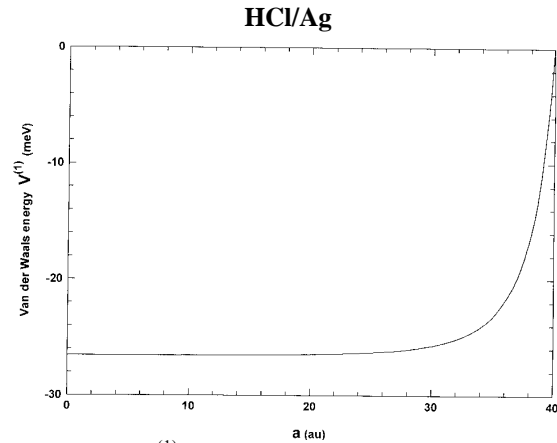


Figure 4b: $V^{(1)}$ as a function of the inner radius a ; $b=40$ au; $R=46$ au. The value at $a=0$ corresponds to a molecule outside a filled spheroid.

5. Conclusion

In this paper, we have presented the dipolar contribution to induction and dispersion energy of diatomic molecules adsorbed on metallic bubbles. The calculation of this energy required the determination of the electric field susceptibility of the spherical bubble surface, based upon the spherical-tensor theory and the RPA and LDA approximations, as well as the determination of second and third rank polarizability tensors of the molecule. These tensors are directly related, through the first Euler angle θ , to the influence of the molecular orientation on the energy. This investigation has been then completed by a numerical study including correlation and exchange effects of the electron response inside the metal.

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