

Response function approach to van der Waals' interaction between atom and metal surface

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Abstract. Van der Waals' attractive interaction between a neutral atom and a metal surface (semi-infinite jellium) is studied via dielectric response approach in the non-retarded limit. It is shown that the interaction energy can be written in terms of the same form factor $F(k, \omega)$, which appears in the formula for dynamic image potential and which depends on the density-density response function of only the metal. The interaction energy written as the change in the zero-point energy of the electromagnetic fluctuations is expressed in terms of a secular determinant whose elements consist of the response function of the metal and the dynamic polarizability of the atom. The usual classical result is obtained when the coupling between the atom and metal is small. In the present analysis, it is shown that for short atom-metal separations, this coupling is important and yields substantial modification over the classical result. Numerical results for such situations are presented for the non-dispersive description of metal and a few inert gas atoms.

Keywords. Form factor; response function; atomic polarizability.

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1. Introduction

An atom or a molecule placed outside a metal surface interacts with the surface via dispersion or van der Waals' (vdW) forces, when the distance between them is large enough to neglect the overlapping of the electronic wavefunctions of the metal and atom. This forms the attractive part of the total interaction and as distance decreases the repulsive part dominates. There is a great spurt in the studies of vdW interaction because of the recent developments in the experimental techniques and increasing applications of metal surfaces in chemical reactions and energy studies. The recent atomic and molecular beam scattering studies (Shih *et al* 1974; Shih 1974; Perreau and Lapujoulade 1982; Mason *et al* 1983; Hill *et al* 1982) and adsorption experiments (Luntz *et al* 1982) on metallic surfaces provide some of the experimental studies. The classical formula for vdW interaction energy based on the method of images was first given by Lennard-Jones (1932) and is of the form (in atomic units, $\hbar = e^2 = m = 1$),

$$E_I^{\text{cl}} = -\frac{\langle r^2 \rangle}{12|z|^3} = -\frac{\omega_0 \alpha^a}{8|z|^3}, \quad (1)$$

where $|z|$ is the distance between the atom and the metal surface, $\langle r^2 \rangle$ is the mean-square displacement of electrons in the atom or molecule, ω_0 an average excitation

energy and α^a is the static polarizability of the atom or molecule. Similar results were obtained subsequently by Bardeen (1940) and Margenau and Pollard (1941) via perturbative approach, except for a multiplying factor (see equation (31) later) which could make the interaction energy smaller than the one obtained from the image method. There exists extensive literature on the subject and we refer the interested reader to the list of references given at the end (in particular, Mahanty and Ninham 1973; Langbein 1974; Mukhopadhyay and Mahanty 1975; Zaremba and Kohn 1976, 1977; Mehl and Schaich 1977, 1980; Harris and Liebsch 1982; Grover 1978; Apell 1981; Persson and Apell 1983; Bruch 1983; Garcia *et al* 1983; Holmberg and Apell 1984). All the existing theoretical work has concentrated on the semi-infinite jellium description of metal, and correction to the z^{-3} dependence at shorter distances, especially in terms of the so called dynamic image-plane position (Zaremba and Kohn 1976, 1977). In this paper, we also regard the metal as a semi-infinite jellium, and use the dielectric response approach in the non-retarded limit, to study the vdW interaction at shorter distances. A brief account of this has appeared elsewhere (Rao and Mukhopadhyay 1984) and we present here the details.

In the following section we develop the theory and obtain an expression for the vdW interaction energy in terms of a form factor which is characteristic of the metallic system only. We note here that this form factor is exactly the same form factor that appears in the evaluation of the dynamic image potential formula (Rao *et al* 1984). Later we calculate the vdW interaction energy in the classical non-dispersive case by solving the secular determinant (see equation (4) later) directly to obtain the eigenvalues, which corresponds to the zero-point energy of the electromagnetic fluctuations. The interaction energy is obtained as the change in the zero point energy, and finally we calculate the vdW interaction in the classical non-dispersive case for a few inert gases outside a metal surface to estimate the difference between the classical formula and the formula derived here.

2. Theory

We consider here a system of a neutral atom placed in vacuum outside a metal surface that is described by a semi-infinite jellium extended in the $z > 0$ region ($z = 0$ defines the edge of the positive background) with the x - y plane parallel to the planar surface. The atom is approximated by a point dipole and the distance between the atom and surface considered is not too large to have significant retardation effects.

The calculation of the vdW interaction usually proceeds along the following lines (for brevity, the spatial dependence is suppressed in the subsequent discussions): For a time-dependent electric field at the atom, the metal responds via the metallic response function and produces a polarizing field at the atom. However, in the absence of any external field, the atom can generate a self-induced polarization field \mathbf{P} via the metal, which we express as,

$$P_i(t) = \int R_{ij}(t-t')P_j(t') dt', \quad (2)$$

where R_{ij} is the response tensor that connects the fields, and i, j are the labels x, y, z referring to the Cartesian components of the fields (sum over repeated indices are understood throughout). The temporal Fourier transform of this equation gives,

$$P_i(\omega) = R_{ij}(\omega)P_j(\omega), \quad (3)$$

so that,

$$D(\omega) = \det |\delta_{ij} - R_{ij}(\omega)| = 0, \quad (4)$$

is the condition for the eigenmodes of the electromagnetic fields of the coupled metal-atom system. The vdW interaction energy E_I is then written as the change in the zero-point energy contribution from these eigenmodes as the separation z between the metallic surface and the centre of the atom is changed from infinity (i.e., no coupling between metal and atom) to a finite value z :

$$E_I(z) = \frac{1}{2} \sum_i [\omega_i(z) - \omega_i(z \rightarrow \infty)] \quad (5)$$

where the sum is over all the eigenmodes ω_i , which are physical (i.e., real positive ω_i) solutions of (4). Note that the determinant $D(\omega)$ in (4) represents the ratio of the secular determinants for the electromagnetically coupled system (i.e., finite separation between metal and atom) to that of the uncoupled system (i.e., infinite separation) here. This means that the zeros of $D(\omega)$ correspond to the eigenmodes of the coupled system while the poles correspond to the eigenmodes of the uncoupled system (Mahanty and Ninham 1973; see also Langbein 1974). These properties of $D(\omega)$ are utilized to rewrite (5) as

$$E_I(z) = \frac{1}{2\pi i} \oint d\omega \frac{\omega}{2} \frac{d}{d\omega} \ln D(\omega) = \int_0^\infty \frac{du}{2\pi} \ln D(iu). \quad (6)$$

Usually it is further assumed that $|R_{ij}(iu)| \ll 1$, so that, $\ln D \simeq \sum_i R_{ii}$, and therefore,

$$E_I(z) = - \int_0^\infty \frac{du}{2\pi} \sum_i R_{ii}(iu), \quad (7)$$

which is the most commonly used formula for calculating the vdW interaction energy.

For the metal-atom system, let $G_{kj}(\mathbf{x}, \mathbf{x}', \omega)$ be the k th Cartesian component of the electric field at \mathbf{x} due to the j th component of a unit dipole source at \mathbf{x}' oscillating with frequency ω , and $\alpha_{ik}^a(\omega)$ be the frequency-dependent polarizability tensor of the atom. Then it follows that, (Mukhopadhyay and Mahanty 1975),

$$\begin{aligned} R_{ij}(\omega) &= - \sum_k \alpha_{ik}^a(\omega) G_{kj}(\mathbf{x}', \mathbf{x}', \omega), \\ &= - \alpha^a(\omega) G_{ij}(\mathbf{x}', \mathbf{x}', \omega), \end{aligned} \quad (8)$$

assuming that the atom is spherically symmetric in its ground state, so that $\alpha_{ij}^a(\omega) = \alpha^a(\omega) \delta_{ij}$. This means that one has to essentially determine G_{ij} from the response behaviour of the metallic surface. For a metallic system as specified earlier, the tensor G_{ij} is obtained within the linear response theory as follows:

In the linear response theory, the induced charge density $\rho_{\text{ind}}(\mathbf{x}, \omega)$ in the metal is related to the external charge density $\rho_{\text{ext}}(\mathbf{x}', \omega)$ as,

$$\rho_{\text{ind}}(\mathbf{x}, \omega) = \int \frac{d\mathbf{x}' d\mathbf{x}''}{|\mathbf{x}' - \mathbf{x}''|} \chi(\mathbf{x}, \mathbf{x}'', \omega) \rho_{\text{ext}}(\mathbf{x}', \omega), \quad (9)$$

where χ is the density-density response function of the metallic system. Now for a unit

dipole source at \mathbf{x}_0 ,

$$\rho_{\text{ext}}(\mathbf{x}, \omega) = \mathbf{e} \cdot \nabla_{\mathbf{x}} \delta(\mathbf{x} - \mathbf{x}_0), \tag{10}$$

where \mathbf{e} is a unit vector along the direction of the unit dipole. This gives,

$$\rho_{\text{ind}}(\mathbf{x}, \omega) = -\mathbf{e} \cdot \nabla_{\mathbf{x}_0} \alpha(\mathbf{x}, \mathbf{x}_0, \omega), \tag{11}$$

where,

$$\alpha(\mathbf{x}, \mathbf{x}', \omega) = \int \frac{\chi(\mathbf{x}, \mathbf{x}'', \omega)}{|\mathbf{x}'' - \mathbf{x}'|} d\mathbf{x}'' \tag{12}$$

Since the electric field due to $\rho_{\text{ind}}(\mathbf{x}, \omega)$ is,

$$E(\mathbf{x}, \omega) = -\nabla_{\mathbf{x}} \int \frac{d\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho_{\text{ind}}(\mathbf{x}', \omega), \tag{13}$$

it follows from the definition of the tensor G_{ij} that,

$$G_{ij}(\mathbf{x}, \mathbf{x}_0, \omega) = \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_{0j}} \int \frac{d\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \alpha(\mathbf{x}', \mathbf{x}_0, \omega). \tag{14}$$

This is then the general expression for G_{ij} within the point dipole approximation for the atom.

For a metal with planar surface described by the semi-infinite jellium, the response properties have translational invariance in the x - y plane parallel to the metal surface. It is then convenient to introduce a two-dimensional Fourier transform in x - y variables and write

$$\chi(\mathbf{x}, \mathbf{x}', \omega) = \int \frac{d\mathbf{k}}{(2\pi)^2} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \chi(k, z, z', \omega), \tag{15}$$

where \mathbf{r}, \mathbf{r}' are the polar vectors in the x - y plane (i.e., $\mathbf{x} = (\mathbf{r}, z), \mathbf{x}' = (\mathbf{r}', z')$) and \mathbf{k} is the Fourier wave vector. From the definition (12) it follows that a similar Fourier transform for α can be written down. In terms of these Fourier transforms, G_{ij} given by (14) now takes the following form for a semi-infinite jellium:

$$G_{ij}(\mathbf{x}, \mathbf{x}_0, \omega) = \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_{0j}} \int \frac{d\mathbf{k} dz'}{(2\pi)^2} \alpha(k, z', z_0, \omega) \frac{2\pi}{k} \exp[-k|z - z'|] \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)], \tag{16}$$

where,

$$\alpha(k, z, z', \omega) = \int_{-\infty}^{\infty} dz'' \chi(k, z, z'', \omega) \frac{2\pi}{k} \exp[-k|z'' - z'|]. \tag{17}$$

We note here that $\chi(k, z, z', \omega)$ vanishes for z or z' outside the metal and therefore $\alpha(k, z, z', \omega)$ vanishes for z outside the metal. From (16) we have,

$$G_{zz}(\mathbf{x}_0, \mathbf{x}_0, \omega) = \int_0^{\infty} dk k \int_{-\infty}^{\infty} dz' \exp[-k|z_0 - z'|] [-\text{sgn}(z_0 - z')] \times \frac{\partial}{\partial z_0} \alpha(k, z', z_0, \omega),$$

$$= \int_0^\infty dk k \left(\frac{\partial}{\partial z_0} - k \right) \int_{-\infty}^\infty dz' \exp[(-k|z_0 - z'|)] \alpha(k, z', z_0, \omega). \quad (18)$$

using $\text{sgn}(z_0 - z') = -1$ for z_0 outside the metal. We now introduce a form factor $F(k, \omega)$ defined as,

$$F(k, \omega) = \int_{-\infty}^\infty dz' \exp[k(z_0 + z')] \alpha(k, z', z_0, \omega), \quad (19)$$

for z_0 outside the metal. This is exactly the same form factor that enters the dynamic image potential formula (Rao *et al* 1984), and is independent of z_0 as long as z_0 is located outside the metal surface. Since $\alpha(k, z, z', \omega)$ vanishes for z outside the metal, it follows that the second integral in (18) equals $F(k, \omega) \cdot \exp(2kz_0)$ and therefore, (18) reduces to,

$$\begin{aligned} G_{zz}(\mathbf{x}_0, \mathbf{x}_0, \omega) &= \int_0^\infty dk k^2 \exp(2kz_0) F(k, \omega) \\ &\equiv G(\mathbf{x}_0, \mathbf{x}_0, \omega). \end{aligned} \quad (20)$$

Following a similar procedure, we obtain from (16), for $z_0 < 0$,

$$G_{xx} = G_{yy} = \frac{1}{2} G_{zz} \equiv \frac{1}{2} G, \quad (21)$$

and,

$$G_{xy} = G_{yz} = G_{zx} = 0, \quad (22)$$

where the arguments $(\mathbf{x}_0, \mathbf{x}_0, \omega)$ are suppressed for brevity. These results along with (7) and (8) then yields,

$$E_I(z) = 2 \int_0^\infty \frac{du}{2\pi} \alpha^2(iu) G(\mathbf{x}, \mathbf{x}, iu). \quad (23)$$

The form factor $F(k, \omega)$ in (20) is characteristic of the metallic system only, and thus once the form factor is known for the system, it is easy to determine the vdW interaction energy. The form factor depends on the density-density response function χ of the metal surface. Construction of χ itself is a formidable task and involves one electron wave functions for the realistic description of the semi-infinite jellium. However, for studying the qualitative features, an approximate model such as the so-called semi-classical infinite barrier (SCIB) model is useful (Mukhopadhyay 1978; Mukhopadhyay and Lundqvist 1978). In this model, the ground state electron density profile coincides with the step-like positive background of the semi-infinite jellium, and the form factor takes a simple analytic form in terms of surface dielectric function (for details, see Rao and Mukhopadhyay 1984):

$$F(k, \omega) = \frac{1 - \varepsilon_s(k, \omega)}{1 + \varepsilon_s(k, \omega)}, \quad (24)$$

where,

$$\varepsilon_s^{-1}(k, \omega) = \frac{k}{\pi} \int_{-\infty}^\infty \frac{dp}{k^2 + p^2} \frac{1}{\varepsilon_B(q, \omega)}, \quad (25)$$

with $q^2 = k^2 + p^2$ and $\epsilon_B(q, \omega)$ is the dielectric function in random phase approximation (RPA) for a infinite homogeneous electron system (jellium) with an electron density equal to that of the metallic system deep inside.

In the following, we obtain the vdW energy first in the classical non-dispersive case and later in the dispersive case (SCIB model) within the limit $|R_{ij}| \ll 1$. Then we obtain the exact expression for the vdW energy by solving directly for eigenvalues in the classical non-dispersive case.

2.1 Classical non-dispersive case

In the classical case, where the metallic system is regarded as non-dispersive, the surface dielectric function ϵ_s equals the corresponding bulk form, i.e., $\epsilon_s = \epsilon_B = 1 - \omega_p^2/\omega^2$, where ω_p is the bulk plasmon frequency. Then the form factor becomes,

$$F_{cl} = \frac{\omega_s^2}{\omega^2 - \omega_s^2}, \quad (26)$$

where $\omega_s = \omega_p/\sqrt{2}$ is the surface plasmon frequency. Then from (20), (23) and (26), we obtain the usual classical result as,

$$E_I(z) = -\frac{\omega_s^2}{4\pi|z|^3} \int_0^\infty du \frac{\alpha^a(iu)}{\omega_s^2 + u^2}. \quad (27)$$

If we assume that the atomic polarizability is given by,

$$\alpha^a(\omega) = \sum_n \frac{f_n}{\omega_n^2 - \omega^2}, \quad (28)$$

where f_n is the dipolar oscillator strength and ω_n is the n th excitation frequency of the atom, then (27) reduces to,

$$E_I(z) = -\frac{1}{8|z|^3} \sum_n \frac{f_n}{\omega_n} \left(\frac{\omega_s/\omega_n}{1 + \omega_s/\omega_n} \right). \quad (29)$$

If we further assume that only one frequency, say ω_0 is contributing significantly to $\alpha^a(\omega)$, then

$$\alpha^a = f_0/\omega_0^2 \quad \text{or} \quad \omega_0 \alpha^a = f_0/\omega_0 = \frac{2}{3} \langle r^2 \rangle, \quad (30)$$

where $\langle r^2 \rangle$ has been defined before in (1). Therefore,

$$E_I(z) = -\frac{\langle r^2 \rangle}{12|z|^3} \left(\frac{\omega_s/\omega_0}{1 + \omega_s/\omega_0} \right), \quad (31)$$

which reduces to (1) if $\omega_s/\omega_0 \gg 1$. This result is the standard one.

2.2 Dispersive case (SCIB model)

In the dispersive description of the metal, (i.e., in the SCIB model here) although the formula (23) is a compact one, the evaluation of ϵ_s and thereby E_I remains a difficult task. This is because ϵ_s itself has a complicated structure. We therefore concentrate on the

order of magnitude effect rather than the actual numerical effect, by using an approximate form for ε_s given by Sunjic *et al* (1972) as,

$$\varepsilon_s(k, \omega) = 1 + \left[\frac{k^2}{\kappa^2} + \frac{k}{\kappa} - \frac{\omega^2}{\omega_p^2} \right]^{-1}, \quad (32)$$

where κ is the Thomas-fermi wave vector ($\kappa \rightarrow \infty$ corresponds to the classical case). In this case, we obtain the form factor as,

$$F(k, iu) = -\frac{1}{2} \frac{1}{k^2/\kappa^2 + k/\kappa + \frac{1}{2} + u^2/\omega_p^2}, \quad (33)$$

so that the interaction energy is,

$$E_I(z) = - \int_0^\infty \frac{du}{2\pi} \alpha^a(iu) \kappa^2 I(|z|, iu), \quad (34)$$

where,

$$I(|z|, iu) = \frac{1}{2|z|} - \frac{1}{4\beta} \text{Im}[\mu^2 \exp(\mu|z|) E_1(\mu|z|)] \quad (35)$$

In the last equation, $\beta = \kappa(k^2 + \omega_p^2/4)^{1/2}/\omega_p$, $\mu = \kappa + 2i\beta$, and E_1 is the standard exponential integral (Gautschi and Cahill 1970). If we now make the approximation (30) for $\alpha^a(\omega)$ then (34) simplifies to,

$$E_I(z) = -\frac{\langle r^2 \rangle}{12} \kappa^2 \left(\frac{1}{|z|} - 2\kappa \text{Re} \{ \exp(c) E_1(c) \} \right), \quad (36)$$

where $c = \kappa|z|(1+i)$, and this result is a new one. Using the standard expressions available for the expansion of $E_1(c)$ in (36) for small as well as large $\kappa|z|$ values (Gautschi and Cahill 1970) it can easily be seen that,

$$\begin{aligned} E_I(z) &\rightarrow -\frac{\langle r^2 \rangle}{12|z|^3} \left(1 - \frac{3}{\kappa|z|} + \frac{1}{\kappa^2|z|^2} + \dots \right), & \text{for large } \kappa|z|, \\ &\rightarrow -\frac{\langle r^2 \rangle \kappa^2}{12} \left(\frac{1}{|z|} + 2\kappa \ln|z| + \text{constant} + O(|z|) \right), & \text{for small } \kappa|z|. \end{aligned} \quad (37)$$

This shows that the classical form is substantially modified at shorter distances. Detailed numerical results show (see Rao and Mukhopadhyay 1984) that such modifications are appreciable for distances smaller than $|z| = 8$ a.u. at metallic densities ($r_s = 3$ and 5).

2.3 Exact expression in non-dispersive case

So far we have obtained the vdW energy E_I within the approximation $|R_{ij}| \ll 1$. For the atom-surface system, the determinant in (4) is diagonal (by (8) and (22)) and therefore the expression for E_I can be obtained exactly. Thus from (4) we have,

$$\begin{aligned} 0 = D(\omega) &= [1 - R_{xx}(\omega)] [1 - R_{yy}(\omega)] [1 - R_{zz}(\omega)] \\ &= [1 + f(\omega)] [1 + f(\omega)/2]^2, \end{aligned} \quad (38)$$

where, $f(\omega) = \alpha^a(\omega)G(\omega)$,

$$= -\frac{\omega_s^2}{\omega^2 - \omega_s^2} \frac{f_0}{\omega^2 - \omega_0^2} \frac{1}{4|z|^3}, \quad (39)$$

in the non-dispersive approximation, using (30) for $\alpha^a(\omega)$, and (20), (26) for $G(\omega)$.

Therefore, either,

$$1 + f(\omega) = 0, \quad (40)$$

$$\text{or, } 1 + f(\omega)/2 = 0. \quad (41)$$

In the second case of (41), the eigenmodes have the degeneracy of two because of the square appearing in (38). From (40) and (41), we can find all the eigenmodes which are physical solutions and thereafter from (5) can obtain the vdW energy. We consider first equation (40), where we substitute for $f(\omega)$ from (39), and solve the resulting equation to obtain the eigenmodes as,

$$\omega_{\pm}^{(1)} = \omega_s p_{\pm}, \quad (42)$$

where,

$$p_{\pm}^2 = \frac{1}{2} [1 + a^2 \pm \{(1 - a^2)^2 + 4\gamma\}^{1/2}], \quad (43)$$

with,

$$a = \omega_0/\omega_s, \quad (44)$$

$$\gamma = \frac{f_0}{4|z|^3 \omega_s^2} = \frac{\langle r^2 \rangle a}{6|z|^3 \omega_s}. \quad (45)$$

For real frequencies p_{\pm}^2 must be positive, so that in (43) we must have $\gamma/a^2 \leq 1$. Substituting the values of $\omega_{\pm}^{(1)}$ in (5), we get

$$\begin{aligned} E_i^{(1)}(z) &= \frac{1}{2} \omega_s [(p_+ + p_-) - (1 + a)], \\ &= \frac{1}{2} \omega_s [1 + a^2 + 2(a^2 - \gamma)^{1/2} - 1 - a], \end{aligned} \quad (46)$$

using $p_+^2 + p_-^2 = 1 + a^2$ and $p_+ p_- = (a^2 - \gamma)^{1/2}$. The superscript (1) above refers to the fact that these expressions correspond to solving (40). Similarly solving (41) we obtain,

$$E_i^{(2)}(z) = \frac{1}{2} \omega_s [1 + a^2 + 2(a^2 - \gamma/2)^{1/2} - 1 - a]. \quad (47)$$

Therefore, the vdW interaction energy is given by,

$$\begin{aligned} E_I(z) &= E_i^{(1)}(z) + 2E_i^{(2)}(z) \\ &= \frac{1}{2} \omega_s [\{1 + a^2 + 2(a^2 - \gamma)^{1/2}\}^{1/2} + 2\{1 + a^2 + 2(a^2 - \gamma/2)^{1/2}\}^{1/2} \\ &\quad - 3(a + 1)], \end{aligned} \quad (48)$$

where we have included the degeneracy factor of two for the eigenmodes resulting from (41). We note now that for large $|z|$, the ratio γ/a^2 becomes small and the above reduces to,

$$E_{I0}(z) = -\frac{\omega_s}{2} \frac{\gamma}{a(1 + a)}, \quad (49)$$

which is identical with the result given by (31).

3. Numerical results

To carry out the numerical calculations with the exact expression (48) in the classical non-dispersive case, we first invoke the condition that $\gamma/a^2 \leq 1$. This means that for the formula (48) to be meaningful, we must have $|z| > |z_m|$, where $|z_m|$ is the minimum value of $|z|$ for which $\gamma/a^2 \leq 1$ is satisfied. This implies that,

$$|z_m| = \left(\frac{\langle r^2 \rangle}{6\omega_0} \right)^{1/3}. \quad (50)$$

Clearly, $|z|$ depends only on the characteristics of the atom, i.e., on the oscillator strength and the excitation frequency of the atom.

Table 1 shows the various rare-gas atoms chosen for calculations, and the respective excitation frequencies ω_0 and the oscillator strengths (Tang *et al* 1976). Also shown are the minimum approachable distance $|z_m|$ determined by (50). Clearly $|z_m|$ is larger for heavier atoms for which the polarizabilities are larger (i.e., larger $\langle r^2 \rangle$ and smaller ω_0 implying larger α^a by (30)).

To see how much modification the new formula (48) yields over the classical formula (31), we have calculated the ratio E_i/E_{i0} corresponding to the electron gas parameter $r_s = 3$ for which $\omega_s = 0.236$ Hartree (relevant for Ag and Au) and a few rare gas atoms, e.g., Ne, Ar, Kr and Xe. The results are shown in figure 1. In the figure, the curve-1 corresponds to Ne, curve-2 to Ar, curve-3 to Kr and curve-4 to Xe. All quantities are in atomic units, where the distances are in a_0 (Bohr radius) and energies are in Hartree. The parameters used are from table 1. It is clear from the figure that the ratio E_i/E_{i0} is significantly larger than unity for $|z|$ close to $|z_m|$ for various atoms, and at $|z_m|$ the ratio is nearly 1.75 (marked by crosses in figure 1). As $|z|$ increases, this ratio becomes smaller and smaller, and at large $|z|$ it approaches unity. This means that, strictly speaking, one cannot always treat $|R_{ij}|$ as small compared to unity, particularly at shorter distances and heavier atoms with large polarizabilities.

4. Conclusions

We have shown that the vdW interaction energy between a metal surface and an atom, calculated via the dielectric response approach, yields two important results. Firstly, the interaction energy can be expressed in terms of a form factor $F(k, \omega)$ which is

Table 1. Rare gas atoms chosen for calculations and the respective values of ω_0 , $\langle r^2 \rangle$ and the calculated minimum approachable distance $|z_m|$.

Atom	$\langle r^2 \rangle$ (a. u.)*	ω_0 (Hartree)*	$ z_m $ (a. u.)
Ne	8.95	0.613	1.35
Ar	28.90	0.427	2.24
Kr	36.30	0.369	2.55
Xe	56.50	0.310	3.12

* Taken from Tang *et al* (1976).

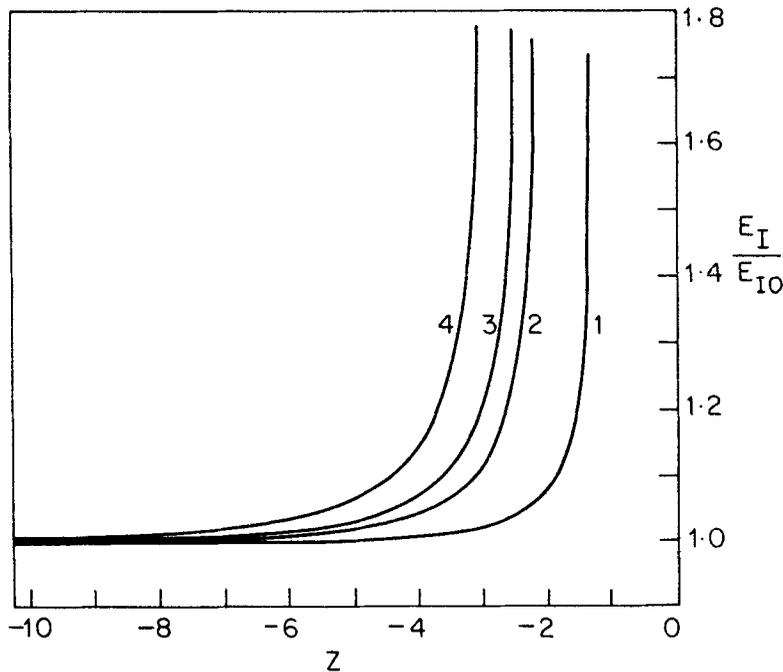


Figure 1. E_I/E_{I0} vs z for $r_s = 3$. 1. Ne; 2. Ar; 3. Kr; 4. Xe.

determined by the density-density response function χ of the metal alone. This form factor is the same one that enters in the formula for the dynamic image potential. Thus a knowledge of this form factor can provide useful information about both the vdW energy as well as latter. Secondly, the interaction energy can be directly and exactly obtained from the secular determinant. To our knowledge, this is a new result (equation (48)). We have found that in the non-dispersive case and heavy atoms with large polarizabilities, the exact formula differs substantially from the classical standard formula for short atom-metal separation, and the difference decreases with increase in separation.

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Note added to the proof: In the analysis of the section 2.3, the effect of dispersion can be incorporated approximately by replacing z everywhere with $z - z_0$ where z_0 corresponds to the effective position of the metal surface (Zaremba and Kohn 1976, 1977) determined by both the atomic polarizability as well as the metallic response (z_0 is typically about one A.U. outside the metal surface). This means that $|z_m|$ would increase by $|z_0|$ and the curves in Fig. 1 would shift to higher $|z|$ region by the corresponding value of $|z_0|$, enhancing the ratio E_1/E_{10} at higher z values.