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Image and van der Waals potentials for a cylindrical (spherical) surface: conductors versus insulators

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Abstract. A second-order perturbative approach is used to derive, respectively, expressions for the image and the van der Waals potentials between a particle and a conducting substrate with a cylindrical (or a spherical) surface. These expressions are valid for all particle-surface separations. Asymptotic forms for these potentials are obtained and have the following forms: for the image potential it obeys a R^{-2} law for a grounded spherical surface and a $(R \ln R)^{-1}$ law for a cylindrical surface; for the van der Waals potential it is a R^{-4} law for a grounded spherical surface and a $(R^3 \ln R)^{-1}$ law for a cylindrical surface, where R is the particle-surface separation. These asymptotic forms are quite different from those of insulating substrates with the same shape of surface. The main difference between a conducting substrate and an insulating substrate is discussed. The difference between a grounded and an insulated conducting substrate is also discussed.

1. Introduction

The image and the van der Waals potentials are important in the studies of the particle-surface interaction. For the former potential the particle involved is a charged one (an electron or an ion), and for the latter potential the particle involved is a neutral one (an atom). So far the theoretical studies have mainly concentrated on the cases in which the surface is either a metal plane surface [1-10] or a spherical surface [11-15]. Little is known about these two potentials when the surface involved is a conducting cylindrical surface (there is an extensive study of the forces between macroscopic bodies with the shapes considered here [16]). Even the asymptotic forms are not known. For a conducting spherical substrate, because of the finiteness of its extent, there is a distinction between a grounded and an insulated substrate. Most of the theoretical studies have concentrated on the insulated substrate. The differences between these two kinds of substrate have not been fully discussed.

However, for insulating substrates there is no distinction between an insulated and a grounded substrate. Moreover, the asymptotic forms of the image and the van der Waals potentials for insulating substrates are well known for various shapes of the surface—planar, spherical and cylindrical. These asymptotic forms can be easily deduced from the well-known asymptotic forms of the atom-ion and the atom-atom interaction potentials by summing over the pair potentials between the foreign particle and the atoms in the substrate. For example, the atom-atom van der Waals potential is well known to have a R^{-6} -dependence (see for example [17]) for a large

interatomic distance R . Therefore the van der Waals potential between an atom and an insulating spherical surface obeys the same R^{-6} law if the atom-surface distance R is much larger than the radius of the sphere. The potential becomes a R^{-5} law if the surface is cylindrical in shape because the sum over the atoms of the substrate contributes a factor R . It is easy to extend the argument to other surface shapes and the asymptotic forms of these potentials, together with the well-known results for the conducting spherical (see for example [18]) and the results of this paper for the conducting cylindrical surfaces, are given in table 1.

Table 1. Asymptotic forms of the image and the van der Waals (vdW) potentials for various shapes of surfaces: conductors versus insulators. R is the distance between the particle and the surface.

Surface \ Potential	Planar		Cylindrical		Spherical		
	Insulator	Conductor	Insulator	Conductor	Insulator	Conductor	
						Insulated	Grounded
Image	R^{-1}	R^{-1}	R^{-3}	$R^{-1}(\ln R)^{-1}$	R^{-4}	R^{-4}	R^{-2}
VdW	R^{-3}	R^{-3}	R^{-5}	$R^{-3}(\ln R)^{-1}$	R^{-6}	R^{-6}	R^{-4}

It is interesting to note that for the most well-known cases of the plane and insulated sphere, the asymptotic R -dependence for both the image and van der Waals potentials are independent of the electrical properties of the substrate. As there is no difference between a grounded and an insulated conducting substrate in the planar surface case (both require the substrate to be at zero potential in classical electrostatics), it is then an interesting question to ask whether the asymptotic behaviour of the particle-surface interaction potentials depends only on the geometrical shape and not on the electrical properties of the substrate, be it an insulator or an insulated conductor. The answer is apparently no. A simple example to test is a thin-slab substrate. If the substrate is a conducting one, the response of the substrate to external charges will differ little from that of a semi-infinite substrate with a planar surface (these two substrates are exactly the same in classical electrostatics). However, for insulators, a thin-slab substrate is different from a semi-infinite one, because the former extends to infinity in two dimensions only.

From this example we see that a conducting substrate which extends to infinity in only one or two dimensions may behave quite differently from an insulating substrate with the same geometry. A substrate with a cylindrical surface belongs to this class of substrates. Moreover the image potential for a conducting cylindrical surface is virtually unknown in classical electrostatics. Therefore the image and van der Waals potentials for a conducting cylindrical surface are interesting subjects to investigate. In this paper we will derive expressions for these two potentials which are valid for all particle-surface separations. The asymptotic forms of these two potentials are shown in table 1. We will also derive the same expressions for a conducting spherical surface, whose explicit forms have not been derived before. A discussion of the differences

between a grounded and an insulated conducting substrate will be given. From this we may gain some insights into the properties of the surface response function.

The main difference between an insulated (uncharged) and a grounded conducting substrate is that in the insulated case the monopole contribution to the surface response function is zero [19] because of the condition of charge neutrality of the substrate. The lowest order contribution comes from the dipole terms. In the grounded case the electrons in the substrate are not confined in the substrate. They are connected to a huge electron reservoir and the electrons are free to move in and out of the substrate, i.e. an electric current may be induced in the substrate in the presence of an external field. The monopole term in the surface response function is therefore non-vanishing (see the explanation in section 3). Thus the asymptotic behaviour of the image and van der Waals potentials will usually give lower inverse- R laws for a grounded than for a neutral insulated conducting substrate, as in the case of a classical conducting sphere. For an infinitely extended conducting substrate the monopole term in the surface response function will always be non-zero because it is the same as grounded.

The situation in an insulating substrate is somewhat different from that of a conducting substrate. The electrons in an insulating substrate are localized and they are not free to move in and out of the substrate even when the substrate is grounded, i.e. there is never an induced electric current in an insulator whether it is grounded or not. Therefore the monopole term in the surface response function is always zero even when the substrate is infinitely extended. The lowest order contribution comes from the sum of the atomic polarizations of the atoms in the substrate. The particle-surface interaction potentials can therefore be approximated by a simple sum over pair potentials between the particle and the atoms in the substrate. Therefore, except for the semi-infinite case, the asymptotic forms of these potentials usually give higher inverse- R laws for an insulating substrate than for a conducting substrate with the same shape (cf table 1).

In section 2, we use a second-order perturbative approach to derive expressions for the image and van der Waals potentials for the particle-metallic surface interactions when the surface is (i) spherical, and (ii) cylindrical in shape. These two potentials are derived in a unified way [10] and the final expressions are valid for all particle-surface separations. In section 3, we discuss the differences between a conducting and an insulating substrate in response to external fields. The effect of grounding a conducting substrate in the surface response function is also discussed. Finally the asymptotic forms for the image and van der Waals potentials for spherical (grounded or insulated) and cylindrical conducting surfaces are obtained to conclude the section.

2. Theory

The image and van der Waals potentials are usually obtained by calculating the self-energy of the particle-substrate system with use of the particle's Green function. In this section we will, however, use a second-order perturbative approach to calculate the self-energy. The usefulness of this approach is that these two potentials can be derived in a unified way [10] and the geometry of the substrate can easily be implemented. If the particle involved is a charged one (e.g. an ion) then the calculated self-energy is the image potential, and if the particle involved is a neutral one (e.g. an atom) then we obtain van der Waals potential. The expressions we obtained for the image and

the van der Waals potentials are valid for all particle-surface separations. We now describe the theory.

The unperturbed system consists of a free particle (an ion or an atom) and an isolated conducting substrate with a surface (spherical or cylindrical in shape). The self-energy of the particle-substrate system is due to the Coulomb coupling between the particle and the substrate. We treat the Coulomb coupling as a perturbation. When the particle is far away from the surface the first-order perturbation is zero because the substrate we considered is a neutral one. Therefore the lowest contribution comes from the second-order perturbation. However, when the particle and the surface are close enough and the wavefunctions of the two unperturbed subsystems overlap, the first-order perturbation will be non-zero. In this situation we may consider the first-order perturbation term as part of the Pauli repulsion and the image or van der Waals potentials comes from second-order terms only. With this definition the expressions we derived for the image and van der Waals potentials are valid for all particle-surface separations.

We now proceed to calculate the perturbation energy between the particle and the substrate. The perturbation \hat{V} is due to the Coulomb coupling between the particle and the substrate,

$$\hat{V} = \int \int d^3r d^3r' \frac{\hat{\sigma}_p(\mathbf{r})\hat{\sigma}_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (1)$$

Here $\hat{\sigma}_p(\mathbf{r})$ and $\hat{\sigma}_s(\mathbf{r})$ are respectively the charge-density operators for the particle and the substrate. The charge-density operator for the particle is

$$\hat{\sigma}_p(\mathbf{r}) = N\delta(\mathbf{r} - \mathbf{R}) - \sum_{i=1}^{N'} \delta(\mathbf{r} - \mathbf{r}_i) \quad (2)$$

where \mathbf{R} and \mathbf{r}_i are respectively the position coordinates of the nucleus and the i th electron. N is the charge on the nucleus and N' is the total number of electrons in the particle (atomic units are used throughout). If $N \neq N'$ the particle is a charged ion, and if $N = N'$ the particle is a neutral atom. The image potential (for an ion) or the van der Waals potential (for an atom) is given by the second-order perturbation energy [10]

$$U = \sum_{n,n'} \frac{|\langle 00' | \hat{V} | nn' \rangle|^2}{\epsilon_0 + E_{0'} - \epsilon_n - E_{n'}} \quad (3)$$

where $|nn'\rangle$ denotes a state with the particle in its n th (unperturbed) excited state (with energy ϵ_n) and the substrate in its n' th (unperturbed) excited state (with energy $E_{n'}$), and $|00'\rangle$ is the unperturbed initial ground state. (The effect of the translational motion of the particle on the image and the van der Waals potential are negligible for thermal ions and atoms. See for example [2] or [20].)

Up to this point the geometry of the surface does not enter the theory. When we want to calculate the interaction potential U in equation (3), we have to expand $1/|\mathbf{r} - \mathbf{r}'|$ in equation (1) in a proper form determined by the geometry of the surface. Because the result for a planar surface is well known ([9] and the references therein), we only consider the spherical and cylindrical surfaces in the following.

2.1. Spherical surface

When the substrate has a spherical surface, it is convenient to use the spherical coordinates $\mathbf{r} = (r, \theta, \phi)$ and the appropriate expansion for $1/|\mathbf{r} - \mathbf{r}'|$ is (see for example [18] p 102)

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r'^l}{r^{l+1}} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi) \quad r > r'. \quad (4)$$

The absolute square of the matrix element $\langle 00' | \hat{V} | nn' \rangle$ in equation (3) becomes, by choosing the centre of the substrate as the origin of the coordinate system,

$$\begin{aligned} |\langle 00' | \hat{V} | nn' \rangle|^2 &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \frac{4\pi}{2l+1} \frac{4\pi}{2l'+1} \langle 0 | \hat{\sigma}_{p,lm} | n \rangle \langle n | \hat{\sigma}_{p,l'm'}^+ | 0 \rangle \\ &\times \int d\mathbf{r} d\mathbf{r}' r^l r'^{l'} Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta', \phi') \langle 0' | \hat{\sigma}_s(\mathbf{r}) | n' \rangle \langle n' | \hat{\sigma}_s(\mathbf{r}') | 0' \rangle \\ &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} 2\pi \frac{(l-m)!}{(l+m)!} |\langle 0 | \hat{\sigma}_{p,lm} | n \rangle|^2 \\ &\times \int d\mathbf{r} d\mathbf{r}' d(\cos \theta) d(\cos \theta') d(\phi' - \phi) [r^{l+2} r'^{l+2} P_l^m(\cos \theta) P_l^m(\cos \theta')] \\ &\times e^{im(\phi' - \phi)} \langle 0' | \hat{\sigma}_s(r, 0, 0) | n' \rangle \langle n' | \hat{\sigma}_s(r', \gamma, \phi' - \phi) | 0' \rangle \end{aligned} \quad (5)$$

with

$$\hat{\sigma}_{p,lm} \equiv \int d\mathbf{r} \hat{\sigma}_p(\mathbf{r}) \frac{Y_{lm}(\theta, \phi)}{r^{l+1}}. \quad (6)$$

The last equality of equation (5) is obtained by the fact that the substrate charge-density-density correlation $\hat{\sigma}_s(\mathbf{r})\hat{\sigma}_s(\mathbf{r}')$ is a rotationally invariant quantity, which depends on r, r' , and the angle γ between \mathbf{r} and \mathbf{r}' only. Therefore in the integral in equation (5) the angles θ, θ' and $\phi' - \phi$ are not all independent variables. They are related by the relationship

$$\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi' - \phi). \quad (7)$$

The interaction potential U of equation (3) becomes

$$U = - \sum_n \sum_{l,m} \int_0^{\infty} \frac{d\omega}{\pi} \frac{4\pi}{2l+1} \frac{|\langle 0 | \hat{\sigma}_{p,lm} | n \rangle|^2}{\epsilon_n - \epsilon_0 + \omega} \text{Im}[D_{lm}(\omega)] \quad (8)$$

where the imaginary part of the frequency-dependent surface density-response function $D_{lm}(\omega)$ is defined as

$$\begin{aligned} \text{Im}[D_{lm}(\omega)] &\equiv 2\pi \frac{(l-m)!}{(l+m)!} \int_{\text{Equation(7)}} d\mathbf{r} d\mathbf{r}' r^{l+2} r'^{l+2} d(\cos \theta) d(\cos \theta') d(\phi' - \phi) \\ &\times P_l^m(\cos \theta) P_l^m(\cos \theta') e^{im(\phi' - \phi)} \text{Im}[\chi(r, r', \gamma, \phi' - \phi; \omega)] \end{aligned} \quad (9)$$

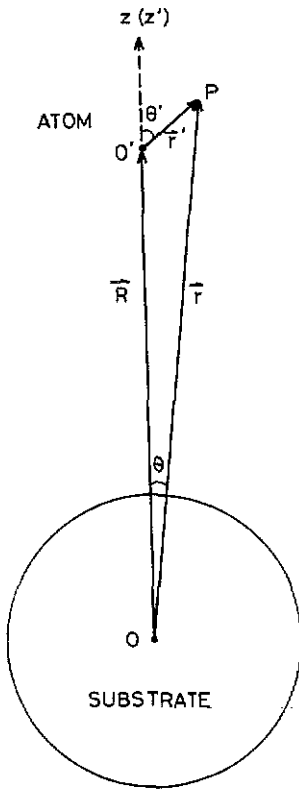


Figure 1. The relation between the position vectors $\mathbf{r} = (r, \theta, \phi)$ and $\mathbf{r}' = (r', \theta', \phi')$. O is the centre of the substrate and O' is the centre of the atom (ion). The $z(z')$ axis is taken along \mathbf{R} , the vector from O to O'.

with (for $\omega > 0$)

$$\text{Im}[\chi(r, r', \gamma, \phi'; \omega)] \equiv \sum_{n'} \langle 0 | \hat{\sigma}_s(r, 0, 0) | n' \rangle \langle n' | \hat{\sigma}_s(r', \gamma, \phi') | 0' \rangle \pi \delta(E_{n'} - E_{0'} - \omega). \quad (10)$$

In evaluating the image and van der Waals potentials one needs to calculate the matrix elements $\langle 0 | \hat{\sigma}_{p,lm} | n \rangle$ in equation (8) in terms of multipole expansions with respect to the centre of the atom (ion). Usually one keeps only the monopole term in the image potential and the dipole terms in the van der Waals potential. This is what we have done here. Consider the coordinate systems shown in figure 1. The position vector $\mathbf{r} = (r, \theta, \phi)$ of the atomic charge-density operator $\hat{\sigma}_p(\mathbf{r})$ (in equation (6)) has the origin at O, the centre of the substrate. Now we have to express \mathbf{r} in terms of $\mathbf{r}' = (r', \theta', \phi')$ with the origin at the centre of the atom (ion) O'. Let the two coordinate systems have a common $z(z')$ -axis parallel to \mathbf{R} , the vector from O to O'. In addition choose the x - and x' -axes such that $\phi' = \phi$. Then to first order in r' (dipole terms), we have

$$\begin{aligned} \cos \theta &= 1 \\ \sin \theta &= \frac{r'}{R} \sin \theta'. \end{aligned} \quad (11)$$

It is easily seen that the matrix element $\langle 0|\hat{\sigma}_{p,lm}|n\rangle$ is zero for $m \geq 2$ if we keep only monopole and dipole contributions. With approximations (11), we have

$$Y_{l0}(\theta, \phi) = \left(\frac{2l+1}{4\pi}\right)^{1/2}$$

$$Y_{l,\pm 1}(\theta, \phi) = (\mp 1) \left[\frac{(2l+1)l(l+1)}{16\pi}\right]^{1/2} \left(\frac{r'}{R}\right) \sin \theta' e^{\pm i\phi'}. \quad (12)$$

For an ion-surface interaction, $N - N' = Q \neq 0$, and by keeping only the monopole contribution, the image potential is given by

$$U_{\text{img}}(R) = -Q^2 \sum_{l=0}^{\infty} \frac{1}{R^{2(l+1)}} \int_0^{\infty} \frac{d\omega}{\pi} \frac{\text{Im}[D_{l0}(\omega)]}{\omega} \quad (13)$$

where R is the distance between the centre of the substrate and the nucleus of the ion. For an atom-surface interaction, $N - N' = Q = 0$, the van der Waals potential is given by

$$U_{\text{vdw}}(R) = - \sum_n \frac{f_{n0}}{2\omega_{n0}} \left\{ \sum_{l=0}^{\infty} \frac{(l+1)^2}{R^{2(l+2)}} \int_0^{\infty} \frac{d\omega}{\pi} \frac{\text{Im}[D_{l0}(\omega)]}{\varepsilon_n - \varepsilon_0 + \omega} \right.$$

$$\left. + \sum_{l=1}^{\infty} \frac{l(l+1)}{2R^{2(l+2)}} \int_0^{\infty} \frac{d\omega}{\pi} \frac{\text{Im}[D_{l,1}(\omega)] + \text{Im}[D_{l,-1}(\omega)]}{\varepsilon_n - \varepsilon_0 + \omega} \right\} \quad (14)$$

where f_{n0} is the dipole oscillator strength for a transition from the atomic state 0 to state n with frequency ω_{n0} .

2.2. Cylindrical surface

When the substrate has a cylindrical surface, it is convenient to express the position vector \mathbf{r} in terms of the cylindrical coordinates (ρ, ϕ, z) . The appropriate expansion for $1/|\mathbf{r} - \mathbf{r}'|$ is (see for example [18] p 118)

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{2}{\pi} \sum_{m=-\infty}^{\infty} \int_0^{\infty} dq e^{im(\phi - \phi')} \cos[q(z - z')] I_m(q\rho') K_m(q\rho) \quad \rho > \rho' \quad (15)$$

where $I_m(x)$ and $K_m(x)$ are the modified Bessel functions. By choosing the axis of the substrate as the z -axis, the absolute square of the matrix element $\langle 00'|\hat{V}|nn'\rangle$ in equation (3) has the form

$$|\langle 00'|\hat{V}|nn'\rangle|^2 = \frac{1}{\pi^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dq' \left\{ \sum_{m=-\infty}^{\infty} \sum_{m'=-\infty}^{\infty} \langle 0|\hat{\sigma}_{p,qm}|n\rangle \langle n|\hat{\sigma}_{p,q'm'}^+|0\rangle \right.$$

$$\times [\langle 0'| \int d\mathbf{r} e^{-iqz - im\phi} I_m(|q|\rho) \hat{\sigma}_s(\mathbf{r}) |n'\rangle$$

$$\times \langle n'| \int d\mathbf{r}' e^{iq'z' + im'\phi'} I'_m(|q'|\rho') \hat{\sigma}_s(\mathbf{r}') |0'\rangle] \left. \right\}$$

$$= 4 \sum_m \int_{-\infty}^{\infty} dq |\langle 0|\hat{\sigma}_{p,qm}|n\rangle|^2 \langle 0'| \int d\rho \rho I_m(|q|\rho) \hat{\sigma}_s(\rho, 0, 0) |n'\rangle$$

$$\times \langle n'| \int d\rho' d(\phi' - \phi) d(z' - z) \rho' e^{iq(z' - z) + im(\phi' - \phi)}$$

$$\times I_m(|q|\rho') \hat{\sigma}_s(\rho', \phi' - \phi, z' - z) |0'\rangle \quad (16)$$

with

$$\hat{\sigma}_{p, gm} \equiv \int d\mathbf{r} e^{iqz + im\phi} K_m(|q\rho) \hat{\sigma}_p(\mathbf{r}). \quad (17)$$

The last equality of equation (16) is obtained by the fact that the substrate charge-density-density correlation $\hat{\sigma}_s(\mathbf{r})\hat{\sigma}_s(\mathbf{r}')$ is invariant under a rotation with respect to the z -axis or a translation parallel to the z -axis. The interaction potential U of equation (3) can be written as

$$U = - \sum_n \sum_{m=-\infty}^{\infty} \int_0^{\infty} \frac{d\omega}{\pi} \frac{2}{\pi} \int_{-\infty}^{\infty} dq \frac{|\langle 0 | \hat{\sigma}_{p, gm} | n \rangle|^2}{\epsilon_n - \epsilon_0 + \omega} \text{Im}[D_m(q, \omega)] \quad (18)$$

where the imaginary part of the frequency-dependent surface density-response function $D_m(q, \omega)$ is defined as

$$\begin{aligned} \text{Im}[D_m(q, \omega)] &\equiv 2\pi \int d\rho d\rho' d\phi' dz' \rho\rho' e^{iqz' + im\phi'} \\ &\times I_m(|q\rho) I_m(|q\rho') \text{Im}[\chi(\rho, \rho', \phi', z'; \omega)] \end{aligned} \quad (19)$$

with (for $\omega > 0$)

$$\begin{aligned} \text{Im}[\chi(\rho, \rho', \phi' - \phi, z' - z; \omega)] &\equiv \sum_{n'} \langle 0' | \hat{\sigma}_s(\rho, 0, 0) | n' \rangle \\ &\times \langle n' | \hat{\sigma}_s(\rho', \phi' - \phi, z' - z) | 0' \rangle \pi \delta(E_{n'} - E_{0'} - \omega). \end{aligned} \quad (20)$$

By using exactly the same approximations of equation (11), except that in the cylindrical coordinates the relevant angles are ϕ and ϕ' instead of θ and θ' , we can expand the matrix elements $\langle 0 | \hat{\sigma}_{p, gm} | n \rangle$ in equation (18) in terms of the monopole and dipole terms of the atomic charge density $\hat{\sigma}_p(\mathbf{r})$. However, except for the $m = 0$ component [21], we do not have closed forms for the expansion of $K_m(q\rho)$. Because the small q contribution will dominate the self-energy U in equation (18), we do the small x expansion for $K_m(x)$. Finally we get the approximate expressions for the image potential and the van der Waals potential, respectively, in the following:

$$\begin{aligned} U_{\text{img}}(\rho) &\approx -Q^2 \frac{4}{\pi^2} \int_0^{\infty} \frac{d\omega}{\omega} \int_0^{\infty} dq K_0^2(q\rho) \text{Im}[D_0(q, \omega)] \\ &- Q^2 \sum_{m=1}^{\infty} \frac{1}{\pi^2} \left[\Gamma(m) \left(\frac{2}{\rho} \right)^m \right]^2 \int_0^{\infty} \frac{d\omega}{\omega} \int_0^{q_c} dq \frac{\text{Im}[D_m(q, \omega)]}{q^{2m}} \end{aligned} \quad (21)$$

and

$$\begin{aligned} U_{\text{vdw}}(\rho) &\approx - \sum_n \frac{2}{\pi^2} \frac{f_{n0}}{\omega_{n0}} \int_0^{\infty} d\omega \int_0^{\infty} dq \frac{q^2 [K_0^2(q\rho) + K_1^2(q\rho)]}{\epsilon_n - \epsilon_0 + \omega} \text{Im}[D_0(q, \omega)] \\ &- \sum_n \sum_{m=1}^{\infty} \frac{1}{\pi^2} \left[\Gamma(m) \left(\frac{2}{\rho} \right)^m \right]^2 \frac{f_{n0}}{\omega_{n0}} \\ &\times \int_0^{\infty} d\omega \int_0^{q_c} dq \frac{[(2m^2/\rho^2) + q^2]}{q^{2m}(\epsilon_n - \epsilon_0 + \omega)} \text{Im}[D_m(q, \omega)]. \end{aligned} \quad (22)$$

In equations (21) and (22), ρ is the distance between the axis of the substrate and the centre of the atom (ion). In the integrals for the $m \geq 1$ components we introduce a cut-off q, q_c , in the upper limit of the integrals over q as the integrands are valid for small q only. The large q contributions are negligible because the integrands are exponentially small, being proportional to $\exp(-2q\rho)$. The expressions (21) and (22) are only approximate and there is no unique way of determining q_c .

3. Discussions and conclusions

In the preceding section, we have derived the expressions for the image and van der Waals potentials between an ion, or an atom, and a conducting substrate with a spherical, or a cylindrical surface. In these expressions, as in the planar surface case [9, 10], an important physical quantity to be noted is the imaginary part of the frequency-dependent surface density-response function of the substrate $\text{Im}[D_{lm}(\omega)]$ in the spherical surface case, or $\text{Im}[D_m(q, \omega)]$ in the cylindrical surface case. The density-response function $D_{lm}(\omega)$, or $D_m(q, \omega)$, is the Fourier transform, with respect to space and time, of the retarded density correlation function $D^R(\mathbf{r}, t; \mathbf{r}', t')$ defined in the linear response theory (see for example [22]),

$$D^R(\mathbf{r}, t; \mathbf{r}', t') \equiv -i\Theta(t - t')\langle 0' | [\hat{\sigma}_{sH}(\mathbf{r}, t), \hat{\sigma}_{sH}(\mathbf{r}', t')] | 0' \rangle. \quad (23)$$

Here $|0'\rangle$ is the normalized ground-state state-vector of the substrate; $\hat{\sigma}_{sH}(\mathbf{r}, t)$ is the charge-density operator of the substrate in the (unperturbed) Heisenberg picture; $[\hat{A}, \hat{B}]$ is the commutator of the operators \hat{A} and \hat{B} ; and $\Theta(x)$ is the usual step function,

$$\Theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0. \end{cases} \quad (24)$$

For insulating substrates electron-electron correlations are negligible and therefore it is no longer valid to expand the surface density-response function $D_{lm}(\omega)$ or $D_m(q, \omega)$ as in equation (9) or (19). Instead, the surface density-response function $D(\omega)$ should depend on four indices ($lm, l'm'$) for a spherical surface or ($mq, m'q'$) for a cylindrical surface. With this expansion of the surface density-response function it is equivalent to express the image and the van der Waals potentials in terms of the more familiar multipole expansions of the atoms in the substrate. The absolute square of the matrix element $\langle 00' | \hat{V} | nn' \rangle$ can be written in the following forms instead of equation (5) or (16):

$$\begin{aligned} |\langle 00' | \hat{V} | nn' \rangle|^2 &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \frac{4\pi}{2l+1} \frac{4\pi}{2l'+1} \\ &\times \langle 0 | \hat{\sigma}_{p,lm} | n \rangle \langle n | \hat{\sigma}_{p,l'm'}^+ | 0 \rangle \langle 0' | \hat{\sigma}_{s,lm}^+ | n' \rangle \langle n' | \hat{\sigma}_{s,l'm'} | 0' \rangle \end{aligned} \quad (25)$$

with

$$\hat{\sigma}_{s,lm} \equiv \int d\mathbf{r} \hat{\sigma}_s(\mathbf{r}) r^l Y_{lm}(\theta, \phi) \quad (26)$$

for the spherical surface case; and

$$\begin{aligned} |\langle 00' | \hat{V} | nn' \rangle|^2 &= \frac{1}{\pi^2} \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dq' \left\{ \sum_{m=-\infty}^{\infty} \sum_{m'=-\infty}^{\infty} \right. \\ &\left. [\langle 0 | \hat{\sigma}_{p,qm} | n \rangle \langle n | \hat{\sigma}_{p,q'm'}^+ | 0 \rangle \langle 0' | \hat{\sigma}_{s,qm}^+ | n' \rangle \langle n' | \hat{\sigma}_{s,q'm'} | 0' \rangle] \right\} \end{aligned} \quad (27)$$

with

$$\hat{\sigma}_{s,qm} \equiv \int d\mathbf{r} e^{iqz+im\phi} I_m(|q|\rho) \hat{\sigma}_s(\mathbf{r}) \quad (28)$$

for the cylindrical surface case. For an insulating substrate the total charge-density distribution may be approximated by the sum of the charge density of each individual atom which consists of the substrate, i.e.

$$\hat{\sigma}_s(\mathbf{r}) \approx \sum_i \hat{\sigma}_{s,i}(\mathbf{r}) \quad (29)$$

where $\hat{\sigma}_{s,i}(\mathbf{r})$ is the atomic charge-density operator for the i th atom in the substrate. The eigenstates of the substrate may be approximated by the linear combination of atomic orbitals with negligible overlaps between neighbouring orbitals. With these approximations, the absolute square of the matrix element $|(00'|\hat{V}|nn')|^2$ in equations (25) and (27) may be decomposed into the sum of pair interactions between the foreign particle and each individual atom in the substrate. Therefore for an insulating substrate, the image and van der Waals potentials may be approximated by the sum of pair potentials between the foreign particle and each individual atom in the substrate. Deviations from the simple sum may exist because overlaps between neighbouring orbitals are not strictly zero. However, the deviations are negligible for good insulators.

On the other hand, for a conducting substrate the valence electrons are delocalized and the charge-density operator $\hat{\sigma}_s(\mathbf{r})$ cannot be approximated by the sum of atomic charge-density operators $\hat{\sigma}_{s,i}(\mathbf{r})$. Electron-electron correlations and, therefore, collective excitations play the most important role in the response of the substrate to external fields. The image and van der Waals potentials should, therefore, be expressed in terms of the density-response function defined in equation (9) or (19), instead of the ion-atom or the atom-atom pair interaction potentials.

An exact calculation of the surface density-response function $D(\omega)$ would need the knowledge of the wavefunctions and eigenvalues of the ground state and the excited states of the substrate and therefore it is not an easy task. However, a simple approximated form of $\text{Im}[D(\omega)]$ can be obtained by noting that there is a simple relation between $D(\omega)$ and the dielectric function $\epsilon(\omega)$. From the approximated form of $\text{Im}[D(\omega)]$ the asymptotic forms of the image and the van der Waals potentials can be easily derived. It can be shown [25] that the dielectric function $\epsilon(\omega)$ and the surface density-response function $D(\omega)$ has, respectively, the following relationship:

$$\frac{1}{\epsilon_{lm}(\omega)} = 1 + D_{lm}(\omega)/a^{2l+1} \quad (30)$$

for a spherical substrate and

$$\frac{1}{\epsilon_m(q, \omega)} = 1 + 2 \frac{K_m(qa)}{I_m(qa)} D_m(q, \omega) \quad (31)$$

for a cylindrical substrate. In equations (30) and (31) a is the radius of the substrate (sphere or cylinder), and the component ($\epsilon_{lm}(\omega)$ or $\epsilon_m(q, \omega)$) of the dielectric function is defined as

$$\epsilon_{lm}(\omega) = \frac{\phi_{lm}^{\text{ex}}(\omega)}{\phi_{lm}^{\text{tot}}(\omega)} \quad (32)$$

for the spherical case, and

$$\epsilon_m(q, \omega) = \frac{\phi_m^{\text{ex}}(q, \omega)}{\phi_m^{\text{tot}}(q, \omega)} \quad (33)$$

for the cylindrical case. In equations (32) and (33) ϕ^{ex} (ϕ^{tot}) is the external (total) potential in the substrate.

From equation (30) or (31) we see that $\text{Im}[D(\omega)]$ can be expressed in terms of $\text{Im}[1/\epsilon(\omega)]$. This has the advantage that it is easier to obtain an approximated form for the imaginary part of the inverse of the dielectric function. If we add an infinitesimal positive imaginary part to the frequency ω , we would obtain $\text{Im}[1/\epsilon(\omega)]$ as a measure of the roots of the equation $\epsilon(\omega) = 0$ (for each component). If we assume that there is at most only one root in each component, we have

$$\text{Im}[D_{lm}(\omega)] = A_{lm}(a)a^{2l+1}\delta(\omega - \omega_{lm}) \quad (34)$$

for the spherical surface case and

$$\text{Im}[D_m(q, \omega)] = B_m(q, a) \frac{I_m(qa)}{K_m(qa)} \delta(\omega - \omega_m(q)) \quad (35)$$

for the cylindrical surface case. In equations (34) and (35), $A_{lm}(a)$ and $B_m(q, a)$ have the dimension of frequency; ω_{lm} ($\omega_m(q)$) is the root for the equation $\epsilon_{lm}(\omega) = 0$ ($\epsilon_m(q, \omega) = 0$). Equations (34) and (35) can be considered as generalizations of the plasmon-pole approximation for a bulk conducting medium [24] and for a planar surface conducting substrate [9, 10]. If we choose $A_{lm}(a) = \pi\omega_{lm}/2$, as in the bulk [24] and the planar surface case [9, 10], equation (13) will give, to lowest order, the well-known classical results of the image potential [18] for the grounded (with $\omega_{00} \neq 0$, and thus $A_{00} \neq 0$) and the insulated (with $\omega_{00} = 0$, and thus $A_{00} = 0$, and $\omega_{10} \neq 0$) conducting sphere. For the cylindrical case we have no classical result with which to compare it, but it seems plausible that $B_m(q, a) = \pi\omega_m(q)/2$ may also be correct.

The physical meaning of the roots of the equation $\epsilon(\omega) = 0$ is well known in electrodynamics. The roots are the characteristic frequencies for which the medium can sustain self-oscillations even when the external potential is zero. These are known as the plasma frequencies. From equations (13), (14), (21) and (22), we see that the asymptotic forms of the image and van der Waals potentials are determined by the $l = m = 0$ mode in the spherical surface case and by the $m = q = 0$ mode in the cylindrical surface case. In either case ($l = m = 0$ or $m = q = 0$), the mode corresponds to a uniform total potential and therefore an excitation with a uniform charge-density distribution in the medium. We may call this mode as the monopole term of the dielectric function. It is therefore important to investigate the roots of the monopole term of the dielectric function $\epsilon_{lm}(\omega) = 0$ and $\epsilon_m(q, \omega) = 0$. From the Maxwell equations we know that the dielectric function of a conducting medium consists of two parts: one from the conduction current (see for example [16] p 17) and one from the polarization of the medium. It is well known that in a bulk conducting medium the current-contributing dielectric function (i.e. the conductivity) will give rise a plasma frequency $\omega_p(q)$, which is non-vanishing for $q = 0$ (this is the mode with a constant external potential or zero external field and therefore is the monopole term). Thus the conduction current contributes a non-vanishing monopole term in

the imaginary part of the surface density-response function. We expect that this conclusion will hold even when the medium has a surface.

For an insulated conducting spherical substrate, there is no electric current and therefore the dielectric function does not contain the contribution of the current. Moreover, for this substrate the polarization of the medium will have no contribution to the monopole term of the dielectric function either as both ϕ_{00}^{ex} and ϕ_{00}^{tot} are zero and the equation $\epsilon_{00}(\omega) = 0$ has no solutions. Therefore for an *insulated* conducting spherical substrate the leading term in the surface density-response function $\text{Im}D_{00}(\omega) = 0$, and the lowest order contributions will come from $l = 1$ terms. The asymptotic forms of the image and van der Waals potentials are, therefore, $U_{\text{img}}(R) \sim R^{-4}$ and $U_{\text{vdw}}(R) \sim R^{-6}$ respectively, the same as in the insulating substrate case. For a grounded conducting spherical substrate, the current term will have a contribution to the dielectric function and thus $\text{Im}D_{00}(\omega) \neq 0$. Therefore the asymptotic forms for the image and van der Waals potentials are $U_{\text{img}}(R) \sim R^{-2}$ and $U_{\text{vdw}}(R) \sim R^{-4}$ respectively.

For a conducting cylindrical substrate, because of its infinite extent, there is no distinction between whether it is grounded or insulated. The conductivity always contributes to the dielectric function, and therefore we always have $\text{Im}[D_0(q = 0, \omega)] \neq 0$. This means that the constant in equation (35) $B_0(q = 0, a) \neq 0$. However in obtaining the asymptotic forms of the image and van der Waals potentials we should also consider the effect of the factor $I_0(qa)/K_0(qa)$ in equation (35). Because both $K_0(x)$ and $K_1(x)$ vanish as e^{-x}/\sqrt{x} for large x and diverge as $|\ln x|$ and $1/x$, respectively, for small x ; $I_0(x)$ approaches a constant for small x and diverges as e^x/\sqrt{x} for large x , therefore the integrals over q in equations (21) and (22) will be dominated by small q contributions. The factor $I_0(qa)/K_0(qa)$ will behave like $1/|\ln(qa)|$. From equations (21) and (22) we obtain the asymptotic forms of the image and the van der Waals potentials as $U_{\text{img}}(\rho) \sim (\rho \ln \rho)^{-1}$ and $U_{\text{vdw}}(\rho) \sim (\rho^3 \ln \rho)^{-1}$, respectively. These asymptotic forms are quite different from those of the insulating cylindrical surface, which predicts a ρ^{-3} and a ρ^{-5} -dependence, respectively. It is to be noted that not only the powers of the inverse of ρ are different, but that in the conducting cylindrical surface a non-power factor $(\ln \rho)^{-1}$ appears. This factor comes from the factor $I_0(qa)/K_0(qa)$ in equation (35) which in turn comes from the boundary condition at the surface. This example tells us that electron-electron correlations and the collective excitations in a conducting substrate play important roles in response to external fields. For an insulating substrate electron-electron correlations are negligible and it may, sometimes, behave quite differently from a conducting substrate with the same shape of surface.

In conclusion, we have derived expressions for the image and the van der Waals potentials, respectively, for a conducting substrate with a spherical and a cylindrical surfaces, which are valid for all ion-surface, or atom-surface, separations. The asymptotic forms of these potentials are obtained and compared with those of the insulating substrate with the same shape of surface. We find that for the case of an *insulated* uncharged spherical substrate, along with the planar surface case, the asymptotic behaviours of the image and the van der Waals potentials are the same for both conducting and insulating substrates. For other cases, however, the asymptotic behaviours are quite different for conducting and insulating substrates. For example, a *grounded* conducting spherical surface gives lower inverse power laws for the image (R^{-2} in contrast to R^{-4}) and the van der Waals potentials (R^{-4} in contrast to R^{-6}) than an insulating spherical substrate does. The most striking case is the

one for a conducting cylindrical surface. The asymptotic forms of the image and the van der Waals potentials can no longer be expressed as simple inverse power laws of the particle-surface separation. It behaves, respectively, like $(\rho \ln \rho)^{-1}$ for the image potential and like $(\rho^3 \ln \rho)^{-1}$ for the van der Waals potential. This is to be compared with a ρ^{-3} -law (for the image potential) and a ρ^{-5} -law (for the van der Waals potential) for an insulating cylindrical substrate. This example demonstrates that a conducting substrate may behave quite differently from an insulating substrate with the same shape of surface. The main difference between these two substrates is that electron-electron correlations are important in a conducting substrate but they are negligible in an insulating substrate.

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References

- [1] Lucas A A 1971 *Phys. Rev. B* **4** 2939
- [2] Lang N D and Kohn W 1973 *Phys. Rev. B* **7** 3541
- [3] Heinrich J 1973 *Phys. Rev. B* **8** 1346
- [4] Harris J and Jones R D 1973 *J. Phys. C: Solid State Phys.* **6** 3585
- [5] Chan D and Richmond P 1976 *J. Phys. C: Solid State Phys.* **9** 163
- [6] Flores F and Garcia-Moliner F 1979 *J. Phys. C: Solid State Phys.* **12** 907
- [7] Echenique P M, Ritchie R H, Barberan N and Inkson J C 1981 *Phys. Rev. B* **23** 6486
- [8] Manson J R and Ritchie H 1981 *Phys. Rev. B* **24** 4867
- [9] Annett J F and Echenique P M 1986 *Phys. Rev. B* **34** 6853 and references therein
- [10] Annett J F and Echenique P M 1987 *Phys. Rev. B* **36** 8986
- [11] Penzar Z and Sunjic M 1984 *Solid State Commun.* **52** 747
- [12] Beck D E 1984 *Phys. Rev. B* **30** 6935; 1987 *Phys. Rev.* **35** 7325
- [13] Ekardt W 1984 *Phys. Rev. Lett.* **52** 1925; 1985 *Phys. Rev. B* **31** 6360
- [14] Puska M J, Nieminen R M and Manninen M 1985 *Phys. Rev. B* **31** 3486
- [15] Ferrel T L and Echenique P M 1985 *Phys. Rev. Lett.* **55** 1526
- [16] Langbein D 1974 *Van Der Waals Attraction* (Berlin: Springer)
- [17] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehart and Winston) p 393
- [18] Jackson J D 1975 *Classical Electrodynamics* 2nd edn (New York: Wiley) pp 57-9
- [19] Apell S P and Penn D R 1986 *Phys. Rev. B* **34** 6612
- [20] Cheng Y C and Lin K C 1988 *Chin. J. Phys.* **26** 212
- [21] Cheng Y C and Yang J S 1990 *Phys. Rev. B* **41** 1196
- [22] Fetter A L and Walecka J D 1971 *Quantum Theory of Many-Particle Systems* (New York: McGraw Hill) p 173
- [23] Cheng Y C and Tu I P to be published
- [24] Tung C J and Kwei C M 1985 *Nucl. Instrum. Meth. Phys. Res. B* **12** 464