Polarizability of a small sphere including nonlocal effects

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We develop a simple semiclassical method for calculating the polarizability of a very small spherical particle by taking into account the nonlocal nature of the dielectric response. Our theory is very general in the sense that it can be applied to any material which can be characterized by a bulk dielectric function of the form $\epsilon_B(\vec{k},\omega)$: We introduce a new additional boundary condition (ABC) which is similar but not exactly equivalent to the Fuchs-Kliewer ABC. The theory is applied to calculate the polarizabilities of dielectric and metallic spheres.

I. INTRODUCTION

It is well known that the optical properties of very small spheres (with radii of the order of 100 Å or less) are very different from those of the corresponding bulk materials because of the surface effects.[1] A particularly important consequence of the small size of the system is that the electric field $\vec{E}$ and the displacement vector $\vec{D}$ are related by a nonlocal relationship of the form

$$\vec{D}(\vec{r}) = \int \epsilon(\vec{r},\vec{r}',\omega)\vec{E}(\vec{r}')d^3r' \ , \qquad (1)$$

instead of the usual local relation, $\vec{D}(\vec{r}) = \epsilon(\omega)\vec{E}(\vec{r})$. Here ω is the frequency and the ω dependence of the fields is kept implicit. In this paper we focus on one specific property, the polarizability, which can be easily related to many other optical constants of the particle. The static polarizability of a small metallic sphere including nonlocal effects has been calculated by a number of authors,[2-4] while the dynamic polarizability has been treated somewhat incompletely.[2,5-7] The case of a dielectric sphere has received relatively less attention.[8] Very recently, Ruppin has calculated the scattering and absorption coefficients of dielectric spheres[9] as well as those of metallic spheres[10] using two additional boundary conditions (ABC). These ABC's are necessary for taking into account the excitation of collective modes (plasmons, excitons, etc.) in the sphere, which arise naturally in a nonlocal treatment.

The purpose of the present paper is to provide a unified approach for calculating the polarizability of a very small sphere including nonlocal effects which can be applied to various types of materials such as metals, insulators, and semiconductors. We assume the sphere to be so small that retardation effects can be neglected. The theory is semiclassical in the sense that effects of the surface on the electronic wave functions or vibrational normal modes are not explicitly included. Surface effects are treated by a method similar to the "specular scattering" or "semiclassical infinite barrier" approximation used previously for a plane surface.[11] This method allows us to express the solution in terms of the bulk dielectric constant $\epsilon_B(\vec{k},\omega)$ which depends on the wave vector $\vec{k}$ and frequency ω.

The paper is organized as follows. In Sec. II we derive a simple expression for the polarizability of a small sphere by assuming that the effect of the surface is taken into account by introducing an "image" system on the other side of the spherical boundary and using the usual Maxwell's boundary conditions, viz., the continuity of the tangential $\vec{E}$ and the normal $\vec{D}$ fields. The ABC implied by our assumption is examined critically in Sec. III, where we show that it is similar to the Fuchs-Kliewer ABC (Ref. 11) for a plane interface, but it does not satisfy the criterion that the component of the polarization vector $\vec{P}$ normal to the boundary should be zero at the boundary. In Sec. IV we modify our ABC so as to make the normal component of $\vec{P}$ vanish at the surface, and give a corresponding modified expression for the polarizability. Section V

is devoted to a numerical calculation of the polarizabilities of dielectric and metallic spheres using simple analytical expressions for the dielectric function $\epsilon_B(\vec{k},\omega)$. We find that the results given by our two expressions for the polarizability are very similar, differing only in quantitative details. These results are compared with the results available in the literature from previous works[4,9,10] and the agreement is impressive. We conclude in Sec. VI by pointing out some possible areas of application of our formalism.

II. A SIMPLE THEORY OF THE POLARIZABILITY

Let us assume that an external electric field, given by

$$\vec{E} = E_0(\omega)\hat{z} \tag{2}$$

is applied to a sphere whose radius is a and whose material is characterized by a bulk dielectric function $\epsilon_B(\vec{k},\omega)$. The sphere is therefore much smaller than the wavelength of light, retardation is being neglected, and $\epsilon_B(\vec{k},\omega)$ is a longitudinal dielectric function. The potential V and the radial component of the displacement vector D_r outside the sphere (assumed to be vacuum) are then given by

$$V(\vec{r}) = -E_0 r \cos\theta_{rE} + (p/r^2)\cos\theta_{rE} \ , \tag{3}$$

$$D_r(\vec{r}) = E_r(\vec{r}) = E_0\cos\theta_{rE} + (2p/r^3)\cos\theta_{rE} \ , \tag{4}$$

where p is the induced dipole moment of the sphere and θ_{rE} is the angle between the vectors $\vec{r}$ and $\vec{E}$. Inside the sphere, we can write

$$\vec{\nabla}\cdot\vec{D} = 0 \ , \tag{5a}$$

$$\vec{\nabla}\times\vec{E} = 0 \ . \tag{5b}$$

To solve for the fields inside the sphere we introduce a fictitious medium in the $r > a$ region, which is a mathematical continuation of the material inside the sphere and which satisfies the following conditions: (i) Maxwell's equations are continued to the $r > a$ region in a form-invariant manner with appropriate definitions of the $\vec{D}$ and $\vec{E}$ fields and the charge density there; (ii) the fields inside the actual sphere are the same as the fields in the $r < a$ region of this infinite medium, the bulk response function of this medium being the same as that of the sphere material; (iii) the component D_r is discontinuous, but the tangential component D_θ is continuous across the surface $r = a$ in this infinite system.

Therefore Eq. (5a) does not hold on the surface of the sphere, where there is a fictitious external surface charge that acts as a source for $\vec{D}$.

It is convenient to introduce the potential function $V_D(\vec{r})$ defined by[12]

$$\vec{D}(\vec{r}) = -\vec{\nabla}V_D(\vec{r}) \ . \tag{6}$$

Next we define

$$V_D(\vec{k}) = \int V_D(\vec{r})\exp(-i\vec{k}\cdot\vec{r})d^3r \ , \tag{7}$$

and its inverse

$$V_D(\vec{r}) = \frac{1}{(2\pi)^3}\int V_D(\vec{k})\exp(i\vec{k}\cdot\vec{r})d^3k \tag{8}$$

in this infinite system, and similar relations for the total potential $V(\vec{r})$ and its Fourier transform $V(\vec{k})$. We note at the outset that $V(\vec{r})$ and $V_D(\vec{r})$ must be of the form

$$V(\vec{r}) = \tilde{V}(r)\cos\theta_{rE} \ , \tag{9a}$$

$$V_D(\vec{r}) = \tilde{V}_D(r)\cos\theta_{rE} \ . \tag{9b}$$

Equation (5) then reduces to

$$\nabla^2 V_D = 0 \ . \tag{10}$$

Multiplying this equation by $\exp(-i\vec{k}\cdot\vec{r})$ and integrating we get

$$-k^2 V_D(\vec{k}) + a^2\delta\left[\int \exp(-i\vec{k}\cdot\vec{r})\right.$$
$$\left.\times \cos\theta_{rE}d\Omega\right]_{r=a} = 0 \ , \tag{11}$$

where[13]

$$\delta = -\left[\frac{d\tilde{V}_D}{dr}\right]_{r=a^+} + \left[\frac{d\tilde{V}_D}{dr}\right]_{r=a^-} \ . \tag{12}$$

Using the expansion

$$\exp(-i\vec{k}\cdot\vec{r}) = 4\pi\sum_{l,m}(-i)^l j_l(kr)Y_{lm}(\theta_{kE},\phi_{kE})$$
$$\times Y_{lm}^*(\theta_{rE},\phi_{rE}) \ , \tag{13}$$

where $j_l(kr)$ is the spherical Bessel function of order l and Y_{lm}'s are the usual spherical harmonics, one gets

$$V_D(\vec{k}) = [4\pi i a^2\delta j_1(ka)/k^2]\cos\theta_{kE} \ , \tag{14}$$

whence

$$V(\vec{k}) = [4\pi i a^2\delta j_1(ka)/k^2\epsilon_B(\vec{k},\omega)]\cos\theta_{kE} \ . \tag{15}$$

We can now go back to the coordinate space using equations like Eq. (8). For $r < a$, this gives

$$V_D(\vec{r}) = (\delta/3) r \cos\theta_{rE} \quad , \tag{16}$$

$$V(\vec{r}) = a^2 \delta F(r) \cos\theta_{rE} \quad , \tag{17}$$

where

$$F(r) = \frac{2}{\pi} \int_0^\infty \frac{j_1(kr) j_1(ka)}{\epsilon_B(\vec{k},\omega)} dk \quad . \tag{18}$$

Since the potentials are the same as those within the actual sphere, we can match $V(\vec{r})$ and $D_r(\vec{r})$ obtained from Eqs. (6), (16), and (17) with the corresponding quantities outside the sphere, given by Eqs. (3) and (4), at $r = a$. The resulting equations can be immediately solved for p and hence for the polarizability, $\alpha(\omega) \equiv p/E_0$. Our final result can be written as

$$\alpha(\omega) = a^3 \left[\frac{1 - 3aF(a)}{1 + 6aF(a)} \right] \quad . \tag{19}$$

Note that in the local limit, i.e., when $\epsilon_B(\vec{k},\omega) \equiv \epsilon_L(\omega)$,

$$F(r) = \frac{r}{3a^2 \epsilon_L} \quad , \tag{20}$$

and α reduces to the familiar expression found in elementary textbooks,[14] viz.,

$$\alpha(\omega) = a^3(\epsilon_L - 1)/(\epsilon_L + 2) \quad . \tag{21}$$

III. THE NATURE OF THE ABC

Before applying Eq. (19) to a more general $\epsilon_B(\vec{k},\omega)$, we will discuss more precisely the nature of the boundary conditions implied by our assumptions. A specific transformation which satisfies all our requirements is suggested by the "inversion theorem"[15] and is defined by

$$V^>(\vec{r}) = (a/r) V^<(a^2\vec{r}/r^2) \quad , \tag{22}$$

$$V_D^>(\vec{r}) = (a/r) V_D^<(a^2\vec{r}/r^2) \quad , \tag{23}$$

where the $>$ ($<$) sign refers to the region $r > a$ ($r < a$) of this infinite system. Furthermore, the nonlocal susceptibility function $\chi(\vec{r},\vec{r}',\omega)$, which relates $V(\vec{r})$ and $V_D(\vec{r})$ for the actual sphere according to the equation

$$V_D(\vec{r}) = V(\vec{r}) + 4\pi \int \chi(\vec{r},\vec{r}',\omega) V(\vec{r}') d^3r' \quad , \tag{24}$$

is assumed to be of the form

$$\chi(\vec{r},\vec{r}',\omega) = [\chi_B(\vec{r} - \vec{r}',\omega) + (a/r')^5$$
$$\times \chi_B(\vec{r} - a^2\vec{r}'/r'^2,\omega)]$$
$$\times \Theta(a - r)\Theta(a - r') \quad , \tag{25}$$

where $\chi_B(\vec{r} - \vec{r}',\omega)$ is the corresponding bulk response function and $\Theta(x)$ is the usual step function

$$\Theta(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x < 0 \end{cases} \quad . \tag{26}$$

The factor $(a/r')^5$ in the second term on the right side is a "weight factor"[16] which allows for the difference in locations of the $\vec{r}'$ and $a^2\vec{r}'/r'^2$. Using Eqs. (22), (23), and (25), the integral over the sphere in Eq. (24) can be transformed into an integral over all space, giving the equation

$$V_D(\vec{r}) = \int \epsilon_B(\vec{r} - \vec{r}',\omega) V(\vec{r}') d^3r' \quad , \tag{27}$$

which is formally the same as a "bulk response" equation in the fictitious infinite medium, as desired. Equations (22) and (23) are also consistent with the Fourier transforms of Eqs. (14) and (15).

Our boundary condition is similar to the "specular reflection" boundary condition of Fuchs-Kliewer (FK) in the sense that the effect of the boundary is assumed to be the same as that of a fictitious medium which is an "image" of the real system (about a spherical boundary in the present case instead of a plane boundary). However, unlike the FK ABC, the present scheme does *not* satisfy the condition that the normal component of the vector $\vec{P} \equiv (\vec{D} - \vec{E})/4\pi$ should be zero at the boundary. This can be seen by differentiating Eqs. (22) and (23), whence we get

$$P_r^<(r = a) = [\tilde{V}^<(a) - \tilde{V}_D^<(a)] \cos\theta_{rE}/8\pi a \quad , \tag{28}$$

unless it is discontinuous at $r = a$. In either case, $P_r^<(r = a) \neq 0$ because it follows from the matching conditions of the fields that $\tilde{V}^<(a) \neq \tilde{V}_D^<(a)$.

In the case of insulators this is not really a restriction because there is no physical condition which requires P_r to be zero at $r = a$. For a metallic sphere, however, the normal component of the current density J_r, which is related to P_r by

$$J_r = \frac{\partial P_r}{\partial t} = -i\omega P_r \quad , \tag{29}$$

must vanish at the boundary. So if $P_r^< \neq 0$ at $r = a$, $J_r^<$ is also nonzero, except in the static case, $\omega = 0$. In the next section we discuss how one can overcome this difficulty.

IV. MODIFIED EXPRESSION
FOR POLARIZABILITY

Although P_r $(r = a)$ is nonzero in our formulation we can make it vanish by slightly modifying our ABC. In order to do that the key observation necessary is the fact that any solution of Eq. (10) can be changed by an amount $Cr\cos\theta_{rE}$, where C is an arbitrary constant, without changing the equation. One can therefore add to the solution $\vec{D} \equiv - \vec{\nabla} V_D(\vec{r})$, where $V_D(\vec{r})$ is given by the Fourier transform of Eq. (14), a $\vec{D}$ field of the form $-C\hat{z}$, which is constant everywhere in the infinite medium. Note that, unlike $\nabla V_D(\vec{r})$, which goes like $1/r^3$ for $r > a$, this additional field remains constant and nonzero even at infinity. This does not contradict any boundary condition on the *real* fields because the real fields coincide with the fields in this mathematical space only for $r < a$. This change would, of course, mean a change in $V(\vec{r})$ also, but since the added $\vec{D}$ field is constant, the change in V is related to the change in V_D by the local dielectric constant $\epsilon_L \equiv \epsilon_B(\vec{k} = 0, \omega)$. Thus we can change Eqs. (16) and (17) to their new values, indicated by the superscript 0,

$$V_D^0(\vec{r}) = (\delta/3)r\cos\theta_{rE} + Cr\cos\theta_{rE} \quad , \tag{30}$$

$$V^0(\vec{r}) = a^2\delta F(r)\cos\theta_{rE} + (Cr/\epsilon_L)\cos\theta_{rE} \tag{31}$$

without changing Maxwell's equations. One can now determine the three unknowns δ, C, and p in our problem by using the two previous matching conditions plus a third condition which we now impose,

$$\epsilon_0\left[\frac{dV^0}{dr}\right]_{r=a^-} = -\left[E_0 a + \frac{2p}{a^3}\right]\cos\theta_{rE} \quad , \tag{32}$$

where ϵ_0 is the background dielectric constant of the sphere. For simple metals $\epsilon_0 = 1$ and this is simply the continuity condition on the radial component of the electric field. For dielectrics this implies that the excitonic part $\vec{\mathscr{P}}$ of the total polarization, given by

$$\vec{\mathscr{P}} = \vec{P} - (\epsilon_0 - 1)\vec{E}/4\pi \quad , \tag{33}$$

must have a vanishing radial component at $r = a$. With this new condition, our final result for $\alpha(\omega)$ takes the form

$$\alpha(\omega) = a^3\left[\frac{1 - 3aF(a) + K(\epsilon_L - 1)}{1 + 6aF(a) + K(\epsilon_L + 2)}\right] \quad , \tag{34}$$

where

$$K = \left[3\epsilon_0 a^2\left[\frac{dF}{dr}\right]_{r=a} - 1\right]\Big/(\epsilon_L - \epsilon_0) \quad . \tag{35}$$

In the local limit, Eq. (34) gives $\alpha(\omega) = 0/0$; this reflects the fact that in the local limit the third condition, given by Eq. (32), is inconsistent with the first two. The correct local limit can be restored either by neglecting the third condition altogether or by evaluating expression (34) using a nonlocal $\epsilon_B(\vec{k}, \omega)$ and then taking the limit $k \to 0$. The second procedure will be discussed in the next section.

Let us note that instead of Eqs. (22) and (23), the "modified" potentials, given by Eqs. (30) and (31), satisfy the transformation equations:

$$V^{0>}(\vec{r}) = (a/r)[V^{0<}(a^2\vec{r}/r^2) - (Ca^2/\epsilon_L r)\cos\theta_{rE}]$$
$$+ (Cr/\epsilon_L)\cos\theta_{rE} \tag{36}$$

$$V_D^{0>}(\vec{r}) = (a/r)[V_D^{0<}(a^2\vec{r}/r^2) - (Ca^2/r)\cos\theta_{rE}]$$
$$+ Cr\cos\theta_{rE} \quad . \tag{37}$$

Using Eqs. (36), (37), and (25), it can again be easily shown that Eq. (24) can formally be written as in Eq. (27) in the infinite mathematical space.

We would like to point out some interesting aspects of these transformations. First of all, if we compare our theory with the FK theory for a plane boundary then it is clear that our Eqs. (22), (23), and (25) are analogous to the following equations in the planar case, which follow from their work in the *nonretarded* limit:

$$V(a + z) = V(a - z) \quad , \tag{38}$$

$$V_D(a + z) = V_D(a - z) \quad , \tag{39}$$

$$\chi(z, z', \omega) = [\chi_B(z - z', \omega) + \chi_B(z + z', \omega)]$$
$$\times \Theta(a - z)\Theta(a - z') \quad , \tag{40}$$

where z is the coordinate perpendicular to the plane interface located at $z = a$ and the real system occupies the $z < a$ half-space. In the case of a plane boundary, these transformations automatically imply that the normal component P_z of the polarization vector (or its excitonic part $\mathscr{P}_z$ in the case of dielectrics) vanishes at the boundary. This is no longer true in the case of a sphere. Equations (22) and (23) were somewhat artificially modified by introducing the constant C to get Eqs. (36) and (37) and the arbitrary constant C was in fact "fixed" in order to make P_r vanish at $r = a$. Secondly, we should emphasize that although our modified ABC does make P_r zero at the boundary it is still not ex-

actly analogous to the FK ABC. This is because, unlike the FK ABC, the normal derivative of the tangential component of $\vec{P}$ (i.e., $\partial P_\theta/\partial r$) does not vanish at the boundary in our work. Finally we note that, if we let $a \rightarrow \infty$, $r \rightarrow \infty$, keeping $|a - r|$ finite, both pairs of transformation equations, viz., (22), (23) and (36), (37), go over the result (38) and (39) for a plane boundary.

V. APPLICATIONS

A. Dielectric sphere

As a simple example of application of our result, consider the expression for $\epsilon_B(\vec{k},\omega)$,

$$\epsilon_B(\vec{k},\omega) = \epsilon_0 + \omega_p^2/[\omega_T^2 + Dk^2 - \omega(\omega + i\gamma)] \ ,$$

$$(41)$$

which is frequently used[17,18] to represent the nonlocal effect in a dielectric medium (also known as spatial dispersion in this case) near an isolated exciton resonance. Here ω_p is a measure of the dipole oscillator strength of the excitation of frequency ω_T, γ is a damping parameter, and the term Dk^2 represents the spatial dispersion. With this form for $\epsilon_B(\vec{k},\omega)$ we can easily determine the function $F(r)$ given by Eq. (18)[19]

$$F(r) = \frac{r}{3a^2}\left[\frac{1}{\epsilon_0} - \frac{C}{\lambda^2}\right] + \frac{C}{\lambda^2\sqrt{ar}}I_{3/2}(\lambda r)K_{3/2}(\lambda a),$$

$$(42)$$

where

$$C = \omega_p^2/D\epsilon_0^2 \ ,$$

$$(43)$$

$$\lambda^2 = \left[\frac{\omega_p^2}{\epsilon_0} - \omega(\omega + i\gamma) + \omega_T^2\right]\bigg/D \ , \quad (44)$$

and I_ν and K_ν are modified Bessel functions[20] of half-integral order $\nu(= \frac{3}{2})$. The polarizability $\alpha(\omega)$ can now be calculated either from Eq. (34) or from Eq. (19). Of particular interest is the imaginary part of $\alpha(\omega)$ because it is proportional to the absorption coefficient of the sphere and its variation with frequency can be compared with the result given in Ref. 9. Note that Ruppin has numerically calculated the extinction coefficient,[9] which is approximately equal to the absorption coefficient for a very small sphere. According to Ref. 9, the main effect of the spatial dispersion is a slight shift in the main absorption peak from its local value of about 1.0003 ω_T to a higher value. This peak arises from the ex-

citation of the so-called Fröhlich mode. We obtained a similar shift using our results. Ruppin has shown that this frequency shift of the absorption peak increases with decreasing particle size in a manner which depends on the choice of the ABC (see the second article in Ref. 9). We have investigated this size dependence using the same values for the various parameters as those employed in Ref. 9, viz., $\omega_p/\omega_T = 0.074\,16$, $D/C^2 = 6.1728 \times 10^{-6}$, $\gamma/\omega_T = 10^{-5}$, $\epsilon_0 = 8.1$, and $\omega_T = 2.8$ eV. These values correspond to a ZnSe sphere. Our result for the frequency of the absorption peak versus the particle radius is shown in Fig. 1 using both Eq. (34) and Eq. (19). It is interesting to note that these results are close to that of Ref. 9 if one uses the FK ABC in that work. This closeness also shows that our approach is similar to the FK formalism as far as the basic physics is concerned, even though the precise boundary condition on the polarization vector is somewhat different.

We can also use Eq. (42) to show that expression (34) has the correct local limit, as mentioned in the last section. This follows by noting that in the $D \rightarrow 0$ (or $\lambda \rightarrow \infty$) limit, the parameter K in Eq. (35) has the form

$$K = -\frac{1}{\epsilon_L} - \frac{3\epsilon_0 C}{2\lambda^2} \ , \quad (45a)$$

while $aF(a)$ goes like

$$aF(a) = \frac{1}{3\epsilon_L} + \frac{C}{2\lambda^3 a} \ . \quad (45b)$$

B. Metallic sphere-dynamic case

If we represent the response of the metal by a hydrodynamic dielectric function,[21]

$$\epsilon_B(\vec{k},\omega) = 1 - \omega_p^2/[\omega(\omega + i\gamma) - \beta^2 k^2] \ , \quad (46)$$
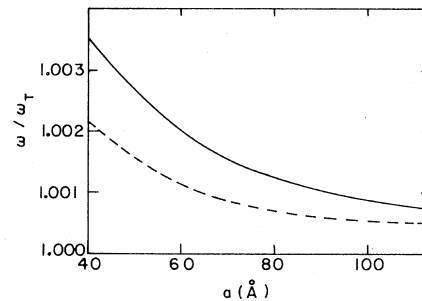

FIG. 1. Variation of the frequency of the absorption peak with radius for a ZnSe sphere. The solid curve is obtained using Eq. (34), while the dashed curve follows from Eq. (14).

where $\beta^2 = 3v_F^2/5$ (v_F being the Fermi velocity) and ω_p is the bulk plasmon frequency of the metal, then the polarizability $\alpha(\omega)$ can be obtained from the dielectric case simply by setting $\epsilon_0 = 1$, $\omega_T = 0$, and $D = \beta^2$. We have plotted $\text{Im}\alpha(\omega)$ versus ω in Fig. 2 for a sphere of sodium ($\omega_p = 5.9$ eV, $v_F = 1.07 \times 10^8$ cm/sec) of radius 15 Å with $\gamma = 0.01\omega_p$. This figure may be compared with Ruppin's result given in Ref. 10. The agreement is excellent. In particular, our result predicts (just like Ref. 10) a shift in the main absorption peak (due to the excitation of $l = 1$ surface-plasmon mode) from its classical value of $\omega_p/\sqrt{3}$ to about $0.62\omega_p$ and a series of small peaks above the bulk plasmon frequency. Our result also agrees with Ref. 10 as far as the relative heights of the main peak and these secondary peaks are concerned. The slight discrepancy in the positions of the secondary peaks is presumably due to the difference in the assumed forms of the dielectric function. Ruppin used the Lindhard expressions and since he considered retardation effects, his formulation involved both the longitudinal and transverse dielectric functions. He also assumed a $\vec{k}$-dependent damping term.

It is also quite striking that our expression for $\alpha(\omega)$ given by Eq. (19) gives essentially the same result as the more rigorous expression, Eq. (34), even though the derivation of Eq. (19) contradicts the continuity of the component P_r at the surface. This suggests that the nonvanishing of the normal current density at the surface is not a very serious limitation in the case of a metallic sphere as long as

the nonlocal effects are included in a "reasonable" way.

One can also investigate the variation of the "dipole" surface plasmon frequency with particle radius using our theory, because this frequency corresponds to the pole in $\alpha(\omega)$. If we use expression (19), the surface plasmon frequency would be given by

$$F(a) = -\frac{1}{6a} \ , \tag{47}$$

which agrees with the $l = 1$ case of a previous surface plasmon dispersion relation derived by Dasgupta.[22] On the other hand, if one uses Eq. (34), the corresponding equation for the surface plasmon frequency is

$$2(\epsilon_L - 1)a\left[F(a) - a\left.\left[\frac{dF}{dr}\right]\right|_a\right] = 1 - 3\epsilon_L a^2\left.\left[\frac{dF}{dr}\right]\right|_a \ . \tag{48}$$

Using the hydrodynamic version of $F(r)$ given by Eqs. (42)−(44) (with $\epsilon_0 = 1$, $\omega_T = 0$, $D = \beta^2$) and a little algebra, Eq. (48) can be reduced to

$$I_{5/2}(\lambda a) = \epsilon_L I_{1/2}(\lambda a)/2 \ . \tag{49}$$

This is precisely the equation for surface plasmon frequency for the $l = 1$ mode derived by Crowell and Ritchie[23] using a hydrodynamic theory. The advantage of Eq. (48) is that it can be applied in conjunction with more rigorous expressions for $\epsilon_B(\vec{k},\omega)$ which go beyond the hydrodynamic model.
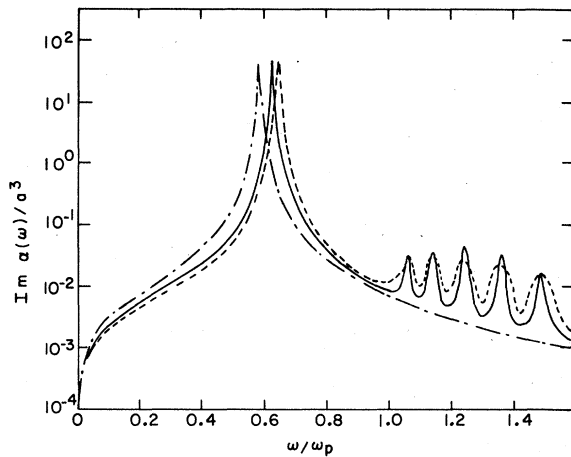

FIG. 2. Variation of the imaginary part of $\alpha(\omega)$ with ω for a sodium sphere of radius 15 Å. The solid curve is obtained using Eq. (34), the dashed curves using Eq. (19), and the dot-dashed curve indicates the corresponding local result.

C. Metallic sphere-static case

If $\omega = 0$, then the dielectric function can be approximated by the well-known Thomas-Fermi expression[24]

$$\epsilon(\vec{k},0) = 1 + k_{\text{TF}}^2/k^2 \ , \tag{50}$$

where k_{TF} is the Thomas-Fermi wave vector. The function $F(r)$ now takes the form

$$F(r) = I_{3/2}(k_{\text{TF}}r)K_{3/2}(k_{\text{TF}}a)/\sqrt{ar} \ . \tag{51}$$

In Fig. 3 the quantity $\alpha(\omega = 0)/a^3$ is plotted against the dimensionless parameter $k_{\text{TF}}a$, using both Eqs. (19) and (34). We obtain very satisfactory agreement with the previous work of Rice et al.[4] provided one uses low values of the parameter r_s $[\equiv (\frac{3}{4}\pi n_0)^{1/3}/a_B$, n_0 being the electron density and a_B the Bohr radius], such as $r_s \simeq 1$ in their work. Since the surface becomes more diffuse in their
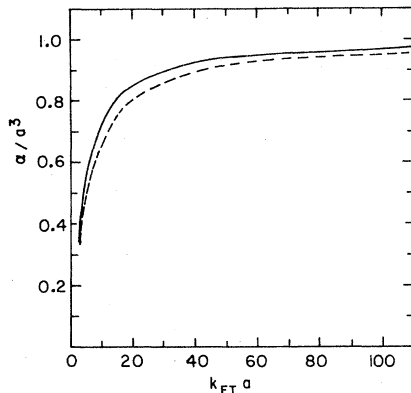
FIG. 3. Variation of the static polarizability $\alpha(\omega = 0)$ with particle radius for a metallic sphere. The solid curve is obtained using Eq. (34) and the dashed curves using Eq. (19).

model for larger values of r_s whereas our model implies a sharp metal-vacuum boundary for all values of r_s, the agreement gets worse as r_s increases. The authors of Ref. 4 calculated $\alpha(\omega = 0)$ using a semiclassical approach as well as a quantum-mechanical random-phase approximation (RPA) approach using the infinite potential barrier model and obtained almost identical values in the two cases.[4] The fact that our numerical calculation agrees with those values in the low-r_s regime indicates that the essential physics of the system is contained in our simple treatment even for particle radii as small as 5 Å. If one could include the effect of the continuous nature of the electron density near the surface in our formalism, we believe that this agreement would continue to larger values of r_s as well. Another advantage of our theory is that one can use Eqs. (30) and (31) to study the spatial variations of quantities like electric field, polarization, induced charge density, etc., within the sphere in a simple analytical way.

V. CONCLUSION

We have derived two simple expressions for the polarizability of a small spherical particle including nonlocal effects. While the second expression, given by Eq. (34), is preferable because it is consistent with the correct boundary condition on the current density in the case of a metallic sphere, the first expression, given by Eq. (19), is even simpler and gives similar results as the second one. Apart from their simplicity, two other major advantages of our formulas are that (a) they can be applied to various different materials and (b) they are capable of giving quantitatively correct results, as can be seen from our calculations in the preceding section. We hope that our work will be useful in studying the optical properties of particles of other materials (such as semiconductors, ionic crystals, etc.) which we did not consider here. In particular, there are two areas of considerable current interest where a theory like ours can play a significant role: (a) It is known that absorption by phonons might be responsible for the anomalously large absorption of infrared radiation by very small metallic particles[25]; one could try to see whether our theory would explain this large absorption by adding a "phonon term" to the dielectric function. (b) Some of the theories of the surface-enhanced Raman scattering are based on an enhancement of the effective polarizability due to image effects.[26] These theories treat the molecules under investigation as point dipoles, which is a very serious restriction since the metal-molecule distances are comparable to the molecular size. As a better approximation, one can assume the molecules to be dielectric spheres[27] and our expressions for $\alpha(\omega)$ can provide a simple but accurate way for taking into account both the size as well as the frequency dependence of the polarizability.

ACKNOWLEDGMENT

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[13]Although $d\bar{V}_D/dr$ is continuous at the actual sphere-vacuum interface, it is discontinuous at $r = a$ in our fictitious medium.

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[16]The factor $(a/r')^5$ is consistent with the facts that (i) the induced charge density $\rho(\vec{r})$ transforms according to the equation (see Ref. 15) $\rho^>(\vec{r}) = (a/r)^5\rho^<(a^2\vec{r}/r^2)$ and (ii) the response function $L_B(\vec{r} - \vec{r}'')$, which relates $\rho(\vec{r})$ with $V(\vec{r})$, is symmetric in $\vec{r}$ and $\vec{r}''$ and should, therefore, transform in the same way with respect to both $\vec{r}$ and $\vec{r}''$.

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