

## Multipolar response of small metallic spheres: Nonlocal theory

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The multipolar response of a small metallic sphere is studied with use of a nonlocal dielectric function. Results obtained with the hydrodynamic and Lindhard-Mermin models are presented and compared to those given by the local Drude model. We find an enhancement of the imaginary part of the multipole polarizabilities at low frequencies and pole order  $l < l_c$ , where  $l_c$  is a cutoff order that corresponds to excitations at the high-wave-vector edge of the electron-hole pair continuum. The absorption coefficient for two very close spheres is calculated and the effect of nonlocality on the number and position of the multipolar absorption peaks is discussed.

### I. INTRODUCTION

The response of small metallic particles to electromagnetic radiation has been the subject of much recent work.<sup>1-27</sup> Of special interest has been the anomalous absorption that composite samples containing these particles exhibit in the far infrared and its dependence on particle size, clustering and volume fraction.<sup>18-27</sup> The most straightforward theories treat spherical particles and assume a local uniform dielectric function for the material. Such spheres have a large absorption peak due to the excitation of a surface plasmon of dipolar character, that appears at a frequency  $\omega_p/\sqrt{3}$  if a Drude dielectric function is adopted. More realistic dielectric functions including a nonlocal character have also been used and give a much richer absorption spectrum.<sup>6,7,13</sup>

When more than one particle is present proximity effects can have a strong influence in absorption. Detailed studies of the two-sphere case show that the presence of a second sphere shifts the dipolar mode to lower frequencies and that new absorption peaks of quadrupolar, octupolar or higher-pole character appear.<sup>28-30</sup> These effects become more apparent as the separation between the spheres decreases and when they are close to touching, the local theory predicts that the absorption peaks approach the bulk static resonance at zero frequency. The multipolar expansion diverges as touching is approached, a clearly unphysical situation since the excitation of modes of very high angular momentum or short wavelength is inhibited by the fact that the electronic wave functions extend over a spatial region of finite size. In this paper we show that the use of a nonlocal dielectric function introduces a cutoff angular momentum that corrects this deficiency in a satisfactory way. In Sec. II we study the multipole polarizabilities of a single sphere in the frequency range  $0 < \omega < 2\omega_p$  using the Drude, hydrodynamic, and Lindhard-Mermin dielectric functions. In Sec. III these polarizabilities are used to obtain the absorption coefficient for a close and a touching pair of spheres. The full

multipolar effects are included since in a nonlocal theory very high-order multipoles have a negligible effect. Still, as we show, the multipolar couplings modify qualitatively the response of a single sphere by introducing additional peaks in the spectrum and broadening significantly the resonance region.

### II. RESPONSE OF A SINGLE SPHERE

We consider the single metallic sphere of radius  $a$ , whose response to an arbitrary electric field is characterized by polarizabilities  $\alpha_l$ , where  $l$  is the pole order of the exciting field component. In a local theory these quantities are given by

$$\alpha_l = \frac{l(\epsilon - 1)}{l(\epsilon + 1) + 1} a^{2l+1}, \quad (1)$$

where  $\epsilon$  is the frequency-dependent dielectric function. Within the Drude model both the real and imaginary parts of  $\alpha_l$  remain finite for arbitrarily large  $l$ . On physical grounds one expects a cutoff at large  $l$  since a metallic particle is not polarized by an electric field which oscillates with a wavelength much smaller than a Fermi wavelength. We shall therefore derive an expression for the polarizability of a single sphere that includes nonlocal effects through a general dielectric function of the form  $\epsilon(\mathbf{k}, \omega)$  and has the desired property of going to zero for sufficiently large values of  $l$ .

In order to excite the multiple of order  $l$  we assume the particle is in an external potential with azimuthal symmetry ( $m=0$ ):

$$V_l(\mathbf{r}) = C_l \left[ \frac{2l+1}{4\pi} \right]^{1/2} r^l P_l(\theta), \quad (2)$$

where  $\mathbf{r} = (r, \theta, \phi)$  are spherical coordinates referred to an origin at the particle center,  $P_l(\theta)$  is a Legendre polynomial of order  $l$ , and  $C_l$  is a constant. A unit charge placed on the  $z$  axis outside the sphere would, for example, produce potential components of the form (2). The

potential (2) excites the multipole  $q_l$  of order  $l$  ( $m=0$ ), which in turn produces a potential outside the sphere of the form

$$V_l^{ind}(\mathbf{r}) = \left( \frac{4\pi}{2l+1} \right)^{1/2} \frac{q_l}{r^{l+1}} P_l(\theta), \quad (3)$$

where the usual definition of  $q_l$  has been adopted.<sup>31</sup> The polarizability  $\alpha_l$  is defined by

$$q_l = -C_l \left[ \frac{2l+1}{4\pi} \right] \alpha_l. \quad (4)$$

The problem of finding  $\alpha_l$  reduces to solving Maxwell's equations with appropriate boundary conditions at the surface of the sphere  $r=a$ . Dasgupta and Fuchs developed a semiclassical infinite-barrier (SCIB) theory for the dipolar ( $l=1$ ) case.<sup>7</sup> We have extended their method to arbitrary  $l$  in a straightforward manner whose details we shall omit here. The result for the polarizability of order  $l$  is

$$\alpha_l = \frac{l(E_l - 1)}{l(E_l + 1) + 1} a^{2l+1} \quad (5)$$

with

$$E_l = \left[ \frac{2}{\pi} (2l+1)a \int_0^\infty \frac{j_l^2(ka)}{\epsilon(\mathbf{k}, \omega)} dk \right]^{-1}, \quad (6)$$

where  $j_l(x)$  is the spherical Bessel function of order  $l$ . For a  $k$ -independent dielectric function  $E_l = \epsilon$  and one recovers the local result (1). The quantity  $E_l$  thus acts like an effective dielectric constant for the excitation of the mode of angular momentum  $l$ . The simplest nonlocal response function is given by the hydrodynamic model<sup>32</sup>

$$\epsilon(\mathbf{k}, \omega) = 1 - \omega_p^2 / [\omega(\omega + i\gamma) - \beta^2 k^2], \quad (7)$$

where  $\gamma$  is a damping parameter and  $\beta^2 = 3v_F^2/5$ ,  $v_F$  being the Fermi velocity. Using this form of dielectric function in (6), we obtain

$$E_l = \left[ \frac{1}{\epsilon} + (2l+1) \left( \frac{a\omega_p}{\beta u} \right)^2 I_{l+1/2}(u) K_{l+1/2}(u) \right]^{-1} \quad (8)$$

where  $u = a[\omega_p^2 - \omega(\omega + i\gamma)]^{1/2}/\beta$ ,  $I_\nu$  and  $K_\nu$  are modified Bessel functions, and  $\epsilon$  denotes the value of the local or Drude dielectric function, obtained from (7) when  $\beta=0$ . The second term in the right-hand side of expression (8) is the nonlocal correction. We have used (7) as well as the Lindhard-Mermin dielectric function<sup>33</sup> to study the effect of nonlocality on the multipole polarizabilities (5). The latter is a better description for response at large wave vector where excitation of electron-hole pairs becomes important. We have used the bulk parameters for tin,  $\omega_p = 1.17 \times 10^{16} \text{ sec}^{-1}$ ,  $v_F = 1.24 \times 10^8 \text{ cm/sec}$  and as a mean free path, the sphere radius.

Figure 1 shows the real and imaginary parts of the multipole polarizabilities of a sphere of radius  $a=30 \text{ \AA}$  for various frequencies. Results using the Drude (D, in Fig. 1) hydrodynamic (H, in Fig. 1), and Lindhard-Mermin (LM) dielectric functions are shown. The frequency dependence is well characterized by the four values we ex-

hibit: one in the low-frequency region ( $\omega \ll \omega_p$ ), two in the resonance region ( $\omega \sim 0.4\omega_p - 0.8\omega_p$ ) and one in the high-frequency ( $\omega > \omega_p$ ) region. A glance at Fig. 1 shows that at all frequencies the nonlocal sphere does not polarize significantly at angular momenta higher than a certain cutoff value  $l_c$ . Using a simple model in which this quan-

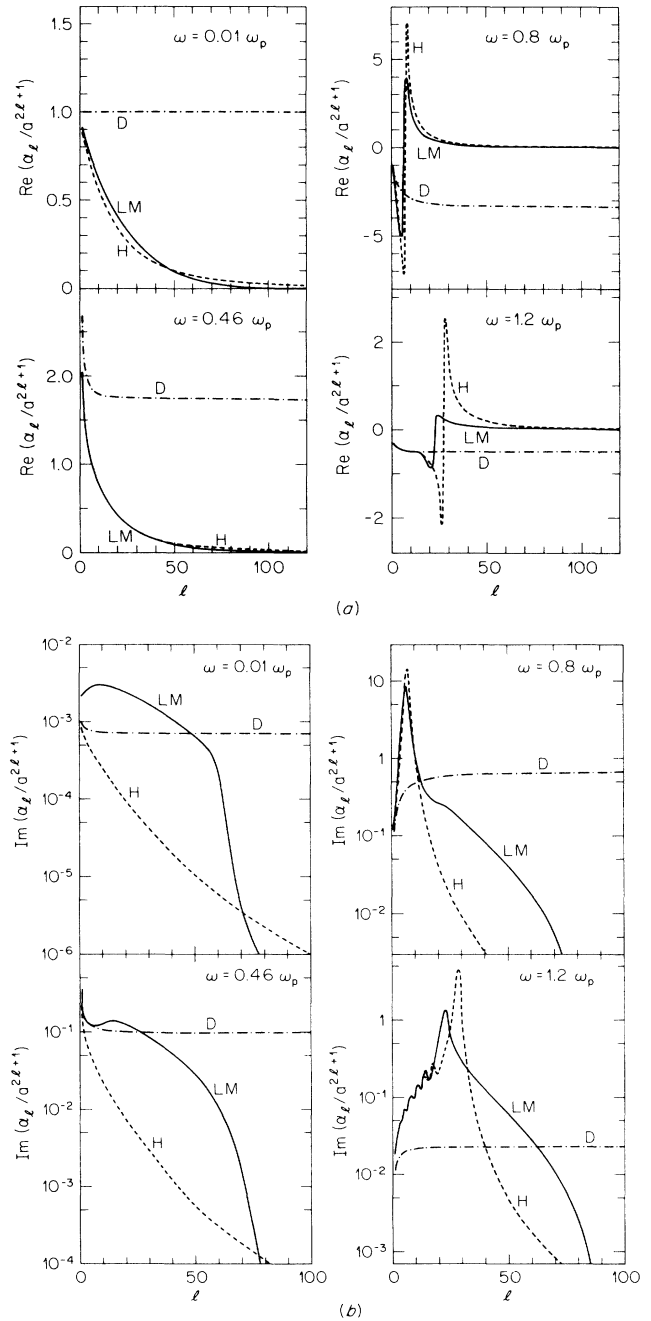


FIG. 1. (a) Real and (b) imaginary parts of the multipole polarizability of a tin sphere of radius  $a=30 \text{ \AA}$  at various frequencies, in the Drude (dotted-dashed curve), Lindhard-Mermin (solid curve) and hydrodynamic (dashed curve) models.

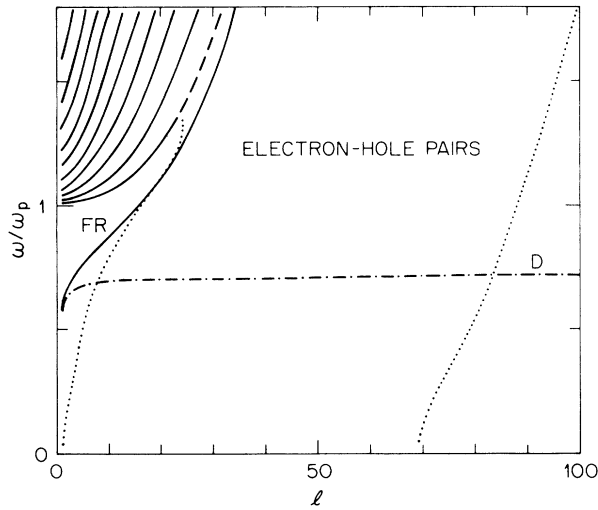


FIG. 2. Dispersion curves of multipolar resonances for a thin sphere of radius  $a=30 \text{ \AA}$  in the  $(\omega, l)$  plane. The curve labeled FR is the nonlocal Fröhlich resonance extended to all pole orders. The local approximation for this Fröhlich resonance is also shown (curve D). The edges of the electron-hole excitation region, marked by dotted lines, are not sharp. These edges are somewhat arbitrarily taken as the  $l$  values (for fixed  $\omega$ ) at which  $\text{Im}(E_l - 1)^{-1} = [\text{Im}(E_l - 1)^{-1}]_{\text{max}}/80$ .

tity is the number of nodes in the waveform of an excitation at the Fermi momentum covering the sphere circumference, we have  $l_c \sim 4\pi a/\lambda_F \sim 70$ , which is a good estimate at frequencies below the resonance region. Another important result is an enhancement in the imaginary part of the polarizabilities at low frequencies in the LM model due to electron-hole excitation. This enhancement amounts to a factor of 5–10 and gives a larger absorption coefficient for the single sphere by about the same factor. It represents the only qualitatively significant distinction between the hydrodynamic and LM models. At low frequencies  $\text{Re}(\alpha_l)$  is proportional to the frequency.

Figure 2 shows the dispersion curves of the multipole

$$M_k^{k'} = (-1)^m \frac{(k+k')!}{\sqrt{(k+m)!(k-m)!(k'+m)!(k'-m)!}} \frac{\alpha_k(\omega)}{D^{k+k'+1}}. \quad (10)$$

Here  $m=0$  for an external field along the center to center axis and  $m=1$  for a polarization perpendicular to this line. We see that the dipole excited in each sphere is proportional to the external field, with a factor of proportionality that acts as an effective polarizability

$$\alpha_{\text{eff}} = - \frac{\text{Cof}(M_1^1 - 1)}{\det(M - I)} \alpha_1(\omega). \quad (11)$$

For infinitely separated particles all matrix elements are zero and  $\alpha_{\text{eff}}$  just equals the single particle dipole polarizability  $\alpha_1$ . At finite separation the local field one of the sphere experiences includes the external field plus those fields that arise from the presence of the other sphere.

resonances for a 30-Å sphere in the  $(l, \omega)$  plane. Although only integer values of  $l$  have physical meaning, curves are drawn as if  $l$  were a continuous variable. This figure is the spherical analog of the excitation structure of an infinite medium in the  $(k, \omega)$  plane. With a local (Drude) dielectric function the only excitation is a Fröhlich resonance (labeled D), given by the condition  $\text{Re}(\alpha_l^{-1})=0$  or  $l = \omega^2/(\omega_p^2 - 2\omega^2)$ . With a nonlocal (LM) model, the Fröhlich resonance (labeled FR) moves to higher frequency with increasing  $l$ , while a series of bulk plasmon resonances in the range  $\omega > \omega_p$ ,<sup>6,7</sup> and a broad electron-hole excitation region also appears. The qualitative behavior of the peaks in Fig. 1(b) can be understood from Fig. 2.

### III. ABSORPTION BY A PAIR OF SPHERES

The simplest system that has its multipoles excited by optical means in the long-wavelength limit  $\lambda \gg a$  is a pair of identical spheres.<sup>34</sup> The nonuniform field that couples to multipoles of order higher than one is provided at the position of one of the spheres by the fields generated by the charge distribution and currents in the other. We are interested in the case of very small spheres where the dominant absorption is by coupling to the electric field and we shall ignore the magnetic contribution to absorption.

We consider two identical spheres of radius  $a$  separated by a center-to-center distance  $D$  and placed in a uniform external electric field  $E_{\text{ext}}$ . The individual response is characterized by the set of polarizabilities  $\alpha_l(\omega)$ . Since the particles are identical they acquire each a dipole moment that is the same in both magnitude and direction. The pair is also capable of an excitation in which both dipoles oppose each other but this mode is not excited in a uniform external field. In the optically active mode the dipole moment is given by<sup>30</sup>

$$p = - \frac{\text{Cof}(M_1^1 - 1)}{\det(M - I)} \alpha_1(\omega) E_{\text{ext}}, \quad (9)$$

where  $I$  is the unit matrix and  $M$  is a two-dimensional matrix with components

These fields are highly nonuniform and are responsible for the excitation of moments of order higher than the dipole in each particle. Such moments must be taken into account when  $D \lesssim 3a$ .<sup>29,34</sup> In the dipole approximation valid for larger  $D$  one assumes all matrix elements (10) to be zero except for  $M_1^1$  and the simple expression  $\alpha_1/(1 - M_1^1)$  for the effective polarizability readily follows. At closer separation one must keep higher-order matrix elements and in fact the dimension of the matrix  $M$  that is required diverges as the spheres approach touching if a local dielectric function is used.<sup>34</sup> The cut-off pole order introduced by nonlocality and described in Sec. II provides convergence of the multipolar series at an

order that can be handled computationally. We shall use this fact to present fully converged absorption curves for very near spheres. In our study we have preferred the LM dielectric function as a nonlocal model in order to include the electron-hole excitations. Thus, only the LM and D model results are discussed in this section.

Figure 3 shows the absorption coefficient per particle for axial excitation and two 30-Å spheres (full curves) at center-to-center distance  $D=61$  Å [Fig. 3(a)], and two 50-Å spheres at  $D=101$  Å [Fig. 3(b)]. In the former case the cutoff pole order  $l_c=80+20\omega/\omega_p$  was used, and for the latter, we chose  $l_c=130$ . The increase was necessary due to the fact that this quantity scales approximately linearly with the radius of the particles. The absorption coefficient is characterized by a number of resonances around  $\omega\sim 0.5\omega_p$  and a smaller oscillatory structure in the range  $\omega\sim 1.1\omega_p-1.6\omega_p$ . The latter is already present in the case of a single sphere,<sup>6,7</sup> which is included in Fig. 2(b) for comparison. We note that for frequencies above the resonance region the response of the pair does not differ significantly from that of two isolated spheres, except for a small decrease in the absorption coefficient in the region  $\omega\sim\omega_p$ . The single-sphere resonance appears slightly blue shifted away from the Fröhlich local resonance at  $\omega_F=\omega_p/\sqrt{3}$ , a known consequence of nonlocality in the SCIB model.<sup>6,7</sup> The main difference occurs in the intermediate-frequency region where there is additional structure and an important enhancement in the absorption by a pair that may reach up to two orders of magnitude. A small enhancement is also apparent in the low-frequency region.

In the resonance region a few peaks appear distinct. Counting from the left, the first resonance is the dipole (Fröhlich) resonance which has been red shifted from its isolated-sphere position. As the spheres move apart one can observe this peak to move continuously towards  $\omega_F$ . The second resonance is entirely due to coupling between the spheres and corresponds to a resonant quadrupolar excitation; the third has octupolar character, and so on. The resonances are fewer and always blue shifted compared to the local response. This is apparent in Fig. 3(a) where the absorption coefficient obtained using the Drude model has been included for comparison (dashed line). As noted in Sec. II this shift to larger frequencies is a nonlocal correction to the multipolar resonances of a single sphere and is maintained as two particles approach each other. The high-frequency oscillations in the region  $\omega>\omega_p$  are absent in the local case. In the low-frequency region the absorption coefficient is proportional to the square of the frequency and shows a nonlocal enhancement by a small factor corresponding to the enhancement of the imaginary part of the polarizability.

Figure 3(c) shows the absorption coefficient per particle for two touching spheres, calculated with the LM dielectric function and the same cutoff pole order  $l_c$  that was used in Figs. 3(a) and 3(b). For touching spheres, a local calculation does not converge. The absorption is similar to that found for almost-touching spheres [Figs. 3(a) and 3(b)] except for minor changes of the peaks in the resonance region. The number and precise location of the peaks may not be accurate because the SCIB model does

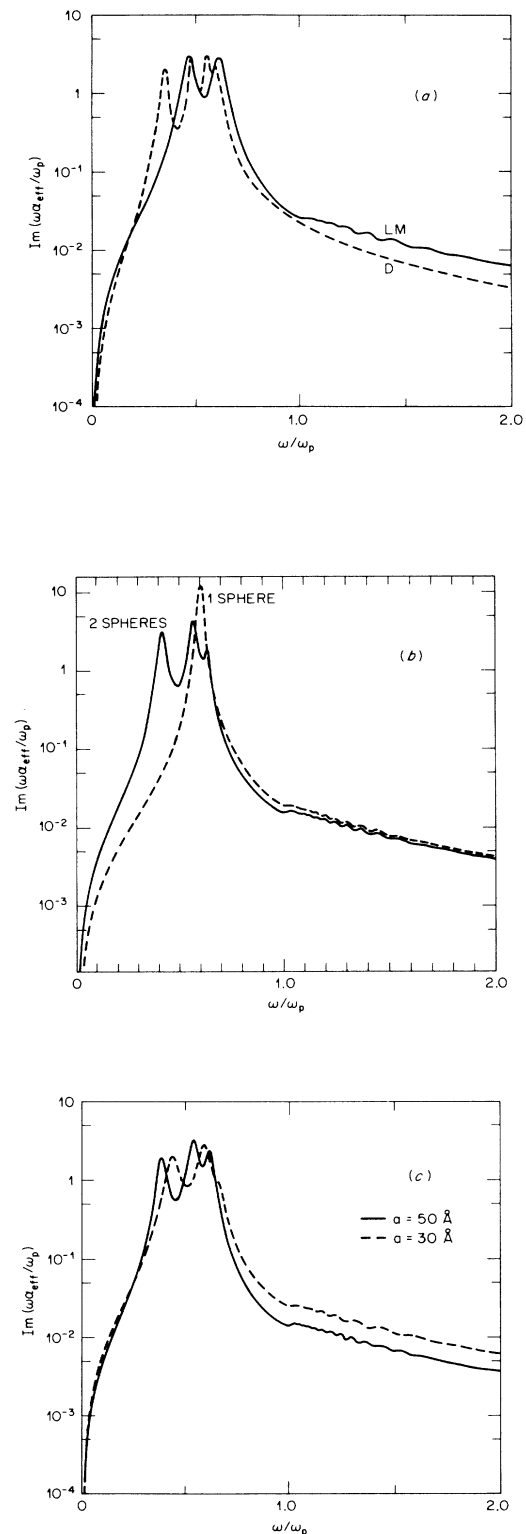


FIG. 3. (a) Absorption coefficient for two equal spheres of radius  $a=30$  Å and distance  $D=61$  Å between centers; (b) two spheres of radius  $a=50$  Å and distance  $D=101$  Å; (c) two touching spheres of radius  $a=30$  Å and radius  $a=50$  Å. The exciting field is along the line joining the sphere centers.

not give a very good description of the surface response. In fact, even an exact calculation of the multipolar resonance of an isolated sphere would give inaccurate results for touching spheres because of the effects of wave function overlap.

Figure 4 is for an external field perpendicular to the line joining the sphere centers. In this case the dipole excited by the external field on each sphere produces a nearly uniform field at the other spheres, with space variations that are mild compared to the case of axial excitation discussed above. As a consequence the effect of high-order multipoles is much smaller. Figure 4(a) is for two 30-Å tin spheres 61 Å apart in the nonlocal LM model (solid line) and local Drude model (dashed line). The main effect of nonlocality is a low-frequency enhancement by a small factor and the oscillations at the other end of the

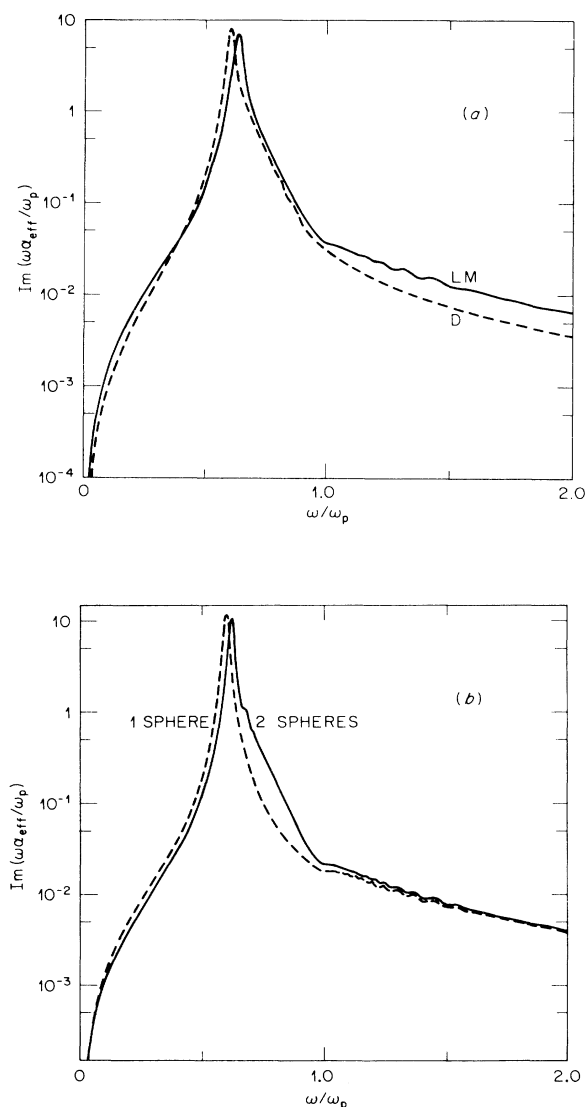


FIG. 4. Same as Figs. 3(a) and 3(b), but with an exciting field perpendicular to the line joining the sphere centers.

spectrum already discussed. Figure 4(b) compares the absorption coefficient per particle of two 50-Å spheres 101 Å apart, with that of a single sphere in the LM model. Coupling between the spheres shifts the spectrum slightly to larger frequencies and produces secondary peaks and a shoulder above the main resonance that are a consequence of multipolar excitations. We note that here the enhancement is by about a full order of magnitude. Finally, just as for axial excitation, the single-sphere oscillations for  $\omega > \omega_p$  are essentially reproduced in spite of the presence of another sphere.

#### IV. DISCUSSION AND CONCLUSIONS

Our results show that nonlocal effects are important in the response of a small metallic particle when multipoles of order higher than dipole are excited. This is because the polarizabilities are very different in the local and nonlocal models, a difference that is also strongly frequency dependent. In numerical computations the existence of a cutoff pole order is of principal importance since it allows a fully converged treatment of multipolar excitation effects. We use this fact to obtain the absorption coefficient of a very close and of a touching pair of tin spheres. We find that nonlocality has an effect on position and number of the multipolar resonances that occur at  $\omega < \omega_p$ . For larger frequencies the spheres respond as if isolated, showing a sequence of small resonances entirely due to the nonlocal form of the dielectric function. At low frequencies we find an enhancement for an external field polarized along the line joining the spheres centers.

Optical experiments done on small metallic particles indeed show that proximity or aggregation broadens the spectrum by way of shifting the low-frequency edge of the surface resonance towards the infrared.<sup>35</sup> The multipolar structure does not appear well resolved, however. Data have been taken using samples where the particles are distributed at random. In disordered arrays one does not expect to find well-defined multipolar resonances since their position is quite sensitive to interparticle separation or relative size between the spheres.<sup>30,36</sup> Also, deformations away from sphericity may introduce additional resonances. We are therefore unable to compare our results in detail with presently available experimental data. Recent experimental techniques that allow a careful control of both position and size when forming the metal spheres<sup>37,38</sup> make it possible that in the near future the multipolar resonances, their location and shape, will be resolved so that the present theory may be tested.

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- <sup>1</sup>L. P. Gor'kov and G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.* **48**, 1407 (1965) [*Sov. Phys.—JETP* **21**, 940 (1965)].
- <sup>2</sup>A. A. Lushnikov and A. J. Simonov, *Phys. Lett. A* **44**, 45 (1973); *Z. Phys.* **270**, 17 (1974).
- <sup>3</sup>M. J. Rice, W. R. Schneider, and S. Strassler, *Phys. Rev. B* **8**, 474 (1973).
- <sup>4</sup>P. Ascarelli and M. Cori, *Solid State Commun.* **18**, 383 (1976).
- <sup>5</sup>L. Genzel and U. Kreibig, *Z. Phys. B* **37**, 93 (1980).
- <sup>6</sup>R. Ruppin, *Phys. Rev. B* **11**, 2871 (1975).
- <sup>7</sup>B. Dasgupta and R. Fuchs, *Phys. Rev. B* **24**, 554 (1981).
- <sup>8</sup>C. G. Grandqvist, R. A. Buhrman, J. Wyns, and A. J. Sievers, *Phys. Rev. Lett.* **37**, 625 (1976).
- <sup>9</sup>P. Apell and A. Ljungbert, *Solid State Commun.* **46**, 1367 (1982); **46**, 47 (1983).
- <sup>10</sup>P. Apell and D. R. Penn, *Phys. Rev. Lett.* **50**, 1316 (1983).
- <sup>11</sup>X. M. Hua and J. I. Gersten, *Phys. Rev. B* **31**, 855 (1985).
- <sup>12</sup>F. Claro and R. Fuchs, *Phys. Rev. B* **33**, 7956 (1986).
- <sup>13</sup>W. Ekardt, *Phys. Rev. Lett.* **52**, 1925 (1984); *Phys. Rev. B* **31**, 6360 (1985); **32**, 1961 (1985); W. Ekardt, Z. Penzar, and M. Sunjic, *ibid.* **33**, 3702 (1986).
- <sup>14</sup>V. A. Davis and L. Schwartz, *Phys. Rev. B* **31**, 5155 (1985).
- <sup>15</sup>D. Penn and R. W. Rendell, *Phys. Rev. Lett.* **47**, 1067 (1981); *Phys. Rev. B* **26**, 3047 (1982).
- <sup>16</sup>N. E. Russell, J. C. Garland, and D. B. Tanner, *Phys. Rev. B* **23**, 632 (1981).
- <sup>17</sup>P. Chylek and V. Srivastava, *Phys. Rev. B* **27**, 5098 (1983).
- <sup>18</sup>D. B. Tanner, A. J. Sievers, and R. A. Buhrman, *Phys. Rev. B* **11**, 1330 (1975).
- <sup>19</sup>G. L. Carr, J. L. Garland, and D. B. Tanner, *Phys. Rev. Lett.* **50**, 1607 (1983).
- <sup>20</sup>R. Ruppin, *Phys. Rev. B* **19**, 1318 (1979).
- <sup>21</sup>R. P. Devaty and A. J. Sievers, *Phys. Rev. Lett.* **52**, 1344 (1984).
- <sup>22</sup>P. N. Sean and D. B. Tanner, *Phys. Rev. B* **26**, 3582 (1982).
- <sup>23</sup>W. A. Curtin and N. W. Ashcroft, *Phys. Rev. B* **31**, 3287 (1985).
- <sup>24</sup>W. A. Curtin, R. C. Spitzer, N. W. Ashcroft, and A. J. Sievers, *Phys. Rev. Lett.* **54**, 1071 (1985).
- <sup>25</sup>S. Lee, T. W. Noh, K. Cummings, and J. R. Gaines, *Phys. Rev. Lett.* **55**, 1626 (1985).
- <sup>26</sup>S. Lee, T. W. Noh, and J. R. Gaines, *Phys. Rev. B* **32**, 3580 (1985).
- <sup>27</sup>P. Sheng, *Phys. Rev. B* **31**, 4906 (1985).
- <sup>28</sup>The terms quadrupolar, octupolar, etc., are here used as labels for the resonances of the pair because as the spheres are separated these resonances evolve into the modes of isolated spheres, which have definite multipole character.
- <sup>29</sup>F. Claro, *Solid State Commun.* **49**, 229 (1984).
- <sup>30</sup>F. Claro, *Phys. Rev. B* **30**, 4989 (1984); **35**, 406(E) (1987).
- <sup>31</sup>See, for example, J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), Chap. 4.
- <sup>32</sup>See, for example, F. Forstmann and R. R. Gerhardts, in *Festkörperprobleme*, Vol. 22 of *Advances in Solid State Physics* (Vieweg, Braunschweig, 1982), p. 291.
- <sup>33</sup>N. D. Mermin, *Phys. Rev. B* **1**, 2362 (1970).
- <sup>34</sup>F. Claro, *Phys. Rev. B* **25**, 7875 (1982).
- <sup>35</sup>U. Kreibig and L. Genzel, *Surf. Sci.* **156**, 678 (1985).
- <sup>36</sup>I. Olivares, R. Rojas, and F. Claro, *Phys. Rev. B* **35**, 2453 (1987).
- <sup>37</sup>P. F. Liao, J. G. Bergman, D. S. Chemla, A. Wokaun, J. Melngailis, A. M. Hawryluk, and N. P. Economou, *Chem. Phys. Lett.* **82**, 355 (1981).
- <sup>38</sup>B. K. Russell, G. Mantovani, V. E. Anderson, R. J. Warmack, and T. L. Ferrell, *Phys. Rev. B* **35**, 2151 (1987).