Surface modes of a pair of unequal spheres

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The surface resonances of a pair of spheres of different radii are studied using a local dielectric function to describe the response of each particle. All modes are characterized by values of $-\epsilon(\omega)$ that diverge as the spheres approach touching. We show that to a good approximation these values depend only on the edge-to-edge separation measured in units of the smaller sphere, and not on the radius of the larger one.

The physical properties of small particles have been the subject of much recent study. In particular their electromagnetic resonant modes are of interest since they determine the structure in the scattering of light and of charged particles, and other properties such as the agglomeration rate through van der Waals forces.[1–4] If particles are very small usually experiments are done in samples involving large numbers of them with a size distribution and interparticle separation that may vary widely. While high-energy electrons can probe a single particle or a pair, optical experiments involve an assembly of them so that dispersion in size, combined with shape and separation, influences drastically the spectrum, in particular making most of the structure disappear. The interpretation of experiments involving more than one particle requires an understanding of the effect of dispersion. To this end we describe here the properties of a pair of spherical particles of unequal radii. Although in most cases a pair will not model adequately a sample involving many small particles, it is known that its behavior gives the proper insight for treating more complex arrays.[1]

Isolated particles may couple to an electromagnetic field through the excitation of surface or bulk modes. If a local dielectric function $\epsilon(\omega)$ is appropriate to describe their response, then only the former are present and they give rise to a multipolar polarizability that for spheres has the form

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

where l is the pole order and a is the radius. Modes are defined by the resonances of this function and for a real dielectric function they are poles located at $\epsilon_l=-(l+1)/l$. For metallic spheres a few nanometers in diameter or smaller one must use a nonlocal dielectric function to account for excitation of bulk plasmons as well as electron-hole pairs. Expression (1) is then no longer accurate and the polarizabilities exhibit a richer structure as a function of l while modes with $l>4\pi a/\lambda_F$ are not excited, where λ_F is the Fermi wavelength.[5,6] It does work well, however, for larger particles and even where it is not accurate it does provide useful insight into the effect we are interested in.

If the particle we are considering is in a polarizable environment the modified local field will change its response to an external potential. In particular, if a second particle is brought nearby then the excitation modes are no longer the resonances in the single-particle polarizabilities. Work on arrays of identical spheres has shown that the resonances are shifted toward the infrared and that the complex couplings between the particles in the sample causes all resonances to be excited even if the external field has a single-pole character, such as an electromagnetic field in the long-wavelength limit.[1,7] In fact, one can write the dipole moment excited in a given sphere for the latter case in all generality as a sum of terms each involving a single mode of excitation.[8] For the pair, this sum has the form

$$P_i=\frac{a_i^3}{3}\sum_{l,j}\frac{f_i^{lj}}{(\epsilon-1)^{-1}+n_{lj}}E\ , \tag{2}$$

where E is the external field, n_{lj} a depolarization factor, and f_i^{lj} the strength of the mode (l,j) whose sum over all modes equals one. The summation index $l=1,2,3,\ldots$ gives the pole character of the mode, while $i,j=1,2$ label the particles.

Expression (2) exhibits all modes explicitly and has the advantage that it gives the location $\epsilon_{lj}=1-1/n_{lj}$ (no damping) and strength of a mode in terms of quantities that depend on geometry only. These quantities are easily computed if the series (2) is cut at a finite $l=L$ (L-order approximation). For instance in the dipole approximation ($L=1$) they are given by

$$n_j=\frac{1}{3}-\frac{(-1)^{m+j}}{1+m}\frac{2}{3}\left[\frac{a_1a_2}{D^2}\right]^{3/2}\ , \tag{3}$$

$$f_1^j=\frac{1}{2}\left[1-(-1)^j\left[\frac{a_2}{a_1}\right]^2\right]\ , \tag{4}$$

$$f_2^j=\frac{1}{2}\left[1-(-1)^j\left[\frac{a_1}{a_2}\right]^2\right]\ , \tag{5}$$

where $m=0$ if the electric field is along the line joining the spheres centers or $m=1$ if it is perpendicular to such line, and D is the separation between the spheres. Notice that if the particles are identical f_i^2 vanishes. These modes ($j=2$) correspond to dipole moments excited on the spheres that are equal and opposite so that the net moment is zero and no coupling to the external field takes place. They are the so-called optically inactive modes. If instead the sphere radii are different, then all modes have nonzero strength. New modes appear when the value of L is increased. Their strength, however, depends strongly on distance since the summation over l is a power series in the ratio a_1a_2/D^2. The number of terms that need to be kept in (2) therefore depends on the value of this ratio. For equal spheres the dipole approximation is sufficient if the particles separation s [see inset, Fig. 1(a)] is more than one radius while the value of L required to achieve 1% accuracy in the position of the first resonance diverges as the particles become closer.[9] The convergence curve $L=L(s)$ given by this criterion was found in our case of unequal spheres to a good approximation to be universal provided the separation is measured in units of the smaller sphere.

Figures 1(a) and 1(b) show for the case $a_2=3a_1$ the resonant values of the dielectric function in terms of separation s measured in units of the radius of the smaller sphere a_1. Solid lines are converged solutions using the 1% criterion in cutting the series (2) and dashed lines represent the dipole approximation. Resonances arising from the dipole and quadrupole modes of isolated spheres as given by the poles of (1) are shown only. Higher-order resonances have a similar qualitative behavior. We note that they all diverge as the particles approach touching. Our study showed that if the larger sphere is increased in size keeping the radius of the smaller one the same, the position of the resonances changed little. This is illustrated by the circles in Fig. 1(a) obtained for the case $a_2=9a_1$. The triangles are solutions for spheres of equal radii. This result is important because it suggests that the relevant space variable in assessing proximity effects on the location of the resonances is the edge-to-edge distance between the particles and not the distance from center to center. The strengths of these resonances do not follow the same universal behavior, however. This is illustrated in Fig. 2 obtained for a pair of NaCl spheres with dielectric parameters $\epsilon_0=5.934$, $\epsilon_\infty=2.328$, $\omega_T=164$ cm^{-1}, and $\gamma=0.02\omega_T$.[10] In this figure the absorption cross sec-

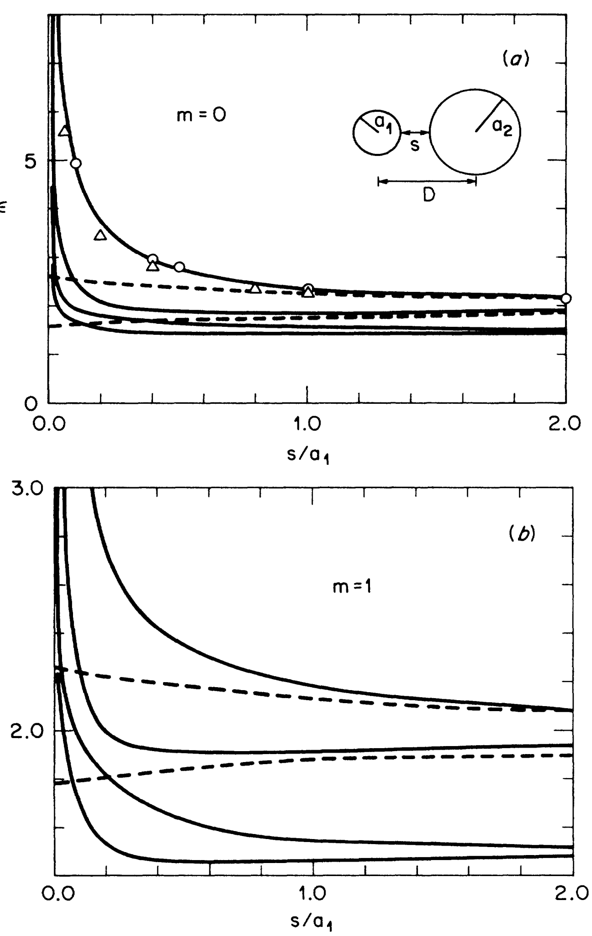

FIG. 1. Resonant values of the dielectric function at different separations s and an exciting field parallel (a) and perpendicular (b) to the line joining the sphere centers. Solid lines are converged solutions, while dashed lines are the dipole approximation as given by Eq. (3). The case shown is $a_2=3a_1$. Triangles and circles correspond to the cases $a_2=a_1$ and $a_2=9a_1$, respectively, and are included for comparison. The inset shows the notation used.

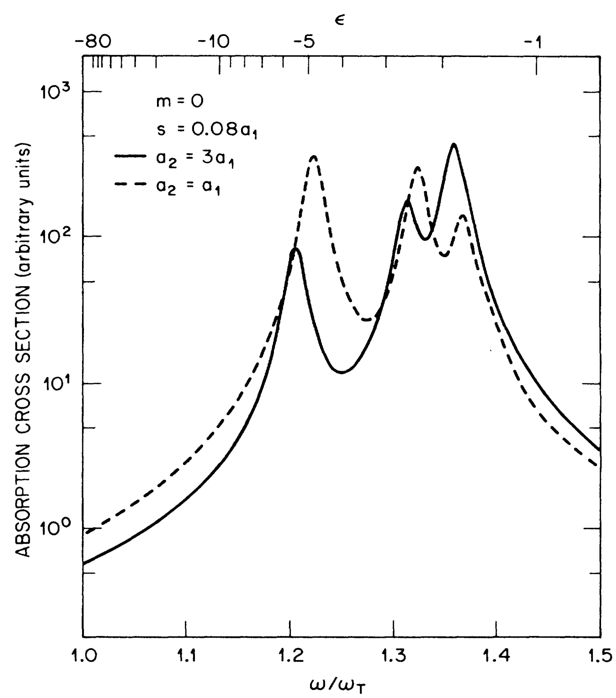

FIG. 2. Absorption cross section for a pair of NaCl spheres of radii $a_2=3a_1$ (solid line) and $a_2=a_1$ (dashed line), and edge-to-edge separation $s=0.08a_1$. The electric field is along the line joining the sphere centers.

tion is shown for the cases $a_2=3a_1$ (solid line) and $a_2=a_1$ (dashed line) both at a separation $s=0.08a_1$ and with the electric field pointing along the line joining the centers ($m=0$). This polarization was chosen because the strength in this case is more evenly distributed among the various resonances than in the $m=1$ case. Notice that while the dipole resonances are almost equal in strength for equal spheres, their amplitude differs by a factor of 2.2 in the unequal case.

The main finding of our study is that the location of resonances in pairs of unequal spheres is determined by the edge-to-edge separation. This result is potentially useful not only in the interpretation of electron scattering experiments probing individual pairs[4] but also in modeling disordered arrays found in samples studied optically where the size dispersion must be taken into account in determining the response of the system.

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