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# Surface modes of two spheres

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The surface-mode frequencies of a system of two spheres are calculated. The results are compared with those of the approximate method due to Clippe, Evrard, and Lucas, and a bound on the range of validity of the latter method is obtained. The implications on some recently proposed interpretations of the results of optical experiments on small metal particles are discussed.

## I. INTRODUCTION

The optical properties of a small metallic or dielectric sphere can be explained in terms of its characteristic surface modes.[1,2] These modes are surface plasmons for a metal sphere and surface phonons for an ionic crystal sphere. However, optical experiments are usually performed on samples containing a large number of particles. Single-sphere theory can only be applied as long as the particles are well separated. When this is not the case, the interactions between the spheres can be introduced in some average way, as in the Maxwell-Garnett theory[3] or other effective-medium theories.[4] It is often found experimentally that particles stick together to form clusters and chains.[5,6] When such clumping of particles exists, effective-medium theories cannot be used and a different approach is needed. A theoretical method which deals with aggregation effects has recently been presented by Clippe, Evrard, and Lucas (CEL).[7] They used a model Hamiltonian in which only dipole-dipole interactions between the spheres in the cluster were included, and all interactions involving higher multipoles were neglected. This approach is certainly valid when the spheres are well separated, but it is not clear whether it provides any useful information in the case of clusters of touching spheres, to which it was applied.

In the present paper we obtain the exact surface-mode frequencies of a two-sphere system and compare them with those obtained from the CEL approximation. This yields a quantitative criterion for the range of validity of the CEL method. The exact calculation is based on the use of bispherical coordinates, in which the solutions of the Laplace equation are known. This approach has previously been employed to calculate the van der Waals energy between two spherical voids in a dielectric medium,[8] and also to obtain the dipole moment of a two-sphere system in an external electric field.[9] In these works, however, perturbation expansions, valid for small ratios of sphere size to intersphere separation were used. We employ an exact numerical algorithm which involves no perturbative method. Aravind *et al.*[10] have recently studied the local electric field intensity in the vicinity of a two-sphere system, which is acted on by a constant field, using the same mathematical approach.

## II. SURFACE MODES OF A SINGLE SPHERE AND OF TWO SPHERES

We first discuss some general properties of the surface modes of the one- and two-sphere systems and their interrelation. The properties of the solid enter only through its frequency-dependent dielectric constant $\epsilon(\omega)$, so that the results are applicable to both metals and dielectrics.

In the nonretarded limit, which is applicable for small enough spheres, the potentials have to satisfy the Laplace equation $\nabla^2 V=0$. The frequencies of the surface modes are obtained by matching internal and external fields using appropriate boundary conditions at the surface (or surfaces) separating the solid from the surrounding medium. For a single sphere of radius $R$ and dielectric constant $\epsilon(\omega)$, embedded in a medium of dielectric constant $\epsilon_m$, the internal and external potentials are[1]

$$V_i = A r^l y_{lm}(\theta,\phi) , \tag{1}$$

$$V_e = B r^{-(l+1)} y_{lm}(\theta,\phi) , \tag{2}$$

where $y_{lm}$ are spherical harmonics, $l=1,2,\ldots$ and $m=0, \pm 1,\ldots,\pm l$. The boundary conditions at the surface of the sphere are

 

$$V_i(R)=V_e(R)\,,$$
$$\epsilon(\omega)\left[\frac{\partial V_i}{\partial r}\right]_R=\epsilon_m\left[\frac{\partial V_e}{\partial r}\right]_R\,, \tag{3}$$

from which the following equation for the surface-mode frequencies is obtained:

$$\frac{\epsilon(\omega)}{\epsilon_m}=-\frac{l+1}{l},\quad l=1,2,\ldots\,. \tag{4}$$

Because of the spherical symmetry for any given $l$ the $2l+1$ modes, $m=0,\pm1,\ldots,\pm l$, are degenerate.

We now consider the two-sphere system. When the spheres are far apart and do not interact the surface-mode frequencies are still given by Eq. (4), but now the degeneracy is doubled, so that the $l$th mode is $(4l+2)$-fold degenerate. When the distance between the spheres is reduced, this degeneracy is partially lifted. In general, there will exist two different frequencies for each $(l,m)$ pair. The $(l,m)$ modes will, however, be degenerate with the $(l,-m)$ modes. Thus, for any $l$ there will exist $2(l+1)$ different frequencies. Of these, $2l$ are doubly degenerate, so that the total number of modes is again $4l+2$. The actual calculation of the surface-mode frequencies can be performed by using bispherical coordinates, as described in the following section.

## III. METHOD OF CALCULATION

Let the two spheres of radius $R$ be centered at $z=\pm D$. In bispherical coordinates $(\eta,\alpha,\phi)$, defined by

$$x=a\sin\alpha\cos\phi\,/(\cosh\eta-\cos\alpha)\,,$$
$$y=a\sin\alpha\sin\phi/(\cosh\eta-\cos\alpha)\,, \tag{5}$$
$$z=a\sinh\eta/(\cosh\eta-\cos\alpha)\,,$$

where $a=(D^2-R^2)^{1/2}$ the two spheres are given by $\eta=\pm\eta_0$ with

$$D=a\coth\eta_0,\quad R=a/\sinh\eta_0\,. \tag{6}$$

We build the potentials inside the spheres and in the surrounding medium from the following solutions of the Laplace equation:

$$V=(\cosh\eta-\cos\alpha)^{1/2}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\{M_n\exp[(n+\tfrac{1}{2})\eta]+N_n\exp[-(n+\tfrac{1}{2})\eta]\}P_n^m(\cos\alpha)e^{im\phi}\,. \tag{7}$$

Because of the axial symmetry of the system, wave functions having different $m$ values are not coupled and we can solve separately for each $m$. We will only solve for the $m=0$ and $m=1$ modes. Higher modes can be obtained in an analogous manner.

For $m=0$ we can choose potentials which are either symmetric or antisymmetric with respect to reflections through the $xy$ plane. For the symmetric case, for example, the potentials inside the upper sphere and in the surrounding medium are given by

$$V_+=(\cosh\eta-\cos\alpha)^{1/2}\sum_{n=0}^{\infty}B_n\exp[-(n+\tfrac{1}{2})\eta]P_n(\cos\alpha)\,, \tag{8}$$

$$V_m=(\cosh\eta-\cos\alpha)^{1/2}\sum_{n=0}^{\infty}A_n\cosh[(n+\tfrac{1}{2})\eta]P_n(\cos\alpha)\,, \tag{9}$$

respectively. Applying the boundary conditions,

$$V_+(\eta_0)=V_m(\eta_0),\quad \epsilon(\omega)\left[\frac{\partial V_+}{\partial\eta}\right]_{\eta_0}=\epsilon_m\left[\frac{\partial V_m}{\partial\eta}\right]_{\eta_0}\,, \tag{10}$$

and eliminating the coefficients $B_n$ from the resulting equations, the following recursion relation is obtained for the coefficients $A_n$

$$\begin{aligned}&n\,[\epsilon(\omega)\cosh(n-\tfrac{1}{2})\eta_0+\epsilon_m\sinh(n-\tfrac{1}{2})\eta_0]\,A_{n-1}\\&-\{2n+1\,[\epsilon(\omega)\cosh(n+\tfrac{1}{2})\eta_0+\epsilon_m\sinh(n+\tfrac{1}{2})\eta_0]\cosh\eta_0\\&\quad+[\epsilon_m-\epsilon(\omega)]\sinh\eta_0\cosh(n+\tfrac{1}{2})\eta_0\}A_n+(n+1)\,[\epsilon(\omega)\cosh(n+\tfrac{3}{2})\eta_0+\epsilon_m\sinh(n+\tfrac{3}{2})\eta_0]\,A_{n+1}=0\,.\end{aligned} \tag{11}$$

The surface-mode frequencies can be obtained from this relation by regarding it as a system of linear homogeneous equations for the coefficients $A_0, A_1, \ldots, A_n$. Truncating the system at some $n_M$, the condition for the existence of a nontrivial solution is that the determinant of the coefficients vanishes, which yields $n_M$ eigenfrequencies. These frequencies will be expressed by equations of the form $\epsilon(\omega)/\epsilon_m = \alpha_i$, $i = 1,2,\ldots,n_M$. Actual frequencies can then be calculated for any solid for which the dielectric function $\epsilon(\omega)$ is known. Our interest is in the first few surface-mode frequencies, and these are found to converge, so as to be independent of $n_M$, provided that $n_M$ is large enough.

For the antisymmetric $m = 0$ modes we obtain the following recursion relation[9]

$$
\begin{aligned}
&n[\epsilon_m \cosh(n-\tfrac{1}{2})\eta_0 + \epsilon(\omega)\sinh(n-\tfrac{1}{2})\eta_0]A_{n-1} \\
&\quad -\{(2n+1)[\epsilon(\omega)\sinh(n+\tfrac{1}{2})\eta_0 + \epsilon_m \cosh(n+\tfrac{1}{2})\eta_0]\cosh\eta_0 \\
&\qquad +[\epsilon_m - \epsilon(\omega)]\sinh\eta_0 \sinh(n+\tfrac{1}{2})\eta_0\}A_n + (n+1)[\epsilon(\omega)\sinh(n+\tfrac{3}{2})\eta_0 + \epsilon_m \cosh(n+\tfrac{3}{2})\eta_0]A_{n+1} = 0 \, .
\end{aligned}
\tag{12}
$$

For the $m = 1$ modes we use expansions analogous to Eqs. (8) and (9) and obtain the following recursion relations for the expansion coefficients of the symmetric and antisymmetric modes

$$
\begin{aligned}
&(n-1)[\epsilon(\omega)\cosh(n-\tfrac{1}{2})\eta_0 + \epsilon_m \sinh(n-\tfrac{1}{2})\eta_0]A_{n-1} \\
&\quad +\{[\epsilon(\omega) - \epsilon_m]\sinh\eta_0 \cosh(n+\tfrac{1}{2})\eta_0 \\
&\qquad -(2n+1)\cosh\eta_0[\epsilon(\omega)\cosh(n+\tfrac{1}{2})\eta_0 + \epsilon_m \sinh(n+\tfrac{1}{2})\eta_0]\}A_n \\
&\qquad +(n+2)[\epsilon(\omega)\cosh(n+\tfrac{3}{2})\eta_0 + \epsilon_m \sinh(n+\tfrac{3}{2})\eta_0]A_{n+1} = 0 \, ,
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
&(n-1)[\epsilon_m \cosh(n-\tfrac{1}{2})\eta_0 + \epsilon(\omega)\sinh(n-\tfrac{1}{2})\eta_0]A_{n-1} \\
&\quad +\{[\epsilon(\omega) - \epsilon_m]\sinh\eta_0 \sinh(n+\tfrac{1}{2})\eta_0 \\
&\qquad -(2n+1)\cosh\eta_0[\epsilon_m \cosh(n+\tfrac{1}{2})\eta_0 + \epsilon(\omega)\sinh(n+\tfrac{1}{2})\eta_0]\}A_n \\
&\qquad +(n+2)[\epsilon_m \cosh(n+\tfrac{3}{2})\eta_0 + \epsilon(\omega)\sinh(n+\tfrac{3}{2})\eta_0]A_{n+1} = 0 \, .
\end{aligned}
\tag{14}
$$

## IV. RESULTS AND DISCUSSION

We have calculated the frequencies of the $m = 0$ and 1 modes corresponding to $l = 1,2,3$ and the results are depicted in Figs. 1 and 2. The curves show the dependence of $\alpha = \epsilon(\omega)/\epsilon_m$ on the intersphere separation. For large values of $D/R$ the modes tend to the single-sphere values of Eq. (4). The method employed here is not applicable at $D/R = 1$, i.e., for touching spheres. In fact, when $D/R$ approaches unity, it is found that larger and larger values of $n_M$ are needed to ensure the convergence of the first few eigenvalues. We have therefore performed the calculations only down to $D/R = 1.1$.

In the CEL approximation only the $l = 1$ modes are derived and the values of $\alpha$ are given by

$$
\alpha = \frac{\lambda - 2}{\lambda + 1} \, , \tag{15}
$$

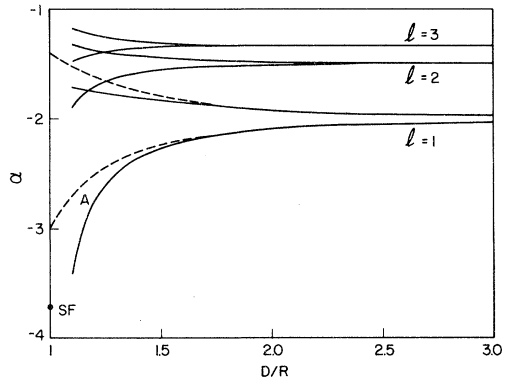


FIG. 1. Surface-mode frequencies of the two-sphere system for $m = 0$. Full curves represent the exact calculation; dashed curves represent the CEL approximation. The optically active branch is denoted by $A$. The circle shows the experimental value measured by Sansonetti and Furdyna (Ref. 11).

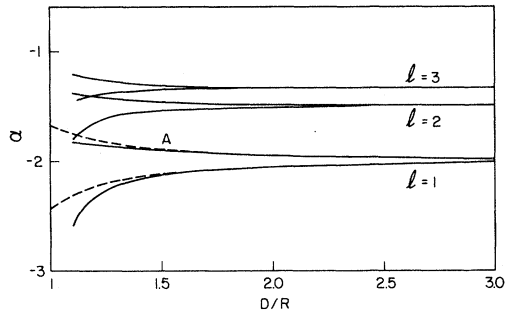


FIG. 2. Surface-mode frequencies of the two-sphere system for $m=1$. Full curves represent the exact calculation; dashed curves represent the CEL approximation. The optically active branch is denoted by $A$.

where $\lambda$ are the six eigenvalues of the tensor

$$\overleftrightarrow{T}=\begin{bmatrix} 0 & \overleftrightarrow{T}^{12} \\ \overleftrightarrow{T}^{12} & 0 \end{bmatrix}, \tag{16}$$

where $\overleftrightarrow{T}^{12}$ is the dipolar tensor

$$\overleftrightarrow{T}^{12}=\frac{R^3}{8D^3}(\overleftrightarrow{I}-3\hat{r}\hat{r}) \tag{17}$$

Here $\hat{r}=(0,0,1)$ is a unit vector in the direction of the line connecting the centers of the spheres.

We have calculated the frequencies using the CEL method and the results are shown by the dashed curves of Figs. 1 and 2. When the spheres are well separated, the dipole-dipole interactions are dominant and the CEL results agree with the exact values. The CEL approximation loses its validity at small separations. From the numerical results we obtain the rough quantitative criterion that the CEL method is applicable for $D/R>1.6$, where it yields results accurate to better than 1%. It is, however, unreliable when the separation between the spheres decreases below this limit.

Sansonetti and Furdyna[11] have devised an experimental method for measuring surface-mode frequencies of arrays of spheres. They employed small InSb spheres ($250\mu\text{m}<R<310\mu\text{m}$) containing free carriers. In the presence of a magnetic field $B$ the dielectric constant of the semiconductor is given by

$$\epsilon(\omega)=\epsilon_L+\frac{ine\mu}{\omega\epsilon_0}\frac{1}{1+i\mu(B-\omega m^*/e)} .$$

Here $\epsilon_L$ is the lattice dielectric constant, $\mu$ is the mobility, $m^*$ the effective mass, and $n$ the concentration of the free carriers. A convenient feature here is that $\epsilon(\omega)$ can be varied by sweeping the external magnetic field. Thus, by placing an array of spheres at the center of a waveguide and measuring the transmission of a microwave signal past the array as a function of the magnetic field, it is possible to determine the frequencies of the optically active modes. Using this technique, Sansonetti and Furdyna have performed measurements on 30 different arrays of touching spheres. Their experimental result for the surface-mode frequency of a pair of touching spheres is shown by the point denoted by SF in Fig. 1. This experimental value $\alpha=-3.73$ is much lower than the value $\alpha=-3$ obtained from the CEL approximation. The curve calculated by the exact method exhibits a trend to lower values of $\alpha$, in qualitative agreement with the experimental result. We do not expect to find complete quantitative agreement with experiment in this region. This is because for $D/R=1$ the measured frequencies could be influenced by small deviations from spherical shape, which inevitably exist in such experiments. Sansonetti and Furdyna[11] found large discrepancies between their experimental results and those of the CEL approximation also for other types of touching-sphere clusters. They suggested correctly that the CEL method is not valid for touching spheres. Although our comparison between the exact calculation and the CEL approximation was performed for the two-sphere system only, it seems reasonable to deduce that for more complicated clusters the CEL method will again be valid only when the separations between the spheres are not too small. For touching or very closely spaced spheres it will not be applicable.

Finally, we note that the CEL theory has recently been invoked in interpretations of the results of optical experiments on ultrafine metal particles.[6,12] In these works the transmittance of thin films consisting of ultrafine gold[6] and nickel[12] particles (usually less than 10 nm in diameter) has been measured. Inspection of electron micrographs has shown that the individual particles tended to stick together to form chains and clusters. The optical spectra were therefore explained in terms of effective depolarization factors of the clusters. In fact, for any eigenvalue $\alpha$ we can define a corresponding effective depolarization factor $L$ by $L=1/(1-\alpha)$. A detailed discussion of this procedure can be found in Ref. 6. Here we only point out that in this application the CEL approximation was employed for cluster of *touching* spheres, i.e., outside its range of validity. It is therefore questionable whether this approach is physically meaningful, and whether it involves more than mere curve fitting.

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