

Absorption spectrum of neighboring dielectric grains

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It is shown that the dipole approximation is inadequate for describing the absorption properties of dielectric powders. The case of a pair of spheres modeling two neighboring grains is solved in a complete multipolar treatment. While the dipole approximation yields one resonance at a frequency in disagreement with experiment, an infinite set of solutions is now found covering in particular the experimental value and predicting the presence of other resonance peaks.

The dipole approximation has been up to now the usual method for treating the polarization of a dielectric in a uniform external field. The local field effective in polarizing the medium consists then of the external field plus the uniform component arising from the dipole polarization of the surrounding medium. Recent results suggest, however, that in real systems this picture excludes some important physical effects. Detailed calculations for ionic crystals give local-field factors that differ significantly from results in the dipole approximation.¹⁻³ The Clausius-Mossotti relation still holds due to a cancellation effect so that the latter approximation here is consistent with experiment.³ This appears not to be the case for arrays of identical dielectric spheres such as have been considered in modeling powders.^{4,5} The magnetoplasma resonances of such arrays have been found to occur at frequencies lower than those predicted by the dipole approximation theory.⁶ This is consistent with the inability of the model to explain actual data for powders that yield assortment of array resonances that cluster at frequencies much too high.⁵ The inclusion of quadrupolar terms has been found to have an important effect on the predicted infrared spectrum of such arrays.^{7,8} We have studied the simplest case where the effect of multipole terms to all orders may be evaluated, that of a pair of dielectric spheres, and we find that results are changed qualitatively by the inclusion of these terms. In particular, we are able to explain the resonance value found in experiment and we predict the occurrence of a sequence of other resonances whose location depends critically on the separation between the spheres.

When a sphere of dielectric constant ϵ is placed in a uniform external field a dipole moment proportional to $(\epsilon + 2)^{-1}$ is formed. Resonant absorption occurs when $\epsilon = -2$, a condition that leads to the so-called Fröhlich surface mode.⁹ If a second sphere is placed nearby it polarizes as well, causing the field at the position of the first sphere to be nonuniform so that higher multipoles are excited. The field effective

in forming the dipole polarization has contributions from all multipole moments in the other sphere. In the dipole approximation all moments but the dipole are ignored, the rationale being that higher multipoles lead to fields that decay as $1/(d)^{2l+1}$, where d is the distance and where l is the multipole order ($l = 1$ for dipole, $l = 2$ for quadrupole, etc.) Through the polarizabilities however, the fields are proportional to $(r)^{2l+1}$, where r is the sphere radius, so that it is conceivable that at short distances their contribution is significant. If the sphere centers are aligned with the external field E both spheres acquire an identical dipole moment along the field, given by

$$P = \frac{\alpha}{1 - \alpha L} E, \tag{1}$$

where α is the dipole polarizability of a sphere and L is given by the series¹⁰

$$\alpha L = M_{11} + \sum_{l=2}^{\infty} M_{1l} M_{l1} + \sum_{l,l'=2}^{\infty} M_{1l} M_{ll'} M_{l'l1} + \dots,$$

$$M_{ll'} = \frac{1}{(2\sigma)^{l+l'+1}} \binom{l+l'}{l} \frac{l(\epsilon-1)}{l(\epsilon+1)+1},$$

where σ is the ratio of half the distance between the sphere centers and their radius. The first term in the series gives the dipole approximation. Indeed, one can easily check that if only this term is kept the condition for resonance is

$$\epsilon^* = -\frac{8\sigma^3 + 1}{4\sigma^3 - 1}, \tag{2}$$

so that for touching spheres ($\sigma = 1$) one gets the expected value, $\epsilon^* = -3$. As spheres separate this value grows monotonically towards -2 . In contrast, experiment gives $\epsilon^* = -3.73$.⁶

There is a simple scheme for solving the resonant condition $\alpha L = 1$ by noting that it may be written in the form

$$A_l = \sum_{l'=1}^{\infty} M_{ll'} A_{l'}, \tag{3}$$

with the constraint $A_1 = 1$. Equation (3) is the condition for the matrix $M_{ll'}$ to have an eigenvalue equal to one so that the equation to be solved is

$$\det |M_{ll'} - \delta_{ll'}| = 0 \quad (4)$$

If convergence allows one may cut this infinite determinant at order \bar{l} thus defining the \bar{l} th-pole approximation. If the dipole approximation were sufficient then ϵ^* as given by (2) would change little in going from this approximation to the 2×2 determinant equation one gets in the quadrupole or second-order approximation. This is not the case, as one gets for touching spheres the value $\epsilon^* = -3.775$, a change of 26% over the $\bar{l} = 1$ result. Further increase of \bar{l} makes $-\epsilon^*$ bigger and bigger, with an approximately linear increase for small \bar{l} . Also, since (4) is an algebraic equation of degree \bar{l} in ϵ with as many real solutions, the quadrupole approximation gives two solutions, the octupole three, and so forth. In fact, to all orders one expects an infinity of values of ϵ for which the denominator of (1) vanishes. We have calculated the lowest-order resonances as a function of the separation between the spheres and these are shown in Fig. 1. For a large separation, convergence of the sums is fast but it slows down as σ decreases. The dashed line in Fig. 1 is the dipole approximation as given by Eq. (2) and it should be compared with the line above which includes the higher multipoles. We see that the approximation is good only for $\sigma \geq 1.5$, all lower values being significantly affected by the inclusion of the multipolar fields.

The multiplicity of solutions is due to the resonant excitation of polarizabilities of all orders. One can see this by noting that as the separation between the spheres grows the curves in Fig. 1 tend to the asymptotic values

$$\epsilon_l^* = -\frac{l+1}{l} + O(\sigma^{-2l-1}) \quad (5)$$

which is just the condition for the vanishing of the denominator of the l th pole polarizability of a single sphere. This result is a direct consequence of the structure of the series in (1) near resonance as can be easily checked. The resonance arises because for ϵ close to ϵ_l^* the effective field each sphere is in has a diverging component coming from the l th pole moment of the other sphere that contributes resonantly to the dipole polarization. Resonances have thus been labeled dipole for $l = 1$, quadrupole for $l = 2$, and so on.

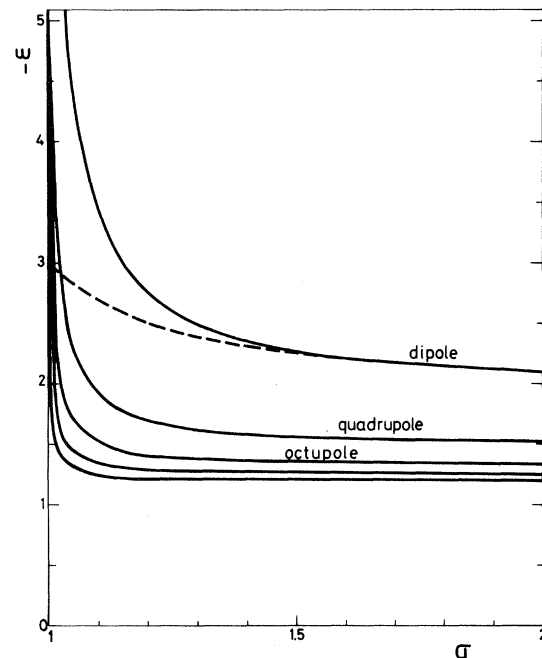


FIG. 1. Resonant values of the dielectric constant ϵ as a function of the separation between spheres σ . Only the first five resonances are included.

According to our results the experimental resonance at $\epsilon^* = -3.73$ could correspond to the quadrupole resonance at a separation $\sigma = 1.013$, or the dipole resonance at $\sigma = 1.077$. Which case it may be decided by a careful measurement of the gap between spheres or by finding one more resonance for the system. We note that at small separation the location of resonances is very sensitive to the distance between spheres. In particular, the dipole resonance covers a broad region of small frequencies (high values of $-\epsilon$) within a small spread in gap values. We expect this shift of the resonance spectrum to lower frequencies to improve the theoretical results for absorption in powders.

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