

## Effective cluster model of dielectric enhancement in metal-insulator composites

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The electrical permittivity of a suspension of conducting spheres at high volume loading exhibits a large enhancement above the value predicted by the Clausius-Mossotti approximation. The permittivity enhancement is a dielectric anomaly accompanying a metallization transition that occurs when conducting particles are close packed. In disordered suspensions, close encounters can cause a permittivity enhancement at any volume loading. We attribute the permittivity enhancements typically observed in monodisperse disordered suspensions of conducting spheres to local metallized regions of high density produced by density fluctuations. We model a disordered suspension as a mixture, or mesosuspension, of isolated spheres and random close-packed spherical clusters of arbitrary size. Multipole interactions within the clusters are treated exactly. External interactions between clusters and isolated spheres are treated in the dipole approximation. Model permittivities are compared with Guillien's experimental permittivity measurements [Ann. Phys. (Paris) Ser. 11, **16**, 205 (1941)] on liquid suspensions of Hg droplets in oil and with Turner's conductivity measurements [Chem. Eng. Sci. **31**, 487 (1976)] on fluidized bed suspensions of ion-exchange resin beads in aqueous solution. New permittivity measurements at 10 GHz on solid suspensions of monodisperse metal spheres in polyurethane are presented and compared with the model permittivities. The effective spherical cluster model is in excellent agreement with the experiments over the entire accessible range of volume loading.

### I. INTRODUCTION

The effective permittivity of an inhomogeneous medium composed of particles of one substance embedded in a continuum of a different material (cermet topology) is, in general, a complicated function of the permittivities of the constituents, of the particle shape and size, and of the volume loading and spatial arrangement of the distribution. When one or more of these parameters has a nonzero variance, the problem is difficult; when all of the parameters have wide variances the problem is completely intractable. Solutions can be found only by limiting the ranges and restricting the variances of the parameters. In the simplest case, that of a regular array of spheres of uniform size, the low-frequency permittivity may be computed exactly.<sup>1,2</sup> Even for regular arrays, small departures from spherical shape, uniformity of size, or regularity of position, greatly increase the complexity of the problem. Disordered suspensions are still harder to handle. The permittivity of a disordered suspension may be calculated only approximately, even for spheres of uniform size.

The permittivity of an isotropic medium is given by the well-known Clausius-Mossotti approximation when only dipole interactions are present. For regular arrays this case occurs in the limit of low volume loading. Higher multipole interactions become important when the particles approach contact, so the Clausius-Mossotti approximation breaks down in regular arrays at high volume loading. In random or disordered distributions close en-

counters can occur at any volume loading, so higher multipole corrections are necessary in disordered media even at low volume loading. The higher multipole interactions have a positive angular average that depends inversely on increasing powers of the interparticle distance. A macroscopic manifestation of their presence is a strong nonlinearity of the permittivity when plotted as a function of volume filling factor. One consequence of this nonlinearity is that any departure from strict constancy of the density of the medium can cause an enhancement of the permittivity above the Clausius-Mossotti value.

Experiments with disordered monodisperse suspensions of conducting spheres almost invariably exhibit substantial permittivity enhancements. Innumerable, more or less empirical, approximate formulas<sup>3-8</sup> have been proposed to account for them. None of these formulas agree with the experimental measurements over the entire range of volume loading. Our aim is to show that density variations produced by particle clustering, alone, can account for the observed permittivity enhancements in monodisperse suspensions of conducting spheres.

### II. EFFECTIVE CLUSTER MODEL

Disordered suspensions contain a wide range of particle clusters of various sizes and shapes, composed of varying numbers of spheres in differing spatial arrangements. No *exact* theoretical method exists for including the contributions of such varied clusters. Persson and Liebsch<sup>9</sup> used a lattice-gas model to simulate random di-

polar interactions in a disordered suspension. Their approach has the advantage that it is not restricted to perfect conductors, but neglect of higher-order multipoles limits this approach to low volume loading when it is applied to conducting spheres. In the absence of an exact method, much effort has been devoted to establishing rigorous upper and lower bounds on effective permittivities.<sup>10–15</sup> The bounds are expressed as functions of the permittivities of the constituents, using more or less detailed statistical properties of the particle distribution. In general, the more that is known about the distribution, the tighter the bounds that can be set. Such theoretical bounds can be stated with considerable generality and offer useful benchmarks that any calculated permittivity must satisfy. For perfectly conducting particles, the higher-order upper bounds are infinite. However, the higher-order lower bounds remain finite and set a tighter limit on the permittivity than does the Clausius-Mossotti relation. We shall compare our measured and calculated effective permittivities with recently evaluated third-order lower bounds on the effective permittivity of a random monodisperse suspension of impenetrable spheres.<sup>14,15</sup> The third-order lower bounds can give a good estimate of the permittivity in the absence of large clusters. We attribute the observed excess permittivity to particle clustering.

None of the available empirical formulas or theoretical calculations are in satisfactory agreement with experiments on monodisperse suspensions of highly conducting spheres over the entire range of volume loading. In the present paper we present a physical cluster model that incorporates higher electric multipole interactions in a very simple way, while allowing particle clusters of arbitrary size. The model is applicable over the entire range of volume loading and it reduces to the Clausius-Mossotti equation in the limit of low particle density.

#### A. Particle clustering

The Lorentz-Lorenz–Clausius-Mossotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \beta = \frac{4}{3}\pi N\alpha = p \quad (1)$$

relates the permittivity  $\epsilon$  and the polarization of a spherical sample of the medium,  $\beta$ , to the number density  $N$  and the polarizability  $\alpha$  of a suspension of point dipoles. The first three members in (1), relating  $\epsilon$ ,  $\beta$ ,  $N$ , and  $\alpha$ , comprise the Lorentz-Lorenz relation and apply to point dipoles. The last assignment, the Clausius-Mossotti relation, equates the volume filling factor  $p$  of a distribution of metal spheres to the polarization  $\beta$  using the *unenhanced* polarizability,  $\alpha = R^3$ , of an isolated conducting sphere of radius  $R$ . It is important to note that the relationships between the first three members of (1) stand on a completely different footing from the last assignment. The latter Clausius-Mossotti relation is only an approximation that holds for conducting spheres under very restricted conditions. The former assignments, the Lorentz-Lorenz relations, are *exact* as we shall use them.

The relations expressed in Eq. (1) are essentially defining equations for  $\beta$  and  $\alpha$ . The polarization  $\beta$  is

defined in terms of  $\alpha$ , while the relationship of either  $\alpha$  or  $\beta$  to the macroscopic permittivity  $\epsilon$  is exact for a macroscopic sphere. Thus, if  $\alpha$  were the actual *in situ* dipole polarizability including the effects of all higher-order multipole interactions, Eq. (1) could be used to calculate the exact permittivity. Of course, this has never been done for atomic or molecular dipoles, since so few higher-order atomic multipole polarizabilities are known. Even when the higher multipole polarizabilities are readily found, as with polarizable spheres, such calculations are laborious and have rarely been made. Nevertheless, it is always possible in principle to get the exact permittivity this way. On the other hand, it is easy to use Eq. (1) the other way around. The relationship remains exact. Thus, we can use a known permittivity in Eq. (1) to calculate the exact effective *in situ* dipole polarizability for the constituents of a sphere. In the following section we use Eq. (1) to find the effective polarizabilities of conducting spheres in spherical clusters.

A collection of *point* dipoles exhibits a Lorentz permittivity “catastrophe” at the density where  $4\pi N\alpha/3 = 1$ . The term “catastrophe” refers to the singularity in permittivity. In Eq. (1) the permittivity singularity takes a less drastic, and more useful, form as a condition on the polarization of a spherical specimen:  $\beta = 1$ . When Eq. (1) is applied to a suspension of identical conducting spheres, the Clausius-Mossotti condition erroneously predicts that the permittivity singularity will occur in the limit  $p = 1$ . This is wrong on two counts: Spheres of uniform size can never meet this condition, since equal-sized spheres cannot fill space. Moreover, the Lorentz catastrophe is preempted by a metallization transition that occurs in any collection of conducting spheres when the spheres touch. The maximum packing density of a suspension of spheres of equal size depends upon their spatial arrangement. For cubic lattices the maximum possible volume filling factors  $p_c$  are 0.52, 0.68, and 0.74, for sc, bcc, and fcc lattices, respectively. Although the Clausius-Mossotti equation does not account for it, each of these lattices exhibits a singularity in the electrical permittivity as the transition is approached from the nonconducting side. It is brought about by *all* the electric multipole interactions acting together, not by the dipolar interactions alone.

Physically, it is clear that even a random or disordered distribution must undergo a metallization transition when the spheres make contact. In regular arrays this transition is sharp, because *all* of the spheres approach contact at once. A sudden onset of metallization occurs when all particles approach contact simultaneously. Thus, even an irregular or random array would exhibit a sudden metallization transition if we could start with a compacted sample and perform a *uniform expansion* by expanding all interparticle distances in concert. In practice, of course, we have no such detailed control over the interparticle spacings in a disordered suspension. Disordered samples generally contain local metallized regions (particle clusters) where the critical density has been reached, and other nonmetallized (dielectric) regions with lower local particle densities. At any filling factor below the critical value, a disordered system acts like a mixture of dielectric regions and metallized particle clusters.

With increasing volume filling factor, the metallized clusters grow at the expense of the dielectric regions. Thus, in contrast with the behavior of regular arrays, the metallization transition in a disordered suspension occurs at different times in different regions of the sample and the dielectric anomaly is spread out over the entire range of filling factors below  $p_c$ . Nevertheless, there is still a singularity at  $p_c$ , when the entire suspension reaches the critical volume filling factor.

### B. Spherical clusters

Exact calculations with regular arrays show that the contributions of higher multipoles responsible for the metallization transition are effectively limited to very small interparticle separations. Figure 1 shows the calculated polarization versus filling factor of a macroscopic sphere containing conducting spheres arrayed on sc, bcc, and fcc lattices.<sup>1</sup> The corresponding curve for a *uniformly expanded* disordered suspension is shown as the dotted line on the left. This curve was interpolated by a method to be described below using the empirical filling factor  $p_c = 0.63$  for random packing of equal-sized spheres.<sup>16,17</sup> The diagonal straight line  $\beta = p$  is the polarization given by the Clausius-Mossotti relation.

In each lattice, the exact polarization deviates more and more from the Clausius-Mossotti value as the spheres approach contact. In contrast with the predictions of the Clausius-Mossotti equation, the exact polarization equals unity when  $p = p_c$ . The permittivity is then infinite. The

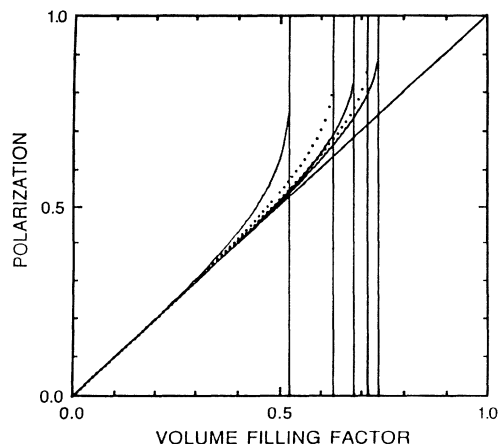


FIG. 1. The polarization  $\beta = (\epsilon - 1) / (\epsilon + 2)$  of a large spherical cluster of small conducting spheres as a function of the volume filling factor,  $p$ , of the cluster. The diagonal line  $\beta = p$  given by the Clausius-Mossotti equation predicts a metallization transition at  $p = 1$ , independent of the spatial distribution of the spheres. The solid lines with vertical asymptotes at 0.52, 0.68, and 0.74 are exact calculations of  $\beta$  for the simple-cubic, body-centered-cubic, and face-centered-cubic lattices, respectively. The cubic lattices undergo a metallization transition when the spheres touch. The dotted lines with vertical asymptotes at 0.63 and 0.71 are effective cluster model calculations of  $\beta$  for *uniformly expanded* disordered suspensions of randomly packed and pair-filled spheres, respectively.

vertical asymptote at  $p_c$  is a macroscopic manifestation of the nonlinear dependence of the higher multipolar interactions on the interparticle distances between the individual spheres. At the microscopic level, the multipole interactions give rise to strong attractive forces between closely spaced spheres in a suspension. These forces are analogous, on an intermediate scale, to the well-known van der Waals dispersion forces on the atomic scale, and to electrorheological and electrostrictive forces on the macroscopic scale. All of these forces have a magnitude proportional to the square of the local electric field, and thus they all vanish in the absence of a field.

Atomic dispersion forces are driven by quantum-mechanical field fluctuations. These fields are negligibly small on the scale of particle sizes in typical composites. In composites, their place is taken by much larger *triboelectric* fields produced by the very act of stirring required to make the medium homogeneous. These random local electric fields polarize the particles, indirectly exciting higher electric multipolar interactions between them. Because higher multipolar interactions fall off so rapidly with interparticle distance, closely spaced conducting particles are strongly attracted to each other, while the forces on other more distant particles are very small. As a consequence, particles in regions of higher particle density tend to condense into more compact close-packed metallized clusters, while particles in regions of lower particle density are relatively unaffected by the short-range forces. The mixing process thus involves two *partially* opposing effects: Electric fields produced by mechanical agitation call into action forces that tend to drive denser regions of the particle distribution all the way to closest packing. At the same time, mechanical stirring continually breaks up clusters (especially long, flat, irregularly shaped, or extended associations), or rearranges them into a more stable regular form. The two processes, while partially opposed, both tend to produce a kind of rough "phase separation" of the suspension into close-packed symmetrical particle clusters immersed in a background suspension of lower particle density.

We shall model a disordered monodisperse suspension as a mixture of isolated spheres of uniform size and close-packed spherical clusters of spheres. This geometry has the advantage that the spherical clusters and the isolated spheres have the same shape and thus make contributions of the same form to the permittivity. The Clausius-Mossotti equation then applies to the dipole interactions of the spheres and clusters of the mixture with the same accuracy as to a heterodisperse suspension of isolated metal spheres. Higher-order corrections arising from small departures from spherical cluster shape and variances in cluster compaction both tend to cancel to first order.

The clusters are spherical regions where the particles of the suspension have the maximum density for random packing. At  $p_c$  the spherical clusters have undergone metallization, so they act electrically simply as larger conducting spheres. Although the isolated metal spheres are of uniform size, no restriction is placed upon the size of the spherical clusters. Rather, we assume that the clusters have a wide range of radii, so that they complete-

ly fill space when the filling factor of the entire suspension reaches the critical value. As the volume filling factor of the metal of the suspension increases from zero to the critical value, the fractional part of the total sample volume occupied by the spherical clusters (and thus the fractional part of the metal in clusters) rises from zero to unity. At the limit of densest packing, the spherical clusters fill the sample space and all of the metal is present in compacted form. At any intermediate volume filling factor  $p$ , a fraction of the spheres,  $f$ , is in clusters and the remaining fraction of the spheres,  $(1-f)$ , is isolated. Thus

$$(1-f)p = p_0, \quad (2)$$

$$fp = p_{\text{cluster}}, \quad (3)$$

where the subscripts on  $p_0$  and  $p_{\text{cluster}}$  identify the respective contributions of the isolated spheres and the compacted spheres to the total volume filling factor. From (2) and (3), we have

$$p_0 + p_{\text{cluster}} = p. \quad (4)$$

Equations (2)–(4) hold exactly for clusters of any shape. They merely state that each metal sphere makes the same contribution to the total volume filling factor, whether it is isolated or part of a cluster. A similar additivity does not hold for their contributions to the total polarization.

The polarization of the isolated sphere fraction of the suspension is given by the value

$$\beta_0 = p_0. \quad (5)$$

The subscripts have been added to distinguish these quantities relating to isolated spheres from corresponding quantities relating to spheres taking part in clusters. Equation (5) is the Clausius-Mossotti relation appearing as the diagonal line in Fig. 1.

As the calculated curves in Fig. 1 show, each sphere in a compact spherical cluster makes a larger contribution than that of an isolated sphere to the polarization of the cluster, and thus to the effective medium as a whole. At the critical volume filling factor, the polarization of a cluster is unity, rather than the Clausius-Mossotti value  $p_c$ . That is, at  $p_c$  the polarization is enhanced by a factor  $1/p_c$ . This enhancement simply reflects the fact the cluster is metallized at a volume filling factor  $p_c$  while the metal within each of the individual spheres has a volume filling factor of unity. The difference,  $(1/p_c - 1)$ , may be expressed as an incremental effective polarizability of the individual spheres making up the cluster. Each sphere in a spherical cluster exhibits a total polarizability  $\alpha = R^3/p_c$  rather than  $\alpha_0 = R^3$ . The difference is the incremental polarizability  $\delta\alpha = (1/p_c - 1)R^3$ .

Physically, the polarizability enhancement is caused by all of the multipole interactions in the cluster acting together. For a disordered medium it would be difficult to calculate this incremental polarizability by a direct summation. Nevertheless, this simple size-independent expression for the average incremental polarizability of a metal sphere within a cluster is *exact* for spherical clusters large enough to justify macroscopic averaging. Ac-

cordingly, we set

$$\beta_{\text{cluster}} = \left[ \frac{1}{p_c} \right] p_{\text{cluster}} \quad (6)$$

for the polarization of the spherical clusters.

Combining Eqs. (1)–(6), we find for the effective polarization of the suspension

$$\beta = (1-f)p + f \left[ \frac{1}{p_c} \right] p = p \left[ 1 + f \left[ \frac{1}{p_c} - 1 \right] \right]. \quad (7)$$

While each metal sphere contributes the same volume to the volume filling factor, each sphere in a spherical cluster makes a larger contribution to the polarization of the cluster, and thus to the effective medium as a whole, than it would if it were acting separately as an isolated sphere.

The effective polarization given by Eq. (6) may be used for arbitrarily large spherical clusters. In the opposite limit of very small cluster size the macroscopic averaging upon which it is based must ultimately break down, since the incremental polarizability of an isolated sphere is zero. Before proceeding to the calculation of effective permittivities, it will be helpful to have some idea of the applicability of the effective spherical cluster model to smaller clusters. We consider the incremental polarizability of the smallest possible cluster: an isolated particle pair. Remarkably, the spherical cluster model applies without much error even to suspensions containing clusters consisting of only two particles.

### C. Particle pairs

Laplace's equation is separable in bispherical coordinates, so the problem of two conducting spheres in a uniform external field may be solved exactly. Using this coordinate system Levine and McQuarrie<sup>18</sup> obtained a series expansion for the total polarizability of a system of two spheres with arbitrary separation. Following their treatment, the polarizability of the pair may be written

$$\alpha_{\text{pair}} = \alpha_1 + \alpha_2 + \alpha_{12}, \quad (8)$$

where  $\alpha_1 = \alpha_2 = R^3$  is the polarizability of either of the two identical spheres when isolated,  $R$  is the sphere radius, and  $\alpha_{12}$  is the incremental polarizability caused by each sphere's *total* field on the other. Since the solution is exact, it includes the effect of *all* higher multipoles induced on these two spheres in a *uniform* external field.

The polarizability tensor of a pair is axially symmetric, so there are two independent components  $\alpha_{12,L}$  and  $\alpha_{12,T}$  longitudinal and transverse to the pair axis, respectively. The average polarizability of an ensemble of pairs with axes distributed isotropically is given by

$$\alpha_{12,0} = \frac{\alpha_{12,L} + 2\alpha_{12,T}}{3}. \quad (9)$$

For an isotropic random medium  $\alpha_{12,0}$  is the important quantity.

The polarizabilities  $\alpha_{12,L}$  and  $\alpha_{12,T}$  are given by

$$\alpha_{12,L} = 4R^3 \sinh^3 \eta_0 \{ [S_0(\eta_0)S_2(\eta_0) - S_1(\eta_0)S_1(\eta_0)] / S_0(\eta_0) \} - 2R^3 \quad (10)$$

and

$$\alpha_{12,T} = 2R^3 \sinh^3 \eta_0 \sum_{s=2}^{\infty} (-1)^{s-1} (\sinh s \eta_0)^{-3}, \quad (11)$$

where  $\eta_0$  is defined by

$$\cosh \eta_0 = \frac{r}{2R} = x. \quad (12)$$

The pair separation parameter  $x = r/2R$  is determined by the interparticle center-to-center distance  $r$  and the sphere radius  $R$ . For spheres in contact  $x = 1$ . The functions  $S_0(\eta_0)$ ,  $S_1(\eta_0)$ , and  $S_2(\eta_0)$  are given by

$$S_k(\eta_0) = \sum_{t=0}^{\infty} \frac{(2t+1)^k}{\exp[(2t+1)\eta_0] - 1}. \quad (13)$$

The incremental polarizabilities given by Eq. (8)–(13) are for pairs of particles. The incremental polarizabilities *per particle* are half as large. To find the total effective polarizability of each particle of the pair,  $\alpha_{\text{pair}}$ , we must add one-half of the incremental polarizability of the pair to the polarizability of an isolated sphere,

$$\alpha_{\text{pair}}(x) = R^3 [1 + \alpha_{12,0}(x)/2R^3]. \quad (14)$$

Calculations using Eqs. (8)–(13) show the isotropic incremental polarizability,  $\alpha_{12,0}(x)$ , to be a very nonlinear function of the separation parameter  $x$ . The effective polarizability  $\alpha_{\text{pair}}(x)$  given by (14) rises very rapidly with decreasing separation of the spheres in a pair as the spheres approach contact. For spheres in contact ( $x = 1$ ), we find  $\alpha_{12,0}(1)/2 = 0.4024R^3$  from Eq. (9). Thus, by Eq. (14), the corresponding total polarizability *per sphere*,  $\alpha_{\text{pair}}(1)$ , is  $1.4024R^3$  when the two spheres in the pair are in contact.

In order to compare the permittivity enhancement of one of the spheres in a compact pair with that of one of the spheres in a larger compact spherical cluster, we use Eq. (1) to relate the microscopic polarizability of an individual sphere in a pair,  $\alpha_{\text{pair}}(1)$ , to the corresponding macroscopic polarization and effective filling factor of a spherical cluster of pairs. We use the condition that the polarization of a pair-filled spherical sample must be equal to unity at the critical filling factor for pairs:  $\beta = 4\pi N_c \alpha_{\text{pair}}(1)/3 = 1$ , or, equivalently,  $\beta = p_c \alpha_{\text{pair}}(1)/R^3 = 1$ , where  $N_c$  is the critical pair density corresponding to  $p_c$ . Thus, for a pair-filled sphere, the critical volume filling factor  $p_c$  is  $1/1.4024 = 0.713$ .

It is interesting to compare the volume loading dependence of the polarization of a uniformly expanded disordered suspension of pairs with those of the cubic arrays. The polarization  $\beta(p)$  of a uniformly expanded pair-filled sphere with a volume filling factor  $p$  may be found by inserting  $\alpha_{\text{pair}}(x)$  from Eq. (14) into Eq. (1). The separation parameter  $x$  may then be replaced by the filling factor  $p$  using the relation  $x = (p_c/p)^{1/3}$ , with  $p_c = 0.713$ . The re-

sulting polarization,  $\beta_{\text{pair}}(p)$ , is given by

$$\beta_{\text{pair}}(p) = p \left[ 1 + \frac{\alpha_{12,0}(x)}{2R^3} \right]. \quad (15)$$

Equation (15) is shown as the dotted curve on the right in Fig. 1. Comparing the dotted polarization curve for the pair-filled sphere with the solid lines for the three cubic lattices in Fig. 1, we see that all of the curves have the same general shape, but the critical volume filling factor  $p_c$  is different for each of them. This shows that in a macroscopically isotropic suspension the effective incremental polarizability scales approximately with the relative volume filling factor,  $p/p_c$ , almost independently of the spatial distribution of the particles, while the critical volume filling factor  $p_c$  is determined by the geometry of the specific particle distribution.

Any of the polarization curves in Fig. 1 could be scaled to represent the polarization as a function of volume loading for other uniformly expanded suspensions. The exact curves for the cubic lattices are inconvenient for this purpose, since they are laborious to calculate and awkward to handle. Equation (15), on the other hand, is easy to evaluate and it can be readily scaled to represent a suspension with a different critical volume filling factor. Using Eq. (15) to scale the polarization of a uniformly expanded suspension, we get

$$\beta_{\text{scaled}}(p) \approx p \left[ 1 + \frac{\alpha_{12,0}(x)}{\alpha_{12,0}(1)} \left[ \frac{1}{p_c} - 1 \right] \right], \quad (16)$$

where  $x = (p_c/p)^{1/3}$  as before, but now the parameter  $p_c$  is the critical filling factor of the suspension to be represented. With the pair filling factor  $p_c = 0.713$ , Eq. (16) reduces to (15), the expression for the polarization of a system of pure pairs. With the filling factor for random close packing,  $p_c = 0.63$ , Eq. (16) was used to interpolate the polarization of a uniformly expanded disordered suspension of spheres in a large spherical cluster as a function of volume loading. This is the interpolation shown as the dotted line on the left in Fig. 1. All of the polarization curves in Fig. 1 exhibit the strong nonlinearity exploited in Eqs. (2)–(7) to model a disordered suspension as a mixture of isolated spheres and effective spherical clusters. Only the vertical asymptote  $p = p_c$  enters the model.

The critical volume filling factor for a close-packed disordered suspension is 0.63. This is about 12% smaller than the value 0.713 calculated for a suspension of pairs. Thus, the spherical cluster model would be a fair approximation, even for a suspension containing clusters consisting entirely of pairs. Actual suspensions, however, contain a wide range of cluster sizes, ranging from pairs to large clusters, so that the error incurred in using the large cluster value for  $p_c$  to model a real suspension will be much smaller. Accordingly, we treat all clusters the same and use the experimental value of  $p_c$  for randomly close-packed spheres,  $p_c = 0.63$ , to calculate the effective permittivity of a disordered suspension.

### III. EFFECTIVE PERMITTIVITY

The effective polarization of the suspension,  $\beta$ , given by Eq. (7) includes all *internal* higher-order electrical multipolar interactions between the spheres in a cluster. These manifest themselves externally as an enhanced *dipole* polarizability of the cluster as a whole. If we limit *external* mutual interactions between isolated spheres, between clusters, and between the clusters and spheres to dipolar terms, the permittivity of the medium is obtained by inserting the polarization, (7), into the Clausius-Mossotti equation

$$\epsilon = \epsilon_0 \left[ 1 + \frac{3\beta}{1-\beta} \right], \quad (17)$$

where  $\epsilon$  and  $\epsilon_0$  are the permittivity of the suspension and the host material, respectively. In order to calculate the permittivity of an actual sample, we need to know, or make some assumption about, the dependence of the fraction of spheres taking part in clusters,  $f$ , as a function of total volume filling factor,  $p$ . In the limit of zero filling factor,  $f = 0$ . At the critical volume filling factor,  $f = 1$ . Since  $f$  ranges from 0 to 1 as the volume filling factor increases from 0 to  $p_c$ , between the limits 0 and  $p_c$  we use a linear interpolation for the volume fraction of the spheres in clusters. Setting  $f = p/p_c$  in Eq. (7), we have

$$\begin{aligned} \beta &= \left[ 1 - \left( \frac{p}{p_c} \right) \right] p + \left( \frac{p}{p_c} \right) \left[ \frac{1}{p_c} \right] p \\ &= p \left[ 1 + \left( \frac{p}{p_c} \right) \left( \frac{1}{p_c} - 1 \right) \right] \end{aligned} \quad (18)$$

for the effective polarization per unit volume of the medium. Inserting the effective polarization  $\beta$  from Eq. (18) into the Clausius-Mossotti equation (17), we get the effective cluster expression for the permittivity  $\epsilon$  of a disordered suspension of conducting spheres.

### IV. COMPARISON WITH EXPERIMENT

Much of the older low-frequency literature<sup>3,5</sup> exhibits permittivity enhancements that have been attributed to variances in both particle shape and spatial distribution. Explanations have invoked a bewildering array of mixture rules incorporating more or less empirical and adjustable particle shape parameters. In order to avoid the arbitrariness required by variations in particle shape, we consider only spherical particles. The low-frequency permittivity measurements of Guillien<sup>19</sup> on emulsions of Hg in oil are of particular interest, because both the particles and the host are liquids. The particles are exceptionally smooth and spherical, so additional enhancements owing to variations in particle shape are completely absent. The conductivity measurements of Turner<sup>20</sup> are of particular interest because of the exceptionally wide range of filling factors accessible to the fluidized bed technique he used. In addition to these low-frequency experiments, we shall also present new permittivity measurements at microwave frequencies.

### A. Low-frequency permittivity measurements

Guillen's permittivity measurements<sup>19</sup> on emulsions of Hg in heavy lubricating oil are noteworthy for their internal consistency. The emulsions were produced directly in the cylindrical sample capacitor and large-scale sample homogeneity was maintained by continuously stirring the sample during measurement. Initially the cell contained only the host oil (Aetna oil,  $\epsilon_0 = 2.263$  at 17.8°C and  $\epsilon_0 = 2.210$  at 24.0°C). Mercury was then injected under air pressure in successive amounts and was further emulsified by a helical stirring paddle. Successive filling factors were accurately determined by weighing. The highest attainable volume filling factor was limited by the increasing viscosity of the emulsion. While the emulsions appeared a uniform pearl grey to the naked eye, microscopic examination revealed the individual perfectly spherical mercury droplets.

Measurements made at 17.8°C and 24.0°C and at frequencies of 0.07, 0.78, and 3.49 MHz showed no temperature or frequency dependence of the reduced permittivity,  $\epsilon/\epsilon_0$ . Guillien's experimental results are shown as open squares in Fig. 2. The lower solid line is the reduced permittivity given by the Clausius-Mossotti equation. The experimental values exhibit a substantial permittivity enhancement that cannot be attributed to shape effects in this liquid system. The lower dotted line shows the Torquato-Lado third-order lower bound on the permittivity.<sup>15</sup> For comparison, the upper dotted line in Fig. 2 shows the permittivity of a random suspension of impenetrable spheres, calculated using an alternative expression of Chiew and Glandt<sup>13</sup> that includes effects of pair

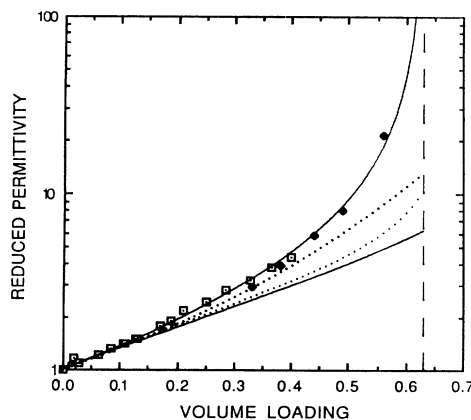


FIG. 2. Reduced permittivity  $\epsilon/\epsilon_0$  (or conductivity  $\sigma/\sigma_0$ ) as a function of volume filling factor,  $p$ . The open squares are Guillien's permittivity measurements on suspensions of Hg droplets in oil. The solid diamonds are Turner's conductivity measurements on fluidized bed suspensions of ion-exchange resin spheres in aqueous solutions of sodium chloride. The lower solid line is the Clausius-Mossotti (or Maxwell) relation. The lower dotted line shows the general Torquato-Lado third-order lower bounds on the permittivity (Ref. 15). The upper dotted line is the Chiew-Glandt equation for the permittivity including pair correlation to order  $p^2$  (Ref. 13). The upper solid line is the reduced permittivity (or conductivity) given by the effective spherical cluster model.

correlations to order  $p^2$ . The permittivity enhancement over the limits set by both the third-order lower bounds and by the pair-correlation calculation is consistent with the presence of larger clusters. The upper solid line in Fig. 2 shows the reduced permittivity predicted by Eqs. (17) and (18), using the empirical value  $p_c = 0.63$  for the critical volume filling factor of disordered suspensions of uniform spheres. With  $p_c$  taken from experiment, there are no adjustable parameters in the effective cluster expression for the permittivity. Agreement is good over this range of volume filling factors. Still larger enhancements are predicted as the filling factor approaches the critical value.

### B. Low-frequency conductivity measurements

Theories of generalized linear susceptibilities apply to electrical conductance as well as to electrical permittivity, so all of our expressions, and in particular Eqs. (17) and (18), may be used to calculate the effective conductance of suspensions of monodisperse spheres, provided the permittivities  $\epsilon$  and  $\epsilon_0$  are replaced by corresponding conductances  $\sigma$  and  $\sigma_0$  throughout. Turner<sup>20</sup> measured the effective electrical conductance of fluidized beds of ion-exchange resin beads in aqueous solutions of sodium chloride for a wide range of particle to host conductance ratios. In fluidized bed experiments, the particles are dynamically suspended and the measured quantity is a time average. This allows reproducible measurements to be made at a higher volume loading than with static suspensions. In Turner's experiments, the particles were nearly perfect spheres with an average diameter of 0.75 mm. The suspensions were made monodisperse by wet sieving followed by fractional separation at high flow rates in the fluidization column. Conductance measurements were made at 25°C on a conductance bridge at 1600 Hz. The volume filling factors were computed from the observed static packing fraction and the column expansion under fluidization. The highest bead-to-host conductance ratio Turner studied was 14 000. These results would be indistinguishable, within experimental error, from measurements using beads of infinite conductance.

Turner's measured effective conductivity ratios  $\sigma/\sigma_0$  are shown as solid diamonds in Fig. 2. Since the same forms of expression govern the effective permittivity and effective conductance of a suspension, the solid and dotted lines plotted in Fig. 2 also hold for effective conductance. The lower solid line, known as Maxwell's relation when applied to conductance, as well as the dotted lines showing the third-order lower bounds and the pair-correlation calculation, are all in poor agreement with experiment at these higher volume loadings. Turner's measured conductances correlate well with Guillien's permittivity measurements at lower loading where a comparison can be made. The trend to still larger enhancements is continued in the neighborhood of the critical volume filling factor. The effective cluster model is in excellent agreement with the permittivity and conductivity measurements over the entire range of volume loading.

### C. High-frequency permittivity measurements

Dynamically sustained suspensions in fluid systems have the advantage of giving excellent time-averaged stability and reproducibility at high volume filling factors and so are particularly suitable for studying enhancements to generalized susceptibility caused by particle clustering. On the other hand, solid suspensions are usually required for use as artificial dielectrics and in other practical applications. Solid systems exhibit the same density fluctuations found in the liquid systems, but in static solid systems there can be even stronger additional variances associated with fabrication, such as incomplete stirring, particle cohesion, settling, substrate distortion, voids, and other factors. Any or all of these fluctuations can occur in a given solid sample, and all can lead to an increase in the measured macroscopic average dielectric constant. Thus, unless special precautions are taken, solid suspension samples can exhibit wide variations in their physical properties.

We have prepared an extensive series of homogeneous monodisperse solid suspensions of metal spheres, taking pains to minimize all density variations but the inescapable statistical fluctuations. Metal magnetic alloy spheres were prepared by atomization from the melt in an argon atmosphere. The spheres were then sieved and air fractionated into a range of monodisperse size classes with mean diameters ranging from 5 to 20  $\mu\text{m}$ . Auger atomic spectroscopy and resistivity measurements on bulk samples of the spheres showed that they had acquired a very thin oxide layer during processing. In our experiments, a thin insulating oxide film is actually helpful, since it prevents zero-frequency percolation while leaving the high-frequency permittivity unchanged. Homogeneous suspensions were made by thoroughly mixing the graded metal spheres with polyurethane powder and then thermally curing the mixed powder under pressure. The volume filling factors of the suspensions were determined by combined density measurements and magnetization measurements below the Curie point of the alloy. Suspensions of spheres were prepared with volume filling factors ranging from less than 0.1 to greater than 0.5. Experimental specimens were then machined from the polymerized suspension material and the permittivity was determined from reflectance and transmittance measurements using a Hewlett-Packard network analyzer over the frequency range from 0.5 to 18 GHz.<sup>21</sup>

Figure 3 shows a scanning electron micrograph of a representative sample of the metal powder fraction of 12- $\mu\text{m}$ -diameter particles. As can be seen, the particles are well-formed spheres of uniform size. Figure 4 shows an electron micrograph of a microtomed section of a typical finished sample containing 12- $\mu\text{m}$ -diameter spheres with a volume filling factor  $p = 0.39$ . Although the microtome blade has pulled some spheres from the host binder, the empty cavities mark the positions of the missing particles. Both isolated particles and compact clusters are present at this intermediate volume loading.

Figure 5 shows the results of permittivity measurements at 10 GHz. As in Fig. 2, the lower and upper solid lines show the predictions of the Clausius-Mossotti equa-

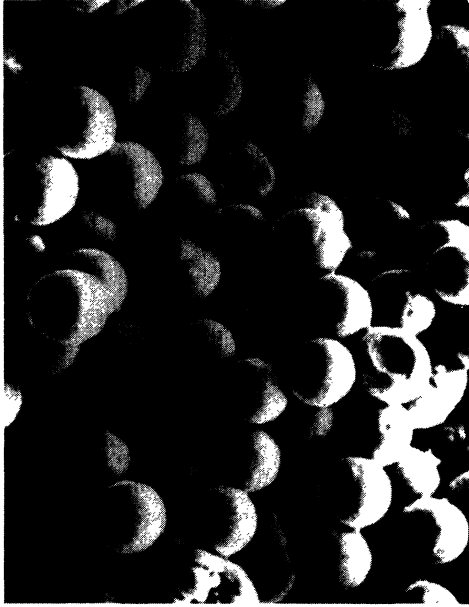


FIG. 3. Scanning electron micrograph of 12- $\mu\text{m}$ -diameter metal-alloy spheres. Atomization from the melt produces well-formed spheres. The narrow size distribution was obtained by sieving and air fractionation.

tion and the effective cluster model, respectively, while the lower dotted line again shows the Torquato-Lado third-order lower bound on the permittivity. The various symbols used show the reduced permittivity ( $\epsilon_0=2.8$ ) in separate series of measurements on monodisperse suspensions containing spheres with mean diameters ranging

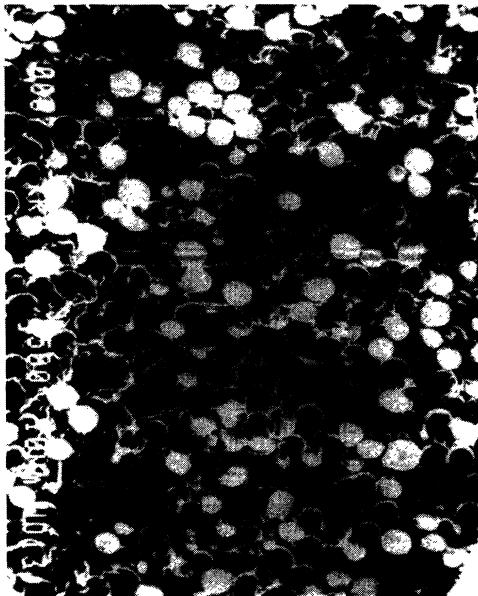


FIG. 4. Scanning electron micrograph of a microtomed surface of a typical solid suspension of metal spheres in a polyurethane binder. The spheres in this sample are from the 12- $\mu\text{m}$ -diameter stock shown in Fig. 3. The volume filling factor is 0.39. Cavities show where the microtome blade has torn some of the spheres from the host. Both isolated spheres and large clusters are present at this volume filling factor.

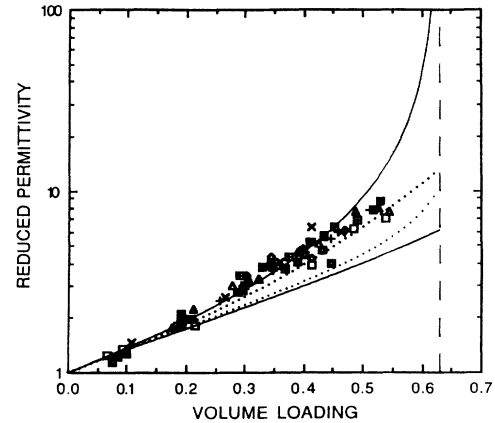


FIG. 5. Reduced permittivity as a function of volume filling factor. Each symbol designates a separate series of permittivity measurements at 10 GHz on samples of mean diameters from 5 to 15  $\mu\text{m}$ . For each measurement a sample was machined from a suspension like that in Fig. 4 containing distributions of spheres similar those in Fig. 3. The lower solid line is the Clausius-Mossotti relation. The lower dotted line shows the general Torquato-Lado third-order lower bounds on the permittivity (Ref. 15). The upper dotted line is the Chiew-Glandt equation for the permittivity including pair correlations to order  $p^2$  (Ref. 13). The upper solid line is the permittivity given by the effective spherical cluster model.

from 5 to 15  $\mu\text{m}$ . No systematic dependence upon particle size is discernible. As with the liquid samples, there is again a substantial permittivity enhancement above the value predicted by the third-order lower bounds. The larger particle clusters responsible for the permittivity enhancement in these samples can be seen in the microtomed specimen shown in Fig. 4. The effective cluster model is again in good agreement with the measurements over a wide range of volume loading. For these solid samples, the Chiew-Glandt equation (upper dotted curve) is in better agreement with experiment at the highest volume loading.

Although pains were taken to minimize extraneous inhomogeneities caused by fabrication the scatter in the data in Fig. 5 is greater than that formed in the time-averaged results for the liquid samples in Fig. 2. This reflects the greater difficulty in preparing homogeneous static solid suspensions. Each individual experimental point in Fig. 5 involved separate fabrication of a machined solid sample of an independently prepared solid suspension. At the highest volume loadings the measured permittivities of the solid suspensions fall somewhat below the corresponding measurements on liquid samples at the same volume loading. This could be due to a physical difference in the behavior of liquid and solid samples, or it could be an artifact of the fabrication at high volume loading. The highest volume loading in our experiments was limited by the difficulty of forming compact, physically stable, machinable solid suspensions.



## V. CONCLUSION

Experimental measurements of electrical permittivity and conductivity of disordered monodisperse suspensions of conducting spheres typically exhibit large enhancements above the values predicted by the Clausius-Mossotti and Maxwell approximations and even above the rigorous third-order bounds on the permittivity. These enhancements are associated with a susceptibility anomaly accompanying the metallization transition that occurs when the volume loading of the spheres reaches the limit of closest packing. None of the myriad of existing empirical relations or theoretical approximations account for these discrepancies or adequately represent the experiments over the entire accessible range of volume loading. Exact calculations for regular arrays of conducting spheres show that the susceptibility enhancement and the metallization transitions are caused by the dipole and *all* higher electric multipole interactions together. Similar calculations for a disordered suspension have not been made and appear prohibitively difficult, but the physical origin of the effects makes it clear that any approach based solely on the dipole approximation must fail. Series approximations and cluster-expansion methods become very difficult with perfectly conducting spheres at high volume loading. The higher-order multipole contributions converge very slowly as the spheres approach contact. In order to get around these difficulties, we have developed a simple physical model that incorporates the metallization transition from the outset, and reduces to the Clausius-Mossotti equation in the limit of low volume loading.

We model a disordered suspension as a mixture, or

mesosuspension, of isolated spheres and localized spherical close-packed metallized clusters with a wide range of radii, suspended in a background host dielectric. The unclustered spheres have the unenhanced polarizability of an isolated sphere, while all internal electric multipole interactions contribute to the enhanced effective polarizability of the spheres taking part in the close-packed clusters. The effective polarizability of a member sphere in a large close-packed spherical cluster is determined by the existence of the metallization transition. It depends only on the critical volume filling factor of the cluster and is independent of cluster size. A single filling factor suffices for all clusters, even for clusters as small as a pair of spheres. The model has no adjustable parameters when the experimental value is used for the volume filling factor for randomly close-packed spheres. Using this experimental value, the effective spherical cluster model is in excellent agreement with experimental permittivity and conductivity measurements on dynamically sustained liquid suspensions and on well-mixed static solid suspensions of monodisperse conducting spheres over the entire accessible range of volume loading.

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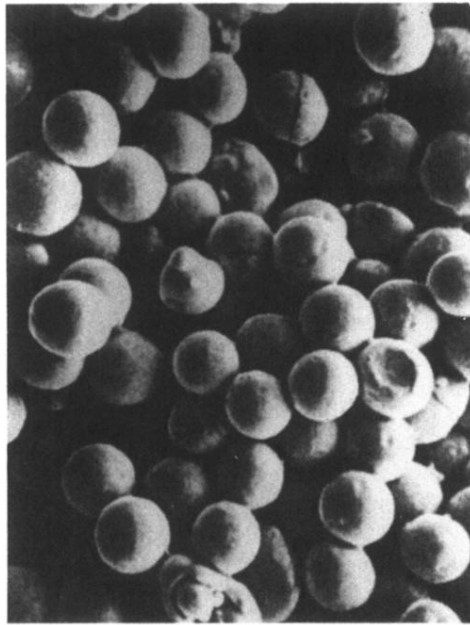


FIG. 3. Scanning electron micrograph of 12- $\mu\text{m}$ -diameter metal-alloy spheres. Atomization from the melt produces well-formed spheres. The narrow size distribution was obtained by sieving and air fractionation.

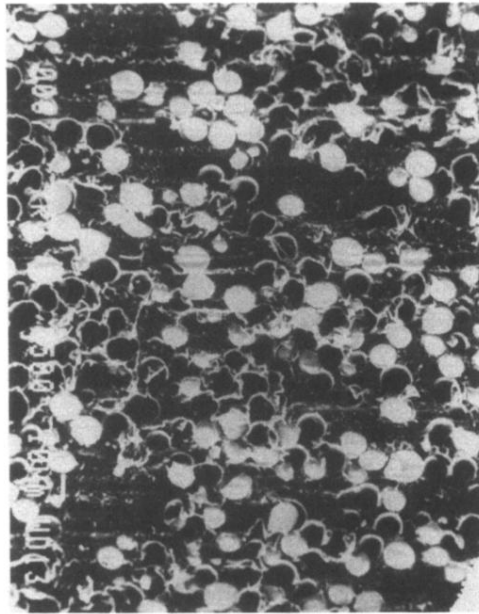


FIG. 4. Scanning electron micrograph of a microtomed surface of a typical solid suspension of metal spheres in a polyurethane binder. The spheres in this sample are from the 12- $\mu\text{m}$ -diameter stock shown in Fig. 3. The volume filling factor is 0.39. Cavities show where the microtome blade has torn some of the spheres from the host. Both isolated spheres and large clusters are present at this volume filling factor.