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Conductivity of inhomogeneous materials: Effective-medium theory with dipole-dipole interaction

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We extend the old effective-medium theory, originally due to Bruggeman, by incorporating dipole-dipole interactions to account for local-field effects. The interactions are represented approximately by use of effective depolarization factors. For close-packed clusters of conducting regions, a description which is appropriate at the percolation threshold, we predict an onset of percolation processes when 15.6 vol% is conducting. This is in very good agreement with numerical simulations as well as with experimental data for the metal-insulator transitions in metal-ammonia solutions and in alkali-tungsten bronzes.

I. INTRODUCTION

In this article we present an improved effective-medium theory for the conductivity of a microscopically inhomogeneous material. Essentially we extend the old formulation, originally due to Bruggeman,[1] by explicitly incorporating dipole-dipole interactions to account for near-field effects. The modified theory will be seen to stand in very good agreement with numerical results simulating a percolative conductivity, as well as with experimental data pertaining to continuous metal-insulator transitions.

The strategy underlying the usual effective-medium theory[1-6] (EMT) is to consider a typical element of the disordered system which is embedded in an effective medium, whose properties are to be determined self-consistently. To achieve this one solves for the exact local field around the element and imposes the condition that the fluctuations of this local field about its effective value should average out. The self-consistency requirement is then sufficient to specify the effective medium. Representing the disordered material as a mixture of conducting and insulating *spheres* it can be seen[2-6] that the EMT predicts an onset of conductivity when the concentration of conducting material is $\frac{1}{3}$, i.e., the theory gives a percolation threshold[3] at a critical concentration

$$C^*_{\mathrm{EMT}} = \tfrac{1}{3}.$$

Another, and at first sight rather different, approach to the conductivity of an inhomogeneous medium is to start with a lattice and connect neighboring nodes one by one with resistors which are placed according to some statistical prescription. Extensive numerical studies by Kirkpatrick[3] demonstrated that the percolation threshold for randomly distributed resistors on a simple cubic lattice occurred at $C^* = 0.25$. This result is not immediately applicable to a disordered material, though, as a real system must be characterized by *percolations on a continuum* rather than on a discrete lattice of any specific type. Such a continuous-percolation problem can be considered as the limit of site or bond percolation on any lattice as the correlations on adjacent sites or bonds are increased. Among the most pertinent computations for the continuous-percolation situation are those by Skal *et al.*,[7] who studied the percolation probability[3,8,9] for a particular random potential in a cubic lattice with site correlation extending up to third-nearest neighbors. Asymptotically they obtained

$$C^* = 0.17$$

for the percolation threshold. This result is reproduced in the numerical work by Webman, Jortner, and Cohen,[10] who investigated bond correlation up to second order. The above value of C^* is also in keeping with the empirical finding by Scher and Zallen,[11] that for three-dimensional regular lattices one has $C^* = FP_c = 0.15 \pm 0.02$, where F is the packing fraction for spheres forming a lattice and P_c is the critical site concentration for the same lattice.

We then have to reconcile that *the accurate numerical computations yield a percolation threshold which is much smaller than the value from the simple EMT.* Several attempts to extend the EMT have been made: Probably the most thorough is by Hori and Yonezawa[12] who employed diagrammatic representation up to high orders in a perturbation expansion and were able to derive upper and lower bounds on the percolative conductivity for a simple cubic lattice. In the low-concentration limits

a "cluster EMT" can be worked out exactly, as shown recently by Bernasconi and Wiesmann[13]; this should accurately represent percolations on a continuum but unfortunately their "cluster EMT" can be justified theoretically only in the limit of very small concentration of either constituent in the inhomogeneous medium. Very recently it has also been suggested by Davidson and Tinkham[14] that the old and well-established EMT should be abandoned in favor of a purely phenomenological amalgamation of percolation theory and the notions behind the effective-medium concept. To our mind the latter approach is too, drastic, and in this paper we present an improved effective-medium theory, where we account for dipole-dipole interactions within clusters of conducting inclusions by introducing effective depolarization factors. This novel extended effective-medium theory (here called EMTDD), which we formulated in another context in a previous paper,[15] is outlined in Sec. II below. In Sec. III we compare this EMTDD with earlier theories and with numerical data, and demonstrate that it simulates accurately the onset of a percolative conductivity. As shown in Sec. IV there is also a satisfactory correspondence with experimental conductivity results on metal-ammonia solutions and on alkali-tungsten bronzes. The main results are summarized in Sec. V.

II. EFFECTIVE-MEDIUM THEORY

A physically very transparent derivation of the EMT was given by Landauer.[2] Following his line of reasoning we consider a spherical inclusion of conductivity σ, which is embedded in an effective medium described by $\bar{\sigma}$. The dipole moment for a sphere of radius r is

$$\vec{E} r^3(\sigma-\bar{\sigma})/(\sigma+2\bar{\sigma}), \tag{1}$$

where $\vec{E}$ is the far field. If the volume fraction C is occupied by such spheres their polarization is

$$\vec{P}=C\vec{E}(\sigma-\bar{\sigma})/(\sigma+2\bar{\sigma}). \tag{2}$$

The rest of the two-phase medium is regarded as spheres of conductivity σ_m (for convenience taken to be smaller than σ) embedded likewise in an effective medium of conductivity $\bar{\sigma}$. Their polarization is then

$$\vec{P}_m=(1-C)\vec{E}(\sigma_m-\bar{\sigma})/(\sigma_m+2\bar{\sigma}). \tag{3}$$

The effective-medium condition is equivalent to stating[2] that the net polarization should vanish, i.e.,

$$\vec{P}+\vec{P}_m=0. \tag{4}$$

By this relation we obtain[16] for *spheres*

$$\tfrac{1}{3}C\alpha+(1-C)(\sigma_m-\bar{\sigma})/(\sigma_m+2\bar{\sigma})=0, \tag{5}$$

where α can be written

$$\alpha=(\sigma-\bar{\sigma})/[\sigma+\tfrac{1}{3}(\sigma-\bar{\sigma})]. \tag{6}$$

Hence α is proportional to the polarizability for a sphere (having a depolarization factor $\frac{1}{3}$). As we discussed in a previous paper[15] the generalization to *randomly oriented ellipsoids* is

$$\alpha=\frac{1}{3}\sum_{i=1}^{3}\frac{\sigma-\bar{\sigma}}{\bar{\sigma}+L_i(\sigma-\bar{\sigma})}, \tag{7}$$

where the L_i's denote the appropriate triplet of depolarization factors which, in its turn, is governed by the ratios between the axes of the ellipsoid. Clearly, the latter definition of an effective medium is nonsymmetric in the two constituents.

Equation (7) inserted into Eq. (5) gives a possibility to discuss the conductivity of nonspherical inclusions. Alternatively, and more important for our present discussion, exactly the same formalism is amenable to a treatment of dipole-dipole interactions among neighboring spherical inclusions. Such a coupling may be insignificant when the concentration of either component in a mixture is small, provided the conducting particles have a possibility of being well separated.[17] However, as the amounts of the two components become increasingly comparable it is obvious that clustering of the conducting regions will become more and more important, until the cluster size eventually diverges at the percolation threshold C^*, where a conducting path opens up throughout a sample of unbounded extension. This *clustering is not accounted for by the simple EMT*, which is the reason for its failure to describe the percolation threshold properly.

Physically, it is clear that the electric field entering the expressions for the polarization of the two components [Eqs. (2) and (3)] is not equal to the far field in the case of spheres which are surrounded by other spheres, but that local-field effects can be significant, or, in other words, that multipole coupling must be considered explicitly. The most important of these interactions, namely dipole-dipole coupling, was studied lately by Clippe, Evrard, and Lucas,[18] who calculated the resonance frequency for several geometrically well determined configurations of identical touching spheres from a dipole-dipole interaction Hamiltonian. As we discussed recently[15] it is possible to represent their computed resonance frequencies by one *triplet of effective depolarization factors*,[19-21] L_i^*, pertaining to each of the geometrical configurations. These quantities replace the L_i's in the expression for the polarizability, i.e., in Eq. (7). An asterisk has been added to the symbol for the depolarization factors to signify that the *effective* depolarization factors are, in a sense,

TABLE I. *Equivalent depolarization factors* for different geometrical configurations of identical touching spheres as extracted from Ref. 18.

Geometrical configuration	Equivalent depolarization factor L_1^*	L_2^*	L_3^*
Single sphere	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
Single-strand chain	0.133	0.435	0.435
fcc lattice	0.0865	0.0865	0.827

fictitious quantities which are not related to any deviations from a spherical shape. Table I contains L_i^*'s for the two most pertinent configurations considered in Ref. 18, viz., infinite linear single-strand chains and close-packed (fcc) clusters; for comparison the values for independent spheres have been included. Formally, the linear chain is seen to behave like a prolate spheroid, whereas the fcc cluster, formally, acts like an oblate spheroid.

To make the significance of the L_i^*'s clear we contemplate spherical conducting inclusions in an insulating matrix. When C is small we have $L_i^* = \frac{1}{3}$ as, in general, the conducting regions are widely apart. However, when C increases the dipole-dipole coupling becomes more manifest and it is then more meaningful to regard the specimen *as consisting of noninteracting aggregates of spheres*. These aggregates can be thought of as the "fundamental particles" to which we apply Bruggeman's theory. A schematic (two dimensional) representation of our conceptual model for the inhomogeneous medium is given in Fig. 1. At C^* (which we know to occur at approx. 17 vol% of conducting material) infinite aggregates form, and then the L_i^*'s for close-packed spheres should be most appropriate. Somewhere in the interval $0 < C < 0.17$ it is reasonable to assume that the two phase material is best characterized by linear chains. Two points are worth making: (i) in general, the effective depolarization factors are concentration dependent; but, (ii) over a large concentration range, from the percolation threshold and up to $C \approx 1$, the L_i^*'s for close-packed clusters should constitute a good approximation for the dipole-dipole interactions.

Before concluding this section we remark that the old EMT is a mean-field theory for which the self-consistency requirement implies that the interactions among the inclusions are accounted for only in so far as they can be represented by a constant far field, whereas, as we pointed out above, all local-field effects are neglected. Our present approach, where we incorporate dipole-dipole interactions via effective depolarization factors should then lead to some overestimation of the coupling at least when C is not very small. On the other hand, the L_i^*'s do not include higher-order multipole-multipole couplings like quadrupole or octupole terms, which may also play some role for neighboring spheres. Physically, we expect the double counting of the dipole-dipole interactions as well as the omission of higher multipoles to be rather unimportant effects in our "local-field approach" to the dipole-dipole coupling in the EMTDD. Furthermore, these two factors counteract one another, which strengthens our contention that by use of the effective depolarization factors, one obtains a good representation of the local-field effects for the pertinent geometrical configurations in the two-phase media.

III. COMPARISON WITH EARLIER THEORIES AND WITH NUMERICAL RESULTS

From Eqs. (5) and (7) it can be seen that the largest depolarization factor determines the onset of conductivity, and hence dipole-dipole interaction will *always* displace the percolation threshold towards lower concentrations of conducting material. Figure 2 shows calculations of effective conductivities for our EMTDD with L_i^*'s appropriate to linear chains and to close-packed clusters. The results apply to the "pure" percolation case for which $\sigma_m = 0$. It can be seen that $\bar{\sigma}$ is zero up to a certain percolation threshold given by

$$C^*_{\mathrm{EMTDD}} = \begin{cases} 0.271 & \text{(chains)}, \\ 0.156 & \text{(clusters)}, \end{cases}$$

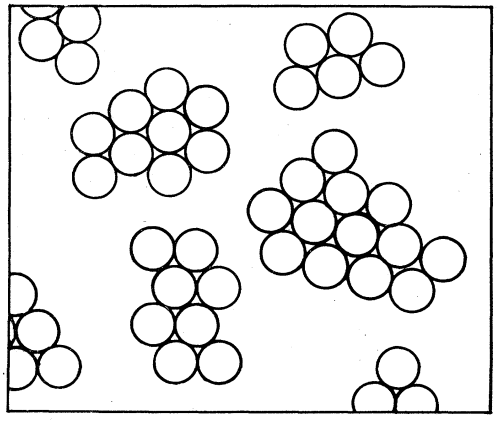

FIG. 1. Two-dimensional representation of our conceptual model for a disordered two-phase medium. The conducting regions (circles) are taken to be aggregated into noninteracting clusters of a well-characterized configurations—here close packed. A triplet of effective depolarization factors approximates the local-field effects within each cluster.

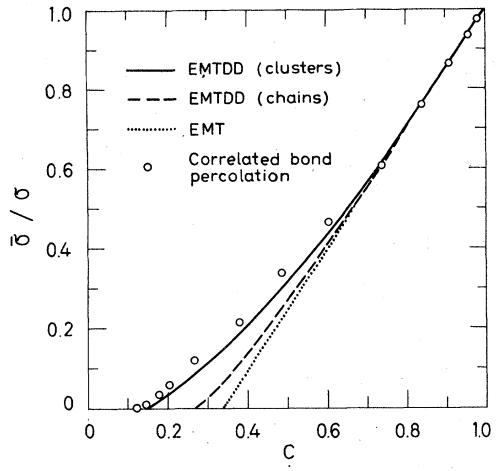

FIG. 2. Normalized effective conductivity vs concentration of conducting material as calculated from our effective-medium theory with dipole-dipole interaction (EMTDD) using the L_i^*'s of Table I to represent spheres aggregated into infinite linear chains or close-packed clusters. Results are shown for the old effective-medium theory (EMT; cf. Refs. 1–6) as expressed by Eq. (8). The circles denote correlated bond percolation on a simple cubic lattice as extracted from Ref. 3; the predicted percolation threshold of $C^* = 0.103 \pm 0.1$ is probably somewhat too low for the continuous-percolation situation.

where the latter value stands in excellent agreement with the result $C^* = 0.17$ obtained from numerical studies[7,10] simulating percolations on a continuum. For comparison the $\bar{\sigma}$-vs-C relation for the simple EMT is also contained in the figure; it can be expressed as[3]

$$\bar{\sigma}_{\mathrm{EMT}} = \sigma \tfrac{3}{2}(C - \tfrac{1}{3}) \quad \text{for } C \geq \tfrac{1}{3}, \tag{8}$$

i.e., by a straight line. At $C \gtrsim 0.7$ the EMTDD is found to be practically indistinguishable from the EMT. The circles in Fig. 2 denote Kirkpatrick's[3] numerical data for site correlated bond percolation networks with a three-dimensional simple cubic lattice. It is immediately clear that the results are very similar to the EMTDD for close-packed clusters, as expected from our considerations in Sec. II above.

It is of interest to study the behavior of the $\bar{\sigma}$-vs-C relations in the immediate vicinity of the percolation threshold, because there the numerical data of Kirkpatrick[3] and of Webman, Jortner, and Cohen[10] can be expressed as

$$\bar{\sigma} = A\sigma(C - C^*)^{\gamma} \quad \text{for } C \gtrsim C^*, \tag{9}$$

where A and γ are constants.

The exponent in the power law is given by[3,10,22]

$$\gamma \approx 1.6.$$

The EMTDD and EMT are investigated close to C^* in the log-log plot of Fig. 3. For the EMT one finds a linear relation with slope unity as predicted by Eq. (8). Sufficiently near the percolation threshold the EMTDD also yields a straight line with

$$\gamma_{\mathrm{EMTDD}} = \gamma_{\mathrm{EMT}} = 1;$$

as can be inferred already from the structure of the effective-medium equations [Eqs. (5) and (7)]. This reflects the simplification in assigning only *one* triplet of L_i^*'s to the complex structure of conducting regions at the percolation threshold. By use of a *distribution* of effective depolarization factors one can, in principle, obtain $\gamma_{\mathrm{EMTDD}} > 1$; however this involves an unwarranted complication to the effective-medium approach.

Evidently, none of the effective-medium theories properly accounts for the critical behavior at C^*, but even so the fact that the right magnitude of the percolation threshold is reproduced proves that the EMTDD for clusters represents a significant improvement over the simple EMT. With this in mind it is interesting to compare our EMTDD with other extensions of the EMT. Recently Bernasconi and Wiesmann[13] (BW) used the correspondence of the effective-medium formalism and the disordered Heisenberg ferromagnet to derive "cluster extensions" of the EMT, which should be exact in the low-concentration limit. In their case of correlated bond percolation, which is most appropriate for our purposes, they found

$$\bar{\sigma}_{\mathrm{BW}} = 1.05\sigma(C - C^*_{\mathrm{BW}}) \quad \text{for } C \geq C^*_{\mathrm{BW}}, \tag{10}$$

with

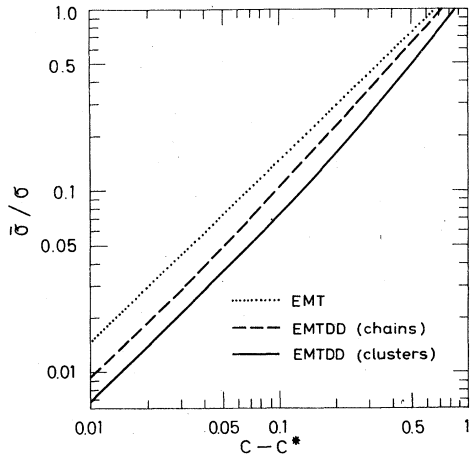

FIG. 3. Log-log plot of normalized effective conductivity vs concentration of conducting material exceeding the value at the percolation threshold. Results are shown for the EMTDD, with L_i^*'s given in Table I, as well as for the old EMT.

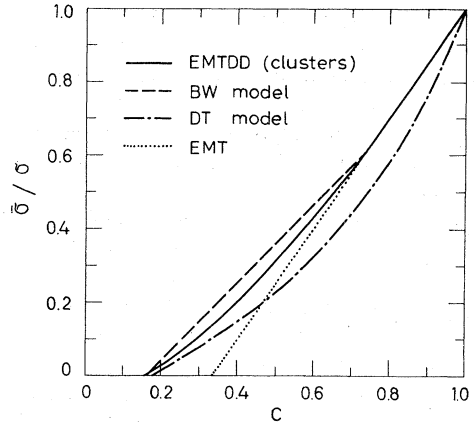

FIG. 4. Normalized effective conductivity vs concentration as obtained from the EMTDD with L_i^*'s appropriate to close-packed spheres (cf. Table I), from the theory by Bernasconi and Wiesmann (BW) given in Ref. 13 [cf. Eq. (10)], from the phenomenological equations by Davidson and Tinkham (DT) given in Ref. 14 [cf. Eq. (12)] and, finally, from the simple EMT. Excepting the EMT the theories predict very similar percolation thresholds.

$$C^*_{\mathrm{BW}} = 0.157.$$

Thus the BW theory yields a percolation threshold which is practically identical with our C^*_{EMTDD} for clusters. Also the exponent in the power law [cf. Eq. (9)] is the same as for the other effective-medium theories. From its derivation Eq. (10) should hold only for small C, but due to the good agreement with numerical data,[3] BW suggested that it could be used for $C \leq \frac{3}{4}$; above this limit the simple EMT was taken to describe the effective conductivity. The dashed line in Fig. 4 represents the BW theory. Comparing with the EMTDD for clusters (solid curve) it is seen that the two approaches give very similar results for the entire $\bar{\sigma}$-vs-C relation. This, we believe, explains the apparent success of Eq. (10) for nondilute two-phase media.

The previously mentioned failure of the EMT to give the correct percolation threshold recently led Davidson and Tinkham[14] (DT) to propose two purely phenomenological equations for the conductivity of microscopically inhomogeneous materials. These were constructed, in the spirit of Padé approximations, to satisfy the percolation result for the threshold while resembling the EMT far from the critical region. For spherical inclusions DT suggested that the effective conductivity could be accurately described by

$$\bar{\sigma}_{\mathrm{DT}} = \begin{cases} \sigma_m(1+3C)/(1-6C) & \text{for } 0 \leq C < \frac{1}{6}, \quad (11) \\ \sigma\frac{2}{5}(6C-1)/(5-3C) & \text{for } \frac{1}{6} < C \leq 1. \quad (12) \end{cases}$$

It is seen that the percolation threshold, taken to be

$$C^*_{\mathrm{DT}} = \tfrac{1}{6} \approx 0.167,$$

is a critical point where Eqs. (11) and (12) diverge in opposite directions. This unphysical behavior is of course not encountered in the pure percolation case, for which the effective conductivity, as obtained from Eq. (12), is plotted in Fig. 4 (dash-dotted curve). The DT model is seen to yield an appreciably more concave $\bar{\sigma}$-vs-C relation than predicted from the EMTDD or BW theories. It should also be noticed that in the limit $C = 1$ the DT model gives a steeper variation than any of the effective-medium theories.

Sensitive tests of the various theories for the conductivity of inhomogeneous media can be carried out if we consider situations for which $\sigma_m \neq 0$. In Fig. 5 we plot results from the numerical simulation by Webman, Jortner, and Cohen[10] appropriate to second-order bond correlation with $\sigma_m/\sigma = 10^{-2}$. The computer data are seen to fall in between the curves for the EMTDD with L_i^*'s pertaining to close-packed clusters and the EMT, although the approximation given by the EMTDD seems to be superior around the percolation threshold. For comparison we have also included in Fig. 5 results from the phenomenological DT equations. The aforementioned divergence at $C^*_{\mathrm{DT}} = \frac{1}{6}$ is clearly observed, and the overall agreement with the numerical simulation is unsatisfactory.

A comparison with numerical simulations[10] is also given in Fig. 6, where we have plotted data for $\sigma_m/\sigma = 10^{-5}$. Results are shown for nearest-

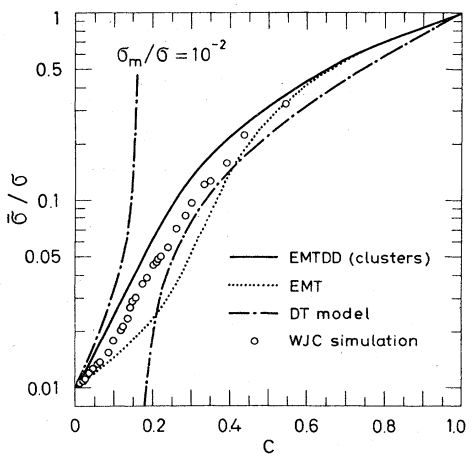

FIG. 5. Normalized effective conductivity vs concentration as obtained from the EMTDD with L_i^*'s appropriate to close-packed spheres (cf. Table I), from the simple EMT, from the phenomenological equations by Davidson and Tinkham (DT) given in Ref. 14 [cf. Eq. (12)] and from the numerical simulation of a percolative conductivity with second-order bond correlation due to Webman, Jortner, and Cohen (WJC) given in Ref. 10.

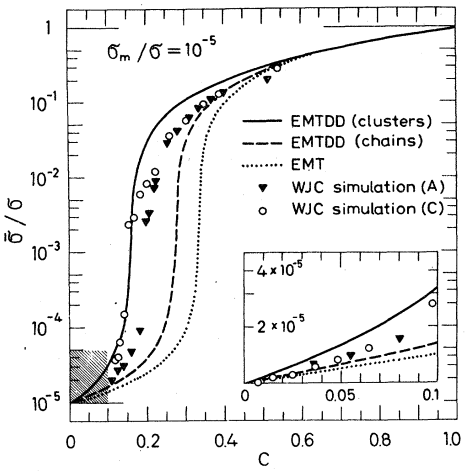

FIG. 6. Normalized effective conductivity vs concentration as obtained from the EMTDD with L_i^*'s appropriate to close-packed clusters and to infinite linear chains (cf. Table I), from the simple EMT and from the numerical simulation of a percolative conductivity due to Webman, Jortner, and Cohen (WJC) given in Ref. 10. Results for their "model A" (nearest-neighbor bond correlation) and "model C" (second-order bond correlation) are denoted by triangles and circles, respectively. The low-concentration regime (shaded area) is shown on a magnified scale in the inset.

neighbor bond correlation (triangles) and second-order bond correlation (circles); the latter model should most accurately represent percolations on a continuum. A comparison with the EMTDD for clusters yields a very good agreement with the circles around the percolation threshold, whereas the fit to the EMTDD for chains and to the simple EMT becomes progressively worse. The inset displays the low-concentration results, showing that the numerical data drop below the solid curve representing the EMTDD for clusters. This behavior is expected, as in this limit the clustering is less pronounced, so that the EMT should be appropriate.

IV. COMPARISON WITH EXPERIMENTAL DATA

The very satisfactory agreement between the EMTDD and the numerical results, which were found in the preceding section, motivates a comparison also with experimental data. In this connection it should be stressed that our treatment applies to spherical conducting inclusions which are touching, so that their electrical fields interact strongly, but are *not* in metallic contact. For the latter situation it might be appropriate to represent the connected parts by ellipsoids which short circuit certain portions of the samples. However, we have chosen not to pursue this further complication of the effective-medium concept, because it does not seem necessary for understanding the experimental results. In this section we will discuss the electrical conductivity of metal-ammonia solutions and alkali-tungsten bronzes. Throughout the discussion we will rely on the extensive compilations of experimental results given in Refs. 10 and 23.

In a recent article Jortner and Cohen[23] analyzed in great detail the properties of metal-ammonia solutions in the intermediate concentration range. Their main conclusion was that the metallic propagation regime was separated from a nonmetallic regime by a microscopically inhomogeneous interval where the concentration fluctuates around either of two well-defined values M_0 and M_1. The limits of the inhomogeneous range for Li-NH_3 and Na-NH_3 solutions were determined to be $M_0 = 2\frac{1}{3}$ mole% metal (MPM) and $M_1 = 9$ MPM from measurements of electrical conductivity, Hall-effect, paramagnetic susceptibility, and concentration-fluctuation data based on small-angle x-ray scattering, neutron scattering, and determinations of the chemical potential. The above results yield the concentration of the metallic component according to[23]

$$C = (M - 2\tfrac{1}{3})/6\tfrac{2}{3} \quad \text{for } 2\tfrac{1}{3} < M < 9, \tag{13}$$

with M in MPM. Using this scale for C the conductivity data for Li-NH_3 at 223 K and for Na-NH_3 at 240 K have been plotted in Figs. 7(a) and 7(b). The curves in the figures were obtained from the EMT and from the EMTDD with effective depolarization factors chosen to represent close-packed spheres and infinite linear chains of spheres (cf. Table I). As in Ref. 23 we take $\sigma_m/\sigma = 1.2\times10^{-3}$ for Li-NH_3 and $\sigma_m/\sigma = 2.4\times10^{-3}$ for Na-NH_3. It is obvious that the EMTDD for clusters gives by far the best description of both metal-ammonia solutions, whereas in particular the simple EMT fails to predict the right percolation threshold. For both sets of data it is found that the solid curves consistently overshoot the experimental results, in particular, at concentrations around 0.3–0.4. This kind of behavior, which is manifest at $C > 0.5$ even for the EMT, was noticed also by Jortner and Cohen,[23] who ascribed it to boundary scattering of the conduction electrons within the metalliclike inclusions.

Our second example of a metal-insulator transition is provided by the alkali-tungsten bronzes, Q_XWO_3, where the alkali metal Q at $0 < X < 1$ occupies a simple cubic sublattice. According to the view expressed in Ref. 10 the interstitial alkali atoms have a nonrandom distribution and tend to form metallic regions. The concentration of the metallic component in the two phase medium is given simply by $C = X$. In Fig. 8 we have plotted

experimental conductivity data for this class of materials and compared with calculated results for the EMTDD and the EMT. Clearly the circles fall in between the curves representing the EMTDD for close-packed clusters and the simple EMT. A very accurate agreement is not to be expected as the value of σ_m/σ, which was set equal to 10^{-3} in Fig. 8, is uncertain and might actually be somewhat smaller,[10] in which case the correspondence with the solid curve becomes better.

V. CONCLUSION

In treating the averaged electric field in a microscopically inhomogeneous material it is customary to set the contribution from the individual inclusions (dipoles) inside a Lorentz cavity equal to zero. However, this view cannot be maintained near a percolation threshold due to the significant clustering of conducting and nonconducting regions. To obtain an approximate description of this complex situation we have in this article extended the old effective-medium theory[1-6] by incorporating dipole-dipole interactions locally. These are represented by use of effective depolarization factors. In the case of close-packed clusters of conducting regions, which is appropriate at the percolation threshold, we predict an onset of percolative conductivity at $C^* = 15.6$ vol%. This is in very good agreement with numerical simulations as well as with experimental data for the metal-insulator transitions in metal-ammonia solutions and in alkali-tungsten bronzes. It would also have been possible to discuss the conductivity of tetrathiofulvalene-tetracyanoquinodimethane[24] (known as TTF-TCNQ) and of vapor-quenched germanium—noble-metal compounds[25] in a similar fashion. Around the percolation threshold our results resemble, and to some extent justify, a simple relation for the conductivity given by Bernasconi and Wiesmann.[13] For spherical conducting inclusions we demonstrate that our novel effective-medium theory is superior to the phenomenological equations recently proposed by Davidson and Tinkham.[14,26]

Exactly the same formalism as the one we use to describe dipole-dipole coupling can also be applied to noninteracting ellipsoidal conducting inclusions and, via a straightforward generalization of Eqs. (5)–(7), to treat the effect of a distribution of conductivities among the inclusions (for example caused by boundary scattering in conducting regions of different size). For the latter case we substitute $C\alpha \to \sum_j C_j \alpha_j$ and $\sigma \to \sigma_j$, where σ_j is the conductivity of regions whose volume fraction is C_j. It is also possible to discuss anisotropic systems[26]; thus prolate spheroids aligned with their major axes parallel with the field direction, to take one example, can be described by letting their unique depolarization factor replace the factor $\frac{1}{3}$ in Eq. (6).

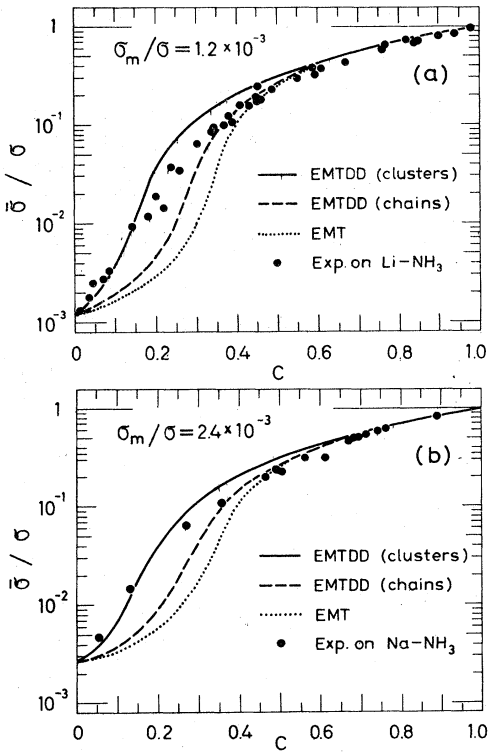

FIG. 7. Data points denote experimental results, as compiled in Ref. 23, (a) for Li-NH_3 solutions at 223 K and (b) for Na-NH_3 solutions at 240 K. The curves represent the normalized effective conductivity vs concentration as obtained from the EMT and from the EMTDD with L_i^{*}'s appropriate to close-packed clusters and to infinite linear chains (cf. Table I). The shown values of the ratios σ_m/σ were used in the theories.

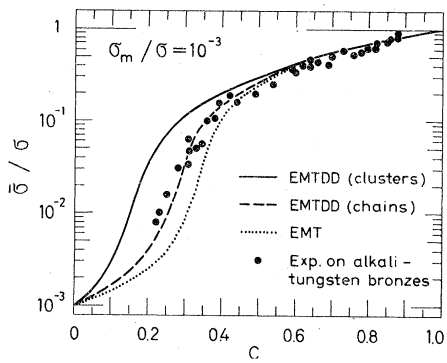

FIG. 8. Data points denote experimental results, as compiled in Ref. 10, for alkali-tungsten bronzes at 300 K. The curves represent the normalized effective conductivity vs concentration as obtained from the EMT and the EMTDD with L_i^{*}'s appropriate to close-packed clusters and to infinite linear chains (cf. Table I).

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