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## A continuum percolation model for dispersed ionic conductors

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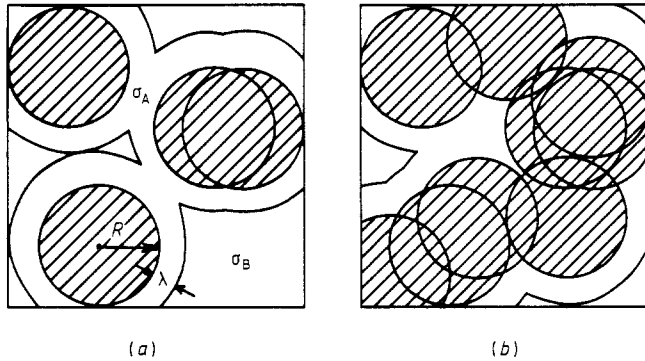
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**Abstract.** A continuum percolation model for heterogeneous mixtures of an ionic conducting solid salt with an insulating second phase is introduced. In this model, the insulating phase is represented by spherical random voids (the Swiss Cheese model) which are allowed to overlap and are randomly distributed in a conducting matrix (the solid salt). A characteristic feature of the model is the existence of a highly conducting spherical shell surrounding the voids, representing the internal interface between the oxide particle and the conducting salt. The relevance of the model for describing the observed effects of insulating particle size on the conductivity of dispersed ionic conductors is critically discussed.

### 1. Introduction

Dispersed ionic conductors are random mixtures of a solid salt, e.g. AgI, LiI, with fine particles of an insulating second phase, such as Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. These composites can show enhancements in ionic conductivity of up to three orders of magnitude compared to the pure homogeneous system (Liang 1973). Generally, this observation is attributed to an increased conductivity along the internal interface between the conductivity salt and the insulating material (Jow and Wagner 1979, Maier 1984, 1985, Poulsen 1985, Dudney 1985). In these composites, the ionic conductivity  $\Sigma$  first increases strongly with concentration  $p$  of the inert phase. After passing its maximum the conductivity drops down and seems to extrapolate to zero at some threshold concentration. The enhancement depends strongly on the size of the inert particles dispersed in the salt. The larger enhancements are found for smaller particles, e.g. the conductivity of AgI containing 30 mole per cent of predried Al<sub>2</sub>O<sub>3</sub> at room temperature is increased by a factor of about 40 for Al<sub>2</sub>O<sub>3</sub> with particle size 0.6  $\mu\text{m}$ , by a factor of 8 for 0.3  $\mu\text{m}$  size particles and by a factor of 2 for 1  $\mu\text{m}$  size particles, while for particles with larger dimensions ( $\sim 8 \mu\text{m}$ ) there is very little or practically no enhancement in  $\Sigma$  (Shahi and Wagner 1981a). Similar results have been obtained for CuCl–Al<sub>2</sub>O<sub>3</sub> (Chang *et al* 1984) and for LiBr–Al<sub>2</sub>O<sub>3</sub> (Nakamura and Goodenough 1982) systems.

Recently, a random resistor model for dispersed ionic conductors (DIC) has been studied (Bunde *et al* 1985, Roman *et al* 1986). Basically, the model assumes that the insulating particles are randomly distributed in the system and the conductivity at the interface between an inert particle and the conducting matrix is *enhanced* with respect to its bulk value. A three-component random resistor network (RRN) model is then



**Figure 1.** The spherical random void model for solid electrolytes in two dimensions. The shaded disks (voids) of radius  $R$  represent the insulating particles which are allowed to overlap. Each particle is surrounded by a circular shell of width  $\lambda$  which delimits the highly conducting interface region (of conductance  $\sigma_A$ ). The remaining free space represents the conducting salt (of conductance  $\sigma_B$ ). (a) Percolation of the interface region at a concentration  $p = p'_c$ ; (b) disruption of conduction paths (conductor–insulator transition) at  $p = p''_c$ .

constructed in which the conducting salt is represented by normally conducting bonds, the inert particles by insulating bonds and the interface region by highly conducting bonds. Effects on the conductivity of the composite due to changes in the size of the dispersed particles are taken into account in a generalised version of the RRN model (Roman and Yussouff 1987), where both size and shape of the particles can be varied; the conductances of the corresponding bonds take the same values as for the original model. An interesting feature of these RRN models is the existence of two percolation thresholds,  $p'_c$  and  $p''_c$ , for percolation of interface (highly conducting) bonds and disruption of conducting paths, respectively. To calculate the conductivity of the system, the resistor model is mapped onto a random walk problem (de Gennes 1976) and studied by Monte Carlo simulations. The calculations show that the RRN model correctly describes the macroscopic conductance properties observed in dispersed ionic conductors (Roman 1990a).

In this paper we introduce a continuum percolation analogue of the RRN model for solid electrolytes which allows us to study analytically particle size effects on the static properties of the system. In addition, the associated non-universality aspects in the critical behaviour of the conductivity for such continuum percolation systems are discussed and compared with the results for percolation models on the lattice. Finally, an attempt is made to calculate approximately the conductivity  $\Sigma$  of the continuum percolation model by using an effective medium approximation (EMA). This approximation provides us with a simple but accurate scheme for obtaining  $\Sigma$  far from the critical region. In this way we expect to describe, at least qualitatively, the macroscopic conduction properties of solid electrolytes.

## 2. Static properties: percolation thresholds

Let us start with the description of the model. Here we consider a variant of the spherical random void model (the ‘Swiss Cheese’ model) which is illustrated in figure 1 for the two-dimensional case. In this model an insulating particle dispersed in a conducting

matrix is represented by a sphere of radius  $R$  (insulator) surrounded by a highly conducting spherical shell of width  $\lambda$ . Typically,  $\lambda$  is of the order of a few hundreds of angstroms as obtained, for instance, from calculations based on space-charge layers for the interfacial region in  $\text{AgCl-Al}_2\text{O}_3$  (Dudney 1985). Here we denote the conductance of the salt by  $\sigma_B$  and the conductance of the interface region by  $\sigma_A$ . A similar description of a solid electrolyte in terms of spherical particles has been worked out recently using an effective medium approach (Brailsford 1986). The present model, however, admits a rigorous treatment of static and dynamic critical properties, near the percolation thresholds, and thus explores a different aspect of the problem. In particular, our aim is to describe the dependence of the conductivity  $\Sigma$  on particle radius  $R$  at low concentrations  $p$ , where particle size-effects play an essential role.

The concentration  $p$  of randomly distributed overlapping spheres of radius  $R$  (the insulating phase) is given by

$$p = 1 - \exp(-cR^d\rho) \quad (1)$$

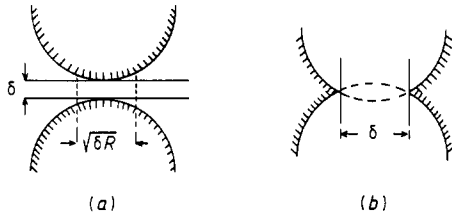
where  $c = \pi$  when  $d = 2$  and  $c = 4\pi/3$  when  $d = 3$ , and  $\rho$  is the particle density. Equation (1) follows from the fact that the number of randomly distributed points (sphere centres) that are found within a distance  $R$  from a given point is determined by a Poisson distribution (see also Vicsek and Kertész 1981). As displayed in figure 1, this model again has two percolation thresholds,  $p'_c$  and  $p''_c$ , for interface percolation and conductor-insulator transition, respectively. The critical concentration  $p''_c$  is known for this model,  $p''_c \approx 0.6766$  when  $d = 2$  (Rosso 1989, Vicsek and Kertész 1981) and  $p''_c \approx 0.966$  when  $d = 3$  (Kertész 1981, Elam *et al* 1984). Note that  $p''_c$  does not depend on the particle radius  $R$ . To determine  $p'_c$  we need to know the percolation threshold  $p_c$  at which percolation of particles occurs. In two dimensions, it coincides with the threshold  $p''_c$  for percolation of the conducting region, while in three dimensions the percolation of spheres occurs at a concentration  $p_c \approx 0.28 \pm 0.007$  which is much lower than  $p''_c$  (Kertész 1981). In this case, insulating particles and the conducting matrix percolate simultaneously for the entire range of concentrations  $p_c \leq p \leq p''_c$ . Clearly  $p'_c$  will depend on the particle radius  $R$  (more precisely on the value of the shell radius  $R + \lambda$  relative to  $R$ ), since the probability for percolation of spheres of radius  $R + \lambda$  is larger than for spheres of radius  $R$  for fixed number of particles.

Let us denote by  $\eta = (R + \lambda)/R$  the parameter which measures the effect of the particle size on  $p'_c$ . To keep the number of parameters in the model to a minimum, we assume that neither  $\lambda$  nor the conductance properties of the interface region depend on the particle radius  $R$ . This may be true for large  $R$ , i.e. in the limit  $R/\lambda \gg 1$ . Accordingly, we expect that most physical situations will occur in the range  $1 < \eta < 2$ , where the lower boundary corresponds to the limit  $R \rightarrow \infty$  and the upper boundary to  $R = \lambda$ .

Now consider the percolation threshold,  $p_c$ , for spheres of radius  $R$ . It is easy to see that for  $R \gg \lambda$ , i.e. for  $\eta \rightarrow 1$ , one obtains  $p'_c = p_c$  since the relative width of the interface region vanishes. However, if the particle radius decreases, such that  $\eta \rightarrow 2$ , we expect that  $p'_c$  will decrease too. Using (1), we can find the actual concentration  $p'_c$  of particles of radius  $R$  at which spheres of radius  $R + \lambda = \eta R$  (highly conducting shells) percolate. First, let us denote by  $\rho_c$  the critical density in (1) for which spheres of radius  $\eta R$  percolate, i.e.  $p = p_c = 1 - \exp(-c\eta^d R^d \rho_c)$ . Since the particle density is  $\rho_c$ , it follows that the concentration  $p'_c$  of spheres of radius  $R$  is  $p'_c = 1 - \exp(-cR^d \rho_c)$ , which can be written using the above expression for  $p_c$  as

$$p'_c = 1 - (1 - p_c)^{1/\eta^d} \quad (2)$$

When  $d = 2$ , equation (2) gives  $0.25 < p'_c < 0.688$ , and when  $d = 3$ ,  $0.04 < p'_c < 0.28$ ,



**Figure 2.** Spherical random voids in two dimensions. (a) The ‘Swiss Cheese’ model where the disks are non-conducting. For small separations  $\delta$  between spheres of radius  $R$  an effective conduction channel of length  $\sqrt{R\delta}$  is obtained. (b) The inverted ‘Swiss Cheese’ model where the disks represent the conducting material. For small apertures  $\delta$  the length of the equivalent channel is  $\sim \delta$ . (After Feng *et al* 1987.)

as  $\eta$  varies from  $\eta = 2$  to  $\eta = 1$ . On the other hand,  $p_c''$  does not depend on  $\eta$  for this model. Equation (2) is exact and constitutes the main result of this work. It gives the interface percolation threshold  $p_c'$  as a function of the highly-conducting shell radius  $R + \lambda$  relative to the particle radius  $R$ .

While the existence of the percolation threshold  $p_c''$  is obvious from the behaviour of  $\Sigma$  at large concentrations  $p$ , the interface percolation threshold  $p_c'$  may be detected when the ratio  $\tau = \sigma_A/\sigma_B$  becomes large (Blender and Dieterich 1987). This is important since near both thresholds a critical behaviour of the conductivity is expected as explained below. Before discussing transport properties, we note that according to (2) the percolation threshold  $p_c'$  in dispersed ionic conductors should be searched for larger particle sizes  $R$ , where  $p_c'$  can become experimentally accessible.

### 3. Dynamical properties: conductivity exponents

It is well known that critical exponents for electrical conductivity in continuum percolation systems can differ considerably from their counterparts in standard lattice percolation models (Feng *et al* 1987). The present continuum percolation (CP) model for solid electrolytes shows similar behaviour. Let us first discuss the possible geometries which arise for the spherical random void model. These are displayed in figure 2 for the case where the voids represent an insulator as in figure 2(a), or a conductor immersed in a poor conductor as in figure 2(b).

The ‘Swiss Cheese’ model (figure 2(a)) can be mapped onto a regular network with randomly occupied bonds, whose associated conductances  $\sigma$  can have a singular distribution of strengths  $P(\sigma) \sim \sigma^{-\alpha}$  for  $\sigma \rightarrow 0$  with  $0 < \alpha < 1$ . If this is the case, the conductivity exponent  $\bar{\mu}$  in the power-law behaviour  $\Sigma \sim (p_c'' - p)^{\bar{\mu}}$ ,  $p < p_c''$ , is given by  $\bar{\mu} \approx \mu + \alpha/(1 - \alpha)$  (Feng *et al* 1987, Bunde *et al* 1985), where  $\mu$  is the standard lattice value (Stauffer 1985). To determine  $\alpha$  for this model, we first note that the channel which determines the critical properties of  $\Sigma$  near  $p_c''$  has an associated conductance  $\sigma$  which scales as  $\sigma \sim \delta^m$  for small channel width  $\delta$  (see figure 2(a)). The value of the exponent  $m$  is obtained by writing  $\sigma$  as the ratio between the cross section of the channel divided by its effective length. Thus,  $m = 1/2$  when  $d = 2$  and  $m = 3/2$  when  $d = 3$ . If the probability for the occurrence of channels with  $\delta \rightarrow 0$  is finite, one then finds  $\alpha = 1 - 1/m$ . We see that for  $d = 2$  the distribution is non-singular ( $\alpha = -1$ ), while for  $d = 3$ ,  $\alpha = 1/3 > 0$  which leads to  $\bar{\mu} \approx \mu + 1/2$ .

The inverted ‘Swiss Cheese’ model (figure 2(b)) is appropriate for studying a system where the spheres represent a very good conductor (with conductance  $\sigma_A$ ) immersed in a poor conducting matrix (conductance  $\sigma_B$ ). If the ratio  $\tau = \sigma_A/\sigma_B$  tends to infinity we can describe either a superconductor/conductor or a conductor/insulator system. In this

case no changes in the transport critical exponents occur since  $\alpha < 0$  in both two- and three-dimensional systems (Feng *et al* 1987).

Returning to our CP model for DIC we see that close to  $p_c''$  it behaves like the ‘Swiss Cheese’ model, while close to  $p_c'$ , for interface percolation, its critical properties for  $\tau \rightarrow \infty$  correspond to the inverted ‘Swiss Cheese’ model. For concentrations  $p \rightarrow p_c''$  we expect that

$$\Sigma \sim (p_c'' - p)^{\bar{\mu}} \tag{3a}$$

with  $\bar{\mu} \approx \mu + \frac{1}{2} \approx 2.6$  when  $d = 3$  (Roman 1990b), while for  $\tau \rightarrow \infty$  close to  $p_c'$  the conductivity diverges as

$$\Sigma \sim (p_c' - p)^{-\bar{s}}, \tag{3b}$$

for  $p < p_c'$ , with  $\bar{s} = s \approx 0.7$  when  $d = 3$ , where  $s$  is the standard lattice superconductivity exponent.

#### 4. Transport properties: DC conductivity

In this section we aim to describe macroscopic features of the conductivity of the system outside the critical region of concentrations. These calculations are relevant for describing the overall behaviour of  $\Sigma$  as a function of composition and particle size observed in the experiments.

Similarly as for RRN models (Bunde *et al* 1985, Roman and Yussouff 1987) one can map the continuum percolation model onto a random walk problem and obtain  $\Sigma$  by calculating the diffusion constant using Monte Carlo simulations. This approach has been already implemented for the random void model (Petersen *et al* 1989), in which a random walk with finite jump distance  $l$  and arbitrary jump direction in the continuum is simulated. For our present purposes, we choose a simple analytical approach to calculate the conductivity  $\Sigma$  based on the effective medium approximation (Kirkpatrick 1973). This scheme has been shown to give accurate results for  $\Sigma$  outside the critical region when  $d = 3$  for the RRN model of dispersed ionic conductors (Rojo and Roman 1988).

To implement the EMA for our model, we first calculate the volume fractions of the three components with conductances  $\sigma_0 = 0$  (the insulating phase),  $\sigma_A$  (the highly conducting phase) and  $\sigma_B$  (the normally conducting phase). We denote the volume fractions, respectively, by  $P_0$ ,  $P_A$  and  $P_B$ . Using (1) we have

$$P_0(p) = p \tag{4a}$$

$$P_A(p) = 1 - p - (1 - p)^{\eta^d} \tag{4b}$$

$$P_B(p) = 1 - p - P_A = (1 - p)^{\eta^d}. \tag{4c}$$

In reality, there is a fourth type of conductance  $\sigma_C$ , of the small channels  $\delta$  between insulating particles (see above) which has been deliberately left out here since it only plays a role close to the critical threshold  $p_c''$ .

In order to calculate  $\Sigma$ , we map the continuum percolation model onto a random resistor model (defined on a  $d$ -dimensional cubic lattice), where the bonds have associated conductances  $\sigma_0$ ,  $\sigma_A$  and  $\sigma_B$ . The corresponding concentrations (or volume fractions) are given by (4) and the probability  $\Pi(\sigma)$  of bonds reads

$$\Pi(\sigma) = P_0(p)\delta(\sigma) + P_A(p)\delta(\sigma - \sigma_A) + P_B(p)\delta(\sigma - \sigma_B). \quad (5)$$

Finally,  $\Sigma$  is obtained in the usual way (Rojo and Roman 1988) and reads

$$\Sigma(p) = \sigma_B \{-A + [A^2 + 2\tau(z - 2 - zP_0)]^{1/2}\}/(z - 2) \quad (6)$$

where  $z$  is the coordination number and

$$A = \tau[1 - (zP_A(p))/2] + [1 - (zP_B(p))/2].$$

From (6) we obtain the percolation thresholds: (i)  $p_c''$  at which  $\Sigma = 0$  occurs for  $P_0 = (z - 2)/z$ , (ii)  $p_c'$  at which  $\Sigma \rightarrow \infty$  for  $\tau \rightarrow \infty$  and which occurs when  $A$  changes sign (for  $\tau$  sufficiently large), i.e.  $P_A(p) = 2/z$ . Strictly speaking, the latter relation admits in general two solutions  $p_{c1}'$  and  $p_{c2}'$  ( $p_{c1}' < p_{c2}'$ ) (Kogut and Straley 1979), of which the smaller value corresponds to  $p_c'$ . For values  $p < p_{c1}'$  and  $p > p_{c2}'$ ,  $\Sigma$  remains finite as  $\tau \rightarrow \infty$ . For the random resistor model in three dimensions it turns out that  $p_{c2}' = p_c''$  (Rojo and Roman 1988).

Some useful properties of  $\Sigma$  can be readily obtained from (6). For  $p_{c1}' < p < p_{c2}'$  and  $\tau \gg 1$  we have

$$\Sigma(p) \approx [2/(z - 2)][(z/2)P_A(p) - 1]\tau \quad (7)$$

which depends linearly on  $\tau$ . The maximum of  $\Sigma$  occurs when  $P_A(p)$  attains its maximum, i.e. at a concentration  $p_{\max} = 1 - \eta^{-d/(\eta^d - 1)}$ .

In the following we restrict our discussions to the three-dimensional case. In mapping the continuum model onto a lattice, we imagine we have made the continuum space discrete by introducing a regular mesh of points separated by a (lattice) distance  $a$  which is sufficiently small,  $a \ll \lambda$ . In doing so, we obtain large portions of the network within which the same type of bonds are present. This would correspond to a highly correlated bond percolation problem, in which the bonds of the lattice are not occupied completely at random. Such correlations may be interpreted in terms of a larger coordination number  $z$  (more than nearest-neighbour interactions) for a completely random system (without correlations). Since we do not know *a priori* the coordination number,  $z$  is treated as a free parameter in this theory. To determine  $z$  we impose that  $P_0(p_c'') = (z - 2)/z = p_c'' \approx 0.966$  ( $d = 3$ ), thus  $z \approx 59$ . Note that one can instead fix  $z$  such that it be consistent with the threshold  $p_c'(\eta)$  as given by (2). Here we follow the first prescription which deals with a constant  $z$ , independent of  $\eta$ , since the final results are qualitatively similar in both cases.

Let us analyse in more detail the EMA predictions for the threshold  $p_c'$ . From (4b) and (6) we obtain  $p_c'$  as a solution of the equation

$$2/z = 1 - p_c' - (1 - p_c')^{\eta^d}. \quad (8)$$

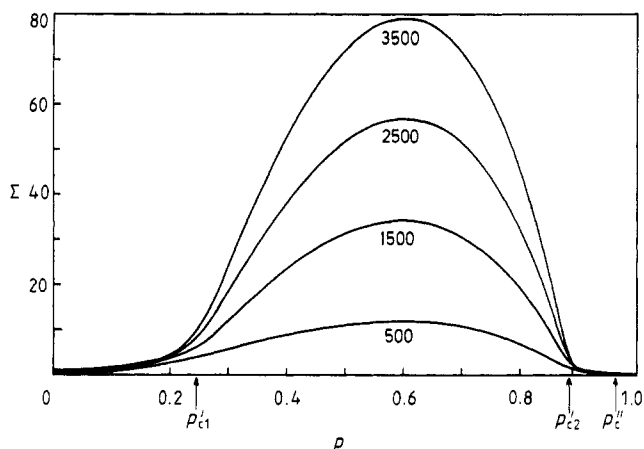
Using the relation  $1 - 2/z = p_c''$ , (8) can be written as

$$p_c'' = p_c' + (1 - p_c')^{\eta^d}. \quad (9)$$

This equation for  $p_c'$  as a function of  $\eta$  can be compared with the exact result (2) or equivalently

$$1 - p_c + p_c' = p_c' + (1 - p_c')^{\eta^d}. \quad (10)$$

The EMA result (9) coincides with the exact value (10) for a  $p_c'$  such that  $p_c'' = 1 - p_c +$



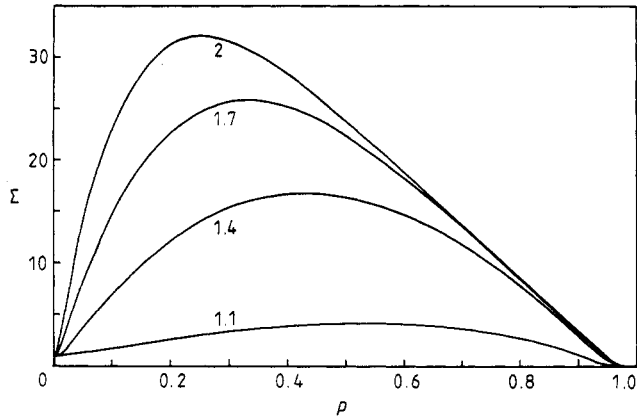
**Figure 3.** Conductivity versus concentration  $p$  of the insulating phase, of the continuum percolation model for solid electrolytes according to the EMA. The curves (from top to bottom) correspond to values  $\tau = 3500, 2500, 1500$  and  $500$ , respectively. In all cases the value  $\eta = (R + \lambda)/R = 1.05175$  was used. The EMA thresholds  $p'_{c1}, p'_{c2}$  and  $p'_c$  are indicated by arrows.

$p'_c$ , which when  $d = 3$  corresponds to  $p'_c \approx 0.246$  and  $\eta \approx 1.05175$ . Compared to (2), the EMA result (9) gives reasonable results in the range  $1.04 \leq \eta \leq 2$ , which corresponds to  $0.35 \geq p'_c \geq 0.005$ . Therefore the present theory applies for particle sizes  $R$  such that  $\lambda \leq R \leq 25\lambda$ .

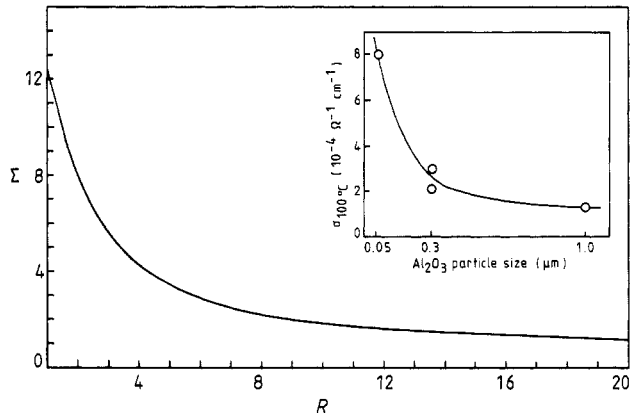
We have now all the ingredients to calculate the conductivity using (6). Results for  $\Sigma$  are shown in figures 3 and 4. The parameters were chosen to illustrate the different shapes of  $\Sigma$  that can be obtained within this scheme. Figure 3 (for  $R/\lambda \approx 19$  and different  $\tau$  values) corresponds to a typical parabolic behaviour of  $\Sigma$ , as observed, e.g. in LiI–Al<sub>2</sub>O<sub>3</sub> (Poulsen 1985), for different temperatures. For this value of  $\eta$  ( $\approx 1.05175$ ), the EMA threshold  $p'_{c1}$  coincides with the exact value from (2) as discussed above. The  $\tau$ -dependence of  $\Sigma$  displayed in figure 3 can be related to the temperature dependence of  $\Sigma$  observed experimentally by assuming thermally activated conduction processes (see, e.g. Roman 1990a). Figure 4 illustrates the effect of varying the particle size, where we see that for  $R \approx \lambda$  a different shape of  $\Sigma$  is obtained, reminiscent of that found in AgI–fly ash (Shahi and Wagner 1981b). Finally, we report in figure 5 calculated values of  $\Sigma$  as a function of particle radius  $R/\lambda$  for fixed  $p$  and  $\tau$ . These results reproduce almost quantitatively the experimental values obtained for LiBr–Al<sub>2</sub>O<sub>3</sub>, and constitute a further support for the validity of the present model.

In summary, we have introduced a continuum percolation model for solid electrolytes which differ substantially from other continuum models described in the literature. We are able to obtain analytical expressions for the particle size dependence of the percolation thresholds of the model in both two and three dimensions. Thus the present study complements previous numerical work on size effects restricted to two-dimensional systems (Roman and Yussouff 1987). These results suggest that the critical behaviour of the conductivity in dispersed ionic conductors, near the so-called conductor–superconductor threshold  $p'_c$ , should be searched for large particle sizes where  $p'_c$  can become experimentally accessible ( $p'_c \approx 0.2:0.3$  in three dimensions). Finally, an attempt is made to calculate the overall dependence of  $\Sigma$  on concentration, enhanced





**Figure 4.** Same as in figure 3 but with  $\tau = 50$ . The different curves correspond, from top to bottom, to different values of  $\eta = 2, 1.7, 1.4$  and  $1.1$ .



**Figure 5.** Conductivity  $\Sigma$  versus particle radius  $R$  (in units of  $\lambda$ ) for  $\tau = 20$  and particle concentration  $p = \frac{1}{3}$ . For comparison, results for  $\text{LiBr} \cdot \text{H}_2\text{O} : \text{Al}_2\text{O}_3$  (2:1) (after Nakamura and Goodenough 1982) are included in the inset.

interface conductance and particle size. The results, obtained within an effective medium approximation for three-dimensional systems, are in good qualitative agreement with the different shapes of  $\Sigma$  found in the experiments.

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