# Frequency-dependent diffusion in a spherical cavity: The effects of domain structure on ionic conduction in polymer electrolytes

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The effects of domain structure on the low-frequency conductivity response of a polymer electrolyte having low carrier concentration are investigated by modeling the domains as spheres. For zero leakage (no dc conductivity), the diffusion equation is solved exactly. The results are also extended approximately to the case of small but nonzero leakage by imposing physically reasonable approximate boundary conditions together with an *ad hoc* procedure for treating the diffusion in the less conductive exterior. Interaction between charge carriers in different domains is taken into account in the Maxwell–Garnet approximation and found to have only a small effect for physically reasonable parameter values. The predicted diffusive behavior is studied and the results are applied to examine the predicted behavior of the frequency-dependent conductivity.

## I. INTRODUCTION

There has been an increasing effort in recent years to understand the ionic transport mechanisms in polymer electrolytes such as polyethylene oxide (PEO) complexed with various salts.[1] The siloxanes and polyphosphazenes, in particular, are characterized by an unusually flexible polymer backbone and exceptionally high conductivity, thereby offering special promise for technological applications. It has been clearly shown[1,2] that some polymer electrolytes, notably those based on PEO, consist microscopically of a mixture of amorphous and crystalline regions; the amorphous regions are mainly responsible for the low-frequency conductivity while the "crystalline" regions, in which the polymer strands are spatially organized with respect to each other, conduct poorly.

Studies of the frequency-dependent conductivity $\sigma(\omega)$ over a range of frequencies near a given $\omega'$ probe those underlying dynamical processes that occur on a time scale of order $2\pi/\omega'$. We might therefore be led to consider carrier diffusion within domains of amorphous material having a distribution of sizes and shapes, and to expect on physical grounds that structure in the observed frequency-dependent conductivity should result at frequencies $\omega$ corresponding to times $\tau \approx 2\pi/\omega$ typically required for a carrier in a domain to diffuse to the domain walls, which may be taken as $\tau = a^2/D_1$ for diffusion coefficient $D_1$ within the sphere of radius $a$. Estimates show that the observed low-frequency structure falls within a reasonable frequency range for such an interpretation; specifically, the reasonable values $a = 100$ Å and $D_1 = 10^{-5}$ cm$^2$/s imply a characteristic frequency of $\sim 10$ GHz, where indeed a marked rise is found in the frequency-dependent conductivity of some mixed amorphous/crystalline polymeric ionic conductors[3]; parameters obtained specifically from our previous fit[3] of $\mathrm{Re}[\sigma(\omega)]$ for $(PEO)_8NH_4SO_3CF_3$ similarly predict approximately this domain size (Appendix A). Furthermore, frequency-dependent conductivity data usually cannot be fitted well at lower frequencies by a small number of Debye functions, and it would seem reasonable on physical grounds that the distribution of relaxation times which is needed arises in part from the domain structure.

Diffusion and conductivity in composite media of this kind are usually studied using one of several effective medium theories[4] in which the macroscopic complex dielectric function of the composite is found from the dielectric functions of the pure components and from whatever information is available about the mixing topography; this determines the frequency-dependent complex conductivity of the overall composite system and, by the Nernst–Einstein relation, the corresponding frequency-dependent diffusion coefficient. In particular, the Maxwell–Garnet effective-medium expression for the dielectric function $\epsilon$ of a system in which spherical particles of phase 1 are surrounded by the host (phase 2) is[5]

$$\frac{\epsilon - \epsilon_1}{\epsilon + 2\epsilon_1} = f_b \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}, \tag{1}$$

where $\epsilon$ is the complex dielectric function whose imaginary part is associated with the conductivity and the diffusion coefficient, and where $f_b$ is the volume fraction of phase $b$.

Equation (1) requires that the dielectric response of the microscopic regions $b$ does not depend on their size, a condition that no longer applies if the density of charge carriers is low and the size of the conducting regions is small. For example, if the conducting phase contains 0.001 M of "free" ions, then the average number of ions in a sphere of diameter 100 Å is $\sim 1/3$. In this case the dielectric response of the small sphere depends on whether it happens to contain charge carriers, and differs from that of the corresponding macroscopic conducting phase. A similar situation may exist also for small semiconductor particles characterized by a low average density of free charge carriers; a small enough particle obviously will have high probability to be without a carrier. If the carrier density is $10^{16}$ cm$^{-3}$, the probability is

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of order 1/2 for particles of radius 100 Å, and even in heavily doped semiconductors the volume per charge exceeds $10^{-18}\,\mathrm{cm}^3$.

In this article, we focus on such systems [to which Eq. (1) is inapplicable] and assume that the conducting regions are small spheres each containing one charge carrier whose behavior is characterized by the given diffusion coefficient $D_1$ within the sphere. The present work is motivated by the spectroscopic study of partly crystalline polymer electrolytes, in which precisely this situation of isolated regions with differing local ionic mobility and differing crystallinity occurs.[3] In Sec. II we solve the problem of single-carrier diffusion in a finite sphere when the mobility in the exterior region is zero. Section III considers how (for nonleaky spheres) the electrostatic interactions between carriers in different spheres affect the conductivity of the overall system, with numerical results for various cases presented in Sec. IV. We conclude, in Sec. V, with a discussion of our results and their relevance to polymer electrolytes.

The effect of small but nonzero carrier mobility outside the sphere (i.e., the "leaky sphere" problem) is considered approximately in Appendix B.

## II. FORMULATION FOR A NONCONDUCTING EXTERIOR REGION

Consider a carrier in a medium with diffusion coefficient $D_1$ inside a spherical region of radius $a$ and diffusion coefficient $D_2$ outside the spherical region. We seek first the probability density $P(\mathbf{r},\mathbf{r}';t)$ defined such that, if the carrier starts at location $\mathbf{r}'$ at time $t=0$, then $P(\mathbf{r},\mathbf{r}';t)\,d^3r$ is the probability that it is found in the volume element $d^3r$ at a later time $t$. Once obtained, the solution for $P(\mathbf{r},\mathbf{r}';t)$ can then be used to evaluate the mean-square displacement $\langle r^2\rangle(t)=\langle|\mathbf{r}-\mathbf{r}'|^2\rangle(t)$ of the diffusing carrier starting from a random initial position within the domain. Linear response theory then yields the low-field complex conductivity as a Laplace transform of $\langle r^2\rangle(t)$. We deal in the present section with the solution for $P(\mathbf{r},\mathbf{r}';t)$ when $D_2=0$ (which allows no diffusion into the external medium), and generalize in the next section to $D_2>0$.

This procedure calculates the response to an applied field from the zero-field diffusive behavior. In the present section, we disregard the electrostatic interactions between charge carriers and electric polarizations in different spheres and consider the dynamics associated with a single isolated sphere. The effect of interaction between carriers in different spheres is considered in Sec. IV.

Our starting point is the continuity equation

$$\nabla\cdot\mathbf{j}+\partial P(\mathbf{r},\mathbf{r}';t)/\partial t=0 \tag{2}$$

combined with Fick's law for the probability flux $\mathbf{j}$:

$$\mathbf{j}=-D_1\nabla P(\mathbf{r},\mathbf{r}';t) \tag{3}$$

which together yield the diffusion equation

$$D_1\nabla^2P(\mathbf{r},\mathbf{r}';t)-\frac{\partial}{\partial t}P(\mathbf{r},\mathbf{r}';t)=0 \tag{4}$$

whose solution, subject to the following three requirements, gives $P(\mathbf{r},\mathbf{r}';t)$. The first two requirements are the assumed initial condition

$$P(\mathbf{r},\mathbf{r}';t)=\delta^3(\mathbf{r}-\mathbf{r}') \tag{5}$$

at $t=0$ and the normalization that Eq. (12) thereby implies for all $t>0$:

$$\int P(\mathbf{r},\mathbf{r}';t)d^3r=1. \tag{6}$$

The third requirement is the boundary condition implied specifically by the assumption $D_2=0$, which forbids any flow of probability into the exterior region ($r>0$) so that, at $r=a$, the radial component of $\mathbf{j}$ given by $\mathbf{j}\cdot\hat{n}$ (for surface normal $\hat{n}$) is zero. This, according to Eq. (3), can be written as

$$\left.\frac{\partial P}{\partial r}\right|_{r=a}=0. \tag{7}$$

We use the method of separation of variables to obtain a set of basis functions that satisfy Eqs. (4) and (6), and then seek the normalized linear combination of these basis functions that satisfy the initial condition (5) at $t=0$ for a given $\mathbf{r}'$. Assuming the desired basis functions to be each the product of a purely time-dependent function and a purely spatially dependent function yields a solution to Eq. (4) of the form

$$P(\mathbf{r},\mathbf{r}';t)=\Phi(\mathbf{r},\mathbf{r}')e^{-\gamma^2t}, \tag{8}$$

where $\Phi(\mathbf{r},\mathbf{r}')$ satisfies the time-independent equation

$$D_1\nabla^2\Phi(\mathbf{r},\mathbf{r}')+\gamma^2\Phi(\mathbf{r},\mathbf{r}')=0, \tag{9}$$

and where the non-negative real coefficient (written as $\gamma^2$) remains to be determined. By expressing Eq. (9) in spherical coordinates $(r,\theta,\phi)$ and by then employing the same procedure generally applied, for example, to the time-independent Schrödinger equation for a particle moving in a spherically symmetric potential, we are led to basis solutions of (9) having the form

$$\Phi_{ilm}=A_{il}j_l\left[\frac{\gamma_{il}}{\sqrt{D_1}}r\right]Y_{lm}(\theta,\phi), \tag{10}$$

where $j_l(x)$ denotes the usual spherical Bessel function and $Y_{lm}(\theta,\phi)$ denotes one of the $2l+1$ corresponding spherical harmonics, and where the index $i$ allows for the possibility of several distinct values of $\gamma_{il}$ for a given $l$. (The coefficients $\gamma_{il}$, which remain to be determined, are later seen to be independent of $m$.) The normalization constants $A_{il}$ are chosen to satisfy

$$\int_{r\le a}|\Phi_{ilm}(\mathbf{r})|^2d^3r=1. \tag{11}$$

The relation[6]

$$I_l=\int_0^z j_l^2(\xi)\xi^2\,d\xi \tag{12}$$

$$=\begin{cases}\dfrac{z^3}{2}[j_l^2(z)-j_{l-1}(z)j_{l+1}(z)], & l\geqslant 1\\[2ex] \dfrac{1}{2}[z-\sin(z)\cos(z)], & l=0\end{cases} \tag{13}$$

with (11) leads to the ($m$-independent) expression for $A_{il}$:

$$A_{il}=\begin{cases}\dfrac{2}{a^3}\dfrac{1}{j_l^2(\lambda_{il})-j_{l+1}(\lambda_{il})j_{l-1}(\lambda_{il})}, & l>0\\[2ex] \dfrac{2\lambda_{il}^3}{\lambda_{il}-\sin(\lambda_{il})\cos(\lambda_{il})}, & l=0\end{cases} \tag{14}$$

where $\lambda_{il} = \gamma_{il} a/\sqrt{D_1}$. The ($m$-independent) allowed values of $\gamma_{il}$ (or $\lambda_{il}$) are determined by the boundary condition $(\partial \phi_{ilm}/\partial r) = 0$ at $r = a$, leading to

$$\lambda_{il} j_l'(\lambda_{il}) = 0. \tag{15}$$

The index $i$ designates the different solutions to this equation for each $l$.

The functions $\Phi_{ilm}$ are assumed to be a complete orthonormal basis set for the expansion of the actual solution in the form

$$P(\mathbf{r},\mathbf{r}';t) = \sum_{i,l,m} B_{ilm} \Phi_{ilm} e^{-\gamma_{il}^2 t}. \tag{16}$$

The specific expansion parameters are next determined by imposing the initial condition (5) at $t = 0$, leading to

$$\sum_{i,l,m} B_{ilm} A_{il} j_l\left(\lambda_{il} \frac{r}{a}\right) Y_{lm}(\theta,\phi) = r^{-2}\delta(r - r')\delta(\cos\theta - \cos\theta')\delta(\phi - \phi'). \tag{17}$$

Multiplication of both sides by

$$A_{il}\, r^2 j_l\left(\lambda_{il} \frac{r}{a}\right) Y_{lm}^*(\theta,\phi) \tag{18}$$

followed by integration over all $(\theta,\phi)$ and all $r \leqslant a$ and use of the normalization property (6) then yields an expression for the expansion coefficients

$$B_{ilm} = A_{il} j_l\left(\lambda_{il} \frac{r'}{a}\right) Y_{lm}^*(\theta',\phi') \tag{19}$$

and thereby to the result

$$P(\mathbf{r},\mathbf{r}';t) = \sum_{i,l} A_{il}^2 j_l\left(\lambda_{il} \frac{r'}{a}\right) j_l\left(\lambda_{il} \frac{r}{a}\right) \times \left[\sum_m Y_{lm}^*(\hat{r}')\, Y_{lm}(\hat{r})\right] \exp(-\gamma_{il}^2 t). \tag{20}$$

The summation formula

$$\sum_m Y_{lm}^*(\hat{r}')\, Y_{lm}(\hat{r}) = \frac{2l+1}{4\pi} P_l(\hat{r}\cdot\hat{r}'), \tag{21}$$

where $P_l(x)$ is the Legendre polynomial of degree $l$ and where $\hat{r} = \mathbf{r}/|\mathbf{r}|$, shows $P(\mathbf{r},\mathbf{r}';t)$ in Eq. (21) to be dependent only on the radial distances $r$ and $r'$ and the angle between $\hat{r}$ and $\hat{r}'$; however, we retain (20) in its present form. For a given $l$ occurring in Eq. (20), the sum is over all $\lambda_{il}$ labeled by the summation index $i$.

Each function $j_l(x)$ is either symmetric (for $l = 0$) or antisymmetric (for $l > 0$) under the transformation $x \to -x$. So if $\lambda_{il}$ satisfies Eq. (15), then $-\lambda_{il}$ satisfies (15) also; because the right-hand side of Eq. (20) is, term by term, invariant under sign change of $\lambda_{il}$, it suffices to consider only nonnegative solutions for $\lambda_{il}$ in the expansion of $P(\mathbf{r},\mathbf{r}';t)$. Furthermore, the solution $\lambda_{il} = 0$ of Eq. (15) is physically acceptable only for $l = 0$, corresponding to the function $j_0(\lambda r) = j_0(0) = 1$ throughout the spherical cavity, but not for $l > 0$ since $j_l(0) = 0$ for $l > 0$. Therefore, the acceptable solutions of Eq. (15) for $\lambda_{il}$ with $l = 0$ are $\lambda_{00} = 0$ together with a set of positive $\lambda_{i0}$, and for $l > 0$ consist only of positive $\lambda_{il}$.

Once the eigenvalues ($\lambda_{il}$) and thereby the probability density $P(\mathbf{r},\mathbf{r}';t)$ are determined, it is necessary to find expressions for the mean-square displacement $\langle r^2 \rangle \equiv \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ of a carrier from its initial position, and then to find its complex Laplace transform[7]

$$D(\omega) = n_d (i\omega)^2 \int_0^\infty e^{-i\omega t} \langle r^2 \rangle(t)\, dt \tag{22}$$

[where $n_d = 1/(2d)$ for dimensionality $d$] which, according to the Nernst–Einstein relation for noninteracting carriers, gives the frequency-dependent conductivity

$$\sigma(\omega) = \frac{nq^2}{k_B T} D(\omega) \tag{23}$$

for density $n$ of carriers each having charge $q$.

The expression for $\langle r^2 \rangle(t)$ is

$$\langle |r - r'|^2 \rangle(t) = \left[\frac{4\pi a^3}{3}\right]^{-1} \int\int P(\mathbf{r},\mathbf{r}';t) \times [r^2 + r'^2 - 2rr' \cos\theta_{rr'}]\, d^3r\, d^3r', \tag{24}$$

where $\cos\theta_{rr'} = \hat{r}\cdot\hat{r}'$. Only the $l = 0$ and $l = 1$ contributions to $P(\mathbf{r},\mathbf{r}';t)$ in Eq. (20) yield nonzero contributions to $\langle r^2 \rangle$ as given by Eq. (24). Then Eq. (24) can be evaluated in spherical coordinates to yield

$$\langle r^2 \rangle(t) = 12a^2 \sum_i \left[N_{i0} e^{-\gamma_{i0}^2 t} - N_{i1} e^{-\gamma_{i1}^2 t}\right] \tag{25}$$

with $N_{i0}$ and $N_{i1}$ given by

$$N_{i0} = \frac{j_1(\lambda_{i0})\,[\lambda_{i0} j_1(\lambda_{i0}) - 2j_2(\lambda_{i0})]}{\lambda_{i0} - \sin\lambda_{i0}\cos\lambda_{i0}}, \tag{26}$$

$$N_{i1} = \frac{[j_2(\lambda_{i1})]^2}{(\lambda_{i1})^2 [j_1^2(\lambda_{i1}) - j_2(\lambda_{i1}) j_0(\lambda_{i1})]}. \tag{27}$$

[Note that $N_{00}$ is seen to be $1/10$ by taking the limit of Eq. (26) as $\lambda \to 0$.] The Laplace transform Eq. (27) can be evaluated immediately using Eqs. (22) and (25) to yield

$$D(\omega) = 12 n_d (i\omega)^2 a^2 \left[\sum_i \frac{N_{i0}}{\gamma_{i0}^2 + i\omega} - \sum_i \frac{N_{i1}}{\gamma_{i1}^2 + i\omega}\right]. \tag{28}$$

## III. INTERCARRIER INTERACTIONS

In the model of Sec. II the conducting region consists of spherical domains each containing a single charge, and interaction between carriers in different domains is disregarded. We once again take each spherical domain to contain at most one carrier and to have radius $a$, with the external medium strictly nonconducting (i.e., the zero leakage case). We seek the dielectric response of the composite medium consisting of the spheres and their nonconducting immediate surroundings.

Consider first a single spherical domain embedded in the external environment. The dielectric functions of the sphere and environment are $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, respectively, and both are assumed real at the (low) frequencies of interest. The sphere contains one charge carrier of charge $q$ whose mobility is $\mu_1$ inside the sphere and is $\mu_2 = 0$ outside, and each $\mu_i$ is related to the corresponding diffusion coefficient via the Nernst–Einstein equation:

$$\mu_i = \frac{q}{k_B T} D_i. \tag{29}$$

We take $\epsilon_1$ to be the dielectric function of the spherical phase in the absence of the charge carrier (and $\epsilon_2$ the corresponding dielectric function of the medium outside the sphere). The polarizability of the sphere in the absence of the carrier is[8]

$$\alpha_1(\omega) = \frac{\epsilon_2(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2} a^3. \tag{30}$$

We seek the excess polarizability $\alpha_2$ of the sphere due to the presence of the charge carrier. (Note that $\alpha_1$ is taken here to include the $\epsilon_2$ factor, in contrast to the conventional definition.)

Consider first the dc ($\omega = 0$) limit. The carrier motion inside the sphere in the presence of a homogeneous electric field is described by the following Fokker–Planck equation

$$\frac{\partial P}{\partial t} = D_1 \nabla^2 P - \frac{D_1 q}{k_B T} \mathbf{E}\cdot\nabla P, \tag{31}$$

where $P$ (as before) is the probability density to find the carrier at a particular location in the sphere. [Equation (31) can be obtained, for example, by decomposing the probability current into a diffusive part and an extra drift part arising from the applied field; the drift contribution is determined by the carrier mobility in bulk, and hence by $D_1$.] The equilibrium solution of Eq. (31) is then

$$P_{\rm eq} = V^{-1} \exp[\, + q\mathbf{E}\cdot\mathbf{r}/(k_B T)\,]. \tag{32}$$

The normalization $V^{-1}$ over sphere volume in (32) applies to the weak-field limit that we consider here. The dipole induced by the field $\mathbf{E}$ is given by

$$\mathbf{m} = q \int_{\rm sphere} \mathbf{r} P_{\rm eq}(\mathbf{r}) d^3 r.$$

In the weak-field limit this yields

$$\mathbf{m} = \frac{q^2 a^2}{5 k_B T} \mathbf{E}, \tag{33}$$

where $\mathbf{E}$ is the (assumed homogeneous) field inside the sphere. If we disregard the position-dependent reaction field resulting from the polarization of the sphere by the carrier itself, $\mathbf{E}$ is related to the external field $\mathbf{E}_0$ by

$$\mathbf{E} = \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2} \mathbf{E}_0. \tag{34}$$

Equations (33) and (34) then lead to an expression for the *excess* dc polarizability of the sphere (i.e., associated with the added carrier)

$$\alpha_c = \frac{q^2 a^2}{5 k_B T} \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2}. \tag{35}$$

The nonzero-frequency result may in principle also be obtained from the Fokker–Planck equation, but it is easier to obtain it by the following argument. First, if we take $\epsilon_2 = \epsilon_1$ so that the only contribution to the sphere polarizability is the excess polarizability $\alpha_c$, then for low density $n$ of spheres the total dielectric response is given by

$$\epsilon = \epsilon_1 + 4\pi p n \alpha_c. \tag{36}$$

Here we have introduced the fraction $p$ of spheres that contain a carrier, so that $pn$ is then the density of such spheres. The presence of the carriers makes $\epsilon$ complex, being related to the conductivity by

$$\epsilon = \epsilon_1 - \frac{4\pi i}{\omega} \sigma(\omega) \tag{37}$$

with the conductivity $\sigma(\omega)$ and diffusion coefficient related by the frequency-generalized Nernst–Einstein equation:

$$\sigma(\omega) = \frac{q^2 pn}{k_B T} D(\omega). \tag{38}$$

Comparison of Eqs. (36) and (37)–(38) leads to

$$\alpha_c(\omega) = -i \frac{q^2}{k_B T \omega} D(\omega), \tag{39}$$

where $D(\omega)$ has been obtained in Sec. III.

Consider next the case $\epsilon_2 \neq \epsilon_1$. Equation (36) is now replaced (in the low sphere-density limit) by

$$\epsilon = \epsilon_2 + 4\pi(n\alpha_1 + pn\alpha_c), \tag{40}$$

where $\alpha_1$ is given by Eq. (30). Equation (37) is similarly replaced by

$$\epsilon = \epsilon_2 + 4\pi n \alpha_1 - \frac{4\pi i}{\omega} \sigma(\omega), \tag{41}$$

so that the $\sigma(\omega)$ term represents the carrier contribution to the total dielectric response. This leaves the relation between $\alpha_c(\omega)$ and $\sigma(\omega)$ intact. However, the effective Nernst–Einstein equation (38) is modified. For charge carriers of charge $q$, density $pn$, and mobility $\mu$ moving in an electric field $\mathbf{E}$, the current is

$$\begin{aligned} \mathbf{j} &= pnq\mu\mathbf{E} \\ &= pnq\mu \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2} \mathbf{E}_0, \end{aligned} \tag{42}$$

where we have used Eq. (34). Therefore, the macroscopic conductivity is

$$\sigma(\omega) = pnq\mu \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2} \tag{43}$$

and use of Eq. (29) leads to

$$\sigma(\omega) = \frac{q^2 pn}{k_B T} \frac{3\epsilon_2(\omega)}{\epsilon_1(\omega) + 2\epsilon_2(\omega)} D(\omega) \tag{44}$$

instead of Eq. (38). This in turn leads to

$$\alpha_c(\omega) = -\frac{iq^2}{k_B T \omega} \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2} D(\omega) \tag{45}$$

instead of Eq. (39). When $\epsilon_2 = \epsilon_1$, we recover Eq. (39).

We note in passing that the argument leading to the result (45) also points out the shortcomings of the Nernst–Einstein relation between macroscopic conductivity and diffusion. While the relation (29) between mobility and diffusion always holds locally, translating it into a relation between the macroscopic transport coefficients should be done with caution.

As a consistency check on the results obtained above, consider again the $\omega \to 0$ limit. Comparing Eqs. (35) and (45) we obtain

$$-i \lim_{\omega\to 0} \frac{D(\omega)}{\omega} = \frac{a^2}{5}. \tag{46}$$

This is identical to the $\omega \to 0$ limit of the general expression (22) (using $n_d = 1/6$ and $\langle r^2 \rangle_{t\to\infty} = 6a^2/5$).

We can now generalize our results to take into account the interaction between spheres in the Maxwell–Garnet ap-

proximation. Each sphere is taken as a polarizable particle with average polarizability

$$\alpha = \alpha_1 + p\alpha_c$$
$$= \frac{\epsilon_2(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2} a^3 + \frac{iq^2 p}{k_B T\omega} D(\omega) \frac{3\epsilon_2}{\epsilon_1 + 2\epsilon_2}. \quad (47)$$

The effective dielectric response of this composite medium is given by

$$\epsilon_2 \frac{\epsilon - \epsilon_2}{\epsilon + 2\epsilon_2} = \frac{4\pi}{3} n\alpha. \quad (48)$$

Note that if $p = 0$ (corresponding to no carriers) we get the usual Maxwell–Garnet result:

$$\frac{\epsilon - \epsilon_2}{\epsilon + 2\epsilon_2} = f \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}, \quad (49)$$

where $f = (4\pi/3)a^3 n$ is the volume fraction occupied by the sphere. If $\epsilon_2 = \epsilon_1$ we obtain from Eqs. (47) and (48)

$$\frac{\epsilon - \epsilon_2}{\epsilon + 2\epsilon_2} = \frac{4\pi np}{3} \frac{iq^2 D(\omega)}{k_B T\omega\epsilon_2}. \quad (50)$$

If $p$ is very small so that $\epsilon \sim \epsilon_2$ we obtain

$$\epsilon \sim \epsilon_2 + 4\pi np \frac{iq^2 D(\omega)}{k_B T\omega}. \quad (51)$$

This is the limit considered approximately in Appendix B.

## IV. BEHAVIOR OF THE SOLUTIONS

For zero leakage, the calculated eigenvalue spectrum leads, in Eqs. (25)–(27), to $N_{i0}$ coefficients that are all zero for $i > 1$ [as can be seen analytically from Eq. (27)]. These values lead to an expression for the mean-square displacement (averaged also over random initial positions within the sphere) that is given by

$$\langle r^2 \rangle \approx a^2(1.2 - 1.187e^{-2.082\tau} - 0.0102e^{-5.94\tau}$$
$$- 0.0017e^{-9.21\tau} - \cdots)$$
$$\approx 1.2a^2[1 - e^{-2.082D_1 t/a^2}], \quad (52)$$

where the time-dependent terms arise from the $l = 1$ contributions to $P(\mathbf{r},t)$. The lowest eigenvalue (equal to zero) in Eq. (52) corresponds to a uniform distribution of the carrier probability throughout the sphere at long times. The quantitative similarity to the simple saturation behavior assumed arbitrarily for related diffusion problems should be of interest in specific applications. In particular, the complex Laplace transformation in Eq. (22) leads to the result

$$D(\omega) \approx 0.867 D_1 \frac{i\omega}{i\omega + (4.335/a^2)D_1} \quad (53)$$

showing structure in the $D(\omega)$ plot at frequencies comparable to the inverse of the time required for a carrier to diffuse from the center of the domain to the domain wall.

For nonzero leakage (as outlined in the Appendix), the eigenvalues used in expanding the interior solution are shifted relative to those for zero leakage. In particular, the lowest eigenvalue, which for zero leakage was zero (corresponding to the uniform distribution of probability throughout the interior approached at infinite time) shifts to a positive value corresponding to an exponential loss of probability in the interior region, and yields nonzero dc conductivity.

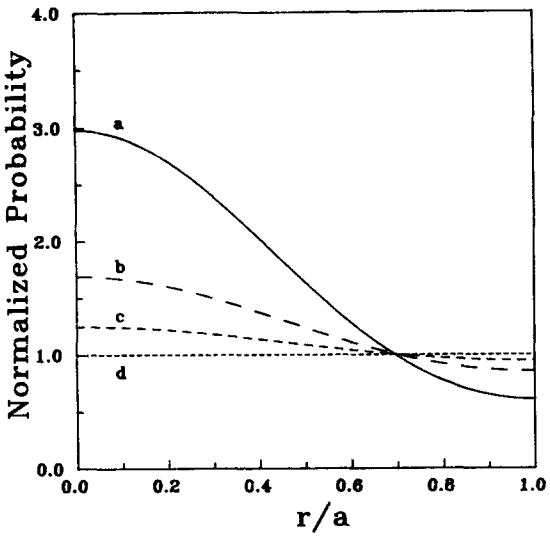


FIG. 1. Probability density for various times $\tau = (D_1/a^2)t$ after the carrier starts at the center of a spherical nonleaky domain. Plotted for (a) $\tau = 0.10$, (b) $\tau = 0.15$, (c) $\tau = 0.20$, and (d) $\tau = 0.50$.

Figures 1 and 2 compare the resulting radial dependence of the probability distribution as a function of time for zero leakage and for nonzero leakage when the carrier starts at the center of the sphere. The approach of the probability to a spatially and temporally independent distribution throughout the sphere (for zero leakage) is replaced for nonzero leakage by an approach toward a spatially nonuniform distribution whose smaller value near the domain edge and continued overall decrease for all values of time are consequences of probability loss through the surface. This is reflected also by the interior contribution $\langle r^2 \rangle_{\text{in}}(t)$ to the

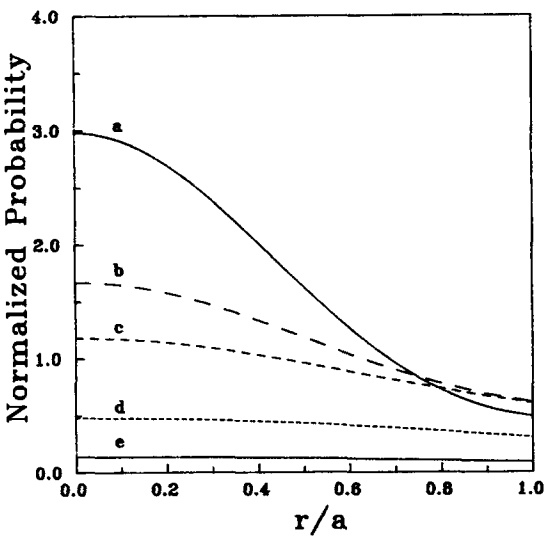


FIG. 2. Probability density for various times $\tau = (D_1/a^2)t$ after the carrier starts at the center of a spherical leaky domain with leakage parameter $\alpha = 1.0$. Plotted for (a) $\tau = 0.10$, (b) $\tau = 0.15$, (c) $\tau = 0.20$, (d) $\tau = 0.50$, and (e) $\tau = 1.0$.

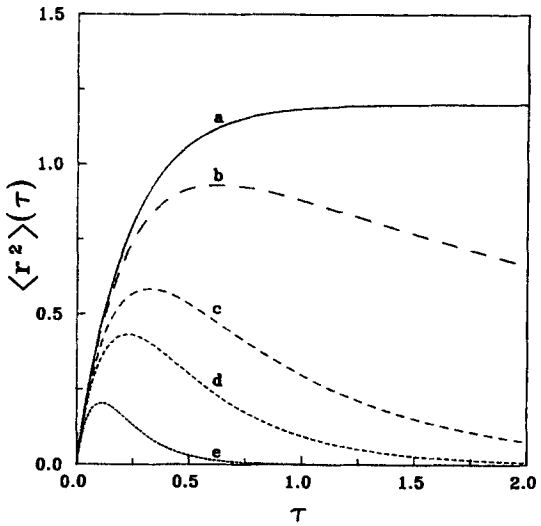


FIG. 3. Interior contribution to the mean-square carrier displacement $\langle r^2\rangle(\tau)/a^2$ in a spherical domain as a function of dimensionless time $\tau = (D_1/a^2)t$ for various values of leakage parameter $\alpha$, specifically (a) $\alpha = 0$, (b) $\alpha = 0.1$, (c) $\alpha = 0.5$, (d) $\alpha = 1.0$, and (e) $\alpha = 5.0$.

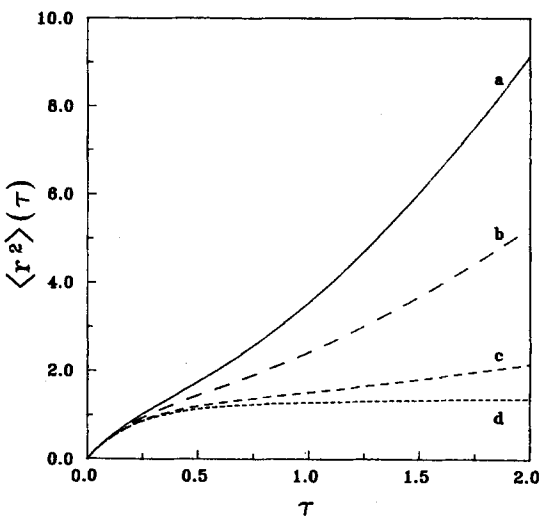


FIG. 5. Total mean-square carrier displacement for a moderately leaky spherical domain ($\alpha = 0.1$) plotted for various values of $r = D_2/D_1$, specifically (a) $r = 1.0$, (b) $r = 0.5$, (c) $r = 0.1$, (d) $r = 0$.

mean-square displacement (Fig. 3). As a consequence of the eventual decrease of $\langle r^2\rangle_{\text{in}}(t)$ (after some time $t_0$), $D(\omega)$ calculated using $\langle r^2\rangle_{\text{in}}(t)$ alone exhibits unphysical negative behavior for $\omega$ less than $\approx 2\pi/t_0$, in accordance with our previous comments about the role of $D_{\text{out}}(\omega)$ [and of $\langle r^2\rangle_{\text{out}}(t)$] in the dc and low-frequency conductivity.

The calculated behavior of the total $\langle r^2\rangle(t)$ in

$$\langle r^2\rangle(t) = \langle r^2\rangle_{\text{in}}(t) + \langle r^2\rangle_{\text{out}}(t)$$

depends (especially at large times) on both the given $D_2/D_1$ and on the leakage parameter $\alpha$. Of course, $\alpha$ should be determined by $D_2/D_1$, but in the present development is an independent adjustable parameter. In our calculations for numerous combinations of $D_2/D_1$ and $\alpha$, we find (as in Figs. 4 and 5) that a value of $D_2/D_1$ somewhat smaller than $\alpha$ appears to be an upper bound for $D_2/D_1$ above which the physically unexpected concave-upward curvature in $\langle r^2\rangle(t)$ vs $t$ develops. Figure 6 shows the calculated behavior of $D(\omega)$ combining both the interior and exterior behavior for the leaky sphere; again, the physically expected behavior occurs for $D_2/D_1$ somewhat smaller than $\alpha$. In practice, using these results, we would expect to treat $D_2/D_1$ and $\alpha$ as parameters to be determined separately, either by fitting or from other experimental measurements.

Figure 7 shows the effect of interactions between carriers, as discussed in Sec. IV. We focus on the case where $\epsilon_0 = \epsilon_i$ and $p = 1$ (i.e., with each sphere containing one particle) so that the $n$ (sphere density) dependence of the con-

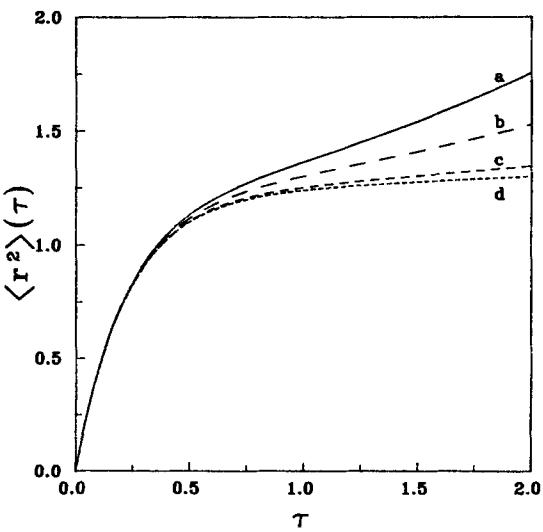


FIG. 4. Total mean-square carrier displacement for a slightly leaky spherical domain ($\alpha = 0.05$) plotted for various values of $r = D_2/D_1$, specifically (a) $r = 0.10$, (b) $r = 0.05$, (c) $r = 0.01$, (d) $r = 0$.

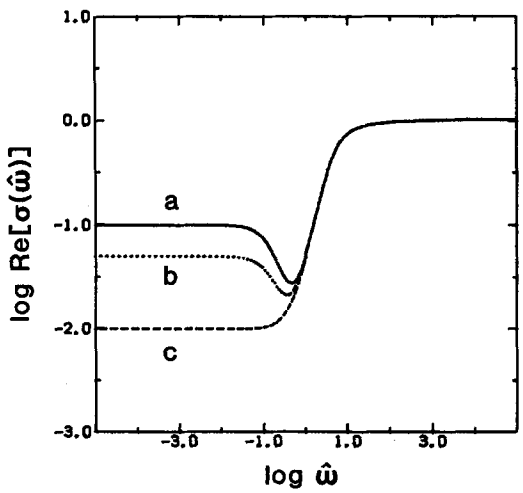


FIG. 6. Real part of the frequency-dependent diffusion coefficient $\hat{D}(\hat{\omega})$ for a slightly leaky sphere ($\alpha = 0.05$) plotted for various values of $r = D_2/D_1$, specifically (a) $r = 0.1$, (b) $r = 0.05$, (c) $r = 0.01$. The dimensionless parameters are defined as $\hat{\omega} = \omega D_1/a^2$ and $\hat{D}(\hat{\omega}) = D(\omega)/D_1$.

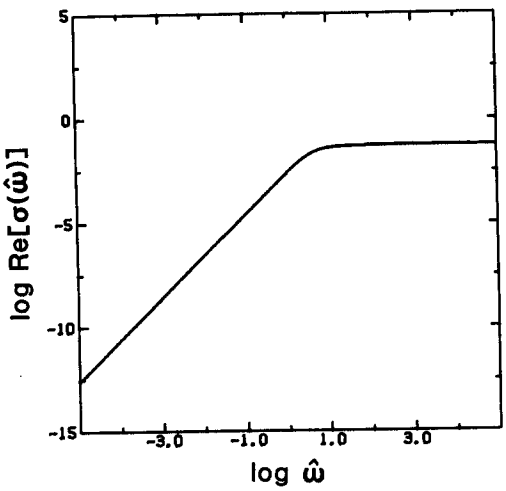


FIG. 7. Real part of the frequency-dependent diffusion coefficient $[\hat{D}(\hat{\omega}) = D(\omega)/D_1$ with $\hat{\omega} = \omega D_1/a^2]$ for various volume fraction $f$ occupied by the interacting nonleaky ($\alpha = 0$) spheres, specifically $f = 5\times10^{-4}$, $f = 5\times10^{-3}$, $f = 5\times10^{-2}$, and $f = 0.5$, for which the plots coincide.

ductivity $\sigma$ reflects exclusively this interaction. Here $\sigma$ is the real part of the complex conductivity, and is given by $\sigma = (\omega/4\pi)\,\mathrm{Im}\,\epsilon$ where $\epsilon$ is the complex dielectric function obtained from Eq. (50). We see that the effect of coupling between spherical domains under these conditions is negligible, an unexpected but useful result allowing the limit given by Eq. (51) to be used as a reasonable approximation even when $p \approx 1$ and $n$ corresponds to a high density of spherical domains. Furthermore, even though the effect of the interaction is small, it is still essential to consider the way in which the $D(\omega)$ for individual domains combine to produce an overall $\sigma(\omega)$. It is particularly noteworthy that the break in the $\sigma(\omega)$ curve occurs at roughly an $\omega = 2\pi/T$ for $D_1 T \approx \frac{1}{2} a^2$, which is a representative time for the particle to diffuse to the walls of the domain. (The same comment of course applies to Fig. 6. for a single domain.) Thus, the structural feature in the diffusion coefficient of the spherical domain corresponds to a structural feature in the diffusion coefficient for the overall system.

## V. SUMMARY AND CONCLUSIONS

We have studied the effects of domain structure on ionic conduction in systems such as polymer electrolytes by modeling each domain as a spherical region containing at most one excess ionic carrier, with the goal of using the behavior of the mean-square carrier displacement $\langle r^2\rangle(t)$ to determine $D(\omega)$ [and $\sigma(\omega)$] for a single domain, and of then considering how the interacting domains combine to produce the effective conduction in the actual many-domain system. For a single spherical domain, our solutions show reasonable physical behavior at short and intermediate times. At long times, as expected, the distribution becomes essentially uniform within the sphere. Our *ad hoc* procedure for including diffusion outside the domain introduces a spurious extra leakage parameter $\alpha$, without yielding an immediate relation giving $\alpha$ in terms of $D_2/D_1$. Intuitively reasonable behavior of the mean-square displacement $\langle r^2\rangle(t)$ and diffusion coefficient $D(\omega)$ is, however, obtained only for a fairly limited range of $\alpha$ for any choice of internal and external diffusion coefficients $D_1$ and $D_2$, suggesting that $\alpha$ can be determined in practice by fitting the theoretical results to experimental or other actual data for a given $D_1$ and $D_2$. An exact solution which does not introduce the extra parameter is indeed possible using Laplace transform methods, but is mathematically tedious compared with the approach followed here.

Using effective medium theory, we have obtained an approximate solution for the overall conductivity with domain–domain interactions taken into account. While under some circumstances the effect of such interactions taken could be important, numerical evaluation shows that the actual effect, for a situation of relevance to the polymer electrolytes, gives essentially the same result as for noninteracting domains. This is an important result, since it indicates that the conductivity and spectroscopic properties deduced from independent-particle transport either in leaky or in nonleaky domain problems are adequate for describing the overall transport and spectroscopic response for carrier concentrations that make more than one carrier per domain unlikely. The effect of the domain walls should be clear, as is indicated in Eq. (53) and Fig. 1, from a measurement of the frequency-dependent conductivity of far-infrared regime. Experimentally, both PEO-based polymer electrolytes (which are semicrystalline at relatively low temperatures) and block copolymers, as prepared, for example, by Smid,[9] should exhibit the domain structure discussed here. The structure in the conductive response for frequency $\omega \approx 2D_1/a^2$ should be indicative of the domain size, and of the intrinsic diffusion coefficient in the conductive region.

There might be interesting applications of materials with single domains as selective absorbers in interesting low-frequency regimes. By control of domain sizes, the frequency of maximum response could be controlled. This might also lead to a spectroscopic probe of domain wall destruction as a function, say, of temperature or physical processing.

For polymer electrolytes in general, a dynamic-disorder model has provided substantial insight into the behavior of the conductivity.[3,10] The combination of dynamic percolation within domains, and static percolation between domains, might well describe semicrystalline polymers in an attractive qualitative way.

The approximate nature of our extension to the leaky sphere case leads us to focus attention on the nonleaky domain (describing the behavior for short and intermediate times, corresponding to intermediate and large $\omega$, which are cases of primary experimental interest). This extension makes clear the conceptual importance of distinguishing between diffusion properties, which are local, and the overall conductivity, which is nonlocal, and provides an effective medium theory for obtaining the overall conductivity with domain–domain interactions taken into account. Under some circumstances the effect of domain–domain interactions could be important, but numerical evaluation shows that the actual effect for situations of relevance to the polymer electrolytes gives essentially the same result as for noninteracting domains.

## ACKNOWLEDGMENTS

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## APPENDIX A: ESTIMATION OF THE DOMAIN SIZE

Assume that the mean-square carrier displacement within a spherical nonleaking domain obeys the simple saturation law

$$\langle r^2\rangle_0(t) = A\,[1-\exp(-\alpha t)], \tag{A1}$$

so that initially

$$\frac{d}{dt}\langle r^2\rangle_0(t)\Big|_{t=0} = \alpha A. \tag{A2}$$

Equation (A1) implies $A=\langle r^2\rangle_0(t\to\infty)$ which, together with the expression for $D(\omega)$ obtained by combining Eq. (A1) with the linear response theory expression Eq. (22), leads to

$$\langle r^2\rangle_0(t\to\infty) = n_d^{-1} D(\omega\to\infty)\tau, \tag{A3}$$

where $\tau$ is $1/\alpha$, $n_d^{-1}=6$, and only the long-range ionic contribution to $D(\omega)$ is considered. Equation (A3) combined with the generalized Nernst–Einstein relation (23) yields

$$\langle r^2\rangle_0(t\to\infty) = \frac{6k_BT}{ne^2}\sigma(\omega\to\infty)\tau. \tag{A4}$$

Because only the long-range ionic contribution to $\sigma(\omega)$ has been included, $\sigma(\omega\to\infty)$ is the estimated upper plateau value in the structure associated with carriers diffusion to the domain walls in the log $\sigma$ vs log $\omega$ curve.

Simple intuition based on the typical time required for carriers to diffuse to the domain wall suggests an expression similar to Eq. (A4) but with the $\omega\to\infty$ limit replaced by $\omega=0$ and with $\sigma$ the conductivity of the bulk material within the domain. Because the plateau described by Eq. (A4) actually is superposed on a monotonically increasing residual $\sigma(\omega)$ dependence from the motions of bound charges, the best values to use in Eq. (A4) actually should not be the apparent maximum plateau, but rather values that indicate roughly where the structure is seen in the log $\sigma(\omega)$ vs log $\omega$ curve, so that both results are actually in agreement.

Using the values $T=300$ K, $n=2\times10^{21}$ cm$^{-3}$, $e=4.803\times10^{-10}$ esu, and a conversion factor of $9\times10^{11}$ s$^{-1}$/($\Omega$ cm), and combining these with data values for crystalline-plus-amorphous $(PEO)_8NH_4SO_3CF_3$, specifically using the $[f=\omega/2\pi,\sigma(\omega)]$ values ranging from [$10^4$ s$^{-1}$, $10^{-6}$ $\Omega^{-1}$ cm$^{-1}$] to [$10^6$ s$^{-1}$, $10^{-5}$ $\Omega^{-1}$ cm$^{-1}$], we obtain corresponding values of $[\langle r^2\rangle_0(\infty)]^{1/2}$ ranging from 22 to 7 Å.

## APPENDIX B: FORMULATION FOR A WEAKLY CONDUCTING EXTERIOR REGION

For small but nonzero exterior diffusion coefficient we assume most of the carriers contributing to the total conductivity at any given time to be also each within a domain, with carrier motion starting from outside neglected as an approximation. Such an approximation would not be strictly applicable at zero frequency where long-range motion produces the nonzero contribution to $\sigma(0)$. But even when carriers initially in the exterior region contribute significantly to the $\omega=0$ conductivity, the structure in the $D(\omega)$ curve at nonzero $\omega$ might still be expected, for small leakage, to arise primarily from carriers inside. Thus while the central point of this article is the analysis of Sec. II, we believe the approach of the present section provides a useful extension of that analysis to lower (but still nonzero) frequencies.

Two further complications enter when the exterior diffusion coefficient is no longer zero. First, the boundary condition (7) must be changed to allow for diffusion into the exterior region in a physically reasonable way. Second, we must apply this boundary condition to find the exterior ($r>a$) solution for $P(\mathbf{r},\mathbf{r}';t)$. Physical considerations imply that the $r>a$ contribution to the spatial probability density dominates at long times, and therefore at low frequencies in $\sigma(\omega)$, when there is any nonzero leakage at all; the exterior solution then becomes essential in determining the dc conductivity.

The most appropriate conditions to apply at the interface would be, first, the continuity of the radial component $\mathbf{j}\cdot\hat{r}$ of the current flux (as before) and, second, the continuity of $P(\mathbf{r},\mathbf{r}';t)$ itself. But application of the separation of variables technique proves difficult. In particular, integrals of the form

$$\int_a^R f_l(\eta r) r^2\,dr,$$

for $f_l$ being either $j_l$ or $n_l$, introduced by attempting a term by term expansion, are ill-defined in the limit $R\to\infty$. This difficulty arises from the unboundedness of the spatial region on which the problem with leakage is defined.

We therefore follow a pragmatic approach: (a) by seeking to describe the physical system using boundary conditions that, while still intuitively reasonable, lead to a simpler interior solution for $P(\mathbf{r},\mathbf{r}';t)$ than does the combined requirement of continuous probability flux and continuous probability density, and (b) by later employing *ad hoc*, but again intuitively reasonable, assumptions about the form taken by the exterior contribution to $\langle r^2\rangle(t)\equiv\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle$.

### 1. Approximate evaluation of the interior solution

For the interior solution, we impose the boundary condition that the probability current density out of the cavity be continuous across any point on the interface and proportional to the probability density $P(\mathbf{r},\mathbf{r}';t)$ at that point, or

$$\mathbf{j}\cdot\hat{r} = \beta P(\mathbf{r},\mathbf{r}';t). \tag{B1}$$

While this condition appears plausible on physical grounds, it is well to consider also its limitations. The coefficient $\beta$ enters as an adjustable parameter which determines the outward flux solely in terms of $P$ inside; thus, this approach does not lead *a priori* to an expression for $\beta$ in terms of exterior properties (i.e., in terms of $D_2$ for the given $D_1$). The appropriate choice of $\beta$ should, in reality, be determined fully by simultaneous specification of $D_1$ and $D_2$. For dilute situations, however, we anticipate that Eq. (B1) is reasonable.

The boundary condition (B1) can be rewritten, using Fick's law, as

$$D_1 \frac{\partial P}{\partial r} + \beta P = 0 \quad (\text{at } r = a) \tag{B2}$$

and reduces to Eq. (7) for $\beta \to 0$. The same procedure used previously for the $D_2 = 0$ case can now be followed. Imposition of the initial condition

$$P(\mathbf{r},\mathbf{r}';0) = \delta^3(\mathbf{r} - \mathbf{r}') \tag{B3}$$

leads to an expansion of $P(\mathbf{r},\mathbf{r}';t)$ in the form (20). Also, as before, linear independence of the separate terms in Eq. (20) implies that Eq. (B2) must hold for each Bessel function in the expansion of $P$, implying the condition

$$j_l'(\lambda_{il}) + \alpha j_l(\lambda_{il}) = 0, \tag{B4}$$

where $\alpha$ is the dimensionless leakage parameter

$$\alpha = \frac{\beta}{D_1 a}. \tag{B5}$$

Thus, the interior solution for $P(\mathbf{r},\mathbf{r}';t)$ in the leaky-sphere problem is already given by Eqs. (20) and (14), except that the eigenvalues ($\lambda_{il}$) are now determined by Eq. (B4) rather than by Eq. (20).

Evaluation of $\langle r^2 \rangle(t)$ requires determining the average over $\mathbf{r}'$ of the mean $r^2$ attained starting from the initial position $\mathbf{r}'$ within the sphere

$$\begin{aligned}\langle r^2 \rangle(t) &= \left[\frac{4\pi}{3} a^3\right]^{-1} \left\{ \int_{r<a} \int |\mathbf{r} - \mathbf{r}'|^2 P(\mathbf{r},\mathbf{r}';t) d^3r\, d^3r' \right. \\ &\quad \left. + \int_{r>a} \int |\mathbf{r} - \mathbf{r}'|^2 P(\mathbf{r},\mathbf{r}';t) d^3r\, d^3r' \right\} \\ &= \langle r^2 \rangle_{\text{in}}(t) + \langle r^2 \rangle_{\text{out}}(t). \end{aligned} \tag{B6}$$

The expression for $\langle r^2 \rangle_{\text{in}}(t)$ is then the same as before (but in terms of the shifted eigenvalues $\lambda_{il}$), as is true also for its Laplace transform $D_{\text{in}}(\omega)$ given by Eqs. (22) and (28). The remaining difficulty, as previously mentioned, lies in calculating $\langle r^2 \rangle_{\text{out}}(t)$ and $D_{\text{out}}(\omega)$.

## 2. Approximate treatment of the exterior solution

Consider the carrier to start at an interior point $\mathbf{r}(0) = \mathbf{r}'$. To evaluate $\langle r^2 \rangle_{\text{out}}(t)$ in an *ad hoc* way, let $\delta P$ be the probability for exit of the particle in the time $(t, t + \delta t)$ through a surface area increment $\delta A$ located at $\mathbf{r} = a\hat{r}$ on the interface, so the $\delta P$ is given by

$$\begin{aligned}\delta P &= (\mathbf{j} \cdot \hat{r}) \delta A\, \delta t \\ &= \beta P(\hat{r}a, \mathbf{r}'; t) \delta A\, \delta t. \end{aligned} \tag{B7}$$

We make the *ad hoc* assumption that each $\delta P$ probability increment leaking through the interface at time $\tau$ (for the given $\mathbf{r}'$ initial position) gives a corresponding contribution to $\langle |\mathbf{r}(t)|^2 \rangle_{\text{out}}$ at a later time $t$ [with $\mathbf{r}(t)$ measured from the center of the sphere] that grows as

$$a^2 + (t - \tau) n_d D_2 \tag{B8}$$

so that the corresponding contribution to $\langle |\mathbf{r}(t)|^2 \rangle$ is

$$\int_0^t [a^2 + (t - \tau) n_d D_2] P(a\hat{r}, \mathbf{r}'; \tau) d\tau. \tag{B9}$$

The quantity $\langle |\mathbf{r}(t)|^2 \rangle$, whose exterior contribution is given by Eq. (B9), is $\langle |\mathbf{r}(t) - \mathbf{r}'|^2 \rangle$ for $\mathbf{r}' = 0$, while the desired quantity, in contrast, is $\langle r^2 \rangle_{\text{out}}(t) = \langle |\mathbf{r}(t) - \mathbf{r}'|^2 \rangle_{\text{out}}$ averaged over both the initial positions $\mathbf{r}'$ and over the subsequent motion of the carrier; this is given by

$$\begin{aligned}\langle r^2 \rangle(t) &= \langle |\mathbf{r}(t) - \mathbf{r}'|^2 \rangle \\ &= \langle |\mathbf{r}(t)|^2 \rangle + \langle |\mathbf{r}'|^2 \rangle - 2\langle \mathbf{r}' \cdot \mathbf{r}(t) \rangle, \end{aligned} \tag{B10}$$

where an average over initial positions $\mathbf{r}'$ within the sphere is included. As an approximation, we ignore the correlation term $\langle \mathbf{r} \cdot \mathbf{r}' \rangle$ in evaluating the exterior contribution $\langle r^2 \rangle_{\text{out}}(t)$. By evaluating $\langle |r'|^2 \rangle$ averaged over the sphere as $0.6\, a^2$, and volume-averaging Eq. (B9) using Eqs. (20) and (14), we obtain

$$\begin{aligned}\langle r^2 \rangle_{\text{out}}(t) = 6\alpha a^2 \Bigg\{ &- \left(1.6 + 12 \frac{D_2}{D_1} \tau\right) \\ &\times \left( \sum_i F_i \frac{\exp(-\lambda_{0i}^2 \tau)}{\lambda_{0i}^2} \right) \\ &+ \left(1.6 + 6 \frac{D_2}{D_1} \tau\right) \left( \sum_i \frac{F_i}{\lambda_{0i}^2} \right) \\ &+ 6 \frac{D_2}{D_1} \sum_i F_i \\ &\times \left( \frac{1}{\lambda_{0i}^4} - \frac{\exp(-\lambda_{0i}^2 \tau)}{\lambda_{0i}^4} \right) \Bigg\}, \end{aligned} \tag{B11}$$

where $\tau = (D_1/a^2)\, t$ is a dimensionless time and

$$F_i = \frac{\sin \lambda_{0i} - \lambda_{0i} \cos \lambda_{0i}}{\lambda_{0i} - \sin \lambda_{0i} \cos \lambda_{0i}} j_0(\lambda_{0i}). \tag{B12}$$

Complex Laplace transformation, after considerable algebraic manipulation, leads to the remarkably simple result

$$\begin{aligned}D_{\text{out}}(\omega) &= n_d (i\omega)^2 \int_0^\infty e^{-i\omega t} \langle r \rangle_{\text{out}}(t) dt \\ &= \left(1.6(i\hat{\omega}) + 6 \frac{D_2}{D_1}\right) \left( \alpha \sum_i \frac{F_i}{\lambda_{0i}^2 + i\hat{\omega}} \right), \end{aligned} \tag{B13}$$

where $\hat{\omega} = (a^2/D_1)\, \omega$, so that $\hat{\omega}\tau = \omega t$. The first term in Eq. (B13) is seen to arise from leakage into the external region (causing the particle to attain a distance $a^2$ from the center of the sphere) while the second comes from subsequent diffusion away from the sphere within the external medium and gives a nonzero dc ($\omega = 0$) conductivity, as is physically reasonable.


[1] C. A. Vincent and J. R. MacCallum, *Polymer Electrolyte Reviews* (Elsevier, London, 1987); M. A. Ratner and A. Nitzan, Solid State Ionics **28/30**, 3 (1988); M. A. Ratner and D. F Shriver, Chem. Rev. **88**, 109 (1988); H. Cheradame, in *IUPAC Macromolecules*, edited by H. Benoit and P. Rempp (Pergamon, London, 1982); L. M. Torrell and C. A. Angell, Brit. Poly. J. **20**, 181 (1988).

[2] M. Minier, C. Berthier, and W. Gorecki, J. Phys. (Paris) **45**, 739 (1984); Y. L. Lee and B. Crist, J. Appl. Phys. **60**, 2603 (1986); P. R. Sorensen and T. Jacobsen, Polym. Bull. **9**, 47 (1983), C. Hardy, Ph.D. thesis, Northwestern University, 1986.

[3] S. M. Ansari, M. Brodwin, M. Stainer, S. D. Druger, M. A. Ratner, and D. F. Shriver, Solid State Ionics **17**, 101 (1985).

[4] R. Landauer, in *Electrical Transport and Optical Properties of Inhomogen-*

*eous Media*, edited by J. C. Garland and D. B. Tanner (AIP, New York, 1978), pp. 2–45.
[5] See, for example, C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983), p. 214 ff.
[6] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw Hill, New York, 1953), p. 1574.
[7] H. Scher and M. Lax, Phys. Rev. B **7**, 4491 (1973).
[8] For example, M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation* (Academic, New York, 1969), pp. 31–32.
[9] D. W. Xia and J. Smid, Solid State Ionics **14**, 221 (1984).
[10] S. D. Druger, A. Nitzan, and M. A. Ratner, J. Chem. Phys. **79**, 3133 (1983); S. D. Druger, M. A. Ratner, and A. Nitzan, Phys. Rev. B **31**, 3939 (1985); S. D. Druger and M. A. Ratner, Phys. Rev. B **17**, 12589 (1988).