Conductivity of disordered solids: Resolution of discrepancies between micro- and macro-response models

J. Ross Macdonald*
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255
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The widely used 1972 macroscopic electric-modulus formalism for conductive-system frequency-response data analysis is corrected to render it properly consistent with purely mobile-charge situations. The corrected model is found to be fully consistent with a 1973 microscopic stochastic-response approach based on continuous-time random-walk hopping when the effect of a limiting high-frequency dielectric constant associated only with charge motion is added to the latter model. When stretched-exponential temporal response with a temperature-dependent β exponent is used to generate the modulus-formalism response model, its temporal dependence is not of stretched-exponential character, and ac conductivity may show non-Arrhenius behavior and an approach to saturation at high temperatures.

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Small-signal frequency-response measurements of the electrical response of disordered materials arising primarily from mobile charges have become a standard approach for characterizing charge-carrier dynamics; see, e.g., Refs. 1–33 in Ref. 1. Full analysis requires not only accurate immittance-spectroscopy (IS) data, but also an appropriate model to represent the response and a powerful complex-nonlinear-least-squares fitting program, such as the freely available LEVM one.[2] Since its development in 1972–1973, the original macroscopic electric-modulus formalism (OMF) approach[3] has provided a widely used fitting model; see, e.g., the 20 references to it in Ref. 4. Unfortunately, unrecognized errors in this model as well as in its application to data analysis have rendered suspect many of the results obtained with it over the last 17 years.[5–7]

Here, I shall show how a corrected modulus-formalism (CMF) approach leads to a physically consistent response and how comparison of it to a slightly corrected version of a microscopic random-hopping model[8] yields mutual consistency and new understanding of the dispersed-relaxation behavior of disordered materials. Although the results are applicable to electronic conduction as well as ionic, I shall concentrate on the latter situation since it is of much current interest, both for gaining basic understanding of dynamic processes and for use in evaluating the limitations of disordered materials in practical applications such as fuel cells and batteries.

Published macroscopic-level IS work has often been ambiguous in not distinguishing clearly between response functions that are appropriate for direct comparison with experimental data and those that are not. Therefore, in the following, a subscript ''E'' will be used where needed to indicate quantities that are appropriate. In addition, the subscripts ''C'' and ''D'' will be employed to distinguish between quantities entirely associated with mobile charge and those that arise from dipole and electronic permittivity effects, respectively. When no such subscripts are included, a quantity is of conductive ''C'' type. Finally, we shall be dealing with two types of conductive-system dispersion (CSD), denoted by the subscript $k=0$ or 1: CSD_0 and CSD_1.

In terms of the complex resistivity, $\rho_{Ck}(\omega)=\rho'_{Ck}(\omega)+i\rho''_{Ck}(\omega)$, of a purely CSD situation, the normalized complex response function $I_k(\omega)$ is given by

$$\begin{aligned}\{\rho_{Ck}(\omega)-\rho'_{Ck}(\infty)\}/\{\rho'_{Ck}(0)-\rho'_{Ck}(\infty)\}&\equiv I_k(\omega)\\&=\int_0^\infty \frac{G_k(x)dx}{[1+i\omega\tau_o x]}\\&=\int_0^\infty \exp(-i\omega t)\{-d\Phi_k(t)/dt\}dt,\end{aligned}\tag{1}$$

where $x\equiv\tau/\tau_o$, and τ_o is a characteristic relaxation time of the response. Equation (1), which follows from linear-response theory,[9,10] shows that $I_k(\omega)$ may be calculated either from knowledge of the normalized distribution of resistivity relaxation times $G_k(x)$ or from a temporal response function $\Phi_k(t)$, sometimes called the correlation or autocorrelation function. It involves t/τ_o. On the other hand, for the microscopic hopping theory of Scher and Lax,[8] $\Phi(t)$ is defined as the probability that a charge carrier not move from its initial position over the time t.

In the usual case where $\rho'_{Ck}(\infty)=0$ or is negligible in the frequency range of interest, the complex conductivity is given by

$$\begin{aligned}\sigma_{Ck}(\omega)&=\sigma'_{Ck}(\omega)+i\sigma''_{Ck}(\omega)\\&=1/\rho_{Ck}(\omega)\\&=\sigma'_{Ck}(0)/I_k(\omega)\\&\equiv\sigma_0/I_k(\omega).\end{aligned}\tag{2}$$

It is important to note that actual data fitting should involve the composite quantity

$$\sigma_{kE}(\omega)=\sigma_{Ck}(\omega)+i\omega\epsilon_V\epsilon_{D\infty},\tag{3}$$

where ϵ_V is the permittivity of vacuum; $\epsilon_{D\infty}$ is the high-frequency-limiting dielectric constant associated with dipolar

and electronic vibrational polarization, present even in the absence of mobile charge; and we assume the absence of dielectric-system dispersion in the frequency range of interest.[5–7] The usual expression for σ_0 is[11,12]

$$\sigma_0=[\gamma N(qd)^2/6kT]/\tau_H, \tag{4}$$

appropriate for low relative charge-carrier concentrations, here taken as cations. Then N is the total cation density; γ is the fraction of mobile ions; q is the cation charge; d is the mean hop distance for a hopping ion; and τ_H is a thermally activated hopping time, discussed below.

The mth moments of the normalized $G_k(x)$ distribution are given by

$$\langle\tau^m\rangle_k\equiv\tau_o^m\langle x^m\rangle_k\equiv\tau_o^m\int_0^\infty x^m G_k(x)dx, \tag{5}$$

and we may also express the first moment or mean value of τ for the $k=0$ situation as

$$\langle\tau\rangle_0=\int_0^\infty t\{-d\Phi_0(t)/dt\}dt=\int_0^\infty\Phi_0(t)dt. \tag{6}$$

Note that $\langle x^m\rangle_k$ is a dimensionless quantity which depends only on the shape of the distribution and is independent of τ_o.

The macroscopic OMF analysis, expressed in terms of the present notation, leads to an expression for the response at the electric-modulus level, $M_{C1}(\omega)\equiv i\omega\epsilon_V\rho_{C1}(\omega)=M'_{C1}(\omega)+iM''_{C1}(\omega)$, by starting with the $I_0(\omega)$ response. The result at the complex conductivity level is

$$\sigma_{C1}(\omega)=i\omega\epsilon_V/M_{C1}(\omega)=i\omega\epsilon_V\epsilon_{D\infty}/[1-I_0(\omega)], \tag{7}$$

where $M_{C1}(\infty)$ was identified as $1/\epsilon_{D\infty}$.[3] In later applications of the OMF, ϵ_∞ has generally been used in place of $\epsilon_{D\infty}$, but this is misleading, as discussed below. The $\omega\rightarrow 0$ limit of Eq. (7) may be readily shown to be[3,5]

$$\sigma_0=\epsilon_V\epsilon_{D\infty}/\langle\tau\rangle_0, \tag{8}$$

a widely used but inappropriate result.

To obtain a specific form for $I_0(\omega)$, Macedo *et al.*[3] used Eq. (1) with the felicitous choice

$$\Phi_0(t)=\exp\{-(t/\tau_o)^{\beta_0}, \tag{9}$$

the stretched-exponential function involving the shape parameter β_0, with $0<\beta_0\leq 1$. The resulting $I_0(\omega)$ is a Kohlrausch-Williams-Watts (KWW) response model, the KWW_0.[13] Although $I_k(\omega)$ cannot be expressed in closed form except for a few fractional values of β_k, very accurate approximations for both KWW_0 and KWW_1 responses are included in LEVM for arbitrary β_k, thus allowing direct fitting of experimental data to a KWW model. When the KWW_0 model is used in Eqs. (2) and (3) for fitting experimental data, it leads to an estimate of β_0, but generally does not yield as good a fit as does the KWW_1 CMF response model involving $\beta_1\simeq 1-\beta_0$.[6,7]

There are several problems with the CSD_1 OMF model of Eq. (7). The authors and later users apparently did not recognize that the $k=1$ complex dielectric constant, given by $\epsilon_{C1}(\omega)\equiv 1/M_{C1}(\omega)=\epsilon'_{C1}(\omega)-i\epsilon''_{C1}(\omega)$, involved a nonzero value of $\epsilon'_{C1}(\infty)\equiv\epsilon_{C1\infty}\neq\epsilon_{D\infty}$, so that $\epsilon_{\infty E}=\epsilon_\infty=\epsilon_{C1\infty}+\epsilon_{D\infty}$. In addition, they did not distinguish between $M_{C1}(\omega)$ and the $M_{C1E}(\omega)$ which follows from the combination of Eqs. (3) and (7). Finally, actual calculation of $M'_{C1}(\infty)$ yields $1/\epsilon_{C1\infty}$,[5] thus showing that such quantities as $M_{C1}(\omega)$ arise directly from pure conductive-system charge motion alone. It follows that for the CMF (Refs. 5, 6)

$$\sigma_0=\epsilon_V\epsilon_{C1\infty}/\langle\tau\rangle_{01}\equiv\epsilon_V\epsilon_{C1\infty}/(\tau_o\langle x\rangle_{01}), \tag{10}$$

and

$$\begin{aligned}\sigma_{C1}(\omega)&=\sigma_0/I_1(\omega)\\&=i\omega\epsilon_V\epsilon_{C1\infty}/[1-I_{01}(\omega)]\\&=i\omega\sigma_0\tau_o\langle x\rangle_{01}/[1-I_{01}(\omega)].\end{aligned} \tag{11}$$

The subscript 01 has been included here to indicate that although $\langle x\rangle_{01}$, for example, involves the $k=0$ $G_k(x)$ distribution, it is now associated with the $k=1$ response, and thus properly must involve a $k=1$ shape parameter β_1 rather than the $k=0$ parameter β_0. If $I_{01}(\omega)$ is calculated from the $\Phi_{01}(t)$ stretched exponential, then the KWW_1 response is given by Eq. (11). It is noteworthy that the associated $\Phi_1(t)$ response is not of stretched-exponential character, however.[14,15]

In an effort to justify the presence of ϵ_∞ (actually $\epsilon_{D\infty}$, since the existence of $\epsilon_{C1\infty}$ was unrecognized) in the OMF approach, Ngai and León[4] have argued that ϵ_∞ inevitably enters in macroscopic measurements. This is certainly true, and it is the reason that $\epsilon_{D\infty}$ is present in Eq. (3). But their approach to producing a $\sigma(\omega)$ expression which arises ''entirely from the motion of ions'' by subtracting the term $i\omega\epsilon_V\epsilon_\infty$ from the OMF σ-level expression, one which intrinsically includes $\epsilon_\infty=\epsilon_{D\infty}$, fails. On the other hand, it is not surprising that a proper mobile-charge theory should yield only conductive-system quantities, such as the $\epsilon_{C1\infty}$ in the CMF and in all the results of the microscopic theory of Scher and Lax.[8]

In recent correspondence,[16] León has stated, ''In my opinion, 'relaxing' mobile charges feel the total high-frequency permittivity in the medium . . . .'' I agree, provided that he is referring to $\epsilon_{D\infty}$ rather than to ϵ_∞ (which could be self-referential). But for situations where τ_o is thermally activated, it is the activation energy itself that one would expect might depend on $\epsilon_{D\infty}$. In fact, as mentioned in Ref. 8, a formula given for the activation energy of low-compensated semiconductors is proportional to $1/\epsilon_{D\infty}$. It seems plausible that some similar or possibly lesser dependence involving screened Coulomb interactions should be present in the activation energy of τ_o for ionic hopping, but there appears to be no justification for the direct presence of $\epsilon_{D\infty}$ or ϵ_∞ in the OMF expressions of Eqs. (7) and (8), since neither follows consistently from a mobile-charge-only analysis.

We are now ready to compare the CMF with the stochastic transport model (STM) of Ref. 8. In terms of the present notation, the STM leads to

$$\sigma_0=[\gamma N(qd)^2/6kT]/\langle\tau\rangle_{01}, \tag{12}$$

where Scher and Lax used the first part of Eq. (6) and identified their resulting $\tau_H=\langle\tau\rangle_{01}$ as the mean time for a hop, or the mean waiting time. We see that it is also the mean relaxation time for the $k=0$ distribution involving the $k=1$ value of the shape parameter. Note that Eqs. (10) and (12) yield the important result

$$\epsilon_{C1\infty}=[\gamma N(qd)^2/6kT\epsilon_V], \tag{13}$$

showing that $\epsilon_{C1\infty}$ should be proportional to T^{-1} when γ is constant, in rough agreement with LEVM fitting of $Na_2O\cdot SiO_3$ data.[6]

An expression identical to that of Eq. (13) except with 3 instead of 6 was recently published by Sidebottom.[12] But Sidebottom did not use the MF, and his derivation was quite different from that leading to Eq. (13). Further, he identified his result as $\Delta\epsilon\equiv\epsilon_0-\epsilon_\infty$, actually equal to $\epsilon_{0E}-\epsilon_{D\infty E}=\epsilon_0$ for $k=0$.[5,14] Note that although the CMF ϵ_{C10} is quite different from $\epsilon_{C1\infty}$, $[\epsilon_{C0}(0)]_{01}$ actually equals $\epsilon_{C1\infty}$, because $G_1(x)=xG_{01}(x)/\langle x\rangle_{01}$.[6] For $k=1$, however, $\Delta\epsilon=\epsilon_{C10E}-\epsilon_{\infty E}=\epsilon_{C10}-\epsilon_{C1\infty}$.[5,6]

When one uses Eq. (13) in the complex conductivity STM result of Ref. 8, specialized for the situation where the spatial and temporal distributions of each hop are considered independent of each other, it becomes just

$$\sigma_{STM}(\omega)=i\omega\epsilon_V\epsilon_{C1\infty}[I_{01}(\omega)/\{1-I_{01}(\omega)\}], \tag{14}$$

not quite the same as the CMF result of Eq. (11). In fact, however, it can be readily shown that this expression has exactly the same real part as that of Eq. (11), but a different imaginary part. To make them exactly equal, it is only necessary to add the effect of the capacitance $\epsilon_{C1\infty}$, namely, $i\omega\epsilon_V\epsilon_{C1\infty}$ to the Eq. (14) response function. Then $\epsilon_{STM\infty E}=\epsilon_{C1\infty}+\epsilon_{D\infty}$, instead of just $\epsilon_{D\infty}$. Since the CMF $I_{01}(\omega)$ function of Eqs. (11) and (14) satisfies the Kronig-Kramers relations at the complex resistivity level, this minor change makes the corrected STM also do so. The resulting detailed agreement established here between the present corrected macro and micro approaches, but not possible using the OMF,[4] justifies them both and underlines the importance and appropriateness of the resulting joint micro-macro model for analyzing relaxation in disordered materials. An important conclusion is that since the STM does not involve long-range Coulomb charge interactions, good fits with the macroscopic KWW_1 CMF response model, as often found for disordered glasses,[5–7,15] indicate that such interactions are then unimportant.

We have already mentioned that there is some evidence that $\epsilon_{C1\infty}\sim 1/T$ as in Eq. (13), but accurate estimation of $\epsilon_{C1\infty}$ (and $\epsilon_{D\infty}$) requires complex-nonlinear-least-squares fitting of the full data, taking proper account of both $\epsilon_{D\infty}$ and possible electrode effects (e.g., Refs. 6,7,15,17). Work in progress shows that CMF fits of various experimental data sets for different materials yield consistent results, while fitting with the OMF, where no separate $\epsilon_{D\infty}$ parameter is included, usually yields not only poorer fits but inconsistent estimates of β_1 from separate fits of $\sigma'_{dat}(\omega)$ and $M_{dat}(\omega)$ or $M''_{dat}(\omega)$. Since the presence or absence of $\epsilon_{D\infty}$ does not affect $\sigma'_{dat}(\omega)$, such inconsistency is a crucial indicator of the inappropriateness of the OMF.

Plotting of an experimental data set at the modulus level, $M_{dat}(\omega)$, generally shows a peak of $M''_{dat}(\omega)$ at $\omega=\omega_{mp}$, $M''_{dat}(\omega_{mp})$, and a limiting value of M'_{dat}, $M'_{dat\infty}=1/\epsilon_{\infty E}=1/[\epsilon_{C1\infty}+\epsilon_{D\infty}]$, at much higher frequencies. Surprisingly, data for different materials show that $M''_{dat}(\omega_{mp})$ may decrease, increase, or remain constant as the measurement temperature increases (e.g., Ref. 18). Thus, it is not proportional to $M'_{dat\infty}$, but simulation shows that for data with constant $\epsilon_{C1\infty}$, where only β_1 varies, $M''_{C1E}(\omega_{mp})/\beta_1$ is approximately constant for $0.4\leqslant\beta_1\leqslant 0.6$. Detailed fitting is needed, however, to elucidate the various interactions properly.

Finally, for the KWW_1 response, the preexponential term of the σ_0 expression of Eq. (12) is proportional to $\beta_1/\{T\Gamma(1/\beta_1)\}$, where Γ is the Euler gamma function. When β_1 increases toward unity as T increases, this term not only leads to a better Arrhenius fit of $\sigma_0(T)$ with a T^{-2} preexponent expression rather than with a T^{-1} one, but $\sigma_0(T)$ tends toward non-Arrhenius saturation at high temperatures, a different cause for limiting high-temperature conductivity, which can be deleterious in practical applications, than that associated with low-τ cutoff of the $G_1(x)$ distribution at constant β_1.[14]

*Email address: macd@email.unc.edu

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