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Relating macroscopic electrical relaxation to microscopic movements of the ions in ionically conducting materials by theory and experiment

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Whatever the preferred representation of the frequency dependence of electrical relaxation experimental data, complex conductivity $\sigma^*(\omega)$, complex permittivity $\varepsilon^*(\omega)$, or complex electric modulus $M^*(\omega)$, there is no escape from the fact that we are dealing with measurements which are macroscopic in nature. The question of how to relate the macroscopic measurement, which contains the high-frequency dielectric constant ε_∞, to the microscopic movement of the ions remains to be answered. Comparing the results of a stochastic transport theory and of the electric modulus formalism, we find that the electric modulus faithfully reproduces the shape of the dispersion of the microscopic ionic movement. However, the electric modulus relaxation time is different from the microscopic relaxation time by a known and calculable factor that is proportional to the product of the high-frequency dielectric constant and temperature. Consequently, the entire electric modulus relaxation time spectrum is shifted uniformly away from the microscopic ion relaxation time spectrum by the same frequency-independent factor, and these two relaxation time spectra have effectively the same dependence on temperature, isotope mass, etc. In contrast to electrical conductivity relaxation, nuclear spin relaxation is a microscopic probe of ionic movement, and from its result we can directly infer the microscopic dynamics of the ions. A combined study of ionic motion using electrical relaxation and nuclear spin relaxation in a crystalline ionic conductor by León *et al.* provides the experimental data to enable us to verify the theoretical relation between the macroscopic electric modulus spectrum and the microscopic ionic hopping relaxation spectrum. [S0163-1829(99)09537-5]

I. INTRODUCTION

The most commonly used experimental technique to characterize the dynamics of diffusing ions in glasses, melts, and crystals is electrical relaxation measurements.[1–30] The usual method of studying electrical relaxation in these materials is to prepare a disk-shaped specimen with thin-film metal electrodes deposited on its two parallel faces. An ac bridge or similar arrangement is used to measure conductance G and capacitance C of the specimen as a function of frequency f. All the experimental information regarding electrical relaxation at a given temperature is contained in $G(\omega)$ and $C(\omega)$ where $\omega\ (=2\pi f)$ is the angular frequency. The real part of the complex conductivity σ' and the real part of the complex permittivity ε' are obtain by the expressions $\sigma'=G(L/A)$ and $\varepsilon'=(C/\varepsilon_0)(L/A)$, where L is the thickness, A is the area of the disk-shaped sample, and ε_0 is the permittivity of a vacuum. The measurements give us immediately the complex permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ and complex conductivity $\sigma^*(\omega)=\sigma'(\omega)+i\sigma''(\omega)=i\omega\varepsilon_0\varepsilon^*(\omega)$, and the complex electric modulus $M^*(\omega)$ is related to the more familiar $\varepsilon^*(\omega)$ and $\sigma^*(\omega)$ by

$$M^*(\omega)=1/\varepsilon^*(\omega) \tag{1}$$

and

$$\sigma^*(\omega)=i\omega\varepsilon_0/M^*(\omega). \tag{2}$$

Thus $\varepsilon^*(\omega)$, $\sigma^*(\omega)$ and $M^*(\omega)$ are just alternative and interchangeable representations of the same data.

In all materials, electrical measurement of $\varepsilon'(\omega)$ at sufficiently high frequencies always gives a constant finite value, which is called the high-frequency dielectric constant ε_∞. Although ε_∞ is unrelated to the microscopic ion dynamics, it comes with the electrical measurement anyway. For any microscopic theory of ion dynamics, which does not contain ε_∞, the challenge that it faces in comparing with experimental data is how to take care of this unwanted quantity. In other words, it is incumbent on the proponent of any microscopic theory to incorporate ε_∞ into the theory before it can be compared with the electrical measurement. Thus there is no escape from dealing with ε_∞ for anyone who wants to deduce microscopic dynamics from macroscopic electrical relaxation data.

The so-called electric modulus (EM) formalism (Refs. 1–4, 6–10, 13, 15–18, 20, 22, and 27–30) for the analysis of electrical relaxation starts with the argument that for mobile ions the appropriate quantity to consider is the decay of the electric field $E(t)$ under the constraint of a constant displacement vector $D(t)$:

$$E(t)=E(0)\Phi(t), \tag{3}$$

where $E(0)$ is the initial electric field imposed and $\Phi(t)$ is the electric field relaxation function $[0\leqslant\Phi(t)\leqslant1]$. In analogy to mechanical relaxation, in the frequency domain the electric field relaxation is related to the electric modulus as

$$\begin{aligned}M^*(\omega)&=M'+iM''\\&=M_\infty\left[1-\int_0^\infty dt\,\exp(-i\omega t)(-d\Phi/dt)\right],\end{aligned} \tag{4}$$

where $M_\infty=\lim_{\omega\to\infty}M'=1/\lim_{\omega\to\infty}\varepsilon'=1/\varepsilon_\infty$ is a measure of the "strength" of the electric field relaxation. In the EM formalism, the macroscopic conductivity $\sigma^*(\omega)$ is obtained from Eq. (2) as $i\omega\varepsilon_0/M_\infty[1-\int_0^\infty dt\,\exp(-i\omega t)(-d\Phi/dt)]$. Therefore, in the EM formalism ε_∞ is incorporated into the formalism from the start. As discussed in the last paragraph, this step is necessary in order to make contact with electrical relaxation measurement.

Workers in the field have used either $\sigma^*(\omega)$, $\varepsilon^*(\omega)$, or $M^*(\omega)$ to represent the data. At the present time there are differences in opinions as to which representation is appropriate to interpret the microscopic movements of the ions. While these differences will be settled in the future, at this time whichever representation is preferred let there be no mistake in recognizing that one is considering the *same* data and the data are obtained from *macroscopic* electrical relaxation measurements. In order to deduce microscopic information of the movements of the ions, a theory of carrier transport and the incorporation of ε_∞ is needed to bridge macroscopic electrical relaxation data and the microscopic motion of mobile ions. One objective of this work is to show that there is a relation between the macroscopic data represented by the normalized electric modulus $M^*(\omega)/M_\infty$ and the theoretical expression of the microscopic complex conductivity $\sigma^*(\omega)$ derived from the stochastic transport theory by Scher and Lax.[31] The results of the present paper show that the *shape* of the $M^*(\omega)/M_\infty$ spectrum is the mirror image of the microscopic ion hopping relaxation spectrum. However, the time scales of the two spectra are not the same and shifted by a factor which is proportional to the product of ε_∞ and temperature. Thus the extent of the connection of the macroscopic electric modulus to the microscopic movements of the ions has now been ascertained and the EM formalism is still the choice to analyze the electrical relaxation of mobile ions.

In contrast to electrical relaxation, nuclear spin relaxation (NSR) is a microscopic technique. Measurement of NSR caused by the motions of ions provides direct information on the microscopic movements of the ions. Recently, León *et al.*[28] have used both electrical relaxation and NSR to study the movement of ions in the crystalline fast ionic conductor $\mathrm{Li_{0.5}La_{0.5}TiO_3}$. We shall show that their results verify the proposed connection between the $M^*(\omega)/M_\infty$ spectrum from electrical relaxation to the microscopic movements of ions as described by the stochastic transport theory of Scher and Lax.

II. THEORY OF SCHER AND LAX

In 1973, Scher and Lax[31] (SL) published a theory of stochastic transport of charged carriers (ions in our case) in disordered systems. These authors started from the Nyquist theorem, which relates admittance (mobility) and noise and generalizes the Einstein relation between mobility μ and diffusion constant D to nonzero frequency as

$$\mu^*(\omega)=(q/kT)D^*(\omega), \tag{5}$$

where q is the ion charge, k is the Boltzmann constant, and T is the temperature.[32] The real part of the frequency-dependent diffusion constant $D^*(\omega)$ is related to the velocity-velocity autocorrelation function $\langle v(t)v(0)\rangle$ by

$$\operatorname{Re} D^*(\omega)=\int_0^\infty \cos\omega t\langle v(T)v(0)\rangle dt, \tag{6}$$

and to the mean-squared displacement of the carrier, $\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle$, by

$$D^*(\omega)=-\frac{1}{6}\omega^2\int_0^\infty e^{-i\omega t}\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle dt. \tag{7}$$

This form for $D^*(\omega)$ naturally obeys the Kramers-Kronig relationship

$$-\operatorname{Im} D^*(\omega)=\frac{1}{\pi}\wp\int_{-\infty}^{\infty}\frac{\operatorname{Re} D^*(\omega)}{\omega'-\omega}d\omega'. \tag{8}$$

The complex conductivity is given by the relations

$$\sigma^*(\omega)=Nq\mu^*(\omega)=(Nq^2/kT)D^*(\omega), \tag{9}$$

where N is the density of the mobile ions. In this work we shall not take into account the possible correlation between successive hops of a mobile ion or cross correlation, which would have introduced into the right-hand side of Eq. (9) the correlation factor or Haven ratio f_H.

Whatever the mechanism of ionic transport, a calculation of $\sigma^*(\omega)$ needs to determine the probability of finding a carrier at any point at time t if it was at the origin at $t=0$. The model used by SL to calculate such a probability function is a generalization of the continuous-time random walk (CTRW) of Montroll and Weiss.[33(a)] These authors have introduced a way of incorporating a continuous-time variable into the basic theory of lattice random walks. In the model the basic quantity is the probability $\psi(\mathbf{s},t)\ \Delta t$ that the time between hops is in the interval $(t,t+\Delta t)$ and the displacement is $\mathbf{s}$. Then $\phi(t)$, defined by

$$\phi(t)=1-\int_0^t\psi(\tau)d\tau, \tag{10}$$

with

$$\psi(t)=\sum_{\mathbf{s}}\ \psi(\mathbf{s},t), \tag{11}$$

is the probability that the ion remains fixed in the time interval $[0,t]$. Although formulated on a lattice, the CTRW [Ref. 33(a)] has general applicability to stochastic transport in disordered systems including the random electron hopping in chalcogenide glasses demonstrated by Scher and Montroll[33(b)] and some other contexts in Ref. 34. Sources of the distribution of hopping times such as different jump probabilities and sites are subsumed in the function $\psi(\mathbf{s},t)$. In this work, neither the ion transport in ionically conducting glasses is described nor any theory of such is subscribed to. Nevertheless, the general applicability of the CTRW and SL theory of stochastic transport in disordered solids ensures the validity of the following description of the microscopic ion conductivity. We shall confine our consideration to the common situation that only one kind of mobile ion contributes to the electrical relaxation. The description can be easily generalized to accommodate the possibility that more than one kind of mobile ions makes their contribution by taking into account their $\psi(\mathbf{s},t)$'s in the description that follows.

Differentiating Eq. (10),

$$\psi(t) = -\frac{d}{dt}\phi(t). \tag{12}$$

If the spatial and temporal probability distribution of each hop of the ion is independent of each other such that $\psi(\mathbf{s},t)$ can be written as a product, $p(\mathbf{s})\psi(t)$ with $\Sigma_{\mathbf{s}} p(\mathbf{s}) = 1$, then calculating $\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle$ by the CTRW method and substituting it into Eq. (7), SL finally obtained the key result:

$$D^*(\omega) = \frac{1}{6} r_{\mathrm{rms}}^2 (i\omega)\tilde{\psi}(\omega)/[1 - \tilde{\psi}(\omega)], \tag{13}$$

where

$$r_{\mathrm{rms}}^2 = \sum_{\mathbf{s}} s^2 p(\mathbf{s}) \tag{14}$$

and $\tilde{\psi}(\omega)$ is the Laplace or causal Fourier transform of $\psi(t)$ defined by

$$\tilde{\psi}(\omega) = \int_0^\infty e^{-i\omega t}\psi(t)\,dt. \tag{15}$$

III. RELATION BETWEEN STOCHASTIC TRANSPORT THEORY AND ELECTRICAL RELAXATION

After the principal results of the stochastic transport theory of SL have been summarized in the above, we are ready to find the relation between the normalized electric modulus function $M^*(\omega)/M_\infty$ [see Eqs. (2) and (4)] and the theoretical expression for the conductivity of SL. A way to show this is to rewrite Eq. (13) using Eqs. (12) and (15), as

$$D^*(\omega) = (r_{\mathrm{rms}}^2/6)(i\omega)\frac{\tilde{\psi}(\omega)}{1-\tilde{\psi}(\omega)} = (r_{\mathrm{rms}}^2/6)(i\omega) \times \left\{ \frac{\int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\phi(t)\right)}{1 - \int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\phi(t)\right)} \right\}. \tag{16}$$

From Eqs. (9) and (16), the complex conductivity can be calculated from $\phi(t)$ by

$$\sigma_{\mathrm{STT}}^*(\omega) = (Nq^2/kT)(r_{\mathrm{rms}}^2/6)(i\omega) \times \left\{ \frac{\int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\phi_{\mathrm{STT}}(t)\right)}{1 - \int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\phi_{\mathrm{STT}}(t)\right)} \right\}. \tag{17}$$

The suffix ''STT'' is introduced in Eq. (17) and from now on in all subsequent equations to indicate that the quantities including $\phi(t)$ are obtained from the stochastic transport theory, which is assumed to describe correctly the microscopic ion dynamics. This theoretical expression is to be compared with the macroscopic one, σ_{EM}^*, obtained from the EM formalism [Eq. (4)] via the Maxwell relation [Eq. (2)],

$$\sigma_{\mathrm{EM}}^*(\omega) = \varepsilon_0 \frac{i\omega}{M^*(\omega)} = (\varepsilon_0/M_\infty)(i\omega) \times \left\{ \frac{1}{1 - \int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\Phi(t)\right)} \right\}, \tag{18}$$

which is obtained from Eqs. (2) and (4). This macroscopic conductivity obtained from electrical measurement can be rewritten explicitly as the sum of two different contributions, a pure imaginary part $i\omega\varepsilon_0\varepsilon_\infty$ and $\sigma_{\mathrm{EM,ion}}^*(\omega)$,

$$\sigma_{\mathrm{EM}}^*(\omega) = \sigma_{\mathrm{EM,ion}}^*(\omega) + i\omega\varepsilon_0\varepsilon_\infty. \tag{19}$$

Here $\sigma_{\mathrm{EM,ion}}^*(\omega)$ is the macroscopic conductivity coming entirely from motion of ions and it is related to the macroscopic decay function $\Phi(t)$ by the expression

$$\sigma_{\mathrm{EM,ion}}^*(\omega) = (\varepsilon_0/M_\infty)(i\omega) \times \left\{ \frac{\int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\Phi(t)\right)}{1 - \int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\Phi(t)\right)} \right\}. \tag{20}$$

By comparing the expressions inside the curly brackets in Eqs. (17) and (20), one finds that the microscopic conductivity $\sigma_{\mathrm{STT}}^*(\omega)$ and the EM macroscopic conductivity $\sigma_{\mathrm{EM,ion}}^*(\omega)$ have similar functional forms. In spite of the similarity in form, we hasten to mention that $\sigma_{\mathrm{STT}}^*(\omega)$ and $\sigma_{\mathrm{EM,ion}}^*(\omega)$ differ in their dependences on ω because $\Phi(t)$ and $\phi_{\mathrm{STT}}(t)$ have different characteristic time scales, the macroscopic τ_{EM} and the microscopic τ_{STT}, respectively. As we shall show later, this similarity between Eqs. (17) and (20) leads us to identify $\Phi(t/\tau_{\mathrm{EM}})$ with $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$. This identification gives a more basic interpretation to the macroscopic $\Phi(t/\tau_{\mathrm{EM}})$ than the decay of the electric field at constant displacement vector, as customarily done in the EM formalism.[1–4,20] The prefactors of the frequency dependent terms in Eqs. (17) and (20) are different. This is understandable because the microscopic conductivity, Eq. (17), is obtained from the mean-square displacement, the frequency-dependent diffusion constant, and the use of the Nyquist theorem, which generalizes the Nernst-Einstein relation between the conductivity and diffusion constant to nonzero frequency. On the other hand, the route to the macroscopic conductivity, Eq. (20), of the EM formalism is through the Maxwell relation. Both approaches, being based on sound physical principles, are legitimate, albeit different ways to obtain information on the dynamics of the ions. $\phi_{\mathrm{STT}}(t)$ as well as $\Phi(t)$ starts from the initial (i.e., at $t=0$) value of unity and decreases monotonically towards zero with time. However, $\phi_{\mathrm{STT}}(t)$ and $\Phi(t)$ are characterized, respectively, by two different characteristic time constants τ_{STT} and τ_{EM}. We can go a step further in relating the STT and EM approaches by rewriting Eq. (17) as

$$\sigma^*_{\mathrm{STT}}(\omega)=(Nq^2/kT)(r^2_{\mathrm{rms}}/6)(i\omega)\left\{\frac{1}{i\omega\tilde{\phi}_{\mathrm{STT}}(\omega)}-1\right\} \tag{21}$$

and Eq. (20) as

$$\sigma^*_{\mathrm{EM,ion}}(\omega)=(\varepsilon_0/M_\infty)(i\omega)\left\{\frac{1}{i\omega\tilde{\Phi}_{\mathrm{EM}}(\omega)}-1\right\}. \tag{22}$$

Here we have introduced $\tilde{\phi}_{\mathrm{STT}}(\omega)$ and $\tilde{\Phi}(\omega)$ as the Laplace transforms of $\phi_{\mathrm{STT}}(t)$ and $\Phi(t)$, respectively, and made use of the relationship between the Laplace transform of the normalized functions $\phi_{\mathrm{STT}}(t)$ and $\Phi(t)$ and that of its time derivative, e.g.,

$$\int_0^\infty dt\, e^{-i\omega t}\left(-\frac{d}{dt}\Phi(t)\right)=1-i\omega\tilde{\Phi}(\omega).$$

Writing out explicitly the time dependences of Φ and ϕ_{STT} as $\Phi(t/\tau_{\mathrm{EM}})$ and $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$ to show explicitly their respective characteristic times and using the identity $\tilde{\varphi}(\omega)=\tau\tilde{\varphi}(\omega\tau)$ from Eqs. (17) and (20), we arrive at the following expressions:

$$\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})=(Nq^2/kT)(r^2_{\mathrm{rms}}/6)\frac{1}{\tau_{\mathrm{STT}}}\times\left\{\frac{1}{\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})}-i\omega\tau_{\mathrm{STT}}\right\} \tag{23}$$

and

$$\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})=(\varepsilon_0/M_\infty\tau_{\mathrm{EM}})\left\{\frac{1}{\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})}-i\omega\tau_{\mathrm{EM}}\right\}. \tag{24}$$

We observe that the expressions inside the curly brackets in Eqs. (23) and (24) have essentially the same structure. Both $\phi(t/\tau_{\mathrm{STT}})$ and $\Phi(t/\tau_{\mathrm{EM}})$ describe the dynamics of the ion motion, the former microscopically and the latter macroscopically. The variables $\omega\tau_{\mathrm{STT}}$ and $\omega\tau_{\mathrm{EM}}$ of the functions inside the curly brackets in, respectively, Eqs. (23) and (24) indicate once again that the microscopic and macroscopic dynamics occur at different times scales of τ_{STT} and τ_{EM}. Except for this difference in time scale, $\phi(t/\tau_{\mathrm{STT}})$ and $\Phi(t/\tau_{\mathrm{EM}})$ are the same functions of the reduced time variables. Similarly, their Laplace transforms $\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ and $\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})$ as well as the entire structures inside the curly brackets in Eqs. (23) and (24) are the *same* functions of the reduced frequency variables $\omega\tau_{\mathrm{STT}}$ and $\omega\tau_{\mathrm{EM}}$. In particular, they have the same value in the limits of $\omega\tau_{\mathrm{STT}}\to 0$ and $\omega\tau_{\mathrm{EM}}\to 0$, respectively. Thus $\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ and $\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})$ will have equal dc conductivity as required if the factors outside the curly brackets in Eqs. (23) and (24) are the same, i.e.,

$$\tau_{\mathrm{STT}}/\tau_{\mathrm{EM}}=(Nq^2r^2_{\mathrm{rms}})/(6kT\varepsilon_0\varepsilon_\infty). \tag{25}$$

Once this relation between the macroscopic conductivity relaxation time τ_{EM} of the EM formalism and the microscopic ionic hopping correlation time τ_{STT} is satisfied, the two expressions for the complex conductivity, $\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ and $\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})$, become isomorphic to each other. However, as a function of the actual frequency ω, $\sigma^*_{\mathrm{STT}}(\omega)$ differs from $\sigma^*_{\mathrm{EM,ion}}(\omega)$. When plotted against $\log_{10}\omega$, $\sigma^*_{\mathrm{STT}}(\omega)$ differs from $\sigma^*_{\mathrm{EM,ion}}(\omega)$ only by a horizontal shift of the whole curve $\sigma^*_{\mathrm{EM,ion}}(\omega)$ parallel to the $\log_{10}\omega$ axis with a shift factor equal to $\log_{10}(\tau_{\mathrm{STT}}/\tau_{\mathrm{EM}})$. This shift factor according to Eq. (25) depends on ε_∞ through the term $\log_{10}\varepsilon_\infty$. The same relation holds between $\mathrm{Re}[\sigma^*_{\mathrm{STT}}(\omega)]$ and $\mathrm{Re}[\sigma^*_{\mathrm{EM}}(\omega)]$ because from Eq. (19) $\mathrm{Re}[\sigma^*_{\mathrm{EM}}(\omega)]$ is exactly equal to $\mathrm{Re}[\sigma^*_{\mathrm{EM,ion}}(\omega)]$.

In general, τ_{EM} is not equal to τ_{STT} and they are related to each other by the ratio shown on the right-hand side of Eq. (25). Hence τ_{EM} cannot be identified with the microscopic ion hopping relaxation time τ_{STT}. Depending on the material parameters on the right-hand side of Eq. (25), the two relaxation times can be very different. In fact, two systems with identical microscopic ion dynamics and the same τ_{STT} but different values of ε_∞ will have two different values of τ_{EM}, each related to the same τ_{STT} by Eq. (25). This dependence of τ_{EM} on ε_∞ is considered by some workers as a shortcoming of the EM formalism. We do not agree with this opinion because this invariably will occur in any representation of the electrical relaxation data because the latter are from macroscopic measurement where ε_∞ inevitably enters. Nevertheless, even considered as a shortcoming of the EM formalism, this is a minor problem that can be overcome. From τ_{EM} the microscopic relaxation time can be readily calculated by the expression

$$\tau_{\mathrm{STT}}=\tau_{\mathrm{EM}}(Nq^2r^2_{\mathrm{rms}})/(6kT\varepsilon_0\varepsilon_\infty). \tag{26}$$

In the EM formalism, the dc conductivity $\sigma_{\mathrm{EM,dc}}$ is calculated by the well-known relation

$$\sigma_{\mathrm{EM,dc}}=\varepsilon_0\varepsilon_\infty/[\tau_{\mathrm{EM}}\lim_{\omega\tau_{\mathrm{EM}}\to 0}\tilde{\Phi}(\omega\tau_{\mathrm{EM}})]\equiv\varepsilon_0\varepsilon_\infty/\langle\tau_{\mathrm{EM}}\rangle. \tag{27}$$

When substituting Eq. (25) into Eq. (27), the macroscopic dc conductivity $\sigma_{\mathrm{EM,dc}}$ turns out to give correctly the microscopic dc conductivity $\sigma_{\mathrm{STT,dc}}$, i.e.,

$$\sigma_{\mathrm{EM,dc}}=Nq^2r^2_{\mathrm{rms}}/[6kT\tau_{\mathrm{STT}}\lim_{\omega\tau_{\mathrm{STT}}\to 0}\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})]=\sigma_{\mathrm{STT,dc}}. \tag{28}$$

The consistency of $\sigma_{\mathrm{EM,dc}}$ with the microscopic dc conductivity explains why $\sigma_{\mathrm{EM,dc}}$ calculated by Eq. (27) are always in good agreement with experimentally measured values.[1–4,10,12–13,20,27–30]

Except for the slowly varying T^{-1} factor in Eq. (25), the temperature dependence of τ_{STT} and τ_{EM} is the same. They have about the same activation energy as long as the activation energy in temperature units is much larger than T. Dependence of τ_{STT} and τ_{EM} on the isotope mass of the mobile ion is exactly the same.[13] Therefore, many of the discussions based on activation energy[35–38] and isotope mass[13,35] of τ_{EM} remain applicable to τ_{STT} and the theoretical interpretations suggested continue to be valid.

It follows from $\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ and $\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})$ being the *same* functions of the variables $\omega\tau_{\mathrm{STT}}$ and $\omega\tau_{\mathrm{EM}}$, respectively, that the normalized electric modulus $M^*(\omega\tau_{\mathrm{EM}})/M_\infty$ of Eq. (4) can be related to the microscopic $\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ by

$$M^*(\omega\tau_{\mathrm{EM}})/M_\infty = i\omega\tau_{\mathrm{EM}}\tilde{\Phi}(\omega\tau_{\mathrm{EM}}) = i\omega\tau_{\mathrm{EM}}\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}}). \tag{29}$$

Since $\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ appears in the expression [Eq. (23)] for $\sigma^*_{\mathrm{STT}}(\omega)$, this result leads to the important conclusion that the shape of the dispersion of $M^*(\omega\tau_{\mathrm{EM}})/(M_\infty\omega\tau_{\mathrm{EM}})$ obtained from the data analysis using the EM formalism can be identified with the shape of the dispersion of $i\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$. The latter originates from the microscopic movement of the ions and determines the frequency-dependent transport coefficients in the microscopic stochastic transport theory [Eq. (23)]. Therefore, the shape of the observed loss peak of $\mathrm{Im}[M^*(\omega\tau_{\mathrm{EM}})/M_\infty]$ is uniquely determined by the movement of the ions. This correspondence between the EM formalism and the stochastic transport theory, though not totally exact [i.e., there is a difference in the relaxation times as given by Eq. (25)], also justifies the fact that the electric modulus has a theoretical basis, e.g., the stochastic transport theory of Scher and Lax. Although τ_{EM} differs from τ_{STT} by a factor, the dispersions of $M^*(\omega\tau_{\mathrm{EM}})/(M_\infty\omega\tau_{\mathrm{EM}})$ and of the quantity $i\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ in the stochastic transport theory are exactly the same. Therefore, any dispersion coming from ion hopping and picked up by the stochastic transport theory in Eq. (23) will be seen exactly in the same shape or form in the EM representation of the data as a function of $\omega\tau_{\mathrm{EM}}$ or at frequencies ω in the neighborhood of $(\tau_{\mathrm{EM}})^{-1}$.

It is worthwhile to point out from Eq. (25) that the quantity $(\varepsilon_0/M_\infty\tau_{\mathrm{EM}})$ on the right-hand side of Eq. (24) is independent of ε_∞. Hence, as a function of $\omega\tau_{\mathrm{EM}}$, the ionic motion contribution to the conductivity, $\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})$, given by Eq. (24), is independent of the value of the high-frequency dielectric constant ε_∞. In the Appendix we summarize the relations between quantities of STT and EM formalism and reemphasize the fact that $\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})$ is uniquely determined by $\Phi(t/\tau_{\mathrm{EM}})$ and *vice versa*, independent of the value of the high-frequency dielectric constant, ε_∞.

Before closing this section, some remarks on the CTRW used by Scher and Lax are appropriate. In the past, Tunaley[39] made a literal interpretation of the CTRW procedure of SL as an ongoing renewal process which led to frequency-independent $D^*(\omega)$ and $\sigma^*(\omega)$. This difficulty is removed by a proper treatment of the CTRW problem as demonstrated by Lax and Scher[40] and others.[41–43] Also, a formal equivalence between the averaged particle transport in disordered systems and the generalized master equation or the CTRW theory was established by Klafter and Silbey.[43] Although the CTRW as a theory is on firm grounds, it may not be general enough to describe any model of charged carrier transport such as that proposed by Maass *et al.*[44]

IV. EFFECT DUE TO THE CONSTANT LOSS CONTRIBUTION TO ELECTRICAL RELAXATION

Experimentally, it has been repeatedly found in electrical relaxation measurements[12,15,19,27–30] that there is an additional contribution to $\sigma'(\omega)$ having approximately the linear frequency dependence $A\omega^{1.0}$ due to processes that are believed to be unrelated to the mobile ion motion.[13,15,19,45–47] This feature of $\sigma'(\omega)$ is general and found in most ionic glasses, in melts such as CKN, and in ionically conducting crystals including Na β-alumina[27] and yttria-stabilized zirconia[28] and $\mathrm{Li_{0.5}La_{0.5}TiO_3}$.[29] There are a number of indications that the $A\omega^{1.0}$ contribution to $\sigma'(\omega)$ is distinctly different in physical origin from the ac conductivity contribution due to the diffusion of mobile ions.[45,46] For example, the temperature dependence of A is extremely weak compared to the thermally activated temperature dependence of the dc conductivity σ_{dc} and of the frequency where $\sigma'(f)$ first begins to rise above σ_{dc}. Likewise, changes in the alkali-oxide mole fraction in glasses have a much weaker effect on the value of A than they do on the dc conductivity. The same is true for the substitution of one alkali for another (the mixed alkali). Finally, changes in the thermal history of the same glass which change the dc conductivity σ_{dc} by nearly half an order of magnitude have no effect on the value of A.[47]

Hence, from the experimental facts, $\sigma'(\omega)$ is the sum of two distinct contributions $A\omega^{1.0}$ and $\sigma'_{\mathrm{ion}}(\omega)$, i.e., $\sigma'(\omega) = \sigma'_{\mathrm{ion}}(\omega) + A\omega^{1.0}$. The former is unrelated to the ion diffusion, and the latter is the contributed by the movement of the ions. When the data are represented by the EM formalism, $\sigma'_{\mathrm{ion}}(\omega)$ is the real part of $\sigma^*_{\mathrm{EM}}(\omega)$ or, in view of Eq. (19), is $\sigma'_{\mathrm{EM,ion}}(\omega)$, the real part of $\sigma^*_{\mathrm{EM,ion}}(\omega)$. Thus, in real ionic conductors, the measured macroscopic conductivity $\sigma'(\omega)$ is the sum

$$\sigma'(\omega) = \sigma'_{\mathrm{EM,ion}}(\omega) + A\omega^{1.0}. \tag{30}$$

The $A\omega^{1.0}$ term is equivalent to a constant dielectric loss $\Delta\varepsilon'' = A/\varepsilon_0$.

When analyzing electrical relaxation data to gain information on ion dynamics, one must bear in mind the omnipresence of the additional contribution in the form of either the constant loss to the dielectric loss or $A\omega^{1.0}$ to the ac conductivity $\sigma'(\omega)$. Ionic conductors, at higher concentrations of ions and temperatures, have $A\omega^{1.0}$ much weaker than $\sigma'_{\mathrm{EM,ion}}(\omega)$ for frequencies extending from low frequencies up to at least some decades above the onset frequency of the conductivity relaxation, $\omega_{2\sigma}$, defined as the frequency at which the measured $\sigma'(\omega)$ has risen to twice the dc conductivity level. The example of sodium trisilicate glass has been given in Fig. 2 of Ref. 46. It can be seen there that at frequencies equal to $\omega_{2\sigma}$ and below the measured $\sigma'(\omega)$ is approximately the same as $\sigma'_{\mathrm{EM,ion}}(\omega)$. In particular, the measured σ_{dc} is practically the same as $\sigma_{\mathrm{EM,dc}}$, which is related to τ_{EM} or the mean $\langle\tau_{\mathrm{EM}}\rangle$ by Eq. (27). The reciprocals of τ_{EM} and $\langle\tau_{\mathrm{EM}}\rangle$ are approximately the same as the frequency ω_p of the $M''(\omega)$ peak exhibited by the data. When the condition above holds, $\sigma'_{\mathrm{EM,ion}}(\omega)$ rises rather rapidly and it is invariably found that $\langle\tau_{\mathrm{EM}}\rangle^{-1} \approx \omega_p$ is comparable to $\omega_{2\sigma}$. For the Na trisilicate glass see Fig. 1 of Ref. 20(c), and for another example see Fig. 5 of Ref. 20(a).

However, the situation is quite different for ionic conductors containing low concentrations of mobile ions. The $M''(\omega)$ peak is nearly Debye-like with $\Phi(t) \approx \exp(-t/\tau_{\mathrm{EM}})$ in Eq. (18). An example can be found in Fig. 3 of Ref. 46. The corresponding $\sigma'_{\mathrm{EM,ion}}(\omega)$ calculated from $M^*(\omega)$ by

Eqs. (18) and (19) has a very slow rise with frequency above $\omega_p \approx \langle \tau_{\mathrm{EM}} \rangle^{-1}$. For the example of the Vycor glass shown in Fig. 3 of Ref. 46, the $M''(\omega)$ peak of which has been fitted by the stretched exponential function $\Phi(t) \approx \exp(-t/\tau_{\mathrm{EM}})^{0.95}$, the corresponding $\sigma'_{\mathrm{EM,ion}}(\omega)$ rises above σ_{dc} slowly with the approximate power law $(\omega/\omega_p)^{0.05}$. Such a slow rise of $\sigma'_{\mathrm{EM,ion}}(\omega)$ has the consequences that (i) $\omega_{2\sigma}$ will be much larger than ω_p had this been the only contribution to the ac conductivity and (ii) the actual $\omega_{2\sigma}$ will be determined by the regime when eventually $\sigma'_{\mathrm{EM,ion}}(\omega)$ is dominated by the much more rapidly rising $A\omega^{1.0}$ contribution. In effect, $\omega_{2\sigma}$ is determined by the rise of $\sigma'(\omega) = \sigma'_{\mathrm{EM,ion}}(\omega) + A\omega^{1.0}$ caused effectively by the $A\omega^{1.0}$ contribution. Therefore, in this case $\omega_{2\sigma}$ can be much larger than ω_p. For the Vicor glass, Fig. 3 of Ref. 46 shows that $(\omega_p/2\pi) \approx 10$ Hz, while Fig. 2 of Ref. 46 indicates that $(\omega_{2\sigma}/2\pi) \approx 4 \times 10^3$ Hz. Also, they could have very difference temperature dependences. Since $\omega_{2\sigma}$ is determined principally by the $A\omega^{1.0}$ contribution unrelated to ion diffusion, its magnitude bears no direct connection to the ion hopping frequency, whether macroscopic or microscopic. Beyond $\omega_{2\sigma}$, $\sigma'(\omega)$ rises rapidly and in a short interval has attained the $A\omega^{1.0}$ dependence. This behavior, shown for the Vicor glass in Fig. 2 of Ref. 46, is found[48] also in the potassium germanate glass $x\mathrm{K_2O}$-$(1-x)\mathrm{GeO_2}$ with $x = 0.0023$ of Jain and Krishnaswami:[49] and in $x\mathrm{Na_2S}$-$(1-x)\mathrm{B_2S_3}$ with $x = 0.001$ of Patel and Martin.[50] Since the rise of $\sigma'(\omega)$ in ionic conductors with low ion concentrations principally reflects the $A\omega^{1.0}$ contribution, it should not be interpreted as originating from the dynamics of diffusion ions. Nevertheless, other workers apparently have not taken these facts into consideration, leading them to make erroneous statements. These statements include, ''The modulus analysis ignores the effect that, for a given conductivity, a lower number density of more mobile charge carriers implies faster ionic relaxation and thus a higher onset frequency of the conductivity dispersion. At very low number densities of mobile charge carriers, the M'' peak therefore occurs in the dc regime, and in shape it approximates to a Debye peak. This does not, of course imply an entirely frequency independent conductivity. The characteristic dispersion in conductivity is still present (Ref. 50 here), but it lies outside the dynamic window of the modulus formalism,'' made by the authors of Ref. 51. Another statement is, ''In glasses where there are few charge carriers, the modulus peak (which scales with σ_{dc}) is shifted to lower frequencies where no dispersion is experienced. The narrowing of the modulus spectrum is identified as an artifact of the data analysis,'' made by the author of Ref. 52. Some authors[51,53] proposed that the ac conductivity data $\sigma'(\omega)$ of ionic glasses at all concentrations can be scaled by one way or the other to a master curve. Reference 53 demonstrated successful scaling for four sodium germanate glasses $x\mathrm{Na_2O}$-$(1-x)\mathrm{GeO_2}$ for $x = 0.1$, 0.03, 0.01, and 0.003. We point out that while the author of Ref. 53 recognized that there is an additive $A\omega^{1.0}$ contribution to the ac conductivity due to processes unrelated to the cation diffusion, no attempt is made to subtract it off. For these glasses, the $A\omega^{1.0}$ contribution is not negligible, and until it is subtracted off from $\sigma'(\omega)$, the result is unclear. The pivotal data of the lowest concentration $x = 0.003$ have a kink which on the one hand enables the data to fall approximately on a master curve with the other glasses, but on the other hand it casts doubts on the data. In similar glasses $x\mathrm{K_2O}$-$(1-x)\mathrm{GeO_2}$ studied by Jain and Krishnaswami the ac conductivity curves for $x = 0.0023$ and 0.20 have different shapes (see Fig. 6 of Ref. 49) and cannot be scaled to a single master curve no matter what scaling factor is used including the form proposed in Ref. 53. The same applies to the data of $x\mathrm{Na_2S} \cdot (1-x)\mathrm{B_2S_3}$ with $x = 0.0010$ and 0.010,[50] and to the comparison of the Vycor glass with the Na trisilicate glass shown in the inset of Fig. 2 in Ref. 46.

V. EXPERIMENTAL VERIFICATION

Unlike electrical relaxation, nuclear spin relaxation (NSR) is a microscopic probe of the motion of the ions. At the Larmor frequency ω_L, the NSR rate $T_1^{-1}(\omega_L, T)$ is given by the expression

$$\frac{1}{T_1(\omega_L, T)} = C[J(\omega_L, T) + 4J(2\omega_L, T)], \tag{31}$$

where C is the coupling constant. $J(\omega, T)$ is the spectral density function which is the real part of the Fourier transform of the spin relaxation correlation function $\phi_s(t/\tau_s)$,

$$J(\omega, T) \equiv \mathrm{Re} \int_0^\infty \phi_s(t/\tau_s) \exp(-i\omega t)\, dt. \tag{32}$$

Let us ignore, for the remainder of this section, the fact that nuclear spin relaxation and macroscopic conductivity relaxation in ionic glasses have different frequency dispersions and hence different time correlation functions,[22–25,36] a point we shall return to discuss in the next section. Such a difference is nonexistent for the crystalline fast ionic conductor $\mathrm{Li_{0.5}La_{0.5}TiO_3}$ (LLTO), as found by León *et al.*[29] Then, in this case, since spin relaxation is a microscopic property, $\phi_s(t/\tau_s)$ is to be identified with the microscopic ion hopping correlation function $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$. Substituting the latter for the former into Eq. (32), we have

$$J(\omega, T) = \mathrm{Re} \int_0^\infty \phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}}) \exp(-i\omega t)\, dt \equiv \mathrm{Re}\, \tilde{\phi}_{\mathrm{STT}}(\omega), \tag{33}$$

where $\tilde{\phi}_{\mathrm{STT}}(\omega)$ is the Fourier transform of $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$ as defined in a previous section.

León *et al.*[29] obtained both the macroscopic electrical relaxation and microscopic lithium nuclear spin relaxation data on LLTO. In the measurement temperature range, the La ion is effectively immobile and Li is the sole mobile ion contributing to both electrical relaxation and nuclear spin relaxation. They fitted their electrical relaxation data in the EM formalism by choosing the stretched exponential $\exp[-(t/\tau_{\mathrm{EM}})^\beta]$ for $\Phi(t/\tau_{\mathrm{EM}})$ and found that the stretch exponent β has the temperature-independent value of 0.40. Instead of working with the numerical values of the Fourier transform of the stretched exponential for $M^*(\omega)$, which is inconvenient, they used the approximate expression

$$M^*(\omega)/M_\infty = i\omega/[\sigma^*_{\mathrm{EM,ion}}(\omega)/\varepsilon_0\varepsilon_\infty + i\omega], \tag{34}$$

which results from Eqs. (2) and (19), and approximated $\sigma^*_{\mathrm{EM,ion}}(\omega)$ therein by the analytic form

$$\sigma^*_{\mathrm{EM,ion}}(\omega)=\sigma_{\mathrm{dc}}\{1+[i\omega/(\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty)]^{1-\beta}\}. \tag{35}$$

As far as LLTO is concerned, the approximate expression given by Eq. (35) has proved to fit the experimental data satisfactorily. From the well-known relation of the EM formalism, $\sigma_{\mathrm{dc}}=\varepsilon_0\varepsilon_\infty/\langle\tau_{\mathrm{EM}}\rangle$, where $\langle\tau_{\mathrm{EM}}\rangle=\int_0^\infty\Phi(t/\tau_{\mathrm{EM}})dt$, one rewrites Eq. (35) as

$$\sigma^*_{\mathrm{EM,ion}}(\omega)=\sigma_{\mathrm{dc}}\{1+[i\omega\langle\tau_{\mathrm{EM}}\rangle]^{1-\beta}\}. \tag{36}$$

By partial integration of Eq. (4), the Fourier transform of $\Phi(t)$ is

$$\tilde{\Phi}_{\mathrm{EM}}(\omega)=\varepsilon_\infty M^*(\omega)/i\omega. \tag{37}$$

Substituting Eq. (34) into Eq. (37), León *et al.* arrived at the result,

$$\tilde{\Phi}_{\mathrm{EM}}(\omega)=1/[\sigma^*_{\mathrm{EM,ion}}(\omega)/\varepsilon_0\varepsilon_\infty+i\omega]. \tag{38}$$

The same expression can be obtained from Eq. (22) given previously. Using the approximation to $\sigma^*_{\mathrm{EM,ion}}(\omega)$ given by either Eq. (35) or (36), $\tilde{\Phi}_{\mathrm{EM}}(\omega)$ can be rewritten as

$$\tilde{\Phi}_{\mathrm{EM}}(\omega)=\frac{1}{(\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty)\{1+[i\omega/(\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty)]^{1-\beta}\}+i\omega}. \tag{39}$$

Since $\tilde{\phi}_{\mathrm{STT}}(\omega)$ and $\tilde{\Phi}_{\mathrm{EM}}(\omega)$ have the same functional form, but differ only in the time scale [i.e., $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})\equiv\Phi(t/\tau_{\mathrm{EM}})$], then we can obtain the former from the latter by scaling all quantities $\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty$ appearing in Eq. (39) (which is $\langle\tau_{\mathrm{EM}}\rangle^{-1}$) by the ratio $\tau_{\mathrm{EM}}/\tau_{\mathrm{STT}}$. According to Eq. (25), this scaling factor is equal to T/T_0, i.e.,

$$\tau_{\mathrm{EM}}(T)/\tau_{\mathrm{STT}}(T)=T/T_0, \tag{40}$$

where

$$T_0\equiv(Nq^2r^2_{\mathrm{rms}})/(6k\varepsilon_0\varepsilon_\infty). \tag{41}$$

After the scaling is performed to obtain $\tilde{\phi}_{\mathrm{SST}}(\omega)$, the spectral density function, Eq. (33), is obtained as

$$J(\omega)=\mathrm{Re}\left[\frac{1}{(\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty)(T/T_0)\{1+[i\omega/(\sigma_{\mathrm{dc}}/\varepsilon_0\varepsilon_\infty)(T/T_0)]^{1-\beta}\}+i\omega}\right]. \tag{42}$$

The parameters of LLTO appearing in Eq. (41) are known. They are $N=2.16\times10^{27}\,\mathrm{m}^{-3}$, $r^2_{\mathrm{rms}}=(3.87\times10^{-10})^2\,\mathrm{m}^2$, and $\varepsilon_0\varepsilon_\infty=7.5\times10^{10}\,\mathrm{F\,m}^{-1}$. The calculated value of T_0 for LLTO is 135 K. León *et al.* used this expression for $J(\omega)$ and Eq. (31) to calculate $T_1^{-1}(\omega_L,T)$ from the macroscopic electrical conductivity relaxation data of LLTO, including σ_{dc}, ε_∞, and the stretch exponent β. There is good agreement between the calculated values and the actual experimental NMR data of LLTO as shown in Fig. 1. This good agreement verifies that $\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})$ and $\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})$, as well as the corresponding $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$ and $\tilde{\Phi}(t/\tau_{\mathrm{EM}})$, are the same function (i.e., having the same β in the stretched exponential functions) of the reduced frequency and reduced time, and τ_{EM} is related to the microscopic τ_{STT} by Eq. (25) in LLTO.

VI. DIFFERENCE BETWEEN LLTO AND IONIC GLASSES

NMR measurements in LLTO by León *et al.*[29] are made in the temperature range from about 170 to 500 K, encompassing the maximum of $T_1^{-1}(\omega_L,T)$. The maximum of $T_1^{-1}(\omega_L,T)$ with $\omega_L=20$ MHz is located at $T_{\mathrm{max}}\approx310$ K. Therefore the ratio T/T_0 is always larger than 1, but no greater than 4 in the entire temperature range. The ratio T_{max}/T_0 is about 2.3. The nuclear spin relaxation correlation time at T_{max}, $\tau_{\mathrm{STT}}(T_{\mathrm{max}})$, customarily is taken to be equal to ω_L because the maximum of $T_1^{-1}(\omega_L,T)$ occurs at a temperature when $\omega_L\tau_{\mathrm{STT}}(T)\approx1$ is satisfied. According to Eq. (40) we have the relation

$$\tau_{\mathrm{EM}}(T_{\mathrm{max}})/\tau_{\mathrm{STT}}(T_{\mathrm{max}})=T_{\mathrm{max}}/T_0, \tag{43}$$

which indicates that, at T_{max}, the NSR time, $\tau_{\mathrm{STT}}(T_{\mathrm{max}})$, is *shorter* than the conductivity relaxation time $\tau_{\mathrm{EM}}(T_{\mathrm{max}})$. Although $\tau_{\mathrm{STT}}(T_{\mathrm{max}})$ is only a factor of 2.3 shorter than $\tau_{\mathrm{EM}}(T_{\mathrm{max}})$ and may be considered to be practically equal to each other, their relation to each other is to be contrasted with a very different one found in several ionic glasses.[23–25]

The experimental data on ionic glasses[23–25,35,36] show that

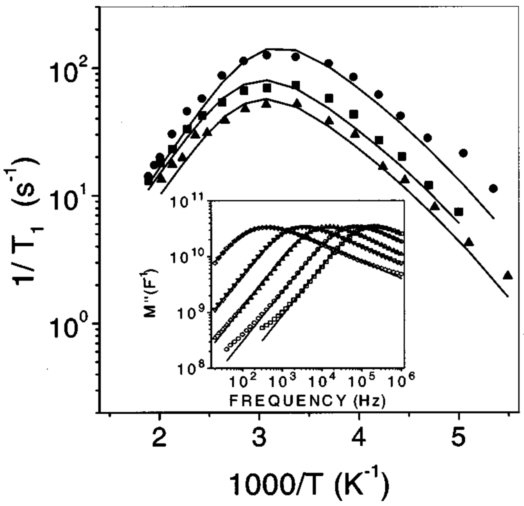

FIG. 1. Temperature dependence of $1/T_1$ at 10.6 MHz (●), 20 MHz (■), and 31 MHz (▲). Solid lines are theoretical values for $1/T_1$ obtained from the experimental electrical conductivity relaxation data at the same frequencies. The inset shows the imaginary part of the electric modulus at several temperatures (179, 193, 206, 221, and 235 K). Solid lines in the inset are fits to a stretched exponential function for the electric modulus relaxation function $\Phi_{\mathrm{EM}}(t/\tau_{\mathrm{EM}})$.

the spin-lattice relaxation time $\tau_s(T_{\max})$ is several orders of magnitude *longer* than $\tau_{\mathrm{EM}}(T_{\max})$. For example, in the glassy fast ion conductor $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$, the ratio $\tau_{\mathrm{EM}}(T_{\max})/\tau_s(T_{\max})$ is about 5×10^{-3} at $\omega_L=4$ MHz. Based on the finding that $[\tau_{\mathrm{EM}}(T_{\max})/\tau_s(T_{\max})]\approx2.3$ for LLTO and the non-Arrhenius temperature dependence of its dc conductivity, León *et al.*[29] suggest that the assumption of an Arrhenius law for the temperature dependence of the dc conductivity of ionic glasses may not be true and it contributes to the large but apparent discrepancy between the two times. All data of $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ cited were taken within the glassy state. It is possible that at the higher temperature $T_{\max}$ of NMR measurement the extrapolated value of $\tau_{\mathrm{EM}}(T_{\max})$ by the Arrhenius law has the order of 10^{-10} s and will exhibit a slight departure from the Arrhenius dependence as seen in some other,[54–56] though not all, glassy fast ion conductors.[57] However, if the behavior of the dc conductivity of $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ is similar to others, the departure at $\tau_{\mathrm{EM}}(T_{\max})\approx10^{-10}$ s is slight and cannot explain the two orders of magnitude difference between $\tau_{\mathrm{STT}}(T_{\max})$ and $\tau_{\mathrm{EM}}(T_{\max})$. Moreover, the same result that $\tau_{\mathrm{STT}}(T_{\max})\gg\tau_{\mathrm{EM}}(T_{\max})$ was found[24] in heavy metal flurozirconate glasses using nuclear spin relaxation in the rotating frame at a much lower frequency. In this case, the measurement of $T_{1\rho}^{-1}(\omega_L,T)$ was at $\omega_L=25$ kHz and in a temperature range in the glassy state where the temperature dependences of τ_{STT} and τ_{EM} undoubtedly have the Arrhenius form. Hence we conclude that the interesting suggestion of León *et al.* cannot be an explanation of the effect found in glassy ionic conductors. From the relation between $\tau_{\mathrm{STT}}(T_{\max})$ and $\tau_{\mathrm{EM}}(T_{\max})$ given by Eqs. (40) and (41) and granted that N and ε_∞ in the glassy ionic conductors and in LLTO are not too different, there is the possibility that r_{rms}^2 is larger for the former than the latter. The value of r_{rms} in LLTO was estimated from $1/T_2$ measurements to be 3.7 Å, a distance close to that found between the A sites of the perovskite structure (3.8 Å).[29] Nevertheless, r_{rms}^2 in the glassy ionic conductors has to be larger by more than two orders of magnitude than the lattice spacing distance of LLTO in order that this can explain the observed value of the ratio $\tau_{\mathrm{EM}}(T_{\max})/\tau_{\mathrm{STT}}(T_{\max})$. Such a large r_{rms}^2 is unphysical, and this possibility can also be ruled out.

One current explanation of the result that $\tau_{\mathrm{STT}}(T_{\max})\gg\tau_{\mathrm{EM}}(T_{\max})$ is based on the proposal that the correlation functions of nuclear spin relaxation and of electrical conductivity relaxation are different in glassy ionic conductors.[36,44] The structural disorder present in ionic glasses engenders a greater importance to interactions between ions at a shorter separation distance in determining the nuclear spin relaxation correlation function $\exp[-(t/\tau_s)^{1-n_s}]$ than the conductivity relaxation correlation function $\exp[-(t/\tau_{\mathrm{EM}})^{1-n_\sigma}]$. As a consequence of the enhanced correlation between the ions, n_s is larger than n_σ, which indicates that the dispersion of spin relaxation is broader, as confirmed by experiment.[22–25,36] The application of the coupling model[36] explained the various differences in the properties of nuclear spin relaxation and of electrical conductivity relaxation including $[\tau_s(T_{\max})/\tau_{\mathrm{EM}}(T_{\max})]\gg1$. Monte Carlo simulation of the closely related disordered Coulomb lattice gas model[44] arrived at the same conclusions. In retrospect, we should have compared $\phi_s(t/\tau_s)=\exp[-(t/\tau_s)^{1-n_s}]$ with the ion hopping correlation function $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})=\exp[-(t/\tau_{\mathrm{STT}})^{1-n_{\mathrm{STT}}}]$ instead of with $\Phi(t/\tau_{\mathrm{EM}})=\exp[-(t/\tau_{\mathrm{EM}})^{1-n_\sigma}]$. Nonetheless, since n_{STT} is equal to n_{EM} because $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$ and $\Phi(t/\tau_{\mathrm{EM}})$ are the same function of the reduced time and τ_{STT} and τ_{EM} have the same activation energy (see near the end of Sec. III), the conclusions reached in earlier works on ionic glasses[36] remained unchanged. In the future we shall revisit this problem in ionic glasses to compare nuclear spin relaxation with the microscopic conductivity relaxation.

In contrast to ionic glasses, LLTO is crystalline. The distances between ions are fixed by the crystalline lattice, and this eliminates the enhancement of the correlation between ions at shorter separation distances for the nuclear spin relaxation in glasses. Hence $n_s\approx n_\sigma$ for LLTO, and it follows from the theoretical explanation of the difference between nuclear spin relaxation and conductivity relaxation[36] that LLTO is a special case, having effectively no difference between $\tau_s(T_{\max})$ and the microscopic conductivity relaxation time $\tau_{\mathrm{STT}}(T_{\max})$. This prediction is consistent with the finding of León *et al.* in LLTO that $[\tau_s(T_{\max})/\tau_{\mathrm{EM}}(T_{\max})]\approx(1/2.3)$ and $[\tau_{\mathrm{STT}}(T_{\max})/\tau_{\mathrm{EM}}(T_{\max})]=(1/2.3)$. Thus we conclude that the LLTO data of León *et al.* lend further support to the explanation of the difference between nuclear spin relaxation and conductivity relaxation given by Ref. 36.

VII. CONCLUSION

Conductivity relaxation is obtained by a macroscopic measurement, and it is not immediately clear how it is related to the microscopic ion hopping motion. By comparing the results of a stochastic microscopic transport theory of the dynamics of ionic movement with the electric modulus representation of the macroscopic conductivity relaxation data, we have shown that the form of microscopic ion hopping correlation function is faithfully reproduced in the electric modulus formalism. This correspondence between the microscopic description and the electric modulus analysis of the macroscopic measurement of ionic motion indicates that the electric modulus M^* is the most suitable representation of macroscopic data compared with other alternatives, e.g., ε^* and σ^*. However, the macroscopic conductivity relaxation time obtained from the electric modulus analysis of the data differs from the microscopic ion hopping correlation time by a known factor, which is a weakly temperature-dependent factor. Consequently, the two times have practically the same thermal activation energy and other dependences on variables such as the isotope mass of the diffusing ion.

Nuclear spin lattice relaxation and conductivity relaxation data of the crystalline ionic conductor $\mathrm{Li_{0.5}La_{0.5}TiO_3}$ obtained by León *et al.* have been employed here to demonstrate that in this crystalline conductor the nuclear spin relaxation correlation function is in every respect the same as the microscopic ion hopping conductivity correlation function. The latter has been calculated from the macroscopic electrical relaxation data, according to the relation between them established in this work. Thus the nuclear spin relaxation data enable us to verify the relation between the macroscopic conductivity relaxation function and the microscopic ion hopping correlation function, the principal result of this work. The property of crystalline LLTO is distinctly different from ionic glasses. The ionic glasses exhibit a large difference between nuclear spin relaxation and conductivity relaxation. The suggestion that the possibility of a non-Arrhenius temperature dependence of the dc conductivity like that found in LLTO can explain the large difference in ionic glasses is examined and dismissed in view of experimental data. However, the property of LLTO turns out to be a special case, which is consistent with the explanation of the large difference offered previously for ionic glasses.[36]

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APPENDIX

The relations between the microscopic (STT) and macroscopic (EM formalism) descriptions are summarized here as follows:

$$\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})=\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}}), \tag{A1}$$

$$\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})=\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}}), \tag{A2}$$

$$\Phi_{\mathrm{EM}}(t/\tau_{\mathrm{EM}})=\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}}), \tag{A3}$$

$$\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})=(Nq^2/kT)(r^2_{\mathrm{rms}}/6)\,\frac{1}{\tau_{\mathrm{STT}}}\times\left\{\frac{1}{\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}})}-i\omega\tau_{\mathrm{STT}}\right\}, \tag{A4}$$

$$\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})=\varepsilon_0\varepsilon_\infty\frac{1}{\tau_{\mathrm{EM}}}\left\{\frac{1}{\tilde{\Phi}_{\mathrm{EM}}(\omega\tau_{\mathrm{EM}})}-i\omega\tau_{\mathrm{EM}}\right\}, \tag{A5}$$

and

$$\tau_{\mathrm{STT}}/\tau_{\mathrm{EM}}=(Nq^2r^2_{\mathrm{rms}})/(6kT\varepsilon_0\varepsilon_\infty). \tag{A6}$$

In spite of the identities (A1)–(A3) as functions of the reduced frequency and reduced time, the corresponding macroscopic and microscopic quantities differ, in general, as a function of the actual frequency ω or time t. Thus, for example, one cannot identify $\Phi(t)$ with $\phi(t)$. However, one can identify $\Phi_{\mathrm{EM}}(t/\tau_{\mathrm{EM}})$ with $\phi_{\mathrm{STT}}(t/\tau_{\mathrm{STT}})$ as stated by Eq. (A3). According to Eq. (A6), $\varepsilon_\infty/\tau_{\mathrm{EM}}$ is independent of ε_∞. Thus $\sigma^*_{\mathrm{EM,ion}}(\omega\tau_{\mathrm{EM}})$ in Eq. (A5) as a function of the reduced frequency $\omega\tau_{\mathrm{EM}}$ is also independent of ε_∞.

Let us consider two systems having one and the same microscopic dynamics of ionic motion (i.e., all the STT quantities are the same for both systems), but they have two different high-frequency dielectric constants, $\varepsilon_{\infty,1}\neq\varepsilon_{\infty,2}$. In the macroscopic electric modulus descriptions, these two systems $i=1$ and 2 require two separate descriptions. Then, applying Eqs. (A1) to the macroscopic conductivity of the two systems, $\sigma^*_{\mathrm{EM,ion,1}}(\omega\tau_{\mathrm{EM,1}})$ and $\sigma^*_{\mathrm{EM,ion,2}}(\omega\tau_{\mathrm{EM,2}})$, we have

$$\sigma^*_{\mathrm{STT}}(x)=(Nq^2/kT)(r^2_{\mathrm{rms}}/6)\,\frac{1}{\tau_{\mathrm{STT}}}\left\{\frac{1}{\tilde{\phi}_{\mathrm{STT}}(x)}-ix\right\}=\sigma^*_{\mathrm{EM,ion},i}(y_i)=\varepsilon_0\varepsilon_{\infty,i}\frac{1}{\tau_{\mathrm{EM},i}}\left\{\frac{1}{\tilde{\Phi}_{\mathrm{EM},i}(y_i)}-iy_i\right\}, \tag{A7}$$

where $x=\omega\tau_{\mathrm{STT}}$, $y_i=\omega\tau_{\mathrm{EM},i}$, and $i=1,2$. From Eq. (A6) it follows that the factors outside the curly brackets on the extreme right-hand side of Eq. (A7) are independent of the system i because

$$\varepsilon_0\varepsilon_{\infty,1}/\tau_{\mathrm{EM,1}}=\varepsilon_0\varepsilon_{\infty,2}/\tau_{\mathrm{EM,2}}=(Nq^2r^2_{\mathrm{rms}})/(6kT\tau_{\mathrm{STT}}). \tag{A8}$$

Furthermore, from Eq. (A2) we have

$$\tilde{\Phi}_{\mathrm{EM,1}}(\omega\tau_{\mathrm{EM,1}})=\tilde{\Phi}_{\mathrm{EM,2}}(\omega\tau_{\mathrm{EM,2}})=\tilde{\phi}_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}}). \tag{A9}$$

Because $\varepsilon_{\infty,1}\neq\varepsilon_{\infty,2}$, Eq. (A7) implies that the macroscopic relaxation times $\tau_{\mathrm{EM},i}$ of the two systems are different, but from Eq. (A1) we have

$$\sigma^*_{\mathrm{EM,ion,1}}(\omega\tau_{\mathrm{EM,1}})=\sigma^*_{\mathrm{EM,ion,2}}(\omega\tau_{\mathrm{EM,2}})=\sigma^*_{\mathrm{STT}}(\omega\tau_{\mathrm{STT}}). \tag{A10}$$

Equation (A10) being valid means that

$$\sigma^*_{\mathrm{EM,ion,1}}(\omega)\neq\sigma^*_{\mathrm{EM,ion,2}}(\omega). \tag{A11}$$

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