Ionic conduction in solids: Comparing conductivity and modulus representations with regard to scaling properties

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In the literature, the electric modulus representation has been used to provide comparative analysis of the ion transport properties in different ion-conducting materials. In this paper we show that the modulus representation is not a suitable tool for such purposes. Our arguments derive from an examination of the scaling properties of both the ac conductivity $\sigma^*(\nu)$ and the modulus $M^*(\nu)$ which demonstrates how scaling that is inherent in $\sigma^*(\nu)$ is lost in $M^*(\nu)$ by inclusion of the high frequency permittivity $\varepsilon'(\infty)$, the latter quantity being unrelated to ion transport processes. Furthermore, we show how highly regarded shape changes of the modulus that occur with varying ion concentration are merely a manifestation of including $\varepsilon'(\infty)$ in the definition of $M^*(\nu)$. We conclude then that the electric modulus formalism has resulted in misleading interpretations of the ion dynamics and, hence, should be discouraged.

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I. INTRODUCTION

For several decades now, researchers have striven to understand the dynamics of the mobile ions in solid ion conductors by interpreting the frequency-dependent features in their electric and dielectric response. These materials share common features such as (1) disordered arrangements of the mobile ions within an otherwise rigid matrix, and (2) thermally activated hopping processes of the mobile ions, giving rise to a dc conduction. Highly conducting solid electrolytes include structurally disordered ionic crystals such as α-$RbAg_4I_5$ and the β-aluminas as well as inorganic ionic glasses.

A remarkable feature of these materials is that their response to an applied electric field as described by an ac conductivity $\sigma'(\nu)$ is very similar.[1] At low frequencies, random diffusion of the ionic charge carriers via activated hopping gives rise to a frequency-independent conductivity. At higher frequencies, however, $\sigma'(\nu)$ exhibits dispersion, increasing roughly in a power-law fashion and eventually becoming almost linear at even higher frequencies. Interestingly, polaronic conductors, both crystalline and glassy, display a behavior that is quite similar to the ionic ones. The physical origins are not yet completely understood, but the dispersion clearly reflects a nonrandom or correlated kind of motion of the ions occurring on relatively short time scales.

Dielectric spectroscopy has been traditionally applied to investigate dipolar relaxation in liquids and solids where reorientation of permanent dipoles gives rise to characteristic frequency-dependent features of the complex permittivity, $\varepsilon^*(\nu)=\varepsilon'(\nu)-i\varepsilon''(\nu)$. In this case, $\varepsilon'(\nu)$ increases with decreasing frequency approaching a limiting value $\varepsilon'(0)$ at low frequencies associated with the polarization resulting from alignment of the dipoles along the direction of the electric field. Concomitantly, the imaginary part $\varepsilon''(\nu)$ passes through a maximum at a frequency which is temperature dependent and whose inverse is commonly associated with the characteristic time required for dipoles to reorient. In the dipolar situation, a dc conductivity is unexpected and when observed usually indicates the presence of impurity ions in the material. This unwanted contribution to the dielectric loss is normally subtracted away in a trivial manner.

For the ion-conducting materials discussed above, one might at first consider a similar subtraction of the dc contribution so as to treat the resulting permittivity as a relaxation process akin to that occurring in the dipolar case. At one level, this appears reasonable, since the mobile ions and the oppositely charged matrix resemble an assembly of dipoles at short times. However, in practice, the polarization is inseparable from the eventual conduction process. The mobile ion, which creates polarization by reorienting locally, is the same ion that later separates from its immediate neighborhood to produce conduction at lower frequencies. In ion-conducting materials polarization and conduction are, therefore, integrated into a single, continuous process.

As a consequence, alternative representations of the dielectric response have been explored in the literature over the past 30 years in attempts to better characterize the ion dynamics in these materials. One prominent representation is the ac conductivity, $\sigma^*(\omega)=i\omega\varepsilon_0\varepsilon^*(\omega)$, which through linear response theory can be related back to fundamental statistical quantities of the ion hopping motions such as the mean squared displacement, $\langle r^2(t)\rangle_{\mathrm{hop}}$.

However, considerably more prominent in the literature is the electric modulus, $M^*(\nu)=1/\varepsilon^*(\nu)$, representation which was developed[2] in 1972. The modulus shares an important analogy with shear stress relaxation measured by mechanical spectroscopy in solids, and in the case of ion-conducting materials, the frequency dependence of $M^*(\nu)$ can be related to a corresponding time-dependent evolution

of the electric field resulting from ion displacements.

Controversy about which of the two representations (if either) provides better insight into the nature of ionic processes in these materials has surfaced and resurfaced over the intervening years. Several researchers have noted discrepancies between interpretations drawn from the two analysis formalisms.[3–5] More recent examinations of the scaling properties of $\sigma^*(\nu)$ and of $M^*(\nu)$ have again shown disturbing differences.[6–8] On the one hand, both $\sigma^*(\nu)$ and $M^*(\nu)$ for a given material exhibit linear scaling as a function of varying temperature (time-temperature superposition principle). This means that spectra of $\sigma^*(\nu)$ or $M^*(\nu)$ measured at various temperatures can be scaled so as to collapse to a single master curve. On the other hand, studies of ion-conducting glasses in which the concentration of the mobile ions is varied by one or two orders of magnitude show pronounced systematic changes in the shape of $M^*(\nu)$ without corresponding changes in the shape of $\sigma^*(\nu)$. This departure between the two formalisms seems paradoxical. Both $\sigma^*(\nu)$ and $M^*(\nu)$ are in principle derived from the same experimental data (i.e., real and imaginary components of the sample impedance). However, as many have recognized, the shape of the modulus is sensitive to $\varepsilon'(\infty)$, the high-frequency limiting permittivity that results from near-instantaneous electronic and atomic polarization which is not directly related to the hopping motion of the mobile ions. This sensitivity has been recognized by Almond and West[3] as early as 1986. Nevertheless, the modulus is still being used and misleading conclusions are still frequently drawn.

In this paper the scaling differences between the conductivity and modulus representations are illustrated in a graphical fashion wherein no model-dependent assumptions are required. This illustration clearly and irrefutably demonstrates how the shape of the electric modulus is corrupted by inclusion of the quantity $\varepsilon'(\infty)$ in its definition. It thus becomes evident that the modulus representation is no suitable tool for a comparative analysis of the ion transport properties of different solid or liquid electrolytes. Therefore, its use for such purposes is strongly discouraged.

II. FEATURES OF THE DIELECTRIC RESPONSE

Typical features of $\sigma'(\nu)$ and $\varepsilon'(\nu)$ are illustrated in Fig. 1. At low frequency the conductivity is a frequency-independent constant $\sigma'(0)$, which arises from a random hopping motion of the ions. This dc conductivity can be interpreted in terms of the Nernst-Einstein relation, $\sigma'(0) = Nq^2D/(VkT)$, where N/V, q, and D denote the number density of the mobile ions, their charge, and their coefficient of self-diffusion, respectively. If the ions perform a random hopping motion with hopping distance x_0 and hopping rate Γ, then D will be given by $x_0^2\Gamma/6$. At higher frequencies, $\sigma'(\nu)$ increases with frequency. Over a limited range which can be roughly characterized by $1<\sigma'(\nu)/\sigma'(0)<100$, the ac conductivity $\sigma'(\nu)$ is reasonably well described by a power law of the form $\sigma'(\nu)=\sigma'(0)(1+(\nu/\nu_0)^n)$, corresponding to correlated ion motion at short times with $\langle r^2(t)\rangle_{\rm hop}\propto t^{1-n}$. At even higher frequencies, the conductivity $\sigma'(\nu)$ merges smoothly to a linear form $\sigma'(\nu)=A\nu$,

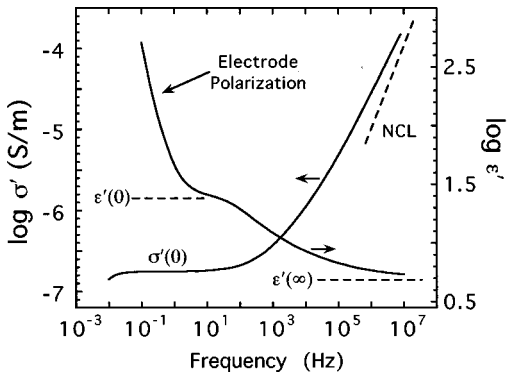

FIG. 1. Characteristic frequency dependence of conductivity and permittivity in ion-conducting materials.

where A is typically about $10^{-12}(\Omega\,\mathrm{m\,Hz})^{-1}$. The origins of this linear regime (the so-called nearly constant loss or NCL regime) are still a subject of debate. While several authors have argued for causes that are unrelated to the ionic motion,[9–12] others have derived models regarding the entire dispersion as resulting from the hopping dynamics of the mobile ions.[13–15]

In the real part of the permittivity (Fig. 1) one observes $\varepsilon'(\nu)$ approach a limiting constant value $\varepsilon'(\infty)$ at high frequencies. This value is unrelated to the hopping dynamics of the mobile ions and instead is the result of much more rapid polarization processes occurring in the material. With decreasing frequency $\varepsilon'(\nu)$ increases and approaches a limiting low frequency plateau $\varepsilon'(0)$ associated with polarization effects of the mobile ions with respect to the immobile matrix. The magnitude of this polarization is then given by $\Delta\varepsilon'=\varepsilon'(0)-\varepsilon'(\infty)$. At even lower frequencies, $\varepsilon'(\nu)$ begins to increase once more. This final increase is substantial and is caused by interfacial phenomena often referred to as electrode polarization. It is the bulk polarization of the sample that results from the presence of metallic or blocking electrodes that do not permit transfer of the mobile ions into the external circuit. Consequently, the mobile ions ''pile up'' near the electrode causing a large bulk polarization of the specimen.

III. ELECTRIC MODULUS FORMALISM

The history of the electric modulus seems to begin with a reference by McCrum, Read, and Williams[16] where the reciprocal complex permittivity is discussed as an electrical analog to the mechanical shear modulus. While McCrum, Read, and Williams used the complex modulus $M^*(\omega)$ to describe the dielectric response of nonconducting materials, Moynihan *et al.*[2] also applied the modulus formalism to materials with nonzero dc conductivities. $M^*(\omega)$ is then simply related to $\sigma^*(\omega)$ via

$$M^*(\omega)=1/\varepsilon^*(\omega)=i\omega\varepsilon_0/\sigma^*(\omega). \tag{1}$$

On the other hand, $M^*(\omega)$ is also related to the function $\Phi(t)$ that describes the decay of an electric field in the material under the constraint of constant dielectric displacement D:

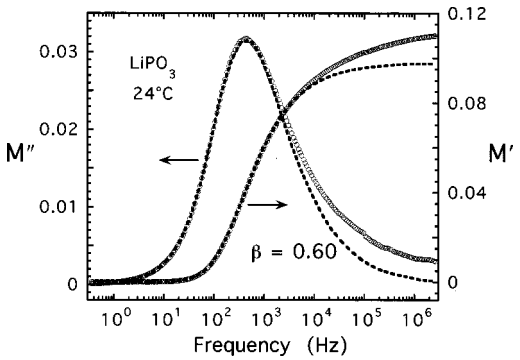

FIG. 2. Real and imaginary parts of the electric modulus for $LiPO_3$ glass at room temperature. The dashed curves are fits of the KWW decay using $\beta=0.60$.

$$M^*(\omega)=M'(\infty)\cdot\left\{1+\int_0^\infty \frac{d\Phi(t)}{dt}\exp(-i\omega t)dt\right\}. \quad (2)$$

Equations (1) and (2) are equivalent to the following Eq. (3),

$$\Phi^*(\omega)=\varepsilon_0\varepsilon'(\infty)/\sigma^*(\omega), \quad (3)$$

where $\Phi^*(\omega)$ denotes the Fourier transform of $\Phi(t)$, i.e.,

$$\Phi^*(\omega)=\int_0^\infty \Phi(t)\exp(-i\omega t)dt. \quad (4)$$

It has long been realized that the stretched exponential KWW (Kohlrausch-Williams-Watts) function,

$$\Phi(t)=\exp(-(t/\tau^*)^\beta), \quad (5)$$

provides a reasonable fit to typical experimental data.[17]

An example of $M^*(\nu)=M'(\nu)+iM''(\nu)$ is shown in Fig. 2 for $LiPO_3$ glass. Typical features include a broad, asymmetric peaked function of ν for $M''(\nu)$ whose frequency at maximum ν_m varies in proportion to the dc conductivity. The real part $M'(\nu)$ exhibits a sigmoidal shape that increases with increasing frequency and approaches $1/\varepsilon'(\infty)$ in the high-frequency limit. Also shown in the figure is a typical fit of the data which emphasizes the frequency range near the peak in $M''(\nu)$ as advocated by Moynihan.[18] While fits of the KWW function are generally successful for frequencies below about $10\nu_m$, the fit quite often underestimates the data at higher frequencies. The rare exception seems to be in materials of ultra low ion concentration where $M''(\nu)$ is nearly symmetrical and where fits with $\beta=1$ are successful over nearly the entire observable frequency range. Proponents of the KWW description argue that this failure at high frequencies is merely an artifact of the data that arises from the presence of the NCL behavior. If the NCL is a separate phenomenon from that of the ionic motion, then it may dominate the data in the high frequency regime and artificially ''lift'' the measured data above the fit.

For a realistic assessment of the modulus formalism it is important to realize that it is based on a description of the electric response of the sample in terms of the macroscopic field-decay function $\Phi(t)$. Empirically, the KWW function is a convenient choice for $\Phi(t)$, and the nonexponentiality parameter β is suitably varied for fitting the data. However, this procedure does not provide a conceptual link for bridging the gap from the macroscopic experimental results to time-dependent functions that characterize the ion hopping dynamics such as, e.g., the mean squared displacement $\langle r^2(t)\rangle_{\rm hop}$.

IV. LINEAR RESPONSE THEORY AND COMPLEX CONDUCTIVITY

In contrast to the modulus approach, which relates $M^*(\omega)$ to the (macroscopic) electric-field-decay function $\Phi(t)$, linear response theory relates $\sigma^*(\omega)$ to functions of time that reflect characteristic properties of the hopping dynamics of the ions. To derive these functions from the experimental data and to extract the information contained in them, one first has to realize that there are two distinctly different contributions to $\sigma^*(\omega)$. One of them, $\sigma^*_{\rm hop}(\omega)$, is entirely due to the hopping motion, while the other, $i\omega\varepsilon_0\varepsilon'(\infty)$, is caused by much faster polarization processes:

$$\sigma^*(\omega)=\sigma^*_{\rm hop}(\omega)+i\omega\varepsilon_0\varepsilon'(\infty). \quad (6)$$

According to linear response theory,[19] $\sigma^*_{\rm hop}(\omega)$ is proportional to the Fourier transform of the autocorrelation function of the current density caused by the hopping motion of the mobile ions, $\langle \mathbf{J}(0)\mathbf{J}(t)\rangle_{\rm hop}$:

$$\sigma^*_{\rm hop}(\omega)=\frac{V}{3kT}\int_0^\infty \langle \mathbf{J}(0)\mathbf{J}(t)\rangle_{\rm hop}\exp(-i\omega t)dt. \quad (7)$$

Here, V denotes the volume of the sample. If there are N mobile ions with charge q and if their velocities at time t are denoted by $\mathbf{v}_{i,\rm hop}(t)$, then the current density and its autocorrelation function will be, respectively,

$$\mathbf{J}_{\rm hop}(t)=\frac{1}{V}\sum_{i=1}^{N} q\mathbf{v}_{i,\rm hop}(t) \quad \text{and}$$

$$\langle \mathbf{J}(0)\mathbf{J}(t)\rangle_{\rm hop}=\frac{q^2}{V^2}\sum_{i,j}^{1,\ldots,N}\langle \mathbf{v}_i(0)\mathbf{v}_j(t)\rangle_{\rm hop}. \quad (8)$$

Therefore, $\sigma^*_{\rm hop}(\omega)$ becomes

$$\sigma^*_{\rm hop}(\omega)=\frac{q^2}{3VkT}\int_0^\infty \sum_{i,j}^{1,\ldots,N}\langle \mathbf{v}_i(0)\mathbf{v}_j(t)\rangle_{\rm hop}\exp(-i\omega t)dt. \quad (9)$$

It is now important to note that on the time scale of the experiment, i.e., at times $1/\omega$, the duration of an individual hop is very short and a hop may, hence, be considered instantaneous. As a consequence, the expressions $\langle \mathbf{v}_i(0)\mathbf{v}_j(t)\rangle_{\rm hop}$ are nonzero only, if hops occur at time 0 and at time t as well. If the hopping is *random*, then each hop will be correlated only with itself. In this case, all the cross terms ($i\neq j$) will vanish, and the self-terms ($i=j$) will be close to δ-functions with weight $\Gamma x_0^2/2$. Again, Γ and x_0 denote the hopping rate and the hopping distance, respectively. According to Eq. (9) a random hopping would, therefore, result in $\sigma^*_{\rm hop}(\omega)=$constant. As this is not observed,

except at low frequencies, there must be a correlation between a hop performed by a mobile ion at time 0 and later hops of this ion and/or other ions. As $\sigma^*_{\rm hop}(\omega)$ is an increasing function of angular frequency, the sum $\Sigma_{i,j}^{1,\ldots,N}\langle \mathbf{v}_i(0)\mathbf{v}_j(t)\rangle_{\rm hop}$ must, in addition to its sharp maximum at $t=0$, have a pronounced negative tail, reflecting the frequent occurrence of ensuing hops whose direction is opposite to the one at $t=0$.

A further important result has been obtained from Monte Carlo simulations,[20] viz., the essential terms in the sum $\Sigma_{i,j}^{1\ldots N}\langle \mathbf{v}_i(0)\mathbf{v}_j(t)\rangle_{\rm hop}$ are, indeed, the self-terms. This immediately implies that correlated back-and-forth hopping of individual mobile ions is a frequent phenomenon in ion-conducting materials. Neglecting the cross terms we arrive at an expression for the hopping-conductivity spectrum $\sigma^*_{\rm hop}(\omega)$, which relates it to the velocity autocorrelation function of the hopping ions, $\langle \mathbf{v}(0)\mathbf{v}(t)\rangle_{\rm hop}$:

$$\sigma^*_{\rm hop}(\omega)=\frac{Nq^2}{3VkT}\int_0^\infty \langle \mathbf{v}(0)\mathbf{v}(t)\rangle_{\rm hop}\exp(-i\omega t)dt. \quad (10)$$

Alternatively, $\sigma^*_{\rm hop}(\omega)$ may now also be expressed in terms of the mean squared displacement, $\langle r^2(t)\rangle_{\rm hop}=\langle(\mathbf{r}(t)-\mathbf{r}(0))^2\rangle_{\rm hop}$. This is possible because of the identity

$$\frac{d^2}{dt^2}\langle(\mathbf{r}(t)-\mathbf{r}(0))^2\rangle_{\rm hop}=2\langle \mathbf{v}(0)\mathbf{v}(t)\rangle_{\rm hop}. \quad (11)$$

Equation (10) hence transforms into

$$\sigma^*_{\rm hop}(\omega)=-\omega^2\frac{Nq^2}{6VkT}\lim_{\varepsilon\to+0}\int_0^\infty \langle r^2(t)\rangle_{\rm hop}\exp(-i\omega t-\varepsilon t)dt. \quad (12)$$

Equation (12) conveys an important message. The shape of the function $\langle r^2(t)\rangle_{\rm hop}$ is uniquely determined as soon as the hopping-conductivity spectrum $\sigma^*_{\rm hop}(\omega)$ is known from experiment. Moreover, if the shape of $\sigma^*_{\rm hop}(\omega)$ turns out to be preserved when parameters such as temperature and composition are changed, then this will imply that the shape of $\langle r^2(t)\rangle_{\rm hop}$ is preserved as well. In other words, any scaling properties that experimental spectra $\sigma^*_{\rm hop}(\omega)$ might display will prove the existence of corresponding scaling properties of the mean squared displacement. Clearly, any observation of such scaling is bound to impact strongly on the assessment of models describing the hopping dynamics of the mobile ions.

V. SCALING PROPERTIES

For many ion-conducting materials, the conductivity spectra as measured at frequencies below a few MHz are found to follow the time-temperature superposition principle. That means that the shapes of the real and imaginary parts of $\sigma^*_{\rm hop}(\omega)=\sigma^*(\omega)-i\omega\varepsilon_0\varepsilon'(\infty)$ do not depend on temperature. This can be expressed by the following scaling law:

$$\frac{\sigma^*_{\rm hop}(\nu)}{\sigma'(0)}=F^*\left(\frac{\nu}{\nu_0}\right). \quad (13)$$

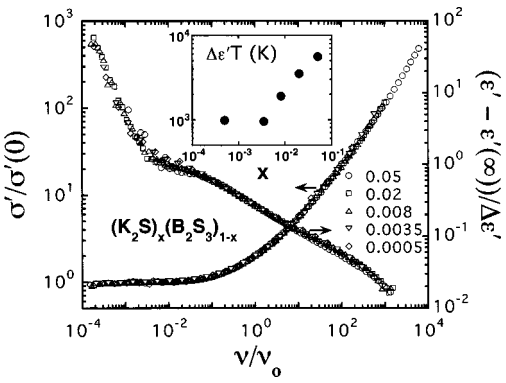

FIG. 3. The master curves [see Eq. (14) and Eq. (15)] of five potassium thioborate glasses (Ref. 26) of substantially differing ion concentration plotted together to demonstrate the common scaling. Inset shows how $\Delta\varepsilon' T$ decreases with decreasing ion concentration.

As shown by Sidebottom[21] and by Schroder and Dyre,[22] an appropriate choice for the scaling factor ν_0 is $\nu_0=\sigma'(0)/(\varepsilon_0\Delta\varepsilon')$. This leads to the following scaling laws, respectively, for the real part of the conductivity:

$$\frac{\sigma'(\nu)}{\sigma'(0)}=F'\left(\frac{\nu}{\nu_0}\right), \quad (14)$$

and for the real part of the dielectric function:

$$\frac{\varepsilon'(\nu)-\varepsilon'(\infty)}{\Delta\varepsilon'}=G'\left(\frac{\nu}{\nu_0}\right), \quad (15)$$

with

$$G'(x)=\frac{1}{\pi^2}\mathrm{P}\int_0^\infty \frac{F'(\tilde{x})}{\tilde{x}^2-x^2}d\tilde{x}. \quad (16)$$

Here, P denotes the principle value of the integral. Equation (16) is obtained by inserting Eq. (14) into the Kramers-Kronig relation

$$\varepsilon'(\nu)-\varepsilon'(\infty)=\frac{1}{\varepsilon_0\pi^2}\mathrm{P}\int_0^\infty \frac{\sigma'(\tilde{\nu})}{\tilde{\nu}^2-\nu^2}d\tilde{\nu}. \quad (17)$$

The scaling laws, Eqs. (14) and (15), can be used to generate master curves of $\sigma'(\nu)$ and $\varepsilon'(\nu)-\varepsilon'(\infty)$.

It has been found that the master curves of different materials have very similar shapes.[1,6,21,23–25] As an example, spectra for $(K_2S)_x(B_2S_3)_{1-x}$ glasses obtained by Patel and Martin[26] are shown in Fig. 3. These spectra are scaled in accordance with Eqs. (14) and (15) for a range of ion concentrations spanning about two orders of magnitude. The conductivity isotherms of a given glass superimpose onto a master curve, and the individual master curves of the glasses cannot be distinguished within the experimental error.

Let us now consider the scaling properties of $M''(\nu)$ spectra. For a given material, $M''(\nu)$ isotherms can usually be collapsed onto a master curve. However, when the $M''(\nu)$ master curves of different materials are compared, significant differences in shape are observed. In materials with high

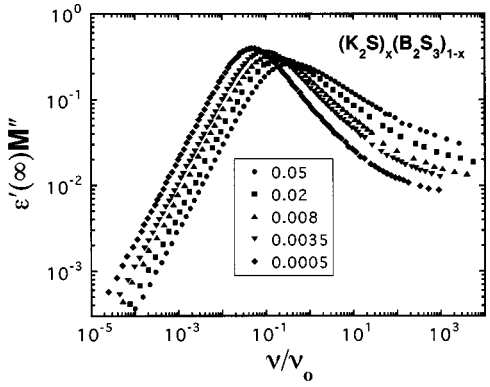

FIG. 4. Master curves of the electric modulus isotherms of the five potassium thioborate glasses shown in the previous figure plotted together to demonstrate the substantial narrowing of the modulus with decreasing ion concentration.

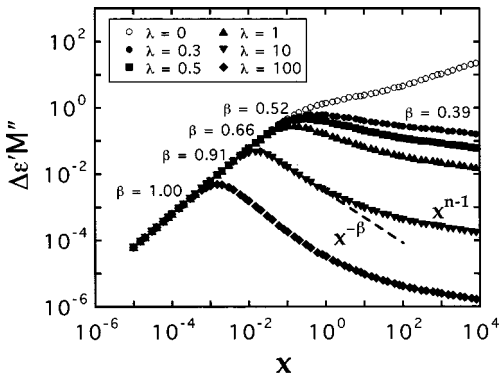

FIG. 6. A demonstration of how retention of $\varepsilon'(\infty)$ in the electric modulus results in a sensitive dependence of its shape upon the ratio $\lambda=\varepsilon'(\infty)/\Delta\varepsilon'$. Increasing λ results in narrowing of the modulus with a concomitant increase of the KWW parameter to unity.

number densities of mobile ions ($N/V\approx 10^{22}\,\mathrm{cm}^{-3}$), the $M''(\nu)$ master curves are considerably broader than a Debye peak. However, with decreasing number density of mobile ions, $M''(\nu)$ narrows and eventually becomes a Debye peak at low number densities.[27–30] This narrowing has often been interpreted in terms of changes in the ion transport mechanism with changing ionic concentrations. As an example, Fig. 4 shows the $M''(\nu)$ master curves of the $(K_2S)_x(B_2S_3)_{1-x}$ glasses. Clearly, the individual master curves do not superimpose, in contrast to the corresponding $\sigma'(\nu)$ and $\varepsilon'(\nu)-\varepsilon'(\infty)$ master curves.

We will now show that the narrowing of $M''(\nu)$ with decreasing ion concentration is not caused by changes in the mechanism of ion transport, but is a trivial effect caused by the influence of $\varepsilon'(\infty)$ on the shape of the $M''(\nu)$ spectra. To do this, we define a quantity $M''_{\mathrm{hop}}(\nu)=1/[\varepsilon^*(\nu)-\varepsilon'(\infty)]$, i.e., a modulus containing only contributions from the hopping motion of the mobile ions. As seen from Fig. 5, the individual $M''_{\mathrm{hop}}(\nu)$ master curves of the $(K_2S)_x(B_2S_3)_{1-x}$ glasses *can* be scaled onto a common master curve simply by using $\Delta\varepsilon'$ as scaling parameter for the $M''_{\mathrm{hop}}(\nu)$ axis. Note

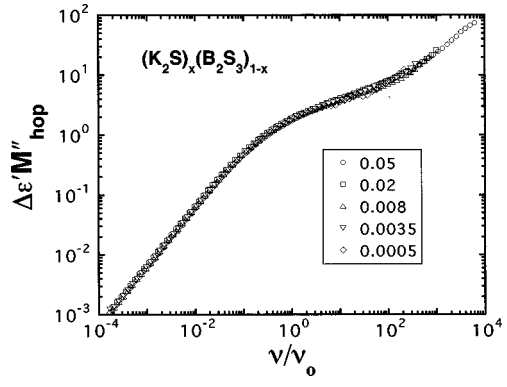

FIG. 5. Master curves of $M''_{\mathrm{hop}}(\nu)$ for the five potassium thioborate glasses plotted together to show how removal of $\varepsilon'(\infty)$ produces common scaling despite substantial changes in ion concentration. Note that unlike $M''(\nu)$ (see Fig. 4), $M''_{\mathrm{hop}}(\nu)$ does not exhibit a peak.

that in contrast to the $M''(\nu)$ master curves, the $M''_{\mathrm{hop}}(\nu)$ master curves do not exhibit a peak. Thus, it is $\varepsilon'(\infty)$ which produces the pronounced folding of $M''_{\mathrm{hop}}(\nu)$ into the peaked shape characteristic of $M''(\nu)$.

However, $\varepsilon'(\infty)$ is not significantly concentration dependent. So why does the shape of $M''(\nu)$ vary systematically with changes in ion concentration? To answer this question we need only form the modulus according to Eq. (1), using the functions $\sigma'(\nu)$ and $\varepsilon'(\nu)$ as described by Eqs. (14) and (15). For the quantity $M''_{\mathrm{hop}}(\nu)$ we find

$$M''_{\mathrm{hop}}(\nu)=\frac{1}{\Delta\varepsilon'}\frac{F'(x)/(2\pi x)}{(G'(x))^2+(F'(x)/(2\pi x))^2}$$

$$=\frac{1}{\Delta\varepsilon'}H(x);x=\nu/\nu_0, \tag{18}$$

which, as was demonstrated in Fig. 5, collapses to a master curve. For the imaginary part of the modulus we find

$$M''(\nu)=\frac{1}{\Delta\varepsilon'}\frac{F'(x)/(2\pi x)}{(\lambda+G'(x))^2+(F'(x)/(2\pi x))^2}, \tag{19}$$

where $\lambda=\varepsilon'(\infty)/\Delta\varepsilon'$. From Eqs. (18) and (19) it becomes apparent that the retention of $\varepsilon'(\infty)$ has destroyed the inherent scaling. In Eq. (19), $\varepsilon'(\infty)$ is introduced in the form of a ratio of $\varepsilon'(\infty)$ (not caused by ion hopping) to $\Delta\varepsilon'$ (caused by ion hopping) that is irreducible in the sense that λ cannot be extracted as a scale factor.

To see how the presence of λ influences the shape of $M''(\nu)$, we use the experimental master curves $F'(\nu/\nu_0)$ and $G'(\nu/\nu_0)$ obtained in Fig. 3, and from Eq. (19) we simply compute $M''(\lambda,\nu)$ for a variety of possible values of λ. The result presented in Fig. 6 shows that $M''(\lambda,\nu)$ exhibits a peak (as a function of ν) only for non-zero values of λ. In this case, $M''(\lambda,\nu)$ may be characterized by three distinct regions of frequency-dependent behavior. At low frequencies, $M''(\lambda,\nu)$ is linear. At high frequencies, $M''(\lambda,\nu)$ varies

like $\sigma'(\nu)/\nu$, i.e., the function is approximately proportional to ν^{n-1} and approaches a constant value at still higher frequencies. It is in the intermediate frequency range just above ν_m where $M''(\lambda,\nu)$ displays a dependence upon λ. Here, the folding of $M''(\lambda,\nu)$ becomes more and more acute for increasing λ. This intermediate frequency range is also that which is emphasized in fitting the KWW decay function. To demonstrate how changes in λ modify this fit, we have included approximate values of β obtained by fitting the KWW function to the spectra in Fig. 6. For $\lambda > 100$, we find a nearly Debye-type form for $M''(\lambda,\nu)$. As is evident from the figure, these fits of the KWW decay function are destined to underestimate the experimental data at high frequencies regardless of issues about the NCL contribution. Furthermore, the inequality of β and $1-n$ as metrics of the dispersion has profound ramifications for how dielectric studies of ion dynamics are to be compared with those of alternative methods, e.g., nuclear magnetic resonance.[31]

VI. DISCUSSION

We are now in a position to offer an interpretation of the experimentally observed narrowing of $M''(\nu)$ which occurs when the ion concentration is drastically reduced (say by orders of magnitude). This narrowing is a consequence of $\Delta\varepsilon'$ present in the denominator of λ. Since $\Delta\varepsilon'$ is due to ion hopping, it is related to the number density of hopping ions. Roling *et al.*, for example, have demonstrated that $\Delta\varepsilon'$ is proportional to $(N/V)^{1/3}$ at very low ion concentrations.[32] So, even if $\varepsilon'(\infty)$ is virtually concentration independent, decreases in $\Delta\varepsilon'$ with decreasing ion concentration will increase λ and produce the observed narrowing in $M''(\nu)$. The narrowing in $M''(\nu)$ is, technically speaking, due to decreasing concentrations of the mobile ions. However, this narrowing is clearly not a reflection of any intrinsic change in the ion transport mechanism, since in the $\sigma'(\nu)$ and $\varepsilon'(\nu) - \varepsilon'(\infty)$ representations, master curves are obtained by linear scaling.

In this context, we would like to comment on the following Eq. (20), which has been presented in a recent paper by Ngai and Rendell:[33]

$$\Delta\varepsilon' = \left(\frac{\beta \cdot \Gamma(2/\beta)}{(\Gamma(1/\beta))^2} - 1 \right) \cdot \varepsilon'(\infty). \tag{20}$$

Here, β is the exponent obtained from a KWW fit to $M''(\nu)$ spectra, while Γ denotes the Gamma function. The authors state that $\Delta\varepsilon'$ can be written as a ''product of $\varepsilon'(\infty)$ and a factor whose value is totally determined by the parameter β that characterizes the dispersion of the conductivity relaxation times.'' Furthermore, the authors claim that this expression is in contrast to other expressions for $\Delta\varepsilon'$, as, e.g., proposed by Sidebottom.[21] We would like to emphasize that this claim is based on a misinterpretation of Eq. (20). This equation does, of course, not imply that $\Delta\varepsilon'$ *depends* on $\varepsilon'(\infty)$ and β, but rather this equation only expresses the fact that β is determined by the ratio $\lambda = \varepsilon'(\infty)/\Delta\varepsilon'$, as illustrated in the previous section. $\Delta\varepsilon'$ is a quantity that depends exclusively on the hopping dynamics of the mobile ions, while $\varepsilon'(\infty)$ is unrelated to the ion hopping. Thus, we note once again that β is a quantity that is not exclusively determined by the ion dynamics.

Finally, we wish to comment on a paper recently published by Ngai and Leon.[34] In that paper, the authors claim that the shape of $M''(\nu)$ is ''uniquely determined by the movements of the mobile ions.'' We can now show that this claim is based on a misinterpretation of the following equations used in the paper:

$$\sigma^*_{EM,\mathrm{ion}}(\omega) = \varepsilon_0 \varepsilon'(\infty) \left(\frac{1}{\Phi^*(\omega)} - i\omega \right), \tag{21}$$

$$M^*(\omega) = \frac{1}{\varepsilon'(\infty)} \cdot i\omega \cdot \Phi^*(\omega). \tag{22}$$

Ngai and Leon define $\sigma^*_{EM,\mathrm{ion}}(\omega)$ as the ''conductivity entirely from the motions of the ions.'' Now, Eq. (21) can be rewritten as

$$\Phi^*(\omega) = \frac{\varepsilon_0 \varepsilon'(\infty)}{\sigma^*_{EM,\mathrm{ion}}(\omega) + i\omega\varepsilon_0\varepsilon'(\infty)}. \tag{23}$$

From this equation it is obvious that the shape of $\Phi^*(\omega)$ does not only depend on $\sigma^*_{EM,\mathrm{ion}}(\omega)$ but also on $\varepsilon'(\infty)$. According to Eq. (22), the same applies to $M^*(\omega)$. Any scaling that exists for $\sigma^*_{EM,\mathrm{ion}}(\omega)$ is thus corrupted by the inclusion of $\varepsilon'(\infty)$. Therefore, $\Phi^*(\omega)$ and $M^*(\omega)$ can *of course* not be regarded as functions that only reflect the hopping dynamics of the ions, nor do they scale with such functions by inclusion of any time constants it their arguments.

VII. CONCLUSIONS

We have compared the scaling properties of electrical conductivity and electrical modulus spectra of ion-conducting solids taking the spectra of $(K_2S)_x(B_2S_3)_{1-x}$ glasses as an example. While the shapes of the conductivity spectra are virtually independent of the number densities of the mobile potassium ions, the modulus spectra narrow considerably with decreasing number density. We demonstrate that this narrowing is *not* caused by changes in the ion transport mechanism, but is a consequence of the inclusion of $\varepsilon'(\infty)$ in the definition of the modulus. We define a ''hopping modulus'' $M^*_{\mathrm{hop}}(\nu) = 1/[\varepsilon^*(\nu) - \varepsilon'(\infty)]$, i.e., a modulus containing only contributions from the hopping motion of the mobile ions, and show that the shape of this ''hopping modulus'' is virtually independent of the number density of the mobile ions. Furthermore, we analyze mathematically in what way $\varepsilon'(\infty)$ influences the shape of $M''(\nu)$. Our analyses clearly lead to the conclusion that the modulus representation is no suitable tool for comparing the ion transport properties of different materials.

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