

Scaling parallels in the non-Debye dielectric relaxation of ionic glasses and dipolar supercooled liquids

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(Received 6 May 1996; revised manuscript received 18 February 1997)

We compare the dielectric response of ionic glasses and dipolar liquids near the glass transition. Our work is divided into two parts. In the first section we examine ionic glasses and the two prominent approaches to analyzing the dielectric response. The conductivity of ion-conducting glasses displays a power law dispersion $\sigma(\omega) \propto \omega^n$, where $n \approx 0.67$, but frequently the dielectric response is analyzed using the electrical modulus $M^*(\omega) = 1/\varepsilon^*(\omega)$, where $\varepsilon^*(\omega) = \varepsilon(\omega) - i\sigma(\omega)/\omega$ is the complex permittivity. We reexamine two specific examples where the shape of $M^*(\omega)$ changes in response to changes in (a) temperature and (b) ion concentration, to suggest fundamental changes in ion dynamics are occurring. We show, however, that these changes in the shape of $M^*(\omega)$ occur in the absence of changes in the scaling properties of $\sigma(\omega)$, for which n remains constant. In the second part, we examine the dielectric relaxation found in dipolar liquids, for which $\varepsilon^*(\omega)$ likewise exhibits changes in shape on approach to the glass transition. Guided by similarities of $M^*(\omega)$ in ionic glasses and $\varepsilon^*(\omega)$ in dipolar liquids, we demonstrate that a recent scaling approach proposed by Dixon and co-workers for $\varepsilon^*(\omega)$ of dipolar relaxation also appears valid for $M^*(\omega)$ in the ionic case. While this suggests that the Dixon scaling approach is more universal than previously recognized, we demonstrate how the dielectric response can be scaled in a linear manner using an alternative data representation. [S0163-1829(97)02725-2]

I. INTRODUCTION

A diversity of scientific disciplines endeavor to understand dynamic processes by examining the dielectric response of materials to an applied time-varying electric field. These include chemists and chemical engineers who study electrolytic solutions, solid state physicists interested in electron transport in semiconductors, materials scientists interested in ionic and dipolar relaxation in solids, and biologists concerned with ion transport through cell membranes.¹ In the linear response regime at moderate field strengths, the dielectric response is completely characterized by the permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, a property of the material alone, where the real and imaginary components represent the storage and loss, respectively, of energy during each cycle of the electric field.

Although all study the same quantity, namely, the permittivity, each of these research fields often focuses upon differing materials and differing physical processes, and in many instances, the dynamics of interest are deemed to be better understood by plotting data in one of several alternative, but in principle equivalent, representations. A partial list of representations seen in the literature include the impedance ($Z^* = 1/i\omega\varepsilon^*$), the conductivity ($\sigma^* = i\omega\varepsilon^*$), and the electric modulus^{2,3} ($M^* = 1/\varepsilon^*$). While each scientific discipline has developed its own preferred style for representing data, alternative representations are equally valid and, as we show, may provide new insight into the dynamics at hand.

Ion relaxation in glass is a good example. The choice of data representation has been⁴ and still remains⁵⁻⁷ a testy subject between those preferring the electric modulus and those preferring the conductivity. Proponents of the modulus approach interpret the broad, asymmetric Gaussian-like shape

of $M^*(\omega)$ as indicative of a nonexponential decay of the electric field in response to an applied displacement field.^{2,5} This decay is reasonably well described by a stretched exponential $e^{-(t/\tau)^\beta}$, where the smallness of the exponent β characterizes the degree of non-Debye behavior. This particular decay function is also used to describe dipolar reorientation in supercooled liquids^{8,9} and is found in a variety of other relaxation phenomena in amorphous materials including mechanical, volumetric, nuclear magnetic resonance, and magnetic relaxation.¹⁰

In the conductivity representation,^{6,7,11,12} the conductivity of ion-conducting glasses exhibits a power law at high frequencies that is terminated at lower frequencies by dc conduction,

$$\sigma(\omega) = \sigma_0 + A\omega^n = \sigma_0[1 + (\omega/\omega_0)^n]. \quad (1)$$

This frequency dependence can be interpreted as the result of ion diffusion through the host compounded by ion-ion interactions.¹³⁻¹⁶ The exponent n similarly characterizes the deviation from Debye behavior and can be regarded as a direct measure of the interionic coupling strength.¹⁷⁻¹⁹

Although the exponent β obtained from $M^*(\omega)$ appears to vary from one material to the next, many have shown that $\sigma(\omega)$ exhibits linear scaling, whereby data plotted on a double-logarithmic scale can be shifted vertically (by σ_0) and horizontally (by ω_0) as indicated in Eq. (1) so as to collapse onto a single scaling curve.^{20,21} Furthermore, the scaling curve obtained is remarkably common to a wide variety of ionic materials with $n \approx 0.67 \pm 0.05$ and suggests that the dynamics of ion motion may be universal.²²

Scaling is an important property for any dynamic process to possess as it implies that one may separate the thermodynamics, entering only through the scales themselves, from

the inherent physics involved in the dynamical process which is completely described by a single scaling function. This separation of the scales from some simpler underlying physics has proved to be of great merit in many scientific fields including second-order phase transitions, percolation, and other critical phenomena.²³

In this paper we examine alternative data representations for both ionic glasses and for dipolar liquids. Our paper is divided into two sections. In the first section, we consider ionic glasses. We review the prevailing standard approaches to data analysis and interpretation of ionic relaxation and then examine two special instances where linear scaling occurs in $\sigma(\omega)$, but is *simultaneously* absent in $M(\omega)$. This previously unrecognized scaling mismatch is resolved by using only model-free general considerations to demonstrate how scales in $\sigma(\omega)$ are incorporated into $M(\omega)$ in an irreducible manner when data are transformed. The importance of these findings is that, in both instances, even the most fundamental notions about ion dynamics drawn from the σ representation are essentially *reversed* from those previously drawn from considerations of $M(\omega)$ alone.

In the second section, we consider the dielectric response of dipolar liquids. We again review prevailing data analysis methods and draw particular attention to numerous similarities with those methods used for ionic glasses. We demonstrate that a scaling approach proposed by Dixon^{8,24} to collapse $\varepsilon''(\omega)$ data for dipolar liquids can also be successfully applied to collapse $M''(\omega)$ of an ionic glass. Guided by the scaling mismatch we observed in the ionic case, we provide evidence that an alternative data representation exists where simple linear scaling prevails.

Throughout the paper, we endeavor to keep our arguments as rudimentary as possible by avoiding the use of any specific model or theory. While these results at present apply only to the ionic glasses and dipolar liquids we have investigated, there is a generic flavor about our findings which suggests straightforward extensions could be made to relaxation phenomena found in other fields.

II. IONIC GLASSES

The dielectric response of ionic glassformers is dominated by the diffusion of cations through the glass matrix. At low frequencies, the random diffusion of these cations results in a dc conductivity $\sigma(\omega) = \omega\varepsilon''(\omega) = \sigma_0$ [i.e., $\varepsilon''(\omega) \propto \omega^{-1}$]. At higher frequencies, a power law dispersion is observed [see Eq. (1)], $\varepsilon''(\omega) \propto \omega^{n-1}$. Thus the presence of mobile ions results in $\varepsilon''(\omega)$ which varies monotonically with frequency and exhibits no peak corresponding to the one seen in dipolar relaxation.

An additional consequence of free charge carriers is the artifact of electrode polarization,² which occurs when ions, unable to exchange with typical metal electrodes, pile up near the interface, resulting in substantial rises in $\varepsilon'(\omega)$ at low frequencies. In the 1970s, many researchers opted to study the dielectric response caused by ion relaxation using the reciprocal quantity $M^*(\omega) = 1/\varepsilon^*(\omega)$, known as the electrical modulus,^{2,3} in which the electrode polarization artifacts are suppressed. Typical features of $M^*(\omega)$ include a broad, asymmetric peak in the imaginary part and a sigmoidal step in the real part. The similarity of these shapes to loss

and storage of mechanical stress associated with relaxation processes is evident and has naturally led to similar interpretations. Since the breadth of $M''(\omega)$ is typically greater than 1.14 decades (characteristic of a Debye or single exponential decay), the shape of $M^*(\omega)$ is commonly associated with a nonexponential time-dependent process. By far, the most common choice is the stretched exponential decay function

$$\phi(t) = \exp\{-(t/\tau)^\beta\}, \quad (2)$$

related to $M^*(\omega)$ as³

$$M^*(\omega) = \frac{1}{\varepsilon_\infty} \left\{ 1 - L \left(- \frac{d\phi}{dt} \right) \right\},$$

where $L(x)$ is the Laplace transform of x . The stretching parameter β is approximately equal to $1/W$, where W is the full width at half maximum (FWHM) of $M''(\omega)$ normalized to that (1.14 decades) of a Debye process. Although the stretched exponential decay function is suitable for describing much of $M^*(\omega)$, from low frequency up to just past the maximum in $M''(\omega)$, it nearly always underestimates the measured data at high frequencies.

Based upon consideration of the high-frequency limiting variations of the fit given by Eq. (2) and of the data, the relation $n = 1 - \beta$ has often served to bridge the analysis of $M''(\omega)$ with that of the power law seen in $\sigma(\omega)$. However, this relationship is not strictly valid²⁵ since in reality the fit of Eq. (1) fails to account for the data at high frequencies. The conductivity scaling exponent n is sometimes referred to as the ‘‘coupling parameter’’ in reference to a popular coupling model¹⁷⁻¹⁹ for non-Debye dynamics. In the instance of ionic relaxation, this model proposes that interionic interactions (coupling) are responsible for the non-Debye response. A situation of $n = 1$ corresponds to maximum coupling strength and would be reflected in $M^*(\omega)$ by an extremely broad ($\beta = 0$) decay, while no coupling ($n = 0$) would yield a Debye relaxation ($\beta = 1$).

In the following we reexamine two special cases: one an ionic glass in the melt above T_g where the modulus shows substantial broadening with increasing temperature and the other a concentration study of alkali-thioborate glasses conducted by Patel and Martin²⁶⁻²⁸ where the modulus exhibits substantial narrowing with decreasing ion concentration. Although both situations appear to suggest that linear scaling is not present, we demonstrate that simple linear scaling is in fact maintained in the conductivity representation of these data.

A. CKN

Measurements on ionic glass formers extending through the glass transition are scarce,²⁹⁻³¹ but indications are that while the shape of $M''(\omega)$ is constant below T_g , it broadens appreciably with increasing temperature above T_g . Consequently, $M''(\omega)$ spectra can be adjusted or ‘‘scaled’’ so as to collapse onto a common curve for temperatures below T_g , but cannot be similarly collapsed above T_g .³² This behavior was nicely demonstrated by the temperature dependence of the electrical modulus of the fragile glass former $0.4\text{Ca}(\text{NO}_3)_2\text{-}0.6\text{KNO}_3$ (CKN) measured by Howell, Bose, Macedo, and Moynihan²⁹ (HBMM). They observed that the

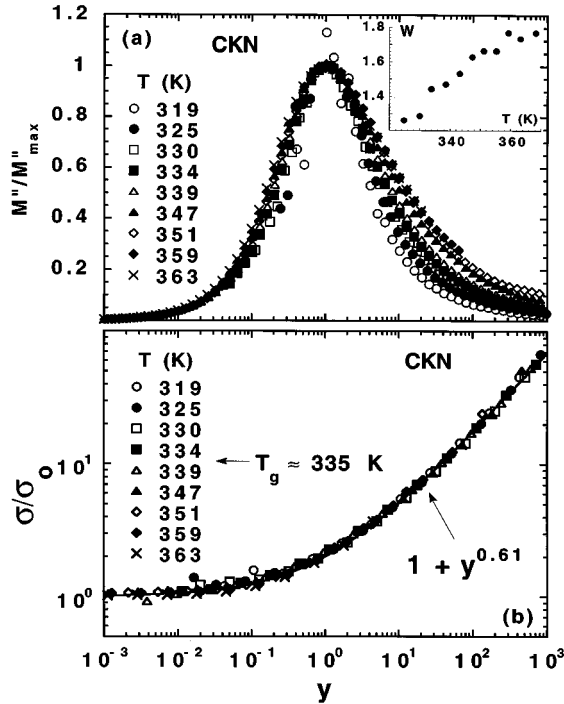


FIG. 1. (a) $M''(\omega)$ of CKN reduced so that peaks coincide showing the failure of scaling. The inset shows how the width of $M''(\omega)$ (normalized to that of a Debye relaxation) narrows with decreasing temperature. (b) $\sigma(\omega)$ of CKN reduced according to Eq. (1). Both above and below T_g , the data collapse upon a common power law with $n=0.61 \pm 0.03$.

shape of $M''(\omega)$ was temperature independent below T_g and hence β was constant. Upon increasing temperature above T_g , $M''(\omega)$ broadened and β steadily decreased, suggesting an increase in the non-Debye behavior. This particular behavior seems to be unique to electrical relaxation, since all other relaxation processes (e.g., mechanical, light scattering) typically exhibit opposite behavior with a tendency toward Debye behavior with increasing temperature.³²

In an effort to understand the puzzling temperature dependence seen in CKN, we have repeated these measurements with an emphasis upon the conductivity. CKN was prepared from reagent-grade materials, dried, and melted at about 600 K. At 450 K, a small commercial air variable capacitor ($C_0 \approx 19$ pF) was placed into the melt and the sample cooled to 333 K ($\approx T_g$) where it was annealed in the manner of HBMM. Impedance measurements¹⁵ were performed from 262.6 to 377.8 K at about 5-K intervals roughly every 30 min.

Figures 1(a) and 1(b) show our results for $M''(\omega)$ and $\sigma(\omega)$, respectively. In Fig. 1(a) we have normalized $M''(\omega)$ by its maximum value and adjusted the frequency scale such that the peaks coincide. As can be seen from the figure, it is not possible to reduce the data to a common curve. As observed by HBMM previously, each spectrum systematically broadens with increasing temperature above T_g . In Fig. 1(b), however, we scale $\sigma(\omega)$ according to Eq. (1) over the same temperature range and find a surprisingly different result, namely, that $\sigma(\omega)$ temperatures *can be scaled*, i.e., collapsed to a single curve, well described by a power law with $n=0.61$.

The discrepancy between $M''(\omega)$ and $\sigma(\omega)$ illustrated in Fig. 1 has not to our knowledge been previously recognized in the 20 years since the electrical modulus formalism was introduced and has a profound impact upon our understanding of ion dynamics. The interpretation commonly drawn from $M''(\omega)$ in Fig. 1(a) is that *significant changes* occur in the mechanism of ion motion near T_g . The power law analysis instead indicates that the mechanism of ion motion is actually *unchanged* over the entire temperature range investigated.

To reconcile the discrepancy between $M''(\omega)$ and $\sigma(\omega)$, we consider explicitly how scaling forms for $\sigma(\omega)$ and $\varepsilon'(\omega)$ become incorporated into $M^*(\omega)$. Again, we strive to avoid model-dependent formulations to keep the development as generally valid as possible. Since $\sigma(\omega)$ varies like

$$\sigma = \sigma_0 + A\omega^n, \quad (3)$$

a form for $\varepsilon'(\omega)$ consistent with the Kramers-Kronig relations would be^{22,33}

$$\varepsilon' = \varepsilon_\infty + B\omega^{n-1}, \quad (4)$$

where $B/A = \tan(n\pi/2)$ and ε_∞ is the background contribution to ε' arising from unrelated processes occurring at higher frequencies. If we now rewrite Eq. (3) in the form of a scaling relation

$$\sigma = \sigma_0 [1 + (\omega/\omega_0)^n], \quad (5)$$

then Eq. (4) becomes

$$\varepsilon' = \varepsilon_\infty [1 + \lambda^{-1} \tan(n\pi/2) (\omega/\omega_0)^{n-1}], \quad (6)$$

where

$$\lambda = \frac{\omega_0}{(\sigma_0/\varepsilon_\infty)}. \quad (7)$$

Although these power law forms fail to describe $\varepsilon'(\omega)$ at low frequencies¹⁵ and $\sigma(\omega)$ at high frequencies where the conductivity is dominated by constant loss phenomena,^{11,21} they do provide an accurate description of the experimental data over a range of frequencies of present interest which bracket the peak in $M''(\omega)$. They are particularly successful at describing the high-frequency wing of $M''(\omega)$, where fits by Eq. (2) consistently fail. Starting from Eqs. (5) and (6), one can now express $M^*(\omega)$ in terms of the reduced frequency $y = \omega/\omega_0$ as³³

$$M'(y, \lambda, n) = \frac{1}{\varepsilon_\infty} \frac{\lambda y [\lambda y + \tan(n\pi/2) y^n]}{(1 + y^n)^2 + [\lambda y + \tan(n\pi/2) y^n]^2}, \quad (8a)$$

$$M''(y, \lambda, n) = \frac{1}{\varepsilon_\infty} \frac{\lambda y (1 + y^n)}{(1 + y^n)^2 + [\lambda y + \tan(n\pi/2) y^n]^2}. \quad (8b)$$

A key feature of Eqs. (8) is the presence of λ as an irreducible parameter. In Fig. 2 we demonstrate the influence of this irreducible parameter upon the shape of $M''(\omega)$ by computing $M''(y, \lambda, n)$ from Eq. (8b) for fixed $n=0.60$ at a variety of λ between 100 and 0.1. As shown in the figure, $M''(y, \lambda, n)$ can generally be segmented, at least for $\lambda > 1$,

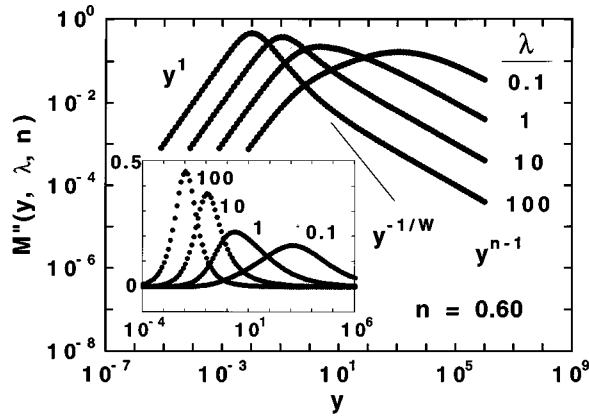


FIG. 2. Plot of $M''(y, \lambda, n)$ evaluated from Eq. (8b) for n fixed at 0.60 and a variety of λ . The three characteristic regions discussed in Eq. (9) are highlighted. The inset shows same plots on a linear scale to highlight the pronounced broadening in $M''(\omega)$ that occurs with decreasing λ .

into three distinct regions of frequency-dependent behavior relative to the position of the peak y_p :

$$\begin{aligned} \text{(I)} \quad & y^1, \quad y < y_p, \\ \text{(II)} \quad & y^{-1/W}, \quad y > y_p, \\ \text{(III)} \quad & y^{n-1}, \quad y \gg y_p. \end{aligned} \quad (9)$$

In the first and second regions, the nonexponential decay function [Eq. (2)] provides an adequate description of $M''(\omega)$. However, that same fit underestimates region III, where the slope is determined solely by the conductivity exponent n . It is only region II that is affected by variations in λ . As λ is increased, *substantial narrowing* (i.e., W decreases) occurs in the modulus (see inset). Again, we stress that this narrowing occurs as a direct result of λ . All the curves in Fig. 2 are obtained *with n fixed*, which implies $\sigma(\omega)$ *remains* scale invariant.

For CKN we can compute λ directly from the data [see Eq. (7)] and the result is shown in Fig. 3. We find that λ

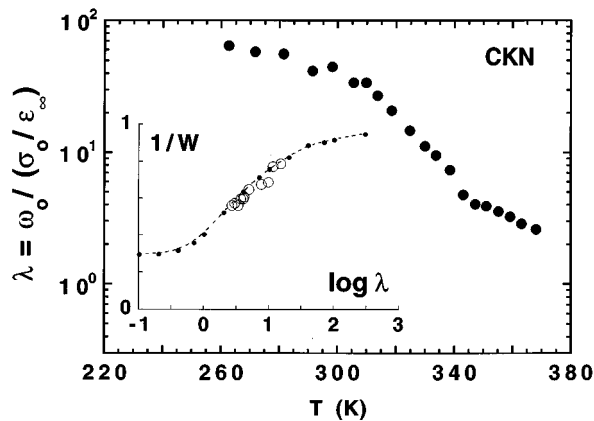


FIG. 3. Plot of $\lambda(T)$ determined from conductivity data for CKN. The inset show $W^{-1}(\lambda)$ obtained from the simulations presented in Fig. 2 (dashed line) together with experimental values of $W^{-1}(\lambda)$ for CKN (open circles) for comparison.

increases with decreasing temperature and, as shown in the inset to Fig. 3, that our experimental $\beta(\lambda)$ is in good agreement with the λ -dependent narrowing found from the simulation. We conclude that the temperature-dependent changes in β occur without corresponding loss of scaling in the conductivity and are merely the result of how scales in the conductivity representation become irreducibly incorporated into the modulus representation. These scales are just a reflection of changing thermodynamic fields, and consequently the shape changes in $M^*(\omega)$ do not indicate any *intrinsic* changes in ion dynamics near T_g . *In sharp contrast* to the findings of HBMM, the present power law analysis of the conductivity indicates a relaxation process that is *invariant with temperature* since the conductivity can be described by a simple scaling relation throughout the entire temperature range *both* above and below T_g .

The value of $n=0.61$ seen here for CKN is slightly less than the 0.67 seen in many other glasses and could indicate that CKN belongs to a different universality class. Whether this exponent exhibits a temperature dependence at much higher temperatures is not known. However, we note the dynamic light scattering measurements³⁴ of the structural relaxation in CKN over the same temperature range of the present study could be described by a stretched exponential with a constant $\beta=0.39 \pm 0.05$ (i.e., $1-\beta=0.61$).

B. Thioborate glasses

In the literature we are aware of only one other example of a system in which substantial changes in β were observed. Patel and Martin²⁶ (PM) studied the sodium-thioborate glasses $x\text{Na}_2\text{S}(1-x)\text{B}_2\text{S}_3$ and observed extreme narrowing (β approaching 1) of $M''(\omega)$ as x was decreased. Their interpretation of this narrowing was based upon the coupling model view that $n=1-\beta$ is a measure of the interaction between ions. Naturally, as x decreases, the average spacing between cations increases, leading to a reduction of the cation-cation coupling (n approaches 0) and eventually a Debye or exponential relaxation ($\beta=1$) of the ions as they move about independent of one another.

On the surface, these findings appear to provide strong support for the coupling model picture of ion motion. Even more importantly, the concentration dependence of β observed by PM suggests a corresponding concentration dependence of n , as implied by $n=1-\beta$. If this is true, then *universality* of n is clearly *ruled out* since n would depend upon the ion separation distance and must necessarily vary from one system to the next. However, the validity of the $n=1-\beta$ relationship is questionable. Indeed, in a more recent publication,³⁵ direct fits of Eq. (1) to $\sigma(\omega)$ of the N-thioborates were reported which indicate little or no systematic concentration dependence of the power law exponent, with $n \approx 0.7$, near the universal value. Thus it again appears that one's perspective on ion dynamics is substantially altered by examining the same data in an alternative representation.

In light of these considerations, we have reexamined the measurements of Patel with an eye towards how the conductivity varies with concentration. Our method follows that used for CKN above where we begin by estimating $\lambda(x)$ from data published in the literature^{26-28,35} and provided by

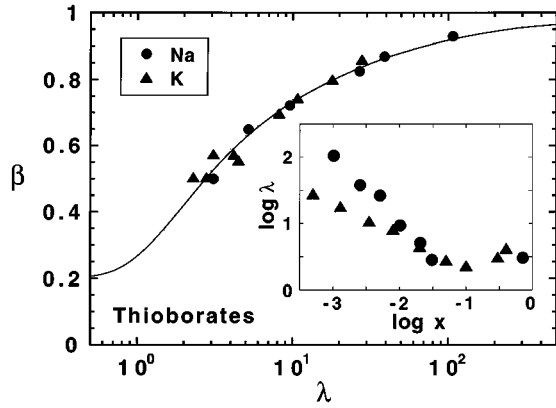


FIG. 4. Comparison of $\beta[\lambda(x)]$ for alkali-thioborate glasses with the theoretical prediction (solid line) based upon Eq. (8b) with n fixed at 0.70. The inset shows $\lambda(x)$ as discussed in the text.

Patel.³⁶ We then compare experimental values of $\beta[\lambda(x)]$ directly with $\beta(\lambda)$ obtained from simulations of $M^*(y, \lambda, n)$ with fixed $n=0.70$. A concurrent analysis is conducted for the comparable potassium-thioborate glasses $x\text{K}_2\text{S}(1-x)\text{B}_2\text{S}_2$, recently presented in thesis work of Patel.^{27,36}

At each composition, values of λ were determined from $\sigma(\omega)$ and $\varepsilon'(\omega)$ over a range of temperatures and an average was obtained. The resulting $\lambda(x)$, shown in the inset to Fig. 4, indicate substantial increases in λ with decreasing x , below about $x=0.03$. For the Na-thioborate glasses $\lambda \propto 1/x$, whereas for the K-thioborate glasses $\lambda \propto x^{-1/2}$. In Fig. 4 we plot the experimentally observed $\beta(x)$ now as $\beta[\lambda(x)]$, together with $\beta(\lambda)$ as determined from simulations of $M''(y, \lambda, n=0.70)$. Despite the differing $\lambda(x)$ exhibited by each glass, the agreement in $\beta(\lambda)$ is excellent.

We can provide some understanding for the increase of λ with decreasing ion concentration. Since the dc conductivity results from random diffusion of ions, each hopping about the lattice at some temperature-dependent rate proportional to ω_0 , it can be expressed through the Nernst-Einstein relation as $\sigma_0 \propto (e^2 \rho_e / kT) \xi^2 \omega_0$, where ρ_e is density of ions and ξ is the rms distance covered in a single hop.¹⁵ It then follows from Eq. (7) that λ is proportional to $kT\varepsilon_\infty / e^2 \rho_e \xi^2$ and, owing to the *explicit inverse dependence upon* ρ_e , should increase with decreasing ion concentration as was observed.

In any event, results of our comparison between $M(\omega)$ and $\sigma(\omega)$ represent an important finding which leads us to draw conclusions regarding the concentration dependence of ion motion which are *opposite* to those drawn by PM. As we have shown, the $\beta(x)$ dependence observed by PM conforms to changes in the shape of $M''(\omega)$ which arise solely from changes in the scales (particularly ρ_e) without the necessity for changes in the interionic coupling as characterized by n . This coupling parameter is independent of ion concentration, and hence $\sigma(\omega)$ is *scale invariant* over the entire range of compositions investigated. Thus there exists a *unique scaling function, determined solely by the exponent n* , which characterizes the fundamental physics underlying ion motion. The specific value of n observed here is approximately the same as that ($n=0.67 \pm 0.05$) seen in a large variety of other ion-conducting glasses and supports the universality

proposal. Furthermore, the absence of a compositional dependence of n rules out the importance of any *interionic* interactions upon the nature of ion motion.

III. DIPOLAR LIQUIDS

In dipolar liquids a dielectric response results from the reorientation of permanent dipoles and is most often studied using $\varepsilon^*(\omega)$. This reorientation is slowed dramatically in the supercooled regime just above the glass transition making the relaxation accessible to traditional radio frequency techniques. The analysis of $\varepsilon^*(\omega)$ is much the same as that applied to $M^*(\omega)$ in ionic glasses since the shapes of these two functions are remarkably similar. For example, both exhibit the same three regions of frequency-dependent behavior outlined in Eqs. (9), both are reasonably well described in the first and second regions by Eq. (1), and in both cases this description underestimates the data in the high-frequency region. Both show temperature dependencies for β , but while $M''(\omega)$ for ionic glasses (M''_i) narrows on approach to T_g from above, $\varepsilon''(\omega)$ in dipolar liquids (ε''_d) broadens.

As a consequence of the temperature-dependent broadening of $\varepsilon''_d(\omega)$, no linear scaling is possible in this data representation. Instead, in a recent series of letters, Dixon and co-workers^{8,37,38} have introduced a scaling approach by which the dielectric response could be collapsed to a single scaling curve. They examined a dozen molecular glass-forming liquids and showed that plots of $Y_\varepsilon = (1/W) \ln(\varepsilon'' \omega_p / \Delta \varepsilon \omega)$, where W is the FWHM of $\varepsilon''_d(\omega)$ normalized to that of a Debye process (1.14 decades) and $\Delta \varepsilon = \varepsilon'_d(\omega=0) - \varepsilon'_d(\omega=\infty)$ is the relaxation strength, versus $X_\varepsilon = (1/W)(1 + 1/W) \ln(\omega/\omega_p)$ did in fact collapse all the spectra onto a single, hence universal, scaling curve. Since then, the dielectric loss of an orientationally disordered crystal, cyclo-octanol, has been included to this same scaling curve and suggests that the approach may be of a more universal nature than previously recognized.³⁷ The scaling approach has also been used to provide indirect evidence for a special divergent susceptibility³⁸ near the glass transition. However, deviations from this universal curve have been noted for polymeric glass formers,⁹ and others³⁹ have recently suggested the scaling is only approximately successful, failing at large values of X_ε . Further, the scaling approach is not linear, and there seems to be no physical explanation for this nonintuitive scaling approach.

Driven by the similarities in the frequency dependence of $\varepsilon''_d(\omega)$ and $M''_i(\omega)$ and the similar manner by which Eq. (1) underestimates the high-frequency data in each, it seems only natural to attempt to Dixon scaling approach for $M''_i(\omega)$, with $Y_M = (1/W) \ln(M'' \omega_p / \Delta M \omega)$ and $X_M = (1/W)(1 + 1/W) \ln(\omega/\omega_p)$. Again, this scaling is motivated entirely from the parallels which we have noted above between $\varepsilon''_d(\omega)$ and $M''_i(\omega)$, including evidence from Menon and Nagel,³⁸ that $\varepsilon''_d(\omega)$ generally exhibits frequency dependencies identical to those outlined in Eqs. (9).

Results for CKN are shown in Fig. 5 where the Dixon scaling approach is quite successful in collapsing $M''_i(\omega)$ for a range of temperatures (including T_g) over which W changes substantially from 1.1 to 1.8. Furthermore, the present scaling curve $Y_M(X_M)$, is virtually identical to the

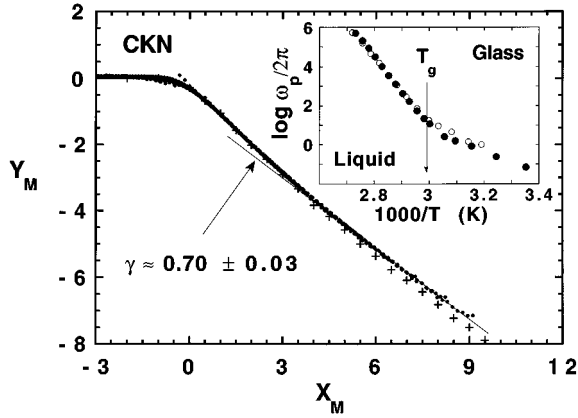


FIG. 5. Dixon scaling approach applied to $M''_i(\omega)$ of CKN from Fig. 1(a). The solid line indicates the approximate slope of the scaling curve at large X_M , $\gamma = 0.70 \pm 0.03$. Crosses locate the position of $Y_\varepsilon(X_\varepsilon)$ observed for several dipolar liquids (Ref. 8). The inset shows how the temperature dependence of $\omega_p/2\pi$ for $M''_i(\omega)$ (solid circles, Ref. 30; open circles, present work) changes significantly near T_g .

universal curve $Y_\varepsilon(X_\varepsilon)$ found for a dozen supercooled dipolar liquids by Dixon *et al.*,⁸ except for $X_M > 4$ where systematic deviations occur. The slope of $Y_M(X_M)$ increases steadily from -0.9 near $X_M = 1$ to about -0.7 near $X_M = 7$, but there is no clear evidence that a limiting power law $Y_M \propto X_M^{-\gamma}$ is attained. We do note though that the data at $X_M > 5$ when fit by a single power law yield a slope $\gamma = 0.70 \pm 0.03$, in close agreement with the value 0.72 ± 0.03 found³⁸ in the dipolar case. Again, all this scaling occurs with apparent indifference to the glass transition $T_g \approx 335$ K, where the temperature dependence of ω_p changes abruptly as shown in the inset of Fig. 5.

The apparent success of Dixon dipolar scaling for ionic CKN is an interesting result since the connection between these two dielectric phenomena is not transparent. The physical processes in each appear to be quite different; $\varepsilon''_d(\omega)$ is associated with dipolar reorientation, whereas $M''_i(\omega)$ results from ionic motion. The finding, however, appears inconsistent with our earlier contention that the ionic spectra for CKN exhibit linear scaling in $\sigma(\omega)$ with a temperature-independent exponent n . To see this, consider how the Dixon scaling acts upon each of the three regions in Eqs. (9). The Dixon approach results in the following corresponding dependences for $Y(X)$:

$$(I) \quad X^0,$$

$$(II) \quad X^{-1},$$

$$(III) \quad X^{(n-2)/[1+(1/W)]} = X^{-\gamma}. \quad (10)$$

So if n is constant and W varies with temperature (as we contend for CKN), γ should likewise be temperature dependent, making the apparent success of the scaling for CKN in Fig. 5 at large X an unexpected result.

To understand one possible source for this discrepancy, we return to our formal expression $M''(y, \lambda, n)$ for assistance. We start by extending the $M''(y, \lambda, n)$ curves shown in Fig. 2 to some arbitrarily wide frequency window (10^{-6}

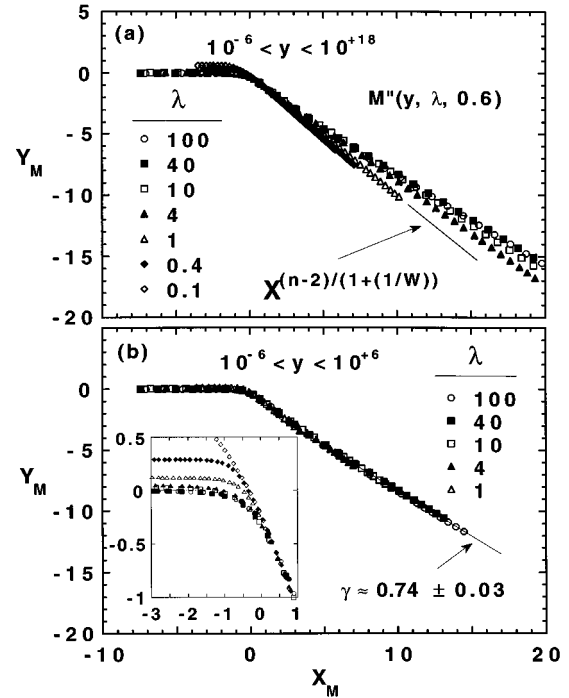


FIG. 6. (a) Plot of the Dixon transformation applied to $M''(y, \lambda, n)$ evaluated from Eq. (8b) for n fixed at 0.60 and $10^{-6} < y < 10^{18}$. The solid line indicates failure of the data to collapse at high frequencies. (b) The same spectra now truncated at $y = 10^6$. The inset shows an expanded view of Fig. 6(a) highlighting deviations from the Dixon scaling curve for small λ .

$< y < 10^{18}$) and then perform the Dixon scaling. The result shown in Fig. 6(a) is what we had expected. We find that while the scaling is successful (for $\lambda \geq 1$) in regions I and II, the tails of each individual spectrum, which vary as ω^{n-1} regardless of λ (or W), project outward in a tangential fashion as $X^{(n-2)/[1+(1/W)]}$ and cannot be incorporated into the Dixon master curve.

The wide frequency window used to construct Fig. 6(a) is experimentally unrealistic though. A more typical window might at best span only ten decades beyond ω_p . Indeed, if the evaluation of $M''(y, \lambda, n)$ is truncated to a narrower window of frequency extending only from $y = 10^{-6}$ to $y = 10^6$, as shown in Fig. 6(b), these tangential tails are no longer visible and the success of the Dixon scaling is enhanced. Hence the apparent success of the Dixon scaling obtained in Fig. 5 for CKN may in fact be a fortuitous consequence of a limited frequency window.

Do the results in Figs. 6(a) and 6(b) for the ionic case imply that the actual success of the Dixon scaling in the dipolar situation likewise depends upon the frequency range accessible? A clarification of this issue will necessarily require spectra which cover a wider frequency range, although we note that an already impressive range of 13 decades was employed in the study by Dixon *et al.*⁸

Nevertheless, high-frequency data are very important for determining the actual success of the scaling. One can show [see Eq. (10)] that application of the Dixon approach to regions I and II amounts to little more than a normalization procedure, in which the slope of $\varepsilon''(\omega)$ in region II ($1/W$) is first extracted and then used to adjust spectra to $Y = X^{-1}$.

This part of the scaling is not particularly insightful. Instead, it is only in region III where actual success of the scaling approach represents a potentially significant finding. Unfortunately, this third region is also the least represented portion of the scaling curve. For any typical finite-frequency window, region III ($X > 5$) is chiefly defined by only the few lowest-temperature data sets where ω_p is positioned to the low-frequency side of the window. Spectra at higher temperatures are not equivalently represented at large X , but instead are systematically truncated by the window edge as ω_p increases with increasing temperature. Since a majority of the individual spectra do not extend into region III, the success of the Dixon transformation at $X > 5$ may only be fortuitous. Some support for this position comes from recent observations^{9,39} that despite agreement in regions I and II, deviations from the DN master curve do occur at $X > 5$.

While we acknowledge that many of the issues we raise regarding the Dixon scaling rely upon our assumption that $M''(y, \lambda, n)$ (developed for the ionic case) behaves in the same fashion as $\varepsilon_d''(\omega)$, we wish to highlight an additional interesting feature in $M''(y, \lambda, n)$ which surfaces at small λ . As shown in the inset to Fig. 6(b), spectra at $\lambda < 3$ exhibit a noticeable deviation ($Y > 0$) from the Dixon curve ($Y = 0$) at negative X . This behavior is interesting since a similar deviation was recently highlighted by Schonhals *et al.*⁹ for polymeric glass formers. This deviation can be traced back to the emergence at small λ of a fourth region of frequency dependence occurring at $y \leq y_p$ (visible in Fig. 2 for $\lambda = 0.1$), where $M''(y, \lambda, n) \propto y^k$ with $k < 1$. While the Dixon transformation precisely compensates the ω^1 behavior of region I, it overcompensates the ω^k behavior of this new region, leading to the observed deviation seen in the inset of Fig. 6(b). This suggests a possible classification of materials—simple molecular liquids with large λ and polymers with small λ —and may be worthy of future investigation.

In any event, the numerous similarities seen in the dielectric relaxation for the dipolar and ionic situations and the apparent success of Dixon scaling, fortuitous or not, suggests to us a new perspective on the absence of linear scaling for $\varepsilon_d''(\omega)$. This perspective results from the one-to-one correspondence between the frequency-dependent features of $M_i''(\omega)$ and $\varepsilon_d''(\omega)$ taken together with our previous finding illustrated in Fig. 1 that when $M_i''(\omega)$ (which violates linear scaling) is transformed into a reciprocal representation, namely, the conductivity given by $\sigma_i(\omega) = \omega \varepsilon_i''(\omega)$, the relaxation then displays linear scaling.

This new perspective is deepened by the improved understanding of $M_i^*(\omega)$ which we have gained through examining its power law origins in an alternative data representation. Specifically, we saw how scaling parameters present in $\sigma_i^*(\omega)$ become convolved into $M_i^*(\omega)$ in a nontrivial fashion such that variations in these scales (i.e., λ) alone, say, with temperature, could cause significant changes in the shape of $M_i^*(\omega)$, resulting in the apparent absence of linear scaling.

Given the similarities in $M_i''(\omega)$ and $\varepsilon_d''(\omega)$ that we have discussed above, it is natural to speculate that there is an alternative representation related to $\varepsilon_d''(\omega)$ just as $\sigma_i(\omega)$ is related to $M_i''(\omega)$, which exhibits linear scaling. Since the

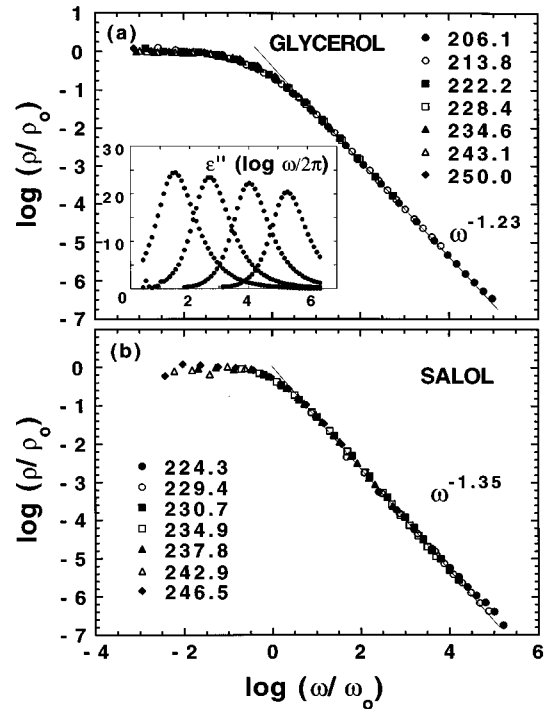


FIG. 7. (a) Plot of $\rho_d(\omega)$ of glycerol at several temperatures linearly scaled (see discussion in text) so as to collapse to the common curve. The solid line indicates the asymptotic power law apparent at high frequencies. Inset shows $\varepsilon_d''(\omega/2\pi)$ of glycerol at 213.8, 222.2, 234.6, and 250.0 K for comparison. (b) Plot of $\rho_d(\omega)$ of salol at several temperatures linearly scaled so as to collapse to the common curve.

immediate corollary to $\sigma_i(\omega)$, $\omega M_d''(\omega)$, has no traditional interpretation for dipolar materials, we instead have chosen to examine the resistivity, $\rho^* = M^*/i\omega$, which like $\omega M_d''(\omega)$ is reciprocal to ε^* , but yet retains a physical identity.

To test these ideas, we have measured $\varepsilon_d^*(\omega)$ of glycerol and salol at several temperatures over a range of frequencies from 1 Hz to 1 MHz using a commercially available impedance analyzer (Schlumberger 1260). Our dielectric cell again consisted of a commercially available air variable capacitor (with a nominal capacitance of 19 pF in air), which was immersed into a small vial of reagent grade melt. The vial was situated in a cryostat and its temperature regulated to better than ± 0.2 K.

Examples of $\varepsilon_d''(\omega)$ for glycerol are shown as an inset to Fig. 7(a), and analysis has revealed that the peak positions and widths are in excellent agreement with other literature values.²⁴ As observed by others, we find a modest broadening of $\varepsilon_d''(\omega)$ with decreasing temperature for glycerol and a more substantial broadening for salol. In neither case, however, are the changes as dramatic as for $M_i''(\omega)$ of ionic CKN. In Figs. 7(a) and 7(b), we plot $\rho_d(\omega) = M_d''/\omega$ for data at several temperatures which have been shifted vertically (ρ_0) and horizontally (ω_0) so as to best coincide. From these figures, we conclude that $\rho_d(\omega)$ can be scaled in a linear manner for both materials. The scaling curves so obtained exhibit two apparent asymptotic trends; a power law at high frequencies of the form $\rho_d(\omega) \propto \omega^{m-2}$ crossing over at lower

frequencies to a constant, ρ_0 . Thus, as we observed in the ionic situation, switching to the reciprocal representation seems to produce a linearly scalable quantity and in principle simplifies the overall description of the dielectric response.

IV. SUMMARY

In conclusion, we have explored similarities in the dielectric response of ionic and dipolar glassformers. We have demonstrated that the scaling approach proposed by Dixon *et al.* previously applied only to dipolar relaxation is also successful for ionic relaxation and seems to be of a more universal nature than previously thought. Despite its successes, however, a physical interpretation of this nonintuitive scaling approach is still missing. In ionic glasses we have demonstrated how acutely the interpretation of relaxation data can be reversed merely by examining different representations of the same data. Two examples were reviewed for

which the data in one representation suggested significant changes in ion dynamics occur in the melt above T_g and in the glass at low ion concentration. In an alternative representation, this same data obey simple linear scaling to reveal *no intrinsic changes* occurring in the ion motion. As a logical extension of our findings for the ionic case, we demonstrate that a similar situation occurs in the dipolar case where response functions for dipolar relaxation exhibit linear scaling in an alternative data representation and can be collapsed onto a master curve in a straightforward manner.

ACKNOWLEDGMENTS

The authors are grateful to Dr. H. K. Patel for valuable discussions and for providing original thioborate data. This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract No. DE-ACO4-94AL85000.

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