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Abstract

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Stretched exponentials with *T*-dependent exponents from fixed distributions of energy barriers for relaxation times in fast-ion conductors

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The conductivity modulus in fast ion conductors (FIC) has often been fitted with stretched exponential relaxation functions of the form $\exp[-(t/\tau_K)^\beta]$, where the β values are taken to be independent of temperature. This analysis corresponds to the assumption of an asymmetric distribution of relaxation times (DRT) that does not have the T dependence observed in the conductivity modulus spectra found for many FIC glasses and expected from a fixed distribution of activation energies (DAE) against the ion hops. In this paper, it is shown, rather, that a fixed DAE leads to the temperature dependence of $\beta \propto T^{0.5}$ for β values near 0.6, and conductivity modulus data for some Li$^+$ glasses are presented where β varies nearly in this way. Similar behavior can be inferred from published data for many other FIC. It is also shown that the DRT calculated from the corresponding stretched exponential relaxation function closely approximates the tail of the DRT calculated from the DAE and truncated at the conductivity percolation limit of 0.3.

I. INTRODUCTION

The ionic conductivity $\sigma(\omega,T)$ in glassy fast ion conductors (FIC) has often been fitted with the Fourier transform of the stretched exponential or Kohlrausch-Williams-Watts (KWW) relaxation function of the form $\varphi_K(t)=\exp[-(t/\tau_K)^\beta]$ for the macroscopic current decay after an electric field change.[1,2] The fits have usually been to the complex conductivity modulus $M^*(\omega,T)=1/\varepsilon^*$ formalism, where the details at high (extra nonconducting relaxation) and low (electrode polarization effects) frequencies are suppressed. The KWW function has also been used[3–5] to describe the relaxation of the local hyperfine fields at the nuclear sites due to the hopping motion of the ions that gives rise to the NMR nuclear spin-lattice relaxation (NSLR) rate, $R_T(\omega_L,T)=T_1^{-1}$. The KWW function has been justified from theories of constrained dynamics,[6] correlation effects in the ionic motion,[7–9] and by numerical simulations.[10,11] The KWW relaxation time $\tau_K(T)=\tau_{K0}\exp(E_k/k_BT)$ is taken to be an average relaxation time for the thermally activated ionic motion, and the exponent β (≤ 1) is often assumed to be independent of T, but how these parameters are related to the microscopic ionic motion is still a matter of debate.

In an alternative treatment, the KWW function can be written as a sum over a distribution $g_K(\tau)$ of simple exponentials with relaxation times τ, i.e., $\varphi_K(t)=\int_0^\infty g_K\exp(-t/\tau)d\tau$, and β is then a measure of the width of g_K, with $\beta=1$ corresponding to the Debye case with a single τ and $\beta<1$ corresponding to the non-Debye case with a distribution of τ. The distribution of relaxation times (DRT) corresponding to a given KWW function can be calculated numerically from the formula by Weron[12]

$$G_K[\log(\tau)]=\tau g_K(\tau)=\frac{\tau}{\pi\tau_K}\sum_{n=1}^\infty$$
$$\times\frac{(-1)^{n+1}\Gamma(n\beta+1)}{n!}\left(\frac{\tau}{\tau_K}\right)^{n\beta-1}\sin(n\pi\beta)$$

$$\text{for small } \tau \quad (1)$$

$$G_K[\log(\tau)]\rightarrow\frac{\Gamma(\beta+1)}{\pi}\sin(\pi\beta)\left(\frac{\tau}{\tau_K}\right)^\beta\propto\tau^\beta \quad \text{for } \tau\rightarrow 0.$$

Such DRT have been little discussed, and how well they reflect the microscopic relaxation times of the ionic motion depends upon how the KWW parameters have been determined. The usual fits to the conductivity modulus incorporate the high-frequency dielectric constant ε_∞, which is due to electronic and ionic vibration polarization, and thus is unrelated to the ionic hopping motion. Hence the resulting fit parameters β, τ_{K0}, E_K, and ε_∞ do not represent the ionic motion alone.

A DRT appears to be a natural model for ions hopping with thermal rates $\tau_a^{-1}=\tau_0^{-1}\exp(-E_a/k_BT)$ over a set of random microscopic activation energy barriers E_a in a disordered glass. The activation energy barriers between the cation sites in the glass are determined mostly by the attractive Coulomb and repulsive overlap forces from the immobile nearest-neighboring anions in the disordered glass structure. The Coulomb repulsion between the mobile ions is weaker, but probably comparable to k_BT such that the thermal mo-

tions of the ions become correlated and the net individual barriers will therefore fluctuate with the hops of the neighboring mobile ions. However, the overall distribution of activation energies (DAE) must remain constant in thermal equilibrium. In a conductivity experiment then, the applied electrical fields make the forward and backward barriers that a particular mobile ion experiences very slightly different, which, in turn, slightly changes the local hopping very little but gives the mobile ions a very small average drift along the field. The NMR radio frequency pulses in NSLR measurements have no measurable effects on the ionic motion.

Our model[13] for the conductivity and the NSLR is based upon a fixed DAE and is able to explain the much longer, by a factor of ~100 to $1\,000$ average correlation times[4,14] derived from measurements of $R_1(\omega_L,T)$ than those derived from $\sigma(\omega,T)$ measurements. The essential idea is that all ionic hops with a correlation time close to $1/\omega_L$ contribute to the NSLR, while the percolating dc current is determined mostly by fast hops over the lowest barriers. Hence, we extract from R_1 a DAE, $Z_{NMR}(E_a)$, for the hops and used the fraction, Z_σ, of the lowest barriers in Z_{NMR} below the percolation limit to calculate σ. The relaxation time $\langle\tau_\sigma\rangle$ averaged over Z_σ is then, naturally, much shorter than $\langle\tau_{NMR}\rangle$ averaged over the entire DAE, Z_{NMR}. We used a continuous-time random walk (CTRW) model[15] to calculate the ac conductivity, $\sigma(\omega,T)$, from the tail of Z_{NMR} and found a fairly good fit, and we stressed the importance of using physically reasonable attempt times, τ_σ, for the ionic hops. Our quantitative method connects the conductivity and the NSLR on a microscopic basis, and it has been shown to work well for several different glasses.[16–19]

In this paper, we compare the temperature dependence of the DRT calculated from a KWW function with fixed β to the temperature dependence of the DRT calculated from a DAE with a fixed distribution. It is demonstrated for one fast ion conductor (FIC) glass, $0.56Li_2S+0.44SiS_2$, that the asymmetric distribution $G_{K\sigma}[\log(\tau)]$ that we calculate from the original KWW fit to the conductivity[4] is indeed almost the same as the DRT we obtain by truncating Z_{NMR} at E_p, the conductivity percolation limit.[13] We will also show that KWW functions that fit the DRT determined entirely by fixed DAE correspond to β exponents increasing approximately as $\beta\propto T^{0.5}$, for β near 0.6. We will present data for the conductivity modulus for some Li FIC, which show this behavior, and data in the literature often show a similar trend although this has been little discussed. That a physically reasonable fixed DAE leads to a T-dependent exponent β, while a constant β corresponds to physically unreasonable T-dependent set of DAE was pointed out in our previous work,[13] but no detailed quantitative analysis was done there.

II. RESULTS

A. Distributions of relaxation times from KWW functions and from DAE

In order to illustrate the DRT generated from KWW functions with fixed β, we refer to the measurements by Borsa et al.[4] for the FIC glass $0.56Li_2S+0.44SiS_2$. By fitting the conductivity to the KWW stretched exponential function in the temperature range $141<T<281$ K, it was found that

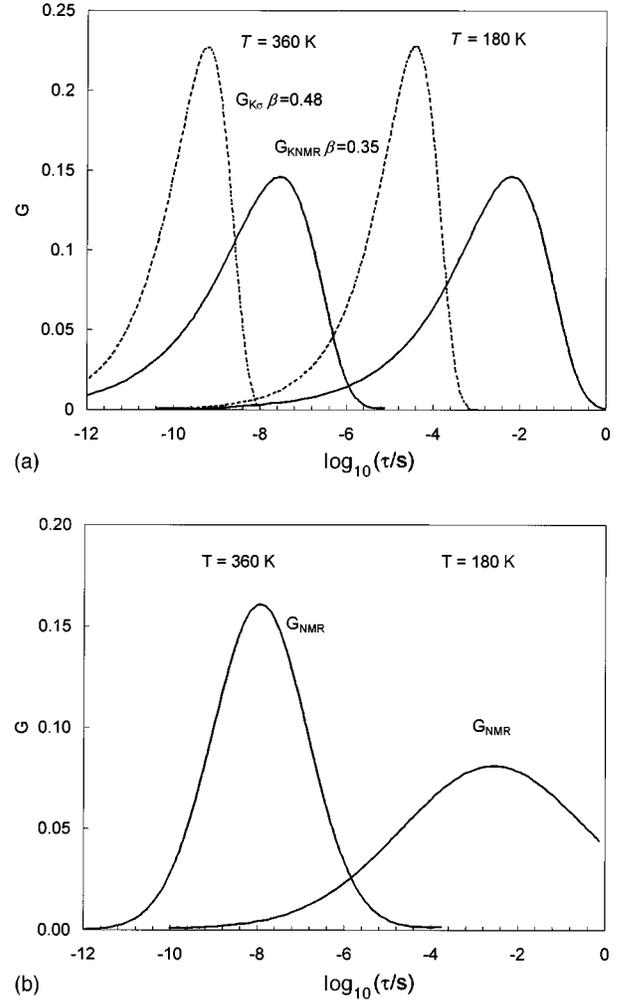FIG. 1. Distributions of relaxation times in $0.56Li_2S+0.44SiS_2$ at 180 K and 360 K. (a): G_K from fitted KWW parameters (Ref. 4) into Eq. (1) for conductivity (dotted lines) and NMR (full lines). (b) G from distribution of barriers fitted to NMR relaxation (Ref. 13).

$$\varphi_{K\sigma}=\exp[-(t/\tau_{K\sigma})^{0.48}]$$

$$\text{with}\quad \tau_{K\sigma}=0.4\times10^{-14}\exp(4000/T), \tag{2}$$

and fitting the ^7Li NSLR in the range $150<T<550$ K gave the quite different function

$$\varphi_{KNMR}=\exp[-(t/\tau_{KNMR})^{0.35}]$$

$$\text{with}\quad \tau_{KNMR}=4.5\times10^{-14}\exp(4500/T). \tag{3}$$

The asymmetric DRT $G_{K\sigma}$ and G_{KNMR} calculated with Eqs. (2) and (3) as inputs in Eq. (1) are compared in Fig. 1(a), and they are strikingly different. The point that we want to emphasize is that each DRT corresponds to a fixed temperature, and by changing T the $G_K[\log(\tau)]$'s are shifted with the T dependencies of the respective τ_1's, but the shape of the G_K's remain the same. The temperatures chosen for the comparison in Fig. 1(a) are 180 K and 360 K, which correspond to about the middle of the T ranges for the measurements of conductivity and NSLR, respectively.
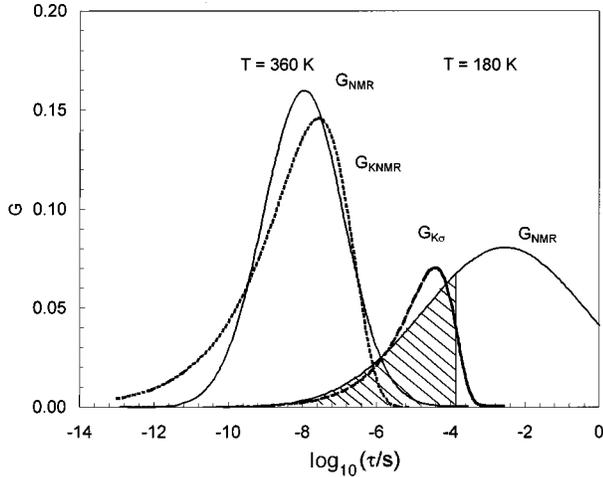
FIG. 2. Distributions of relaxation times in $0.56Li_2S+0.44SiS_2$ at 180 K and 360 K. Full lines are the same as from NMR relaxation in Fig. 1(b), hatched area is G_σ from the low-barrier fraction giving conductivity by percolation (Ref. 13). Dotted line is G_{KNMR} from Fig. 1(a) at 360 K, dashed line is $G_{K\sigma}$ from Fig. 1(a) at 180 K multiplied by 0.3.

The DRT behave differently if one starts from a model where the data are fit to a T-independent DAE, $Z_{NMR}(E_a)$, for the microscopic hopping of each ion. By assuming a Gaussian DAE,

$$Z_{NMR}(E_a)=[1/(2\pi)^{0.5}E_b]\exp[-(E_m-E_a)^2/2E_b^2], \quad (4)$$

the fit to the same NSLR data for the $0.56Li_2S+0.44SiS_2$ FIC glass as above gave[13] the parameters $E_m/k_B=4500\,K$ and $E_b/k_B=900\,K$. The normalized DAE can be directly converted into a DRT, $G_{NMR}[\log(\tau_a)]$, of microscopic hop times by using $\log(\tau_a)=\log(\tau_0)+E_a/2.303k_BT$. We use the same prefactor $\tau_0=4.55\times10^{-14}$ s as for the NSLR data fit with Eq. (4) to calculate the G_{NMR} that are plotted in Fig. 1(b) for the same two temperatures as in Fig. 1(a). We see that, contrary to the distributions G_K obtained from KWW functions, the G_{NMR} are symmetric and broaden as $1/T$ when the temperature is changed.

The DRT G_{NMR} and G_{KNMR} are compared in Fig. 2 at 360 K, which is about where the NSLR relaxation has its peak. Although the two distributions are quite different, G_{KNMR} is broader and shifted slightly to longer relaxation times, both give satisfactory fits to the NLSR data since at this T they are approximately equal for correlation times around $1/\omega_L \approx 10^{-8}$ s, which are most efficient for the relaxation.

Our model[13] for the dc conductivity emphasized the percolation of ions along paths over the lowest barriers, and as such we truncated $Z_{NMR}(E_a)$ for the $0.56Li_2S+0.44SiS_2$ glass at the percolation limit $E_p/k_B=4000\,K$ to find the effective distribution $Z_\sigma(E_a)$ for σ_{dc}. The corresponding DRT G_σ at 180 K is shown as the shaded area in Fig. 2 and is compared with the KWW DRT $G_{K\sigma}$ from Fig. 1(a) reduced in amplitude by the percolation fraction 0.3. We see that the truncated and very asymmetric G_σ is indeed about the same as the more rounded $G_{K\sigma}$ at this T.
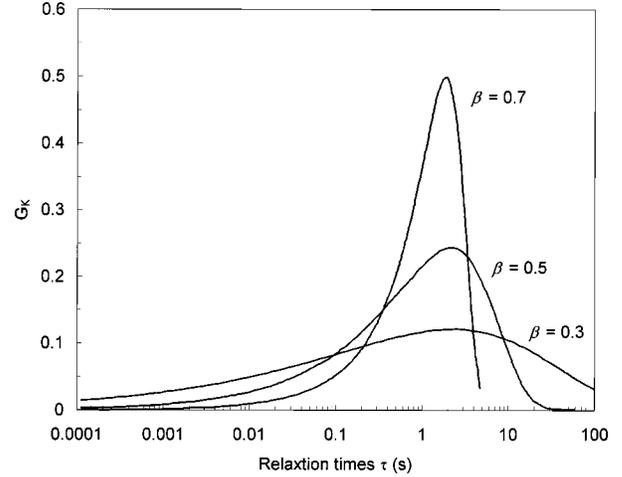

FIG. 3. Distributions of relaxation times G_K with $\tau_K=1$ for some values of β.

B. Temperature dependence of β

Figures 1 and 2 illustrate the basic difference between the normalized $\log(\tau)$ DRT that are based on T-independent DAE, and those that are based on stretched exponentials with fixed β. The height G_{max} and the inverse width of the former vary as T, while the latter have a fixed shape and correspond to DAE that would have to broaden as T. Thus, if a model based on a fixed DAE is more applicable, as we believe, then precise KWW fits should yield different values of β at different T. We will analyze and check this by presenting new data and revisiting published values of β_σ.

In order to determine the T dependence of β to be expected from a fixed DAE without considering the effects of ε_∞ as discussed above, we show in Fig. 3 the DRT, $G_K[\log(\tau)]$, from Eq. (1) for some values of β and a constant $\tau_K=1$. Note that the maximum of G_K occurs at about $\tau/\tau_K \approx 2$, and its position is slightly dependent on β. We see that the peak value of G_K increases by a factor two going from $\beta=0.3$ to $\beta=0.5$, and by another factor two going on to $\beta =0.7$, while the widths are halved in each step. We have checked in more detail that the normalized distributions G_K retain almost exactly the same shape when we vary β and reduce the horizontal axis by the same factor as the vertical axis is expanded. Now since Fig. 1(b) shows that the symmetric DAE automatically gives a temperature dependent DRT, hence, temperature dependent FWHM, it follows that the β values corresponding to the DAE at each temperature shown in Fig. 1(b) must likewise be temperature dependent. A series of calculations were then preformed as a function of temperature and the temperature dependence of β was thus determined. Figure 3 was used to "calibrate" the determination of β from the DAE calculations. In this way, we can connect β to the width of G_K and find the numerical relation between β and T shown as the full line in Fig. 4, where we have arbitrarily set $\beta=0.4$ at $T=200\,K$. The relation can be shifted horizontally on the $\log(T)$ scale, and one dashed line in Fig. 4 is the full line shifted by multiplying T by 1.5 effectively broadening the DAE, and the other is shifted by dividing T by 1.5 effectively narrowing the DAE. From the slope of the lines it is seen that $\beta(T)$ varies approximately as $T^{0.5}$ near the typical value $\beta_\sigma=0.6$ for conductivity, and about as $T^{0.6}$ around $\beta_\sigma=0.4$.
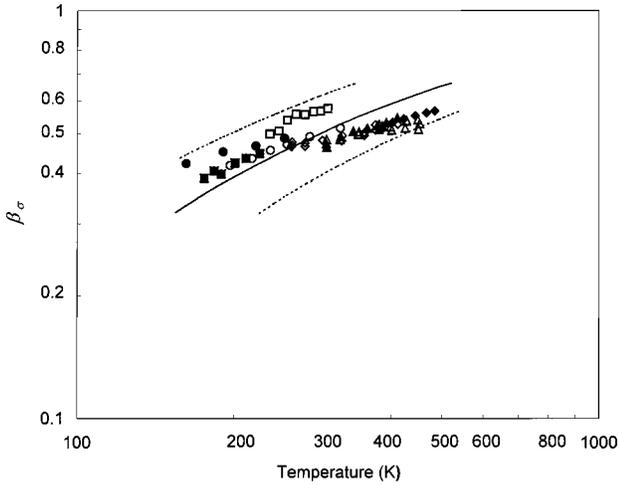
FIG. 4. Stretched exponent β_σ as function of temperature. Calculated relation is solid line with possible shifts (dashed), measured data from modulus are symbols: ($\bigcirc$) $0.35Li_2S+0.65GeS_2$, Ref. 17; ($\bullet$) $0.45Li_2S+0.55GeS_2$, Ref. 17; ($\blacklozenge$) $Li_2O\cdot3B_2O_3$; ($\diamond$) $Na_2O\cdot3SiO_2$, Ref. 23; ($\blacktriangle$) $Na_2O\cdot3SiO_2$, Ref. 24; ($\triangle$) $K_2O\cdot3SiO_2$, Ref. 23; ($\blacksquare$) $LiLa\cdot2TiO_3$, Ref. 25; ($\square$) $0.6LiCl-0.7Li_2O\cdot B_2O_3$, Ref. 14.

The experimentally determined values of β_σ are usually found from experiments by fitting the imaginary part $M''(\omega)$ of the complex conductivity modulus:[20]

$$M^*(\omega)\equiv 1/\varepsilon^*(\omega)=i\omega\varepsilon_0\sigma^*(\omega) \quad \text{with} \quad (5)$$

$$M_K^*(\omega)=M_\infty\left[1-\int_0^\infty \exp(i\omega t)(-d\varphi 0_K/dt)dt\right], \quad (6)$$

where $\varphi_K(t)$ is the KWW relaxation function, M_∞ is the high-frequency dielectric modulus, $1/\varepsilon_\infty$, and $\varepsilon_0=8.85\times10^{-12}$ F/m. As discussed above, this latter expression can be transformed to a DRT (individual Debye responses) using Eq. (1) and hence:

$$M_K^*(\omega)=M_\infty\left[1-\int_0^\infty g_K(\tau)d\tau/(1+i\omega\tau)\right]. \quad (7)$$

However, since ε_∞ is unrelated to the ionic motion of interest, the dc conductivity is not directly seen in these formulas, and the contributions to the total ε^* from several physical processes are mixed in the inversion to M, the modulus from Eqs. (6) and (7) must be viewed as a phenomenological approximation for the total conductivity motion, where the resulting parameters are numbers without clear microscopic meaning. In particular, the fitted β_σ may show less T variation than we derived above from a DAE alone. Other such details of the conductivity modulus will be further discussed in the next section.

For fixed values of β_σ and M_∞, Eq. (6) gives $M_k''(\omega,T)$ peaks that have constant height and constant FWHM values on a $\log(\omega)$ scale when $\tau_K(T)$ is varied, and the width (or height) of the peaks gives the β_σ directly.[21] However, experimental data for M'' for a range of different FIC are often similar to those[17] of the FIC glass $0.35Li_2S+0.65GeS_2$ shown in Fig. 5, where the peaks clearly become narrower

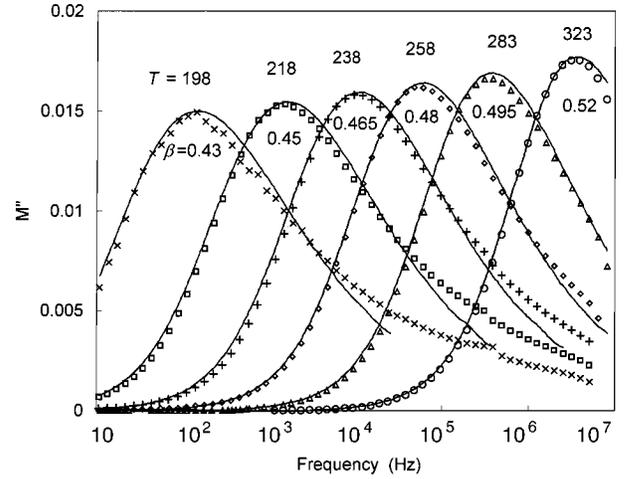

FIG. 5. Imaginary part of dielectric modulus in $0.35Li_2S+0.65GeS_2$ as function of temperature from Ref. 17, with stretched exponential fits.

and increase in height with increasing T. The fitted values of β_σ in Fig. 5 are plotted in Fig. 4 and grow approximately as $T^{0.4}$, slightly slower than the dependence derived from a fixed DAE.

Some additional problems we find in the KWW fit of the measured M'' data with Eq. (6) for the typical FIC glass $0.35Li_2S+0.65GeS_2$ should also be mentioned. The relaxation times in this case are $\tau_{k\sigma}(T)=3\times10^{-15}\exp(5200/T)$ s, which corresponds to about the inverse frequencies $1/\omega_{max}(T)$ at the M'' peaks. However, the unphysically short prefactor (by a factor of about 100) cannot be readily interpreted as an attempt time for single ion hops, and the NMR relaxation in the same glass gave much longer relaxation times with the activation temperature 6100 K. Only our microscopic theory[13] with a DAE from NMR and conductivity from percolation over the lowest barriers, can connect such different results for the relaxation times quantitatively.

The value of $M_\infty=1/\varepsilon_\infty$ in the heights of the peaks is often ignored in fits with Eq. (5). For example, a value of $\varepsilon_\infty=16$ was needed to produce the fits on Fig. 5 instead of the directly observed $\varepsilon_\infty=14$ found at high frequencies and low T for this FIC glass. This indicates that there must be a dielectric contribution from fast ion motion that is not a part of the process that is assumed to be describable with a single KWW function. Deviations from the calculated KWW behavior are often observed at high frequencies, and the simplest explanation is that the DAE has relatively more low barriers than those corresponding to Eq. (1) alone. Their Debye contributions to the conductivity will increase the measured M'' at frequencies well above its peak.

Literature data where the height of the $M''(\omega)$ peaks increase with T are common, and we plot some of the available data for $\beta_\sigma(T)$ in Fig. 4 for comparison. As an example of this, we also report T-varying modulus results for $0.45Li_2S+0.55GeS_2$,[17] where we find β_σ ranging from 0.42 at $T=173$ K to 0.515 at 273 K. Sometimes the variation in β_σ is derived explicitly as for $Li_2O\cdot3B_2O_3$,[22] for $Na_2O\cdot3SiO_2$,[23,24] $K_2O\cdot3SiO_2$,[23] and $LiLa\cdot2TiO_3$,[25] and sometimes a clear T dependence of β_σ can be inferred from published graphs of M'' as for $0.6LiCl+0.7Li_2O+1.0B_2O_3$

(Ref. 14) and $1.0Na_2O+0.4Al_2O_3+2.2SiO_2$.[26] However, the published modulus data are sometimes normalized to uniform heights and plotted together in a master plot, and any information about small changes in β_σ with T is then easily lost. There are also compounds with no apparent variation in β_σ, at least over small temperature ranges, like $0.56Li_2S+0.44SiS_2$,[4] $LiPO_3$,[21] and in $0.7Li_2S+0.3B_2S_3$ glass,[18] where there is only a small and hardly significant change of β_σ from 0.53 to 0.55 with T from 163 to 223 K. In $0.6AgI+0.4(Ag_2O+2B_2O_3)$, the β from ultrasonic damping[27] increases rapidly with T, but it does not seem to change for the conductivity. We have found no fast ion conductor where β_σ *decreases* with T.

The general trend in the data collected in Fig. 4 is that β_σ increases with T but somewhat slower than we have derived from a fixed distribution of barriers. Note that the β_σ points for different compounds do not have to lie on the same line in the plot because their T scales can be shifted, i.e., their unique DAE will necessarily generate a unique temperature dependence to β.

Other ways of fitting conductivity data have been suggested,[28] but most of these are little used. For example, it may be reasonable to subtract ε_∞ off from the complex dielectric constant and fit the ionic contribution in nonconductors with the alternative stretched exponential[29]

$$\varepsilon^*(\omega)-\varepsilon_\infty=[\varepsilon(0)-\varepsilon_\infty]\left[-\int_0^\infty \exp(-i\omega t)(d\varphi/dt)dt\right].$$

(8)

Depending upon the relative magnitudes of $\varepsilon(0)$ and ε_∞, this leads to quite different KWW parameters for the ionic motion than the more commonly used Eq. (5).

III. DISCUSSION

We have compared the DRT derived from fitting conductivity data with a KWW relaxation function to the one obtained from a DAE, and we have demonstrated the striking similarity of the very asymmetric $G_{k\sigma}$ from the KWW fit and G_σ from the truncated G_{NMR}. This result may not be so surprising since both distributions are based on fits to the same experimental data. Phenomenological stretched exponentials may also fit the conductivity modulus data well because this mathematical form can approximate the cutoff fraction of barriers that permits rapid hops for percolation of the mobile ions.

However, we have also shown that if the non-Debye type relaxation observed in ionic conductivity is due to a T-independent DAE, then one should find different β values when fitting the data to KWW relaxation functions in different temperature ranges. This is what is indeed found in many experiments, although the experimental T dependencies of the conductivity moduli are somewhat smaller than the approximation $\beta_\sigma \propto T^{0.5}$ we expect from a fixed DAE alone. The T dependence is probably reduced because the constant ε_∞ and the macroscopic σ_{dc} are mixed into the modulus. In another paper we will discuss the conductivity as a sum of

dc, ac, and ε_∞ contributions and how this influences M and β.

On comparing and contrasting the treatment of the conductivity and NSLR dynamical data with a DAE approach or the intrinsically nonexponential relaxation KWW treatment, we find that the DAE approach is able to treat both sets of data within a single formalism. Two different functions are required for the two different sets of data using the KWW formalism. We also find that while a DAE can be easily and naturally identified with the disordered glassy state, a similar natural association cannot be found for the KWW function. Other than qualitative interpretations, it is not clear for example, if a value of β close to unity or close to 0 can be interpreted in any straight forward manner in terms of the structure of the glass under study. In a similar way, the DAE approach can be easily tailored to handle the systematic change in the dynamics with glass composition and even multiple ion dynamics, where as such is not the case with the KWW approach. In the case of the multiple ion dynamics, where one ion population has significantly different dynamics than another, this must be treated as two separate relaxations in the KWW approach, where as in the DAE approach, the different ion dynamics are simply treated as a (slightly) more complex set of DAE.

Although we have shown above that the use of the macroscopic dielectric modulus and Eq. (6) has to be viewed with caution when one wants to obtain precise information about the microscopic ionic hopping motion,[30,31] the comparison of $M''(\omega)$ at different temperatures seems to be a rapid and sensitive way to decide whether the phenomenological β_σ for the conductivity depends upon T and thus supports a model with a DAE.

NSLR is usually measured and fitted as function of T rather than of ω, and hence a perfect KWW fit with a fixed β_{NMR} over a large T range should not be expected. However, there is no reason to prefer a macroscopic stretched relaxation function for the microscopic NSLR, since the radio frequency pulses cannot slow down the ionic motion and give an intrinsic KWW behavior to the spin-lattice relaxation.

Because fitted values of β may vary with temperature and the fitted prefactors τ_{K0} may be unphysically small, and since we see from Fig. 1 that the distributions derived from KWW-functions have components with unphysically short relaxation times $<10^{-13}$ s at high T, we conclude that any physics derived from extrapolations of KWW functions will be very uncertain. It should be remembered in discussions of KWW parameters β and E_K that the prefactors τ_{K0} must also be considered, and it is much better to compare the relaxation times or functions directly than through the more insensitive exponents from KWW or Arrhenius fits.

IV. CONCLUSION

The conductivity modulus spectra for a number of FIC is observed to exhibit a slight but systematic temperature dependence where the modulus spectra broadens with increase in the temperature. To accurately model the data, a temperature dependence of the nonexponential relaxation parameter, β, of $\beta \sim T^{0.5}$ is required and not *a priori* expected from the

KWW formalism where it is expected that β should be a fixed parameter. It is found, however, that our alternative treatment of using a fixed Gaussian DAE truncated at the conductivity percolation limit to model the ion dynamics through the conductivity modulus spectra does produce the correct approximate temperature dependence of $\beta \sim T^{0.6}$ using a fixed parameter set. It is found that some FIC exhibit stronger temperature dependencies than others, but no FIC are found where β decreases with temperature.

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