A new problem in the correlation of nuclear-spin relaxation and ionic conductivity in superionic glasses

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Abstract
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Keywords
glasses, activation energies, ionic conduction, conducting polymers, electrolytes

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A new problem in the correlation of nuclear-spin relaxation and ionic conductivity in superionic glasses

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Following the recent resolution of the longstanding problem of reconciling constant frequency nuclear-spin lattice relaxation (SLR) activation energies and d.c. conductivity activity energies in ion conducting glasses, we point out a new problem which seems not to have been discussed previously. We report conductivity data measured at a series of fixed frequencies and variable temperatures on a lithium chloroborate glass and compare them with SLR data on identically prepared samples, also using different fixed frequencies. While phenomenological similarities due to comparable departures from exponential relaxation are found in each case, pronounced differences in the most probable relaxation times themselves are observed. The conductivity relaxation at 500 K occurs on a time scale shorter by some 2 orders of magnitude than the 7Li SLR correlation, and has a significantly lower activation energy. We show from a literature review that this distinction is a common but unreported finding for highly decoupled (fast-ion conducting) systems, and that an inverse relationship is found in supercoupled salt/polymer “solid” electrolytes. In fast-ion conducting glasses, the slower SLR process would imply special features in the fast-ion motion which permit spin correlations to survive many more successive ion displacements than previously expected. It is conjectured that the SLR in superionic glasses depends on the existence of a class of low-lying traps infrequently visited by migrating ions.

I. INTRODUCTION

The failure of the classical Blombergen, Purcell, and Pound (BPP) theory to describe nuclear-spin lattice relaxation (SLR) in ionically-conducting glasses,1-4 and the need for a nonexponential relaxation assumption to provide accord with experiment,5-8 has been known for a long time. However, although Ngai5 recognized that relationships between SLR and conductivity anomalies were to be expected, it has only recently been pointed out9-11 that the longstanding discrepancy between activation energies for dc cationic conductivity and for SLR for the same cation in the same glass can be the direct and artificial consequence of the nonexponential nature of the relaxation. It is a simple consequence of the facts that (i) nonexponential relaxation leads to frequency-dependent conductivity,9 and also frequency-dependent SLR for frequencies above that of the system’s internal relaxation frequency; (ii) in the frequency-dependent range, the isochronal (constant frequency) activation energy is smaller than the dc value by a factor which depends largely on the nonexponentiality factor. The more nonexponential the relaxation, the greater the difference. The origin of the difference in dc conductivity activation energy and the usual ~10–100 MHz SLR activation energy is then primarily a consequence of the fact that almost all of the early SLR data were acquired in the frequency-dependent (ac) range (in consequence of

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accord between SLR and conductivity phenomenologies was obtained. For instance, Martin et al.\textsuperscript{13} reported that the high-temperature (dc) $T_1$ activation energy was now consistent with the dc conductivity energy, while Niklasson and Borjesson,\textsuperscript{15} by analyzing the high-frequency conductivity using power-law fits, rather than the previous\textsuperscript{1,19,20} modulus formalism, found agreement between the spectral densities, or correlation functions, for conductivity and SLR.\textsuperscript{21} Elliott\textsuperscript{22} has since constructed a microscopic theory for the SLR based on the assumption that the correlation function for the fluctuations involved in SLR is identical with that used in his diffusion-controlled-relaxation model for ionic conductivity\textsuperscript{23} (a development of the original one-dimensional Glarum model for dielectric relaxation). Unless the diffusion-independent term in Elliott’s model is important, the characteristic times for conductivity (or dielectric) relaxation and SLR should then have the same temperature dependence—both being controlled by the arrival of a diffusing ion at the site of a “defect” or relaxable subunit—and should have comparable magnitudes.

The aim of this paper is to show that, in a favorable case, the relation of SLR to conductivity is not so clear cut. The case is that of Li$^+$ motion in a LiCl–Li$_2$O–B$_2$O$_3$ glass in which the Li$^+$ motions are so free from the matrix that their jumping frequency can cause maximum damping of 30 GHz acoustic phonons, i.e., $\omega T_\text{g} \geq 1$, more than 100 K below $T_g$ (Ref. 24) (as for the AgI–Ag$_2$O–B$_2$O$_3$ case mentioned earlier). In such a case, the $T_1$ minimum for a~30 MHz SLR experiment would be expected far below $T_g$, but this has not been borne out in the recent experimental study of Martin et al.\textsuperscript{17} We show, using samples identical to those provided by one of us (M.T.) for Martin et al.’s SLR study, that the conductivity relaxation time (which is close to the mechanical relaxation time) is some 2 orders of magnitude shorter than the SLR correlation time. Furthermore, we will show that the activation energies are significantly different. These findings, coupled with the additional recent observation\textsuperscript{25} that the kinetics of a process as complicated as crack nucleation and failure in glass fibers from the same system, match with the kinetics of the conductivity, suggest that there is something yet to be understood about SLR in ionic glasses. Our observations will then be used as a basis for reexamining the conductivity/SLR relations of other recent studies.

II. EXPERIMENT

Starting materials were reagent-grade LiCl (Mallinkrodt), Li$_2$CO$_3$ (Fisher), and B$_2$O$_3$ (99.9% from Apache Chemicals). LiCl and B$_2$O$_3$ were vacuum dried at about 100°C for several days before use. The ground and mixed materials were heated in a platinum crucible with cover at temperatures between 700 and 850°C for 1 h and then melted at $\approx 960°C$ for 15 min. The very fluid melt was poured onto a stainless-steel plate and pressed quickly to a thickness of about 0.5 mm using a second plate. The quenched samples were then annealed at 320°C for 10 h in a dry He atmosphere. The glass obtained was slightly colored, presumably due to traces of Pt$^{2+}$ from the Pt cruci-

![FIG. 1. Conductivity as a function of frequency on log-log plot for the chloroborate glass 0.6LiCl–0.7Li$_2$O–1.0B$_2$O$_3$, at 5 K intervals. The temperature of measurement is indicated on the left of selected isotherms.](image)

This was assumed to have negligible effect on the conductivity. The composition studied was (LiCl)$_{0.6}$(Li$_2$O)$_{0.7}$(B$_2$O$_3$)$_{1.0}$ this being chosen after the higher LiCl content composition studied successfully by Borjesson\textsuperscript{24} proved difficult to measure reproducibly.

Taking precautions to protect the sample from moisture-induced surface deterioration, gold electrodes were sputtered onto the disc samples using a ring mask to provide a well-defined electrode dimension. The cell constant, 0.0559 cm$^{-1}$, was determined by micrometer determination of the disc thickness (to ±0.002 cm) and knowledge of the diameter of the smaller gold electrode. The sample was then mounted in a sealed metal cell in which it was suspended between spring-loaded contacts, and the conductivity and capacitance were determined over the frequency range 8 Hz–4 x 10$^6$ Hz using a Hewlett Packard model 4192 A frequency analyzer. The temperature range covered by the measurements was $-88°C$ to $+62°C$, though here we use a restricted sample of the results in the analysis to avoid any errors due to lead impedances and capacitances at high frequencies or from measurements made too near the bridge high impedance limits. The temperature was measured using a Cr–Al thermocouple in close contact with the sample inside the sealed cell. The whole assembly was mounted in a temperature smoothing controlled to ±0.02 K by a Eurotherm temperature controller. The whole data-taking process was automated as described in Ref. 26. The glass transition temperature was determined using a Perkin Elmer DSC-4 at 10 K/min.

III. RESULTS

The data are presented in the usual form of $\log(f)$ vs. $f$ for various isotherms in Fig. 1. Figure 2 shows a reduced set of these data in the same form and as transposed to the less common isochronal (constant probe frequency) Arrhenius plot form, in order to show their relationship. The dashed and dotted lines are explained later.

Finally, we present in Fig. 3 the combined conductivity and capacitance data in the complex electrical modulus form, since the $M''$ peak frequencies allow us to define the
conductivity relaxation times, we need to compare with those for SLR. For clarity, the real part of the modulus $M'$ is not shown. It rises to the value 0.07 at $10^6$ Hz in the manner seen in many previous cases. This value corresponds to a high-frequency dielectric constant $\varepsilon_{\infty}$ of 14 at the lowest temperature of the study, although a limiting low value of $\varepsilon_{\infty}$ has not been reached even at $10^6$ Hz and $-62$ °C.

IV. DISCUSSION

The isochronal Arrhenius plots of Fig. 2 again confirm the lower activation energies yielded by constant frequency measurements of relaxation processes under $\omega \tau > 1$ conditions. However, the "activation energy" in the ac ($\omega \tau > 1$) regime does not accord well with the SLR low-temperature ($\omega \tau > 1$) regime activation energy, even with our conservative data set. Since the SLR activation energy has been found for many glasses to be related to the d.c. conduction activation energy by the simple expression

$$E_a(\omega \tau > 1) = \beta E_{a(d.c.)},$$  \hspace{1cm} (1)$$

where $\beta$ is the parameter which measures the departure of the conductivity relaxation from exponentiality in the Kohlrausch-Williams-Watts (KWW) approximation

$$\theta(t) = \exp[-(t/\tau)^{\beta}],$$ \hspace{1cm} (2)$$

this is a matter for some concern. The pattern we see, one of curvilinear a.c. plots with average Arrhenius slopes that decrease with increasing frequency, is one common to previous studies. While the difference at the highest frequencies and lowest temperatures in some studies may in part be due to measurement inaccuracies in these conditions, its continued presence in the more reliable mid-frequency ranges suggests real differences between the conductivity and SLR response functions. Master plots of conductivity $\sigma''$ spectra of superionic glasses always show positive deviations from the transformed KWW function at or above half height (see Fig. 3 and Refs. 20 and 28), so the source of the deviation from Eq. (1) in the case of conductivity can be assigned to the onset of the excess loss mechanisms. This is also implied in a recent discussion by Jain et al. The point at which these should begin to influence the slope of the a.c. conductivity is marked by an arrow on selected isochrones in Fig. 2(b), and is seen to be quite close to the point of departure from the d.c. conductivity line. These additional mechanisms, which anticipate the transition to the limiting high-frequency $\sigma - f^\alpha (\alpha - 1)$ regime, evidently do not affect the SLR response, at least not at $\omega \tau$ values as close to 1.0 as in the case of conductivity. In this respect, the SLR response behaves more like that of conductivity in poorly conducting glasses (low decoupling indexes) in which the conformity to the transformed KWW function extends over a wider $\omega \tau$ range.
This is, in fact, quite consistent with the main point of this paper to which we now turn attention.

Rather than focusing attention on the ac “activation energies,” we now examine the relationship between the actual characteristic times, $\tau_0$, for the two processes. These are determined from the conditions under which maximum coupling between the fixed frequency probe field ($\omega_p$) and the relaxing system occurs, using the general relation $\omega_p \tau_c \approx 1$ [in the particular case of SLR, it is more accurate to write $\omega_0 \tau_c \approx 0.6$ for the maximum (but still very weak) coupling condition in BPP theory, but the effect of this refinement is negligible compared with the differences in characteristic times we will be discussing].

For the SLR process, this condition is signaled by arrival at a minimum value of the spin-lattice relaxation time $T_1$. At the $T_1$ minimum $\omega L \tau_c \approx 1$, where $\omega L$ is the Larmor frequency in radians s$^{-1}$ for the chosen magnetic field. For conductivity, this condition is defined by the arrival at a maximum value of $M''$ (Fig. 3), and we obtain a characteristic time $\tau_0$ from the relation

$$\tau_0 = (2\pi f_{\text{max}})^{-1}. \quad (3)$$

Under conditions in which the maximum cannot be observed, an average conductivity relaxation time can be obtained$^{19}$ from the d.c. conductivity using the Maxwell-like relation

$$\langle \tau_0 \rangle = \frac{\sigma_0 \epsilon_\infty}{\sigma_{\text{d.c.}}} \quad (4)$$

in which $\epsilon_0$ is the permittivity of free space and $\epsilon_\infty$ is 14 (see Sec. III).

Because the modulus analysis suppresses electrode capacitance effects, $\tau_0$ and $\langle \tau_0 \rangle$ defined in these ways are always in close agreement [c.f. comparisons of Eq. (4) values with those made using tan $\delta$ maxima],$^{29}$ although small differences must be expected because of the relationship$^{28}$

$$\langle \tau_0 \rangle = \frac{\tau_c \Gamma(1/\beta)}{\beta}, \quad (5)$$

where $\Gamma$ is the gamma function and $\beta$ is the nonexponentiality parameter of the “universal” KWW function, Eq. (2). For $\beta$ values of 0.64 and 0.5, the differences amount to 0.1 and 0.3 log units, respectively.$^{28}$

We will use this treatment of the conductivity data in an initial comparison with the SLR results of Martin et al.$^{17}$ but it should be recognized here that there is currently an increasing interest and persuasion$^{30-32}$ in a return to the conventional treatment of electrical relaxation in glasses in which the glass is treated as a relaxing dielectric with a d.c. conductance in parallel. This alternative data treatment will be considered as part of the later discussion.

The conductivity relaxation times obtained from the $M''$ peak frequencies ($\tau_0$), and from d.c. conductivities ($\langle \tau_0 \rangle$), are plotted in Fig. 4 along with the values of $\tau_0$ for the SLR process defined from the maxima in $\log(T_1)$ vs $1/T$ curves of Ref. 17 for three different spectrometer frequencies. The $\tau_0$ values are obtained using the usual assumption that, at the $T_1$ minimum, the relationship $\omega L \tau_c \approx 1$ holds (where $\omega L$ is the Larmor frequency for the particular spectrometer field). Of course this does not define a unique correlation time any more than does the maximum loss frequency in Fig. 2, since in neither case is the relaxation process exponential. However, if the correlation function is the same or similar for each process, then the characteristic, or most probable time, should differ from the average in the same way. In any case, the difference of $\tau$ from the average value $\langle \tau \rangle$ should be small, as seen for $\tau_0$ and $\langle \tau_0 \rangle$ in Fig. 4.

It is clear from Fig. 4 that there is a rather large difference between the time scales for the two processes, not only in the value of $\tau_0$ at any chosen temperature, but also in the temperature dependences of the two processes. The fact that both processes can be extrapolated to give photon-like $\tau_0$ values$^{20,2c}$ (as indicated by the far IR Li$^+$ “rattling” time, $1/\omega_0$ in Fig. 4) encourages belief that both sets of measurements are free from artifacts (the conductivity $\tau_0$ is usually$^{20,2c}$ a little shorter than $10^{-14}$ s). We note additionally the mechanical (longitudinal) relaxation time $\tau_m$ obtained by Borjesson$^{24}$ for a glass of similar composition (LiCl)$_{0.7}$(Li$_2$O)$_{0.7}$(B$_2$O$_3$)$_{1.0}$ using an even higher frequency probe than SLR, viz., Brillouin scattering, in Fig. 4. This relaxation time, due to Li$^+$ ion jumping, accords quite well with the value extrapolated in the present conductivity relaxation study when it is taken into account that the difference is in the direction expected from the higher LiCl content and higher conductivity of Borjesson’s glass.
The difference in conductivity and SLR relaxation activation energies seen in Fig. 4 is much larger than the difference ($\Delta E = pRT \sigma_E$) arising from the difference between conductivity and diffusion processes ($\sigma = D/T$). This implies that the SLR correlation time is longer mainly because the fluctuation needed to optimize the intrinsically weak relaxation of the spin system is less probable. This could mean that more particles, more or different jumps, or higher degrees of correlation are involved in SLR than in conductivity relaxation. In this respect the observation that, in the cases quoted, the complete $T_1$ curve requires a greater nonexponentiality parameter for its fitting than does the complete conductivity relaxation curve ($M''$ spectrum, Fig. 3), would be consistent. However, this cannot be used as an argument supporting different kinetics for the two processes without due consideration (given later) of alternative ways of treating the conductivity/dielectric relaxation. What does seem immediately implicit in Fig. 4 is that the fluctuations (electric field gradient etc.) which couple most effectively to the spin system (hence, which minimize $T_1/\tau_c$) are not those determined by the frequency of ionic jumping unless there is some error in the common view that the conductivity relaxation time and mobile ion jump time are very similar when many ions are present. An obvious question is whether or not there are data on other systems which show the same trend. However, before answering this question, we should first consider a possible source of the discrepancy which would require no revision of the previous expectation of common electrical and SLR correlation functions.

We must ask whether the difference between $\tau_\sigma$ and $\tau_c$ could be an artifact of the formalism used to analyze the conductivity relaxation. It could be argued that our complex modulus treatment of the electrical relaxation phenomenon as opposed to the parallel dc conductor plus dielectric relaxation treatment causes a distortion of the electrical relaxation which is the origin of the discrepancy. That this possibility does not resolve the discrepancy in time scales is most easily seen from Johari's treatment of the phenomenon of the latter standpoint. Rather than subtracting a contribution to the susceptibility due to the dc conductance, Johari attributes the low-frequency part of the modulus spectrum to the dc conductivity and subtracts out a corresponding Lorentzian component. It is clear in this case that the frequency of the maximum in the residual $M''$ spectrum (which it is argued should give the true dielectric relaxation time) would occur at higher frequencies, corresponding to shorter characteristic times. Thus, in this analysis the difference between electrical (now dielectric) and spin relaxation times would be accentuated rather than removed. We therefore conclude that the relaxation time discrepancy revealed by this study is nontrivial, and turn to the other published works in the area to see if similar differences can be identified.

Of the other studies of Li$^+$-containing glasses for which both types of data are available, one included SLR data at the low frequency of 4 MHz, which is within the common conductance measurement frequency range. An isochronal conductivity scan at 400 KHz (one decade below the lowest-frequency SLR scan) was published in Ref. 13 and showed a break from the dc curve at 250 K, considerably below the temperature of the $T_1$ minimum at 4 MHz (345 K) as expected for the lower frequency. However, based on the break temperatures at 40 and 4 KHz, that at 4 MHz (the SLR frequency) would also occur at a lower temperature, 300 K, than for the SLR $T_1$ minimum. This implies that conductivity relaxation is the faster process since conductivity is evidently able to follow the field oscillations to lower temperatures. The direct comparison is made as before by using the dc conductivities to calculate the conductivity relaxation time, via Eq. (2), at the temperature of the $T_1$ minimum. This requires a short extrapolation of the dc conductivity data available in Ref. 13. The result is $\tau_\sigma = 10^{-9.7}$ s—more than 2 orders of magnitude shorter than the $^7$Li $\tau_c$ value ($1/\omega_c = 10^{-7.4}$ s). Since this study, like that with which we make comparison in the present paper, was performed at several frequencies, we can compare the activation energies of $\tau_\sigma$ and $\tau_c$. As in Fig. 4, that for SLR proves to be considerably larger, suggesting that our observation is general. It should be noted here that the $T_1$ findings of Martin et al. are well supported by the single-frequency study of Pradel et al. The latter authors analyzed their data using a Davidson–Cole relaxation function and found both the spectral width parameter $\sigma_{DC}$ and $E_{ac}$ to be greater than for dc conductivity.

Turning to $^{109}$Ag relaxation, we note that in Ref. 14 a difference between $\tau_\sigma$ and other relaxation times associated with Ag$^+$ motion in (AgI)$_{0.6}$(Ag$_2$O·2B$_2$O$_3$)$_{0.4}$ was recognized, but the difference was only cited as evidence for the failure of BPP theory for SLR. If we quantify the $\tau_\sigma$ vs $\tau_c$ difference, we find $\tau_\sigma$ for $^{109}$Ag (obtained from 12.5 MHz studies) is $10^{-7.8}$ s at the $T_1$ minimum (308 K) and this is 1.5 orders of magnitude longer than the value $10^{-9.3}$ s for conductivity relaxation at the same temperature. Although smaller than in the previous case, this is still a large difference, especially in view of the fact that the longitudinal mechanical relaxation time interpolated from Brillouin scattering and ultrasonic data agrees with the conductivity relaxation time within 0.1 orders of magnitude at this temperature.

The remaining $^{109}$Ag study is that of Roos et al. on (AgI)$_x$(Ag$_2$S–GeS$_2$)$_{1-x}$ glasses which were characterized electrically by Pradel and Ribes. The SLR correlation time for the glass of $x=0.5$ is $10^{-7.8}$ s at 282.5 K compared with $10^{-10.0}$ for $\langle \tau_\sigma \rangle$ at the same temperature. This discrepancy is comparable to that found by Chung et al. and Roos et al. found that the Davidson–Cole distribution function was incapable of giving a satisfying fit to the log($T_1$) vs $1/T$ plot, hence, gave no DC parameters which could be compared with those for the conductivity relaxation.

From the aforementioned review, it would appear that the $\tau_c$ vs $\tau_\sigma$ gap to which we have drawn attention is real and general. Its resolution should provide additional insights into mechanisms of, and cooperative effects in, ionic transport processes in glasses and supercooled liquids.

In seeking to clarify this problem, it would be helpful to pursue joint conductivity/SLR studies into the viscous
liquid state above \( T_g \) to see to what extent the differences we have identified disappear as the conductivity and structural relaxation times approach each other. One case is already available since one of the first systems ever characterized with respect to conductivity relaxation, \( \text{LiCl-H}_2\text{O} \), has recently been studied by both conventional \( ^7\text{Li} \) and \( \beta \)-radiation detected \( ^6\text{Li} \) NMR techniques. Comparing the latter studies on \( \text{LiCl-D}_2\text{O} \) with short extrapolations (to the same composition) of conductivity relaxation data on \( \text{LiCl-H}_2\text{O} \) solutions, we find that the \( ^7\text{Li} \) SLR relaxation time and the conductivity relaxation time are the same within \( 10^{\pm 1} \). This seems consistent with the pattern we have unfolded because in the \( \text{LiCl-H}_2\text{O} \) system it was shown that the decoupling index above \( T_g \) was close to unity implying that conducting and matrix species relax on the same time scale. For fast-ion glass systems such coincidence of time scales is only approached as \( T \to \infty \) in the liquid state.

Such consistency suggests we should look for a case in which the decoupling index is in the inverse sense, i.e., in which the conductivity relaxation is slower than the matrix relaxation. Although such a system cannot easily be studied in the glassy state, its liquid-state behavior could be expected to show the opposite relation of NMR correlation times and conductivity relaxation times to that observed for superionic glasses. A suitable case in which supercoupling of conducting modes to matrix modes has been demonstrated is the salt-in-polymer type of “solid” electrolyte, in which it would indeed appear that the SLR effective fluctuations occur on shorter time scales than does conductivity relaxation. This has been noted without quantification by Greenbaum et al. and data provided by these workers suggest that the differences in \( \tau_c \) and \( \tau_\sigma \) are of the order of \( 10^0 \). Whether or not there are any differences in the temperature dependence in this case cannot be determined at this time. However, the inversion of the \( \tau_c/\tau_\sigma \) ratio, under the same circumstances that the \( \tau_c/\tau_\sigma \) ratio (i.e., the decoupling index) is large, provides a coherent pattern which we believe deserves further quantitative exploration.

We conclude with further consideration of the origin of the difference between \( \tau_c \) and \( \tau_\sigma \) in these systems since the explanation is necessary of interest in connection with migration mechanisms. We invoke two scenarios. The first attributes the difference to correlation effects and the second to site distinction effects.

First, let us suppose that the \( \text{Li}^+ \) ion hops do not occur randomly but rather are highly correlated through the long range Coulomb interaction (because of the need to maintain overall electrical neutrality with the immobile anion network). Then the effect of individual ion hops on the damping of the excess nuclear spin energy should be diminished because the correlations serve to smooth out the field gradient differences between different sites. Thus, instead of the damping maximum time scale corresponding to the ion jump time scale, it may be longer by an amount which reflects the efficiency of the intercation coupling. It seems reasonable to suppose that the correlations will become stronger the lower the temperature, hence the difference between \( \tau_\sigma \) (reflecting individual jumps) and \( \tau_c \) (reflecting correlation-corrected jumps) could increase with decreasing temperature, as observed.

On the other hand, one could argue that the larger activation energy for \( \tau_c \) implies the presence of a distinct class of deep traps in which the electric field gradient and/or the dipolar interactions which couple to the spin system are very different from those in the shallower traps in which the ions must spend most of their time. To understand the domination of conductivity by shallow-trapped ions, one must suppose the shallower traps to be highly degenerate. Because of the field gradient/dipolar effect, however, the less frequent visits to the deeper traps would dominate the SLR. An increase in shallow trap depth in poorer conducting glasses would explain the tentative correlation of \( \tau_c/\tau_\sigma \) with \( R_g \).

This latter picture has much in common with that underlying the weak electrolyte model. The emphasis on a trapping topology we invoke here over the more common energy landscape picture of ion migration, however, implies an analogy with models of electron transport in glasses and helps to rationalize their common features. To broaden the picture even further, we should add that if studies in the liquid state of moderately fast-ion conductors can show that \( \tau_c \) varies in a non-Arrhenius fashion with changing temperature so as to approach both \( \tau_\sigma \) and \( \tau_c \) at high temperature, then the phenomenon to which we have drawn attention would be identified as another participant in the serial decoupling phenomenon discussed recently by several authors.

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