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# Regarding the correlation of nuclear spin relaxation and electrical conductivity relaxation in ionic glasses

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Much attention has been focused recently on the apparent differences between ion dynamics in ion-containing glasses as probed by electrical conductivity relaxation (ECR) and by nuclear spin relaxation (NSR) techniques. In both relaxation processes, a power law frequency dependence is observed. Based upon fluctuation-dissipation arguments, the power law exponents should be equivalent. However, experimentally, it appears that the conductivity exponent is generally smaller than the NSR exponent. While an explanation for this discrepancy based upon fundamental differences in the correlation functions probed by the two techniques has been proffered, we show how this discrepancy may simply arise from differing analyses of the ac conductivity. We review several cases taken from the literature in which the conductivity exponent was obtained from analysis of the electrical modulus. We demonstrate how this analysis approach generally underestimates the conductivity exponent. When we instead determine the exponent directly from the ac conductivity, we find near equivalence between the NSR and ECR exponents. (© 1998 American Institute of Physics. [S0021-9606(98)51514-0]

# I. INTRODUCTION

It is well established that the motion of ions in ioncontaining glasses produce a non-Debye response in both the ac conductivity,  $\sigma(\omega)$ , and the spin lattice relaxation time,  $T_1(\omega)$ , at frequencies above the characteristic relaxation rate.<sup>1-5</sup> The ac conductivity exhibits a power law at high frequencies, but is constant ( $\sigma_0$ ) at low frequencies, and can be described empirically by

$$\sigma(\omega) = \sigma_0 + A \,\omega^{n_\sigma}.\tag{1}$$

This non-Debye behavior is reflected as well in the electrical modulus representation,<sup>6</sup>  $M^*=1/\epsilon^*$ , where  $\epsilon^*=\epsilon'-i\sigma/\omega$  is the complex dielectric permittivity, as a distinctly asymmetric loss modulus,  $M''(\omega)$ . This loss modulus is often described over a limited range of frequencies near its maximum by a Fourier transform of the Kohlrausch–Williams–Watts (KWW) relaxation function,

$$\phi_m(t) = \exp\{-(t/\tau_m)^{\beta_m}\},\tag{2}$$

where the KWW exponent,  $\beta_m < 1$ , is a measure of the degree of deviation from Debye relaxation.

Corresponding frequency-dependent behavior is also observed in the nuclear spin lattice relaxation time,  $T_1(\omega)$ , which is frequency independent at high temperatures (below the maximum of  $1/T_1(\omega)$  vs.  $T^{-1}$  plots) but varies as

$$T_1(\omega) \approx B \omega^{2-n_{\rm NSR}} \tag{3}$$

at low temperatures.<sup>3</sup>

Both the electrical conductivity relaxation (ECR) and nuclear spin relaxation (NSR) track the motion of ions in glasses, albeit in somewhat different contexts since the correlation functions of these two processes are different.<sup>2</sup> The conductivity is related to ion diffusion via the currentcurrent correlation function and in the absence of cross correlations is given by the velocity *auto*correlation function or the mean square displacement of a tagged particle. The spin lattice relaxation rate  $1/T_1(\omega)$  arises from two contributions involving magnetic dipole–dipole interactions and interaction of the nuclear quadrupole with the local electric field gradient (both interactions vary as an inverse cube of the separation distance). Thus NSR involves a correlation of mutually interacting *pairs* of particles.<sup>1</sup>

In the last five years or so, much work<sup>1-5,7-9</sup> has been devoted to drawing connections between the non-Debye behavior of ECR and NSR. Strom et al<sup>10</sup> noted that such a connection might be obtained in the first approximation via the fluctuation–dissipation theorem of statistical mechanics which predicts

$$1/T_1(\omega) \propto \frac{kT\sigma(\omega)}{\omega^2}.$$
(4)

In this instance it is assumed the two processes share a common correlation function despite the physical differences in the correlations probed by NSR and ECR.<sup>1</sup> As defined above [see Eqs. (1) and (3)], this approximation leads to an equivalence between the two exponents,  $n_{\rm NSR}$  and  $n_{\sigma}$ .

While early studies<sup>1,11</sup> conducted primarily for low conductivity oxide glasses at low temperatures indicate  $n_{\text{NSR}} \approx n_{\sigma} \approx 1.0$ , results for so-called superionic glasses<sup>3,4</sup> at higher temperatures indicate  $n_{\text{NSR}} \approx 0.65$  and  $n_{\sigma} \approx 0.5$ ; that is  $n_{\text{NSR}} > n_{\sigma}$ .

An additional striking dissimilarity is seen<sup>7,12</sup> in the characteristic timescales,  $\tau_{\text{NSR}}$  and  $\tau_{\sigma}$ . Both are commonly described by Arrhenius laws,  $\tau_i = \tau_i^{\infty} \exp(E_i/kT)$ , and appear to behave quite differently such that (1) over a substantial temperature range,  $\tau_{\sigma} \ll \tau_{\text{NSR}}$ , (2) in the high-temperature limit,  $\tau_{\text{NSR}}^{\infty} < \tau_{\sigma}^{\infty}$ , and (3)  $E_{\text{NSR}} > E_{\sigma}$ . These differences are not surprising and suggest that a first approximation such as fluctuation–dissipation may be insufficient. A tentative explanation of these peculiar trends has been offered within the framework of the coupling model.<sup>13–15</sup> The model assumes that both ECR and NSR can be described by KWW decays of the form

$$\phi_i(t) = \exp\{-(t/\tau_i)^{1-n_i^{\kappa}}\}.$$
(5)

The superscript denotes exponents that are determined by fits of the KWW as opposed to those obtained from analysis of the power law alone [see Eqs. (1) and (3)] and is a distinction which will become clearer in later discussion. Owing to the inverse cube dependence upon separation distance of ion pairs, it is proposed that the NSR correlation is enhanced at short distances such that the "coupling parameter",  $n_{\text{NSR}}^K$ , of NSR is larger than that of conductivity (i.e.,  $n_{\text{NSR}}^K > n_{\sigma}^K$  From this inequality between the exponents, the coupling model predicts that the ratio of activation energies is

$$\frac{E_{\rm NSR}}{E_{\sigma}} = \frac{1 - n_{\kappa}^{K}}{1 - n_{\rm NSR}^{K}},\tag{6}$$

and that the pre-exponential factors are related by

$$\frac{\tau_{\rm NSR}^{\infty}}{\tau_{\sigma}^{\infty}} = \frac{\left[(1 - n_{\rm NSR}^{K})\omega_{c}^{n_{\rm NSR}^{K}}\tau_{0}\right]^{1/(1 - n_{\rm NSR}^{K})}}{\left[(1 - n_{\sigma}^{K})\omega_{c}^{n_{\sigma}^{K}}\tau_{0}\right]^{1/(1 - n_{\sigma}^{K})}}.$$
(7)

For the values<sup>3</sup> of  $\omega_c = 10^{12}$  Hz and  $\tau_0 = 10^{-13}$  s together with  $n_{\text{NSR}}^K = 0.65$  and  $n_{\sigma}^K = 0.5$ , Eqs. (6) and (7) lead to  $E_{\text{NSR}}/E_{\sigma} = 1.4$  and  $\tau_{\text{NSR}}^{\infty}/\tau_{\sigma}^{\infty} \approx 3 \times 10^{-2}$ . Thus the coupling model appears to offer a qualitative explanation for observed differences in ECR and NSR experiments.

In the present paper, however, we reexamine these comparisons between ECR and NSR in light of recent realizations regarding the analysis of ECR data using the electrical modulus formalism. We show that in many of the previous comparisons, the conductivity exponent as typically determined from traditional fits of a KWW to the electrical modulus is significantly smaller than that obtained from the ac conductivity. Instead, we find that when  $n_{\sigma}$  is determined directly from the frequency dependence of the conductivity, the exponent so obtained is comparable to that obtained from a similar power law analysis of NSR, hence suggesting that previous findings of an inequality between the two exponents may be only an artifact of the modulus analysis.



FIG. 1. Conductivity of  $0.1 \text{Li}_2 \text{O}/0.9 \text{GeO}_2$  for temperatures 296, 355, 396, 434, 471, and 514 K. Inset shows the temperature dependence of the effective power law exponent ( $n_{\text{eff}}$ ) and highlights the eventual approach to  $n_{\sigma}$  at high temperatures.

## **II. DATA ANALYSIS**

We begin by reviewing salient features of ECR data in both the conductivity and electrical modulus representations. As an example,  $\sigma(\omega)$  for 0.1Li<sub>2</sub>O/0.9GeO<sub>2</sub> is presented in Fig. 1, and displays the characteristic frequency dependence described by Eq. (1). At low frequencies  $\sigma(\omega)$  approaches a plateau,  $\sigma_0$ , and increases at higher frequencies as a power law with  $n_{\sigma} \approx \frac{2}{3}$ . Also apparent in the figure is an increase in the slope of  $\sigma(\omega)$  at high frequencies with decreasing temperature. At our lowest temperature, the slope is approximately unity. This approach to unity slope at low temperatures is well documented<sup>16-18</sup> and is generally attributed to the presence of a secondary mechanism,  $\sigma_{II}(\omega) \approx \omega^1$ , which displays a roughly linear frequency dependence and possibly a weak temperature dependence. Often referred to as the "excess" or "constant loss" contribution, this second mechanism contributes significantly to the total measured conductivity when that due to ionic relaxation [see Eq. (1)] is small (i.e., at either low temperatures or high frequencies). The exact nature of this excess contribution is still unclear, as is the exact limiting value of the exponent which some claim may exceed unity.<sup>19</sup> Furthermore, while these two contributions are suitable for describing  $\sigma(\omega)$  at frequencies up into the gigahertz range, they become inadequate at higher frequencies (far infrared) where vibrational processes begin to dominate.<sup>20</sup>

In the inset to Fig. 1, we plot the effective exponent,  $n_{\rm eff}$ , obtained from fits of Eq. (1). We refer to this as an effective exponent, since it in principle includes contributions from two power law mechanisms,  $\sigma_{I}(\omega) \approx \omega^{n\sigma}$  and  $\sigma_{II}(\omega) \approx \omega^{1}$ . As can be seen from the figure, a transition occurs from  $\sigma(\omega)$  dominated by the excess contribution at low temperatures with  $n_{\rm eff} \approx 1$  to  $\sigma(\omega)$  dominated by ionic relaxation at higher temperatures with  $n_{\rm eff} \approx n_{\sigma} \approx \frac{2}{3}$ . A key point we wish to stress here, and which will be important in later discussion, is that  $n_{\rm eff}$  approaches to a high-temperature limiting plateau. This plateau  $(n_{\sigma} \approx 0.66)$  is reached for T >400 K in the case of 0.1Li<sub>2</sub>O/0.9GeO<sub>2</sub>. Similar behavior has been observed by others<sup>16</sup> and it is clear that a temperature range exists over which the contribution to  $\sigma(\omega)$  from the constant loss mechanism  $[\sigma_{II}(\omega)]$  is negligible, and thus where  $n_{\rm eff} = n_{\sigma}$ .



FIG. 2. The  $M''(\omega)$  of 0.1Li<sub>2</sub>O/0.9GeO<sub>2</sub> at 434, 471, and 514 K. Solid lines are KWW fits with  $\beta_m = 0.55$ . Inset shows  $M''(\omega)$  at 434 K on a double logarithmic scale and highlights the differences between the traditional KWW fit and the experimental data at high frequencies.

We turn now to the electrical modulus. In Fig. 2, we present  $M''(\omega)$  of the  $0.1 \text{Li}_2 \text{O}/0.9 \text{GeO}_2$  data for temperatures *above* 400 K.  $M''(\omega)$  typically exhibits a well-defined maximum to which a characteristic relaxation rate can be associated and displays an asymmetric frequency dependence whose FWHM is significantly larger than the 1.14 decades seen in Debye processes.

A procedure for describing  $M''(\omega)$  by a KWW decay function was outlined several years ago by Moynihan et al<sup>21</sup> and has been widely adopted by others but recently criticized by some.<sup>22,23</sup> We include examples of such traditional KWW fits in Fig. 2 with  $\beta_m(=1-n_{\sigma}^K)=0.55$ . We refer to these fits as "traditional" since they focus most attention toward describing the region of  $M''(\omega)$  near the peak,  $\omega \approx \omega_p$ , and sacrifice the data at higher frequencies.<sup>24</sup> While the fits do a good job of describing much of  $M''(\omega)$ , from low frequencies up to and just beyond  $\omega_p$ , these fits clearly fail to describe the high-frequency wing of  $M''(\omega)$ . Indeed, the fit varies as  $\omega^{-\beta_m}$  at high frequencies while the experimental data vary as  $\omega^{n_{\text{eff}}-1}$ . These two limiting behaviors are evident in the double logarithmic scale shown as an inset to Fig. 2.

The failure of the KWW to completely describe  $M''(\omega)$ is widely acknowledged, and has been recognized from the outset.<sup>21</sup> Many insist that this failure stems from the presence of the excess or constant loss mechanism  $[\sigma_{II}(\omega)]$  known to dominate at low temperatures (or high frequencies) and which, as we saw in Fig. 1, artificially increases the effective exponent from its true value of  $n_{\sigma}$ . This constant loss will likewise lift  $M''(\omega)$  at high frequencies, leading to the apparent underestimate of the fit to the data. Based on this interpretation of the mismatch between the KWW fit and the data at high frequency, it is tacitly assumed that the exponent  $\beta_m$  obtained from fitting just around the peak of  $M''(\omega)$  is the "true" exponent, that is, the exponent which would have described all of  $M''(\omega)$  if the constant loss were not present. Under this assumption, the exponent  $\beta_m$  is related to  $n_{\sigma}$ simply as<sup>15,25</sup>

$$\boldsymbol{\beta}_m = 1 - \boldsymbol{n}_{\sigma}^K = 1 - \boldsymbol{n}_{\sigma} \,. \tag{8}$$

However, as our results for  $0.1Li_2O/0.9GeO_2$  demonstrate, the constant loss contribution alone is not an acceptable explanation for the inability of the KWW fit to describe

 $M''(\omega)$  over the entire frequency range. It is clear from Fig. 1 that, for T > 400 K, the contribution from any constant loss mechanism is negligible, and  $n_{\rm eff}$  has settled to a plateau value of  $n_{\rm eff}=n_{\sigma}=0.66$ . Over this same temperature range, though, fits of a KWW ( $\beta_m=0.55$ ) continue to underestimate the high-frequency wing of  $M''(\omega)$ . Consequently, the equality in Eq. (8) is *invalid*, even in the absence of excess loss contributions. This non-equivalence between  $\beta_m$  and  $1-n_{\sigma}$  was recently demonstrated<sup>25</sup> for a wide variety of glassformers which exhibited  $n_{\sigma}=0.67\pm0.05$  as compared with  $\beta_m=0.58\pm0.1$  (i.e.,  $n_{\sigma}^{K}=1-\beta_m\approx0.4$ ) and an explanation has been proposed.<sup>26</sup>

We now reexamine three ion-conducting glasses which have been studied both by NSR and ECR (electric modulus) techniques and which have suggested significant differences exist between the respective exponents,  $n_{\text{NSR}}$  and  $n_{\sigma}$ . In each instance, we demonstrate how analysis of the conductivity given by Eq. (1) provides an exponent,  $n_{\sigma}$ , that is significantly larger than that,  $n_{\sigma}^{K} = 1 - \beta_{m}$ , obtained by traditional KWW fits of the electric modulus and is nearly identical to the power law exponent obtained by NSR.

# A. 0.6LiCI-0.7Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>

The NSR measurements on 0.6LiCl-0.7Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> were reported by Trunnel et al.<sup>27</sup> who analyzed the power law characteristics of  $T_1(\omega)$  [slope of log(1/ $T_1$ ) vs log( $\omega$ ) from Fig. 6 of Ref. 27] to obtain  $n_{\text{NSR}} = 0.65$ . Tatsumisago et al.<sup>4</sup> performed ECR measurements and provided data for several temperatures in both  $\sigma(\omega)$  and  $M''(\omega)$  representations (Figs. 1 and Fig. 3 of Ref. 4, respectively). In their study, traditional fits of a KWW were performed which failed to describe the high-frequency wing but did describe the region of  $M''(\omega)$  near the peak with  $\beta_m = 0.50$ . Assuming the equivalence given in Eq. (8) they concluded  $n_{\sigma}$  $=n_{\sigma}^{K}=1-\beta_{m}=0.50$ , which is significantly smaller than  $n_{\rm NSR}$ . In Fig. 3, we have reproduced some of the conductivity data from Tatsumisago, et al.4 (extracted directly from Fig. 1 of Ref. 4), including their lowest temperature spectrum which exhibits a near unity slope (i.e., arrival at the constant loss dominated regime). Included are fits of Eq. (1) to the five higher temperatures, where we find  $n_{\sigma} \approx 0.62$  $\pm 0.05$ , a value significantly larger than that obtained from the KWW fit of  $M''(\omega)$  and reasonably equivalent to that reported for NSR ( $n_{NSR} = 0.65$ ). We conjecture that the value of  $n_{\sigma}$  obtained from Fig. 3 does represent the hightemperature plateau value for  $n_{\rm eff}$  since no significant temperature dependence is evident. This conjecture is also supported by the spectrum at 181 K, which indicates the excess contribution  $[\sigma_{II}(\omega) \approx \omega]$  is roughly an order of magnitude smaller than most of the higher temperature spectra analyzed in Fig. 3.

## B. 0.56Li<sub>2</sub>S-0.44Si<sub>2</sub>S

Next we consider the lithium thiosilicate glass,  $0.56\text{Li}_2\text{S}-0.44\text{Si}_2\text{S}$ . Borsa *et al.*<sup>5</sup> analyzed measurements of  $T_1(\omega)$  as a power law [slope of  $\log(1/T_1)$  vs  $\log(\omega)$  from Fig. 3b of Ref. 5] and reported  $n_{\text{NSR}}=0.65$ , identical to the value observed in the previous case for  $0.6\text{LiCl}-0.7\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ . In the same paper, ECR data were



FIG. 3. Conductivity of  $0.6LiCl-0.7Li_2O-B_2O_3$  taken from Ref. 4. Solid lines are fits to Eq. (1) with the effective exponents shown.

presented and analyzed using the traditional KWW fitting to the electrical modulus with  $\beta_m = 0.48(n_{\sigma}^K = 1 - \beta_m = 0.52)$ . Conductivity data (extracted directly from Fig. 1a of Ref. 5) is reproduced in Fig. 4, and once again analyzed in terms of Eq. (1). Although  $n_{\sigma} \approx 0.64 \pm 0.05$  at high temperatures, a noticeable increase occurs for the exponent at the lowest temperature (141 K where  $n_{\rm eff} \approx 0.75$ . This is likely a result of encroachment of the constant loss at this reduced temperature. For comparison, we include the lowest temperature spectra from 0.1Li<sub>2</sub>O/0.9GeO<sub>2</sub> (296 K and 0.6LiCl- $0.7Li_2O-B_2O_3$  (181 K), which are consistent with the location of  $\sigma_{II}(\omega)$  found for a large variety of materials in a recent survey28 and which suggest the high-frequency portion of the last spectrum might indeed be influenced by such a constant loss mechanism. In fact, fitting the 141 K spectrum only out to  $10^4$  Hz reduces  $n_{\rm eff}$  to 0.66. We conclude that  $n_{\sigma} \approx 0.64 \pm 0.05$ , again significantly larger than the value previously obtained from KWW analysis of  $M''(\omega)$  but comparable to that seen by NSR ( $n_{\rm NSR} = 0.65$ ).

# C. ZBLAN

Last we review the studies of a flourozirconate glass of composition (mol %) 27.4  $ZrF_4$ , 27.4  $HfF_4$ , 19.8  $BaF_2$ , 3.0  $LaF_3$ , 3.2  $AlF_3$  and 19.2 NaF (ZBLAN) in which both ECR and NSR data have previously been presented. In this final example the limitations on available data have made our analysis more tenuous than in the previous two cases. Analy-



FIG. 4. Conductivity of  $0.56\text{Li}_2\text{S}-0.44\text{Si}_2\text{S}$  taken from Ref. 5. Solid lines are fits to Eq. (1). The dashed line is a fit to Eq. (1) for frequencies only to  $10^4$  Hz. Included for comparison are data for  $0.6\text{LiCl}-0.7\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  at 181 K (crosses) and  $0.1\text{Li}_2\text{O}/0.9\text{GeO}_2$  at 296 K (diamonds) which are dominated by the excess contribution [ $\sigma_{II}(\omega)$ ].



FIG. 5. The ac portion of conductivity of ZBLAN taken from Ref. 3. Solid lines are fits of a single power law with  $n_{\sigma} = 0.68 \pm 0.05$ . A slope of 0.59 is shown for comparison. Inset shows  $M''(\omega)$  for ZBLAN at approximately 370 K. A power law description of the high-frequency side indicates  $n_{\sigma}^{K} \approx 0.6$ .

sis of  $T_1(\omega)$  by Kanert *et al.*<sup>3</sup> concluded  $n_{\rm NSR} = 0.75 \pm 0.07$ , a value which is somewhat larger than in the previous two examples. In that same paper, a value of  $n_{\sigma} = 0.59$  was also quoted. While it is not precisely clear how this value was determined, it appears to result from a power law analysis of  $M''(\omega) \approx \omega^{\beta_m}$  at  $\omega \ge \omega_p$ . An example of  $M''(\omega)$  at approximately 370 K (taken from Fig. 4 of Ref. 3) is shown in the inset to Fig. 5, where a single power law fit through the last few data indeed results in a slope  $(-\beta_m) \approx -0.4$ , thus suggesting  $n_{\sigma}^{K} = 0.6$ , consistent with the value (0.59) quoted.

Although we consider this approach of directly evaluating the power law behavior of  $M''(\omega)$  to determine  $n_{\sigma}$  to be an improvement over using the traditional KWW fit outlined earlier, the slope of  $M''(\omega)$  will only reach its asymptotic limit  $[M''(\omega) \propto \omega^{n_{\sigma}-1}]$  at  $\omega \gg \omega_n$ , and hence the value of  $n_{\sigma}$ can in principle be underestimated if the fit extends only to frequencies close to  $\omega_p$  (e.g., see inset Fig. 2). To avoid this dilemma, we turn our attention to  $\sigma(\omega)$ , which upon removal of  $\sigma_0$  exhibits only a single power law at all frequencies. In Fig. 5 we reproduce conductivity data for ZBLAN (taken from Fig. 3 of Ref. 3) with the dc conductivity (also determined from Fig. 3 of Ref. 3) already subtracted. Although only four data points are available for each of four tempertures, roughly three decades of both frequency and conductivity are encompassed and fits to a single power law display a reasonably common slope,  $n_{\sigma} \approx 0.68 \pm 0.05$ . This value of  $n_{\sigma}$  is again considerably larger than the estimate obtained from the slope of  $M''(\omega)(n_{\sigma}^{K}=1-\beta_{m}=0.59)$  and agrees (within error) with that of NSR ( $n_{\rm NSR} = 0.75 \pm 0.07$ ).

## **III. DISCUSSION**

Results of these analyses are summarized in Table I, where the following observations can be made. First,  $n_{\sigma}$  determined from  $\sigma(\omega)$  is roughly some 20% larger than its counterpart  $(n_{\sigma}^{K})$  determined from traditional KWW fits of  $M''(\omega)$ . Second, as a consequence of this,  $n_{\sigma}$  is now seen to be more comparable to the NSR exponent, and within error it is reasonable to conclude the two exponents are equivalent. Furthermore, all these exponents are narrowly bracketed around a common and thus apparent *universal* value of  $n_{\text{NSR}} = n_{\sigma} \approx 0.67 \pm 0.07$ .

TABLE I. Summary of relaxation exponents. The exponents  $n_{\sigma}^{K}$  and  $n_{\rm NSR}$  are from the original reference and  $n_{\sigma}$  is determined from analysis of the conductivity data.

SYSTEM [reference]	$n_{\sigma}^{K}$	$n_{\sigma}$	n <sub>NSR</sub>
0.6LiCl-0.7Li <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub> [4,27]	0.50	$0.62 \pm 0.05$	0.65
0.56Li <sub>2</sub> S-0.44Si <sub>2</sub> S [5]	0.52	$0.64 \pm 0.05$	0.65
ZBLAN[3]	0.59	$0.68 \pm 0.05$	0.75±0.07

These results indicate that the short time dynamics of ion motion are similar in both NSR and ECR experiments provided the latter is interpreted by the high-frequency behavior of the conductivity and not by  $M''(\omega)$  at limited frequencies near its maximum. What impact do these findings have upon the coupling model expressions for ratios of activation energies and of relaxation times given by Eqs. (6) and (7)? This may be difficult to say. According to Ngai<sup>29</sup>, these expressions are defined only in terms of the KWW correlation functions for NSR and ECR whose coupling exponents  $(n_{\text{NSR}}^{K} \text{ and } n_{\sigma}^{K})$  are to be obtained from KWW fits of  $T_{1}(\omega)$ and the electric modulus. Hence, within the limits of this definition of the coupling model exponent, the differences between  $n_{\sigma}^{K}$  and  $n_{\sigma}$  would be viewed as inconsequential to the coupling model predictions discussed earlier [Eqs. (6 and 7)]. However, it seems clear from fluctuation-dissipation arguments alone [see Eq. (4)] that the power law exponents derived from  $T_1(\omega)$  and  $\sigma(\omega)$  are the proper ones to compare.

Differences in the ECR and NSR timescales may still be the result of fundamental differences in the correlation functions involved in ECR and NSR measurements. In both cases the short-time (high-frequency) dynamics appear to be described by power laws with a common exponent  $(n \approx \frac{2}{3})$ . Power laws possess a unique scale invariant feature in the sense that no characteristic time scale can be associated with them.<sup>30,31</sup> Characteristic time scales only emerge as a consequence of these power laws crossing over to some alternative functional frequency dependence as occurs for  $\sigma(\omega)$  at low frequencies when the dc conductivity is encountered. In some models of ion dynamics,<sup>32,33</sup> the power law regime is thought to result from a local process involving either some form of ion "rattling" within a given Coulombic well or alternatively a rapid "back-forth" exchange of the ion between two adjacent wells. For  $\sigma(\omega)$  the crossover is commonly understood as a direct consequence of long-range ion displacements involving one or more barrier crossings.<sup>34,35</sup> In the case of ECR the electric field acts to bias the migration of ions along the direction of the field and in doing so terminates the power law at time scales larger than  $\tau_{\sigma}$ . Consequently, it is the onset of dc conductivity which establishes the characteristic time scale,  $\tau_{\sigma}$ . Likewise,  $\tau_{\rm NSR}$  can only be defined by crossover of  $T_1(\omega)$  at low frequencies to a frequency-independent behavior. However, there is no compelling reason to expect this crossover to occur at the same frequency of applied field as it does for  $\sigma(\omega)$ . In the NSR experiment, the magnetic field does not supply a corrsponding bias to promote long-range ion displacements and might allow the power law to be monitored out to lower frequencies and longer times ( $\tau_{\rm NSR}$ ). Borsa *et al.*<sup>5</sup> have stressed that NSR dynamics are driven by fluctuations while for ECR the dynamics are driven by relaxation. While these differences may not show up in the short-time dynamics (as indicated by the similarity in power law exponents discussed here), it may well be displayed at longer times where the characteristic time scales ( $\tau_{\rm NSR}$  and  $\tau_{\sigma}$ ) in both approaches are defined.

In any event, our purpose in the present paper is not so much to provide a final answer for the observed differences between NSR and ECR timescales as to clarify an important issue concerning data analysis and hopefully make others aware of the how different analyses of ECR can lead to significantly differing estimates of the conductivity exponent. It is imperative that these differences be recognized when making comparisons between NSR and ECR experiments.

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- <sup>1</sup>O. Kanert, R. Kuchler, J. Dieckhofer, X. Lu, and H. Jain, Phys. Rev. B **49**, 629 (1994).
- <sup>2</sup>P. Maass, M. Meyer, and A. Bunde, Phys. Rev. B 51, 8164 (1995).
- <sup>3</sup>O. Kanert, R. Kuchler, K. L. Ngai, and H. Jain, Phys. Rev. B **49**, 76 (1994).
- <sup>4</sup>M. Tatsumisago, C. A. Angell, and S. W. Martin, J. Chem. Phys. **97**, 6968 (1992).
- <sup>5</sup>F. Borsa, D. R. Torgeson, S. W. Martin, and H. K. Patel, Phys. Rev. B **46**, 795 (1992).
- <sup>6</sup>P. B. Macedo, C. T. Moynihan, and R. Bose, Phys. Chem. Glasses **13**, 171 (1972).
- <sup>7</sup>K. L. Ngai, J. Chem. Phys. **98**, 6424 (1993).
- <sup>8</sup>M. Meyer, P. Maass, and A. Bunde, Phys. Rev. Lett. 71, 573 (1993).
- <sup>9</sup>P. Maass, M. Meyer, and A. Bunde, Phys. Rev. B 51, 8164 (1995).
- <sup>10</sup>U. Strom, K. L. Ngai, and O. Kanert, J. Non-Cryst. Solids **131-133**, 1011 (1991).
- <sup>11</sup>K. L. Ngai, U. Strom, and O. Kanert, Phys. Chem. Glasses 33, 109 (1992).
- <sup>12</sup>I. Svare, F. Borsa, D. R. Torgeson, and S. W. Martin, Phys. Rev. B 48, 9336 (1993).
- <sup>13</sup>K. L. Ngai, Solid State Ionics 5, 27 (1981); Comments Solid State Phys. 9, 141 (1980).
- <sup>14</sup>K. L. Ngai, R. W. Rendell, and H. Jain, Phys. Rev. B **30**, 2133 (1984).
- <sup>15</sup>K. L. Ngai and O. Kanert, Solid State Ionics **53-56**, 936 (1992).
- <sup>16</sup>W. K. Lee, J. F. Liu, and A. S. Nowick, Phys. Rev. Lett. 67, 1559 (1991).
- <sup>17</sup>A. S. Nowick, B. S. Lim, and A. V. Vaysleyb, J. Non-Cryst. Solids **172-174**, 1243 (1994).
- <sup>18</sup>D. L. Sidebottom, P. F. Green, and R. K. Brow, Phys. Rev. Lett. **74**, 5068 (1995).
- <sup>19</sup>S. R. Elliott, Solid State Ionics **70-71**, 27 (1994); M. LeStanguennec and S. R. Elliott, Solid State Ionics **73**, 199 (1994).
- <sup>20</sup>K. Funke, C. Cramer, B. Roling, T. Saatkamp, D. Wilmer, and M. D. Ingram, Solid State Ionics 85, 293 (1996).
- <sup>21</sup>C. T. Moynihan, L. P. Boesch, and N. L. Laberge, Phys. Chem. Glasses 14, 122 (1973).
- <sup>22</sup>S. R. Elliott, J. Non-Cryst. Solids 170, 97 (1994).
- <sup>23</sup>A. S. Nowick and B. S. Lim, J. Non-Cryst. Solids 172-174, 1389 (1994).
- <sup>24</sup>C. T. Moynihan, J. Non-Cryst. Solids 172-174, 1395 (1994).
- <sup>25</sup>D. L. Sidebottom, P. F. Green, and R. K. Brow, J. Non-Cryst. Solids 183, 151 (1995).

- <sup>26</sup>D. L. Sidebottom, P. F. Green, and R. K. Brow, Phys. Rev. B 56, 170 (1997).
- $^{\rm 27}\,M.$  Trunnell, D. R. Torgeson, S. W. Martin, and F. Borsa, J. Non-Cryst. Solids 139, 257 (1992).
- <sup>28</sup>D. L. Sidebottom, P. F. Green, and R. K. Brow, J. Non-Cryst. Solids 203, 300 (1996).
- <sup>29</sup>Personal correspondence.

- <sup>30</sup>H. E. Stanley, Nature **378**, 554 (1995).
- <sup>31</sup>J. J. Binney, N. J. Dowrick, A. J. Fischer, and M. E. J. Newman, The Theory of Critical Phenomena (Oxford U.P. Oxford, 1995).
- <sup>32</sup>K. Funke, Prog. Solid State Chem. 22, 111 (1993).
   <sup>33</sup>A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics Press, London, 1983).
- <sup>34</sup>O. L. Anderson and D. A. Stuart, J. Am. Ceram. Soc. **37**, 573 (1954).
- <sup>35</sup>S. R. Elliott and F. E. N. Henn, J. Non-Cryst. Solids 116, 179 (1990).