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Correlation functions for ionic motion from NMR relaxation and electrical conductivity in the glassy fast-ion conductor $(Li_2S)_{0.56}(SiS_2)_{0.44}$

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The ^{7}Li NMR spin-lattice relaxation and the electrical conductivity in the typical glassy fast-ion conductor $(Li_2S)_{0.56}(SiS_2)_{0.44}$ are discussed from models of Li^+ ionic motion with distributions of activation energies, as well as from stretched-exponential time-correlation functions. The measured correlation times from the two effects differ by two orders of magnitude, and the derived distributions are shifted greatly relative to each other. We relate the great differences to percolation around the high barriers in the distribution. We present a phenomenological theory that yields good quantitative fits to the observed NMR relaxation with a Gaussian distribution, and to the conductivity and related dielectric properties with the continuous-time random-walk model and the same Gaussian truncated at the percolation limit. This correlates the two effects in a simple and effective way; both time-correlation functions can be calculated approximately from the distributions, and even the dc conductivity can be calculated from the NMR results. The present approach is discussed and compared with previously proposed models to explain the anomalies in ac electrical-conductivity and NMR relaxation rates in glassy fast-ion conductors.

I. INTRODUCTION

The electrical conductivity $\sigma(\omega,T)$ in fast-ion conductors (FIC) has been studied and discussed extensively, but no clear picture has emerged of how the conductivity is related to the thermally activated hopping rates of individual ions. Measurements of other properties like the NMR spin-lattice relaxation (NSLR) rate $R_1(\omega,T)$ which depends significantly upon the microscopic motion in different ways are being used to more fully characterize the ionic conduction process. To our knowledge, no detailed studies of σ and R_1 on the same materials in wide or overlapping ranges of frequency ω and temperature T have been made besides the recently reported study of the glassy FIC $(Li_2S)_{0.56}(SiS_2)_{0.44}$.[1] The purpose of this paper is to point out again[1] the great differences between the correlation times (two orders of magnitude) derived from NMR and from conductivity and to explain these differences. We will analyze the conductivity, the related dielectric properties, and NMR relaxation due to Li^+ ion motion in the FIC glass $(Li_2S)_{0.56}(SiS_2)_{0.44}$ and correlate the similarities and differences between them. This composition shows behavior typical of glassy FIC: (i) The ac conductivity is strongly T dependent and increases almost proportionally to ω at high frequencies and (ii) the NMR relaxation R_1 deviates from the simple Bloembergen-Purcell-Pound (BPP) (Ref. 2) behavior by being very asymmetric around the maximum in a plot of $\log_{10}(R_1)$ vs $1/T$. There are many models that can explain separately the anomalous behavior of $\sigma(\omega)$ and of $R_1(\omega,T)$. However, since both of these are related to the cation dynamics on a microscopic scale, a model that can explain both the behaviors of $\sigma(\omega)$ and of $R_1(\omega,T)$ starting from the same microscopic picture should give enlightening information.

The conductivity $\sigma(\omega,T)$ is often described using a stretched exponential, or Kohlrausch-Williams-Watts (KWW),[3] time-correlation function of the form $\exp[-(t/\tau)]^{\beta}$ with $0<\beta\leq 1$, but there is no general agreement on how the exponent β or the correlation time $\tau(T)$ is related to the individual hopping motions of the ions. The NSLR $R_1(\omega,T)$ may also be fitted with a KWW function, and it has often been assumed the two correlation functions should be approximately equal since they result from the same basic ionic motion. However, this is not found in the FIC glass $(Li_2S)_{0.56}(SiS_2)_{0.44}$. From $\sigma(\omega,T)$ in the ranges $0<\omega/2\pi<4$ MHz and $141<T<281$ K we find[1] the correlation function

$$f_{\mathrm{cond}}(t)=\exp^{-(t/\tau_{\mathrm{cond}})^{0.48}} \quad \text{with } \tau_{\mathrm{cond}}=0.4\times10^{-14}\exp^{4000/T} \tag{1}$$

and from the measured $R_1(\omega,T)$ of ^{7}Li in the ranges $4<\omega/2\pi<40$ MHz and $150\le T\le 550$ K we found[1]

$$f_{\mathrm{NMR}}(t)=\exp^{-(t/\tau_{\mathrm{NMR}})^{0.35}} \quad \text{with } \tau_{\mathrm{NMR}}=4.5\times10^{-14}\exp^{4500/T}\,. \tag{2}$$

These functions at $T=250$ K are plotted in Fig. 1, and apart from the somewhat different shape due to the different β's we see $f_{\mathrm{cond}}(t)$ is shorter than f_{NMR} by several orders of magnitude. The difference is so large that τ_{cond} and τ_{NMR} must result from different aspects of the ionic motion, and the purpose of this paper is to explain this difference. We assert a single ion hop attempt frequency, quite reasonably, should be connected to the activation energy E_a, the hop length and the ion mass, and this relation is far from fulfilled in the prefactor of τ_{cond} in Eq. (1).

The great difference in correlation times for the two effects can be seen directly from the temperature shift with ω of the peak in the NMR relaxation R_1 and of the peak in the imaginary part of the dielectric modulus $M''(\omega,T)=\mathrm{Im}[i\omega/\sigma(\omega,T)]$, and is not related to our choice of stretched exponentials for the fit. These properties have maxima near $\omega\tau_{\mathrm{NMR}}(T)\approx1$ and $\omega\tau_{\mathrm{cond}}(T)\approx1$, respectively, and the resulting Arrhenius plots are shown in Fig. 2. Although the two sets of values for τ do not overlap in temperature, we see that the extrapolated correlation times differ by a factor of 100.

To obtain a better understanding of the physics involved other models will be examined and applied to the measured $R_1(\omega,T)$ and $\sigma(\omega,T)$ in glassy $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$; in particular we will consider distributions of barrier heights E_a against the ionic motion. This approach has been used in the analysis of NMR relaxation, and a Gaussian distribution has been shown to work well for R_1 vs $1/T$.[4] It is not immediately clear how $\sigma(\omega,T)$ can be calculated from the same distribution of barriers, so we will first study the ω and T dependencies of σ as derived by Dyre,[5,6] Macdonald,[7] and others from the continuous-time random-walk model with a rectangular distribution of activation energies. This method yields a good fit of the complex $\sigma(\omega,T)$ when we use the measured $\sigma(\omega\to0,T)$ as a parameter. The fitted curves also show, however, that the distribution of E_a for $R_1(\omega,T)$ and $\sigma(\omega,T)$ are strikingly different reflecting the differences of correlation functions Eqs. (1) and (2). We suggest a quantitative explanation for the differences, based upon the dc percolation motion through the lattice. This approach also permits us to calculate approximately the magnitude of $\sigma'(\omega\to0,T)$ and the time correlation function.

II. NMR RELAXATION WITH A DISTRIBUTION OF BARRIER HEIGHTS

The NMR spin-lattice relaxation of a given ^{7}Li nucleus is determined by the local electric field gradient (EFG) fluctuations arising from the Li ionic motion. Hops of the ion will take it to a randomly different local field and thus contribute in the same way to R_1, and it does not matter whether the hopping is locally back and forth over the same barrier or part of long-range diffusion. The fluctuating field may be magnetic dipolar from nearby spins or electric quadrupolar from neighboring ions. The immobile S^{2-} ions surrounding the Li^+ ions in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass have no magnetic moments, therefore the ^{7}Li relaxation is expected to be quadrupolar in nature arising from the hopping of the ions to other sites with different EFG magnitudes and principal axes.

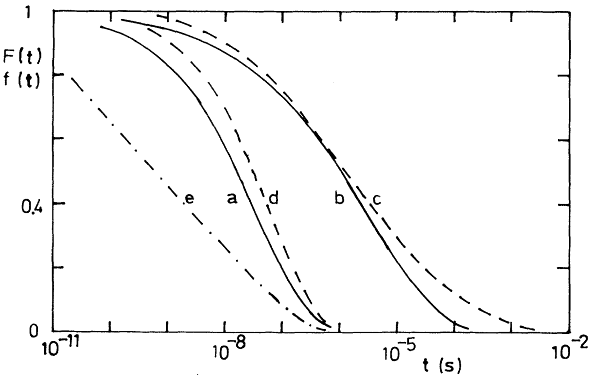

FIG. 1. Stretched exponential time-correlation function for Li^+ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ at 250 K. (a) $f_{\mathrm{cond}}(t)$ from the conductivity and Eq. (1). (b) $f_{\mathrm{NMR}}(t)$ from the NMR relaxation and Eq. (2). (c) $F_{\mathrm{NMR}}(t)$ from the distribution of barriers in Eq. (12). (d) $F_{\mathrm{cond}}(t)$ from the barriers below the percolation limit in Eq. (14). (e) $F_D(t)$ from the rectangular distribution of barriers in Eq. (15).

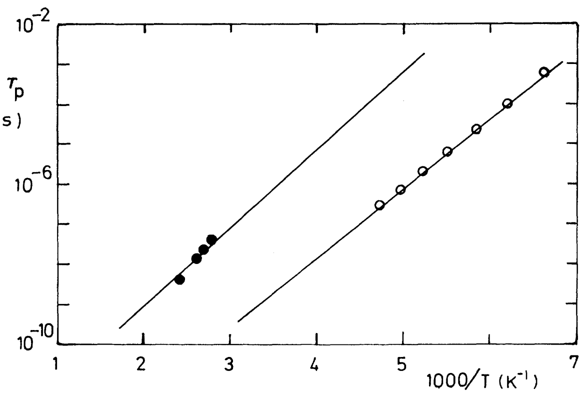

FIG. 2. Correlation times τ_p for Li^+ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ from $\omega\tau_p=1$ at the maxima of imaginary dielectric modulus M'' (open circles) and NMR relaxation R_1 (filled circles), plotted as functions of inverse temperature. Lines through the points are drawn with the activation temperatures of Eqs. (1) and (2).

The potential energy wells in a structurally disordered glass differ in shape from site to site so the ions see a distribution of barrier heights E_a against hops to the next energy well. Hence the ions will hop with different rates;

$$r=1/\tau=r_0\exp^{-E_a/k_BT}\ , \tag{3}$$

over each of the z barriers to the nearest empty wells, and we might therefore expect a distribution of NSLR rates. However, a sample of nuclear spins will still show one well-defined rate R_1 if the spin-spin relaxation is sufficiently fast. The spin energy diffuses to those nuclei which have the optimum hopping rate for fast relaxation to the lattice, and we expect the measured relaxation rate will be an average, defined as

$$R_1(\omega,T)=M\int_0^\infty\left[\frac{\tau/z}{1+\omega^2(\tau/z)^2}+\frac{4\tau/z}{1+4\omega^2(\tau/z)^2}\right]Z_{\rm NMR}dE_a\ . \tag{4}$$

The coefficient M depends upon the average change in the local field caused by each hop. We assume a Gaussian distribution of E_a;

$$Z_{\rm NMR}(E_a)=\frac{1}{(2\pi)^{1/2}E_b}\exp^{-(E_m-E_a)^2/2E_b^2} \tag{5}$$

with a half-width E_b around the average E_m. In most cases, especially for the $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass, the observed NMR relaxation recovery curves are good exponentials[1] so the condition of fast spin-spin relaxation for Eq. (4) is fulfilled.

The classical attempt rate r_0 against one barrier in Eq. (3) is given by the oscillation frequency $f_{\rm osc}$ of the ion in the well, $r_0=f_{\rm osc}$ (without the 2π factor). This depends on the curvature of the potential in the well, and for a reasonable sinusoidal barrier shape between wells[8] it is $f_{\rm osc}\approx(E_a/2m)^{1/2}/d$, where m is the Li mass. The distance d between the neighboring wells must be estimated from the structure of the glass.

The phase diagram[9,10] of $(\mathrm{Li_2S})_x(\mathrm{SiS_2})_{1-x}$ shows that it is a mixture of $\mathrm{Li_2SiS_3}$ and $\mathrm{Li_4SiS_4}$ with some 5 to 10% additional free volume. In $\mathrm{Li_2SiS_3}$, the distances from each Li ion to the three nearest Li neighbors are about 3.5 Å and about 4 Å to the next three. $\mathrm{Li_4SiS_4}$ has $\frac{1}{4}$ of the Li ions on $\frac{1}{4}$-filled tetrahedral sites, which permits motion from the filled to the empty sites. Also in this structure, the distances between the Li neighboring sites are about 3.5 Å. In the mixture $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ with more random distances between sites and more and larger voids than in the separate compositions, we expect that many empty sites permit motion of the ions. Hence we assume each ion can, on the average, hop to $z=6$ neighboring wells about $d=3.6$ Å away. This gives the rate prefactor $r_0=6.75\times10^{10}E_a^{0.5}$ s^{-1} for Eq. (3), where E_a has the units of K. A good fit of Eq. (4) to the R_1 data[1] using Eq. (5) with $E_m/k_B=4500$ K and $E_b/k_B=900$ K is shown in Fig. 3. The shape of the distribution $Z_{\rm NMR}(E_a)$ is shown in Fig. 4 and it appears reasonable. We see that the peak E_m is the same as the activation energy of $\tau_{\rm NMR}$ fit in Eq. (2), and the total attempt rate $zr_0=2.7\times10^{13}$ s^{-1} at E_m is very close to the prefactor 2.2×10^{13} s^{-1} of $(\tau_{\rm NMR})^{-1}$. The magnitude $M=8\times10^9$ s^{-2} is much greater than that expected from the magnetic nuclear dipolar interactions and indicates the relaxation mechanism must be electric quadrupolar in nature.

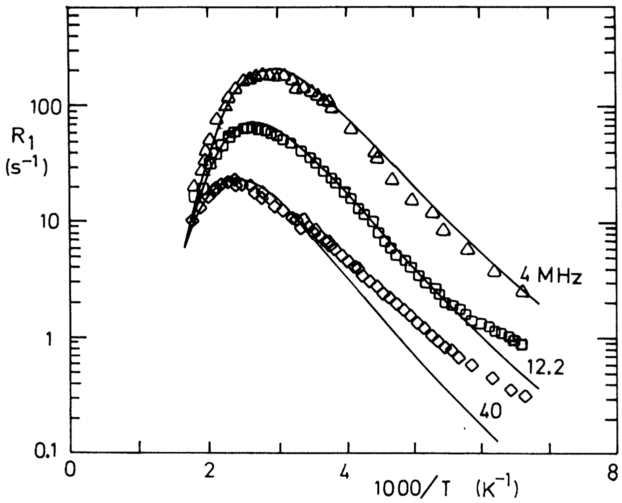

FIG. 3. Spin-lattice relaxation R_1 of ^{7}Li in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ at 4.0, 12.2, and 40.0 MHz from Ref. 1 fit as described in the text with calculated R_1 from Eq. (4) with a Gaussian distribution of barriers.

We have assumed a distribution of the z rates r_i out of a well and used $\sum_z r_i\approx r(E_a)z$ with the same distribution $Z_{\rm NMR}(E_a)$ for r as for r_i. This is good if all barriers are nearly equal. It is also permitted on the low-T side of the relaxation curve where most of the ions have $rz\ll\omega$, where Eq. (4) simplifies to $(2M/\omega^2)\int rzZ_{\rm NMR}dE_a$ and it does not matter whether we average r_i first or not. The use of $Z_{\rm NMR}(E_a)$ on the high-T side of the relaxation vs the $1/T$ curve may be more doubtful, since z uncorrelated barriers are unlikely to be all higher than the average

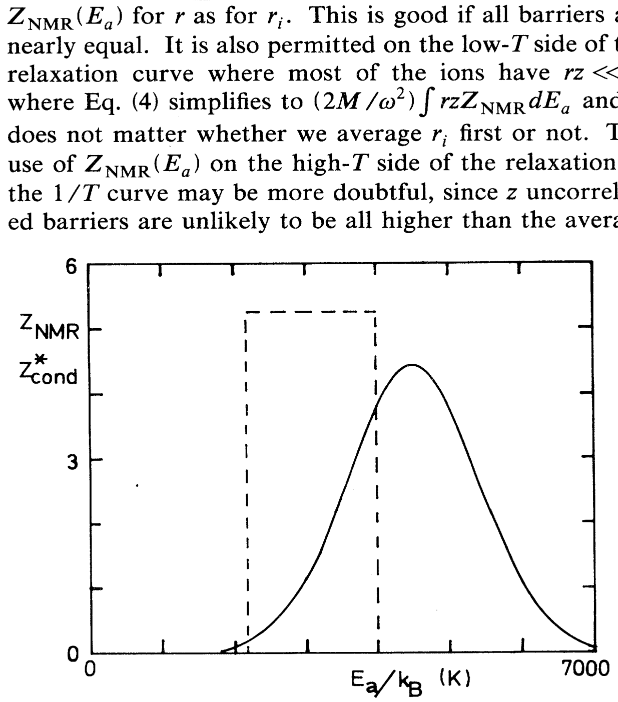

FIG. 4. Distribution of activation energies in the motion of $\mathrm{Li^+}$ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ derived as described from NMR relaxation (full line) and from electrical conductivity (dashed line).

E_m, and the lowest barrier will largely determine the rate out of a well. However, the fast rates $rz \gg \omega$ simplify Eq. (4) to $5M\int(1/rz)^2 Z_{\mathrm{NMR}}\,dE_a$ which contributes little to the relaxation and is unimportant for the fit. Anyway, in so far as the derived distribution Z_{NMR} differs from that of individual barriers, it reflects the total rate out of a well, and so it would be relevant also for the conductivity. We have disregarded the distribution of depths of the wells (site energy disorder).

III. CONDUCTIVITY FROM A DISTRIBUTION OF BARRIERS

To calculate the conductivity of Li^+ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass from the same distribution Z_{NMR} of barriers, we also need some information about the special correlation of the ionic diffusion. Locally restricted hopping over low barriers gives only high-frequency conductivity, while the dc conductivity requires continuous percolation paths for the ions through the disordered lattice. We use the continuous-time random-walk model discussed by Dyre,[5,6] Macdonald,[7] and earlier workers to derive the approximate frequency dependence of $\sigma(\omega)$. Here the basic equation is the assumption

$$\frac{1}{\sigma(\omega,T)+i\omega}\sim\left\langle\frac{1}{\gamma(E_a,T)+i\omega}\right\rangle , \tag{6}$$

where the average over the relaxation times should be taken over the distribution of activation energies E_a for the current decay rate γ. The complex conductivity $\sigma=\sigma'+i\sigma''$ has the same units as γ, and the units are taken care of by fitting the calculated $\sigma(\omega\to 0,T)$ to the measured value.

The connections between the rates τ and the Gaussian distribution are not immediately clear, so we follow the literature[5,7] where Eq. (6) has been averaged analytically over a rectangular distribution with limits $E_{\max}$ and $E_{\min}$ corresponding to $\gamma_{\min}$ and $\gamma_{\max}$, respectively, to give

$$\sigma(\omega)=Ki\omega\left[\frac{\ln(\gamma_{\max}/\gamma_{\min})}{\ln\dfrac{1+i\omega/\gamma_{\min}}{1+i\omega/\gamma_{\max}}}\right] . \tag{7}$$

We will try to fit this approximation first, and although a strictly rectangular distribution is clearly unphysical, this will help us to calculate the magnitude of the current decay rates and the relations to the Gaussian distribution. In the next section we will average Eq. (6) numerically over the tail of the Gaussian below the percolation limit.

The imaginary part of σ is related to the complex dielectric constant

$$\sigma''(\omega,T)=\omega\epsilon_0\mathrm{Re}[\epsilon(\omega,T)-\epsilon(\infty)] , \tag{8}$$

where the real $\epsilon(\infty)$ is the electronic contribution which dominates at high frequencies. The complex coefficient K in Eq. (7) must be chosen to fit the measured low-frequency conductivity. This model thus avoids the great problem of calculating the magnitude of the conductivity, and agreement at both low and high frequencies is ensured by the fits of $\sigma(\omega\to 0,T)$ and $\epsilon(\infty)$.

At moderate frequencies $\omega \ll \gamma_{\max}$, Dyre[5,6] has shown that Eq. (7) reduces to

$$\sigma_D(\omega)=\sigma(0)\frac{i\omega\tau_D}{\ln(1+i\omega\tau_D)} , \tag{9}$$

where $\tau_D=1/\gamma_{\min}$, and he argues that the limit $\tau_{\max}$ does not matter for σ' in most cases.

The measured conductivity σ' of $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ (Ref. 1) is shown in Fig. 5 and the dc limit plotted in Fig. 6 can be described with

$$\sigma'(0,T)=6.25\times 10^{4}\exp(-4000/T)$$

$$=2.5\times 10^{-10}/\tau_{\mathrm{cond}}(T)\ (\Omega\,\mathrm{cm})^{-1}$$

if we use τ_{cond} from Eq. (1). The calculated σ' from Eq. (7) and σ'_D from Eq. (9) are almost identical, as discussed by Dyre,[5,6] and fit our measurements in Fig. 5 fairly well in the whole ω and T range when we set

$$\tau_D=1/\gamma_{\min}=2\tau_{\mathrm{cond}}=0.8\times 10^{-14}\exp(4000/k_BT) .$$

This associates $1/\tau_{\mathrm{cond}}$ from the KWW fit, Eq. (1), with the *slowest* decay rate $\gamma_{\min}$ in the model, and the derived $\gamma_{\min}$ differs clearly from any individual hopping rate zr from Eq. (3). We note $\omega\tau_D\approx 1$ marks the bend in the graphs in the curves in Fig. 5 where $\sigma'(\omega)$ flattens out to constant dc conductivity. The factor 2 between τ_D and τ_{cond} may come from the definitions, since there is a similar factor between the theories of Dyre[5] and Bryksin.[11]

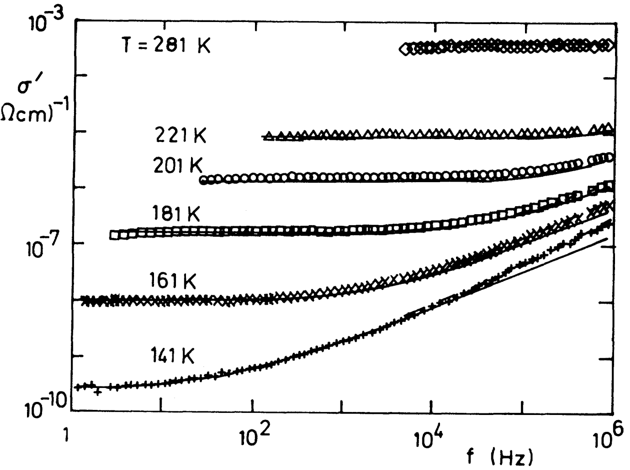

FIG. 5. Real conductivity σ' in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ from Ref. 1 as a function of frequency at several temperatures, and fit as described from Eq. (6) with a numerical average over the distribution Z_{NMR} truncated at $E_{\max}$ (full lines) and from Eqs. (7) and (9).

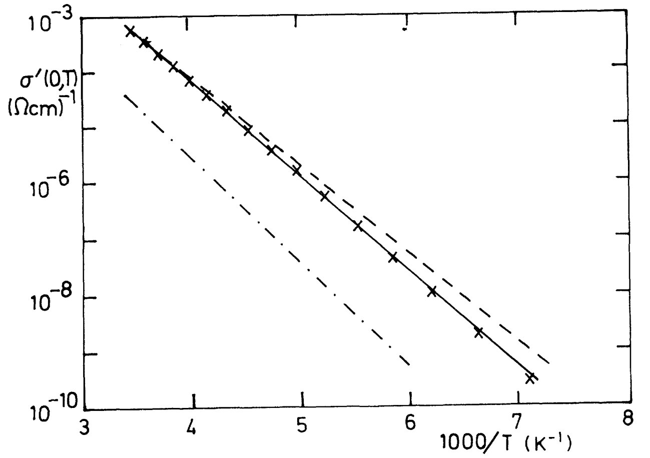

FIG. 6. Measured dc conductivity $\sigma'(0,T)$ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ from Ref. 1 as a function of inverse temperature (crosses), the fit $\sigma'(0,T)=6.25\times10^{2}\exp(-4000/T)$ $(\Omega\,\mathrm{cm})^{-1}$ (solid line), calculated $\sigma'(0,T)$ from Eq. (11) (dashed line) and from the assumption that all barriers are equal to $E_m=4500$ K (dashed-dot line).

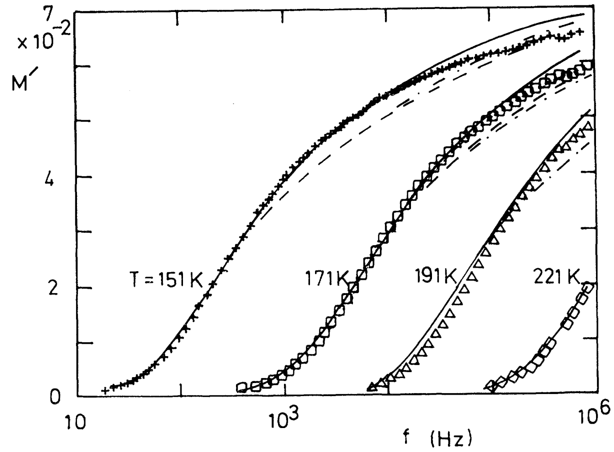

FIG. 8. Real dielectric modulus $M'(f,T)$ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass measured as a function of frequency at several temperatures, and fit as described from Eq. (6) with a numerical average over Z_{NMR} truncated at $E_{\max}$ (full curves), and from the approximations Eq. (7) (dashed curves) and Eq. (9) (dash-dot curves).

The calculated imaginary parts of Eqs. (7) and (9) are also quite similar when we fit different electronic contributions $\epsilon(\infty)$ in the two approximations. In Fig. 7 we use the constant ratio $\sigma''(1\ \mathrm{Hz},T)/\sigma'(\omega\to0,T)=0.02$ for both fits, $\gamma_{\max}=1.25\times10^{14}\exp(-2200/k_BT)$ and $\epsilon^*(\infty)=14$ for σ'' from Eq. (7), and $\epsilon_D(\infty)=9$ for σ''_D from Eq. (9).

The dielectric properties of FIC are often displayed as the complex modulus $M^*=1/\epsilon^*$, which more clearly shows the effects of the motion in the middle frequency range. The calculated modulus compared to the measured data is shown in Figs. 8 and 9 for several temperatures. The frequency dependence calculated from Eqs. (7) and (9) does not fit perfectly but fits much better than one might expect in view of the simplicity of the models.

The crude rectangular distribution $Z^*_{\mathrm{cond}}(E_a)$ used in Eq. (7) for the $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass must have $E_{\max}/k_B\approx4000$ K from $\gamma_{\min}$, a much smaller $E_{\min}/k_B$ of about 2200 K, and the normalized shape shown in Fig. 4. It is obvious Z^*_{cond} is shifted relative to Z_{NMR}, so the two distributions must represent different aspects of the ionic motion and be manifestations of the same differences which give rise to the different KWW functions Eqs. (1) and (2).

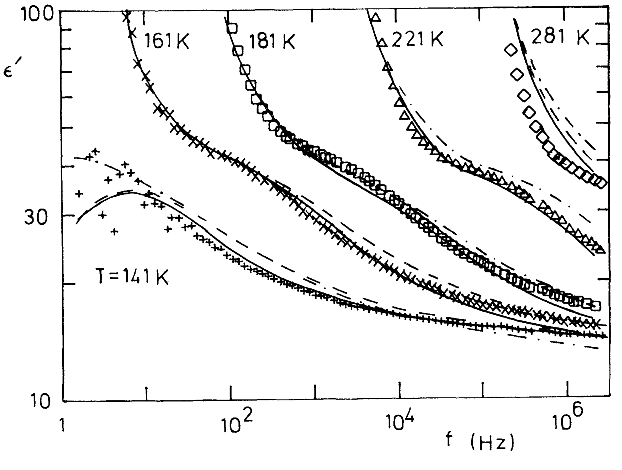

FIG. 7. Real dielectric constant $\epsilon'(f,T)$ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ measured as a function of frequency at several temperatures, and fit as described from Eq. (6) with a numerical average over Z_{NMR} truncated at $E_{\max}$ (full curves), and from the approximations Eq. (7) (dashed curves) and Eq. (9) (dash-dot curves).

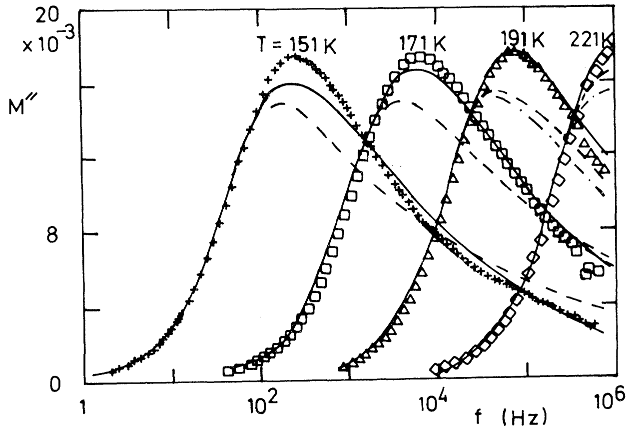

FIG. 9. Imaginary dielectric modulus $M''(f,T)$ in $(\mathrm{Li_2S})_{0.56}(\mathrm{SiS_2})_{0.44}$ glass measured as a function of frequency at several temperatures, and fit as described from Eq. (6) with a numerical average over Z_{NMR} truncated at $E_{\max}$ (full curves), and from the approximations Eq. (7) (dashed curves) and Eq. (9) (dashed-dot curves).

IV. CONDUCTIVITY FROM PERCOLATION

The dc conductivity is quite likely associated with the percolation motion of the ions through the low-energy pathways in the lattice. The limit $E_{\max}$ associated with $\sigma(\omega \rightarrow 0, T)$ is taken as approximately the bottleneck barrier E_p against hopping in the percolation limit where a sufficient fraction of the barriers is lower than E_p and thus easy to pass. This fraction is 0.247 in the case of a simple cubic lattice with $z=6$ and a random distribution of high and low barriers.[12] This fraction increases to 0.388 for the diamond lattice with $z=4$. If we set in the NMR derived Gaussian distribution the condition that the fraction of barriers below E_p should be 0.247 (corresponding to $z=6$ as it should be in our case) we find $E_p=E_m-0.68E_b \approx 3900$ K which is indeed almost equal to $E_{\max}$. The real distribution Z_{cond} for the Li^+ conductivity is certainly not rectangular, but it is reasonable to associate Z_{cond} with the wing of the Gaussian Z_{NMR} below the percolation limit $E_{\max}$. There are of course occasional hops over higher barriers, which are important for the NMR relaxation, but these hops are unimportant for the dc conductivity since the ionic current can percolate around these barriers. The fit is insensitive to the other limit $E_{\min}$ and the shape of the tail of Z_{NMR} with the fastest hop rates and is not important for the conductivity, since the rapid hops take little time in the random walk.

With this interpretation we can average Eq. (6) numerically over the distribution Z_{NMR} truncated at the percolation limit $E_{\max} \approx 4000$ K and renormalized. We still use $\gamma = 1.25 \times 10^{14} \exp(-E_a/k_B T)$, $\sigma''(1\text{ Hz}, T)/\sigma'(0,T)=0.02$, and $\epsilon(\infty)=14$. The results are shown in Figs. 5 and 7–9 and the overall fit is better than from the approximations of Eqs. (7) and (9). The rather high value of $\epsilon(\infty)=14$ could be checked with measurements at higher ω or lower T.

This approach to the random walk diffusion appears to be new and it is very important because it also allows us to estimate the correlation time for the conductivity and even the magnitude of $\sigma(0,T)$. In the next section an approximate KWW time-correlation function for the conductivity is derived.

We assume the fraction

$$P=\int_0^{E_{\max}} Z_{\text{NMR}} dE_a$$

of the ions are in wells with barriers below the percolation limit $E_{\max}$ and we assume these ions essentially determine $\sigma(\omega \rightarrow 0, T)$. Their average time between jumps is

$$\tau_{\text{av}}(T)=\int_0^{E_{\max}} \frac{1}{6r} \frac{Z_{\text{NMR}}}{P} dE_a \tag{10}$$

with $E_{\max}/k_B=4000$ K. This time is very close to $\tau_D=2\tau_{\text{cond}}$ so it must also be interpreted as the correlation time for the ions determining the dc current. The decay rates γ in Eq. (6) corresponding to lower values of E_a must likewise be given by the inverse analogs of Eq. (10) with $E'_{\max}=E_a$ and the corresponding P', and this is important for the ac conductivity.

We may argue that the percolation limit in this random glass is unlikely to be completely sharp and that the cutoff at $E_{\max}$ should be somewhat gradual due to local variations. A gradual cutoff could easily be included in Eq. (10), but this would mean the fitting of an additional parameter whose significance is doubtful.

The average hop length of the ions is about $d/\sqrt{3} \approx 2.08$ Å along the field, and perhaps a little less for the lower barriers. The dc conductivity from random diffusion should therefore be approximately

$$\sigma'(0,T)=CP\frac{e^2 d^2}{6k_B T \tau_{\text{av}}} . \tag{11}$$

The concentration C of Li^+ ions in $(\text{Li}_2\text{S})_{0.56}(\text{SiS}_2)_{0.44}$ must lie between the density $1.7 \times 10^{28}\ \text{m}^{-3}$ reported[9,10] for Li_2SiS_3 and $2.4 \times 10^{28}\ \text{m}^{-3}$ reported for Li_4SiS_4, and we assume $C=1.9 \times 10^{28}\ \text{m}^{-3}$. With $e=1.6 \times 10^{-19}$ C and $k_B=1.38 \times 10^{-23}$ J/K we then indeed find Eq. (11) fits the measured $\sigma'(0,T)$ in Fig. 6 quite well. The fit may have been even better with shorter hops for the lower barriers. If we use the whole distribution Z_{NMR} or just the mean E_m in Eq. (10) we find conductivities that are far too small. It is quite remarkable that the dc conductivity in this fast-ion conductor can thus be calculated essentially from the NMR relaxation data and the percolation limit for the maximum barrier probed by the long-range ionic diffusion. The fit may have been better with shorter hops for the lower barrier and a distribution of percolation limits.

V. CORRELATION FUNCTIONS FROM DISTRIBUTION OF BARRIERS

The time-correlation function for the local field in the spin system which leads to the NMR relaxation must be the weighted average of the correlations for the individual spins

$$F_{\text{NMR}}(\tau,T)=\int_0^{\infty} e^{-tz/\tau} Z_{\text{NMR}} dE_a . \tag{12}$$

This function has been calculated numerically with the fit parameters in Fig. 1 for $T=250$ K, and we see it is close to, but not exactly equal to f_{NMR} from Eq. (2).

It would be interesting to have an exact analytical relation between F_{NMR} from a Gaussian distribution of barriers and a stretched exponential function with fixed parameters, but it is easy to show this is impossible. We write Eq. (12) with $x=E_m-E_a$ and $\tau_m(T)=(\tau_0/z)\exp(E_m/k_B T)$, use the approximation $\exp(x/k_B T) \approx 1+x/k_B T+(x/k_B T)^2/2$ which is permitted in the integral if the distribution Z_{NMR} is narrow with $E_b/k_B T=\alpha \ll 1$, and integrate to find

$$F_{\text{NMR}}(t,T)=\frac{e^{-(t/\tau_m)[1-0.5/(1+\tau_m/t\alpha^2)]}}{\left[1+\alpha^2 \dfrac{t}{\tau_m}\right]^{1/2}} . \tag{13}$$

The form of Eq. (13) shows that the correlation function $F_{\text{NMR}}(t,T)$ derived from a Gaussian $Z(E_a)$ can never be exactly equal to a KWW function $\exp[-(t/\tau_m)^{\beta}]$. We see that attempts to fit stretched exponentials to

$F_{\rm NMR}(t,T)$ must always give $\beta_{\rm NMR} \to 1$ for $t \to 0$, so the resulting parameters will depend upon the time range fitted. We also see the fit will depend upon the ratio $\alpha = E_b/k_BT$, so if a fitted $\beta_{\rm NMR}$ depends upon the width of the distribution E_b, it will also depend upon the temperature T. This conclusion can easily be checked by comparing Eq. (2) and Eq. (12) numerically.

We have associated the fraction of barriers below the percolation limit $E_m/k_B \approx 4000$ K with the distribution of activation energies for the conductivity. This permits us to approximate the time correlation function for the fraction P of the ions contributing most to the conductivity with

$$F_{\rm cond}(t,T) = \int_0^{E_{\max}} e^{-tz/\tau} \frac{Z_{\rm NMR}}{P} dE_a \tag{14}$$

on the condition that each hop destroys the memory of the local polarization. Equation (14) has been plotted in Fig. 1 for $T = 250$ K, and it is indeed close to the stretched exponential $f_{\rm cond}(t)$ from Eq. (1). The correlation function calculated from the rectangular distribution behind Eq. (7)

$$F_D(t,T) = \frac{\int_{E_{\min}}^{E_{\max}} e^{-tz/\tau} dE_a}{\int_{E_{\min}}^{E_{\max}} dE_a} \tag{15}$$

with $E_{\min}/k_B = 2200$ K is quite different from $f_{\rm cond}$ as seen in Fig. 1, and the approximation $E_{\min} \to 0$ corresponding to Eq. (9) is very unreasonable in the time-correlation Eq. (15).

We have demonstrated the relations between the distribution of barriers for the hopping ions and the time-correlation function of the motion for NMR relaxation and conductivity, and in Figs. 10 and 11 we compare the correlation function at various temperatures. The agreement varies somewhat with T and it is best in the middle ranges 250–400 K for $f_{\rm NMR}$ and around 200 K for $f_{\rm cond}$, which are most important in the fits of the experimental data.

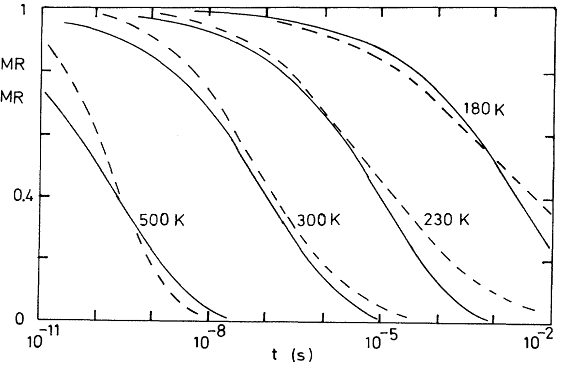

FIG. 10. Time-correlation function $f_{\rm NMR}(t,T)$ from Eq. (2) (solid curves) compared to $F_{\rm NMR}(t,T)$ calculated from Eq. (12) (dashed curves) at several temperatures.

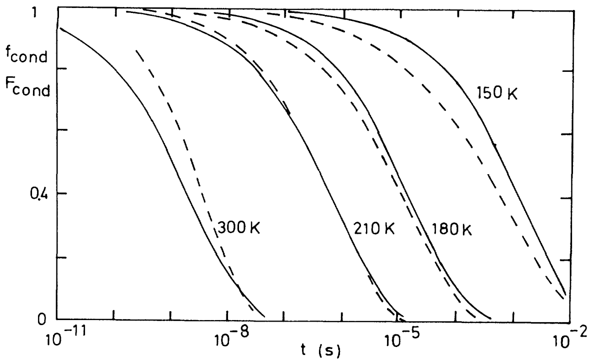

FIG. 11. Time-correlation function $f_{\rm cond}(t,T)$ from Eq. (2) (solid curves) compared to $F_{\rm cond}(t,T)$ calculated from Eq. (14) (dashed curves) at several temperatures.

VI. DISCUSSION AND COMPARISON WITH OTHER MODELS

The salient feature of the present work in the paper gives clear evidence for the difference in the correlation function for ionic motion as derived for NMR relaxation and from ac conductivity. Formally, the difference comes from the fact $\sigma(\omega)$ is the $q=0$ component of the generalized conductivity $\sigma(q,\omega)$ which is related to the qth Fourier component of the local current density fluctuations $J(r,\omega)$, while $R_1(\omega)$ is given by the local ionic motion and thus probes all q components of $\sigma(q,\omega)$. To illustrate this point more specifically we can consider the case in which the time-dependent part of the electric field gradient tensor $V_{ij}(t)$, responsible for the NMR relaxation, can be expanded in terms of the atomic displacements $u_l(t)$ of mobile cations: $V_{ij}(t) = \sum_l a_l u_l(t)$. Thus introducing collective variables a_q one can express the spectra density as[13]

$$J(\omega_L) = \frac{1}{N}\int \sum_q \sum_{l,m} a_l a_m \langle V_q(0) V_q(t) \rangle e^{iqr_{lm}} e^{i\omega_L t} dt$$

$$= \sum_q A_q S(q,\omega_L) \tag{16}$$

and the NSLR as

$$R_1 = \sum_q A_q S(q,\omega_L) \propto k_B T \sum_q A_q \frac{\chi''(q,\omega_L)}{\omega_L} , \tag{17}$$

where we used the fluctuation-dissipation theorem to relate R_1 to the imaginary part of the generalized susceptibility $\chi(q,\omega_L)$ at the Larmor frequency ω_L. Since the ionic displacements $a_l(t)$ give rise to the dielectric response and thus the conductivity of the system, it is justified to relate $\chi(q,\omega_L)$ to the generalized dielectric constant $\epsilon(q,\omega)$ and write

$$R_1 \propto k_B T \sum_q A_q \frac{\epsilon''(q,\omega_L)}{\omega_L} \propto k_B T \sum_q A_q \frac{\sigma'(q,\omega_L)}{\omega_L^2} , \tag{18}$$

where we have used the relation $\sigma'(q,\omega) \propto \omega\epsilon''(q,\omega)$ between the real part of the conductivity and the imaginary part of the dielectric constant. If, and only if, the ionic motions are uncorrelated we can expect no q dependence and Eq. (18) reduces to

$$R_1 \propto \frac{T}{\omega_L^2}\sigma_{ac}(\omega,T) \ . \qquad (19)$$

The simplified Eq. (19) has been considered previously[14] and has been applied to analyze R_1 and σ_{ac} data in β alumina[15] at temperatures below $T \approx 50$ K.

The diffusion-controlled relaxation model[16] and the jump relaxation model[17] are microscopic models which incorporate ionic correlations and lead to non-Debye-like relaxation behavior in both conductivity and NMR relaxation. However, the above models fail to predict different correlation functions for R_1 and σ_{ac} as found instead experimentally.[1] Furthermore, the correlation function proposed by Elliott and Owens[16] can be approximated only by a stretched exponential with $\beta \geq 0.5$ while we find $\beta = 0.35$ [see Eq. (2)].

The dramatic difference between NMR and conductivity correlation times has been noted[18] from the comparison of conductivity data with ^{7}Li NSLR data[19] in Li-chloroborate glassy FIC. The difference between τ_{NMR} and τ_{cond} is attributed either to correlation effects or to site distribution effects.[18] Actually both effects should be considered. In the case of a distribution of barriers, as assumed here, the generalized conductivity should be q dependent affecting τ_{NMR} and τ_{cond} in different ways. By looking at the problem from another point of view, τ_{NMR} is an average of the correlation times between hops of each ion, while τ_{cond} is the correlation time of the electric current driven by the remaining polarization after the applied electric field E is switched off. The average polarization is small, only $Ee^2d^2/2k_BT$ for an ion hopping between two wells separated by d in the field direction or possibly 10^{-4} of the polarization change ed in one hop. Thus just a few hops in a large group of ions are enough to cancel most of the polarization in the group, and τ_{cond} will be much shorter than τ_{NMR}. We have used this argument to write the correlation function Eq. (14).

A distribution of barriers would also be able to describe the gradual progression from long-range cationic migration along preferential paths at high temperature to essentially localized ionic displacements within clusters with local barriers at low temperature.[20]

A homogeneous correlation function (CF) displaying the stretched-exponential functional behavior was derived in the framework of a general semiphenomenological coupling model.[21] However, the CF obtained from the coupling model is q independent and thus, in its original formulation, it does not account for the difference in β exponents found for R_1 and σ_{ac} data.[1] It was originally suggested[22] $E_L^{NMR} = \beta E^{dc}$, where E_L^{NMR} is the activation energy obtained from the R_1 vs T data on the low-temperature side of the maximum (see Fig. 3) and E^{dc} is from dc conductivity whereby $E_L^{NMR} = E_a$ is the true microscopic barrier to ionic motion. After we reported[1] the difference observed between the β values obtained from NMR and conductivity it has been argued[23] that the coupling model leads to the prediction $\beta_{NMR} < \beta_\sigma$ and that the microscopic barrier E_a should be identified as $E_a = \beta_\sigma E_\sigma^* = \beta_R E_{NMR}^*$. Our experimental values for the β coefficients and for the effective activation energies [see Eqs. (1) and (2)] are only in qualitative agreement with the prediction of the coupling theory. Thus, although the coupling theory may indeed include effects of interactions and correlations among mobile ions, one should also incorporate into the model a distribution of microscopic barriers which we believe to be the main source for the difference in NMR and conductivity correlation functions. As was pointed out by Dyre[5] a distribution of barriers with only site energy disorder is not a sufficient condition to ensure a frequency-dependent conductivity. The same conclusion was reached for the asymmetry of the NSLR curve vs temperature by using Monte Carlo simulations.[24] In both cases one finds a distribution of barriers with the same saddle-point energy leads to an average correlation time with a single average activation energy, i.e., Debye-like relaxation. On the other hand for a distribution of barriers with the same site energies, the average correlation time deviates from a simple activated law.[21] In the second case, the ionic hopping motion is strongly correlated because of the asymmetry of the barriers at the different local sites. Both correlations in space and in time should be included in a general theory for $\sigma'(q,\omega)$ which then would explain the differences between $R_1(\omega)$ and σ_{ac}.

VII. SUMMARY AND CONCLUSIONS

We have fit the non-BPP NMR relaxation vs $1/T$ curves in the glassy structure by assuming independent ionic hops over a distribution of barriers E_a. A Gaussian distribution is the natural first choice and we have shown this indeed gives a good fit to the NMR relaxation in this glassy fast-ion conductor. We have also used the fact that the attempt rate for the hops cannot be fit arbitrarily, but, being the oscillation frequency in the well, it must be related to E_a, the hopping distance d and the ion mass m.

The local barriers change somewhat with a hop of a neighboring ion, and clearly there must be some ion-ion correlations that keep the average ionic density and the number z of available neighboring wells approximately constant. There have been many attempts in the literature to include a "memory effect" from previous hops in the probability for the next hop.[17] However, the surrounding lattice readjusts rapidly after a hop and in a time short compared to the hop rate in the local cluster. Even if the local conditions change after each hop, we argue the distribution $Z_{NMR}(E_a)$ over the whole sample is constant, and the average hopping rates and the resulting spin relaxation and conductivity are of course independent of the time.

We have shown the relative ω and T dependencies of the conductivity are described surprisingly well with Eq. (7) from the rectangular distribution of activation energies in the continuous-time random-walk model, although the way of fitting $\sigma(\omega \rightarrow 0, T)$ and $\epsilon^*(\infty)$ ensures at least a partial agreement and the distribution of low barriers is not significant in the model. However, the derived rectangular distribution Z^*_{cond} is shifted compared to the Gaussian Z_{NMR}. Aided with the derived rates, we concluded Z^*_{cond} must be a crude approximation for Z_{NMR} truncated at the percolation limit $E_{\max}$, and we have shown it gives an even better fit to use the truncated Z_{NMR} directly in the numerical average in Eq. (6). The bottlenecks for the dc conductivity are the barrier heights $E_{\max}$ which define a sufficient fraction $P \approx 0.25$ of easy barriers for percolation when $z \approx 6$. The hopping between the bottlenecks is fast and contributes little to the total diffusion time. Therefore the precise distribution of low barriers is unimportant. The ac conductivity has similar bottlenecks at lower $E'_{\max}$ which determine the γ rates in the model Eq. (6).

Hence, the correlation time τ_{cond} of the current from Eq. (1) can be approximated with the average Eq. (10) where the ions in the bottlenecks determine the decay rate for most of the polarization. Likewise, the KWW function Eq. (1) can be approximated with the average Eq. (14) over the time-correlation functions of the individual ions. And most important, the magnitude of the dc conductivity can be simply estimated from Eq. (11) and the average hopping rate of the fraction of ions P. In most discussions of conductivity, $\sigma(0,T)$ is a necessary fit parameter and it is remarkable we can calculate it rather well from the distribution of barriers derived from the NMR spin-lattice relaxation and the assumption of percolation.

We have established quantitative connections between rates of motion derived from NMR relaxation and from conductivity and dielectric properties of the glass starting from a microscopic description of the ionic motion. We find the differences in correlation functions derived from NMR vs conductivity is intimately related to the local vs macroscopic character of the two CF's which becomes a relevant factor in the presence of disorder. The good fit for this particular glassy fast-ion conductor may of course be in part fortuitous, but the overall quantitative consistency of our analysis indicates the conclusions should be generally valid for glassy FIC.

We recognize that the differences between the time-correlation functions and the effective distributions are related to the average number z of neighboring wells to which an ion can hop. We therefore predict that more ordered samples with fewer z and thus greater difficulty for percolation, must have effective distributions Z_{cond} and Z_{NMR} which are more equal. More ordered samples are also likely to have distributions Z_{NMR} that are narrower and thus fit stretched exponents β which are closer to 1.

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