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Reply to “Comment on ‘Correlation functions for ionic motion from NMR relaxation and electrical conductivity in the glassy fast-ion conductor (Li2S)0.56(SiS2)0.44’”

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Abstract
Hunt’s Comment criticizes our recent article for combining concepts from percolation theory and effective-medium theories to calculate the dc and ac conductivities in ionic conducting glasses. Our approach was an attempt to describe the dc and ac conductivity with input information from our NMR measurements. We used the continuous-time random-walk theory and reasonable assumptions for the glasses which yielded good fits of the dc and ac conductivities at many temperatures.

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Comments

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Reply to "Comment on 'Correlation functions for ionic motion from NMR relaxation and electrical conductivity in the glassy fast-ion conductor \((\text{Li}_2\text{Si})_{0.56}\text{Si}_2)_{0.44}\)" 

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Hunt's Comment criticizes our recent article for combining concepts from percolation theory and effective-medium theories to calculate the dc and ac conductivities in ionic conducting glasses. Our approach was an attempt to describe the dc and ac conductivity with input information from our NMR measurements. We used the continuous-time random-walk theory and reasonable assumptions for the glasses which yielded good fits of the dc and ac conductivities at many temperatures.

Hunt in his Comment lists several inconsistencies in our attempt\(^1\) to fit the conductivity data for the fast-ion glass conductor \((\text{Li}_2\text{Si})_{0.56}\text{Si}_2)_{0.44}\) with information from the NMR spin-lattice relaxation of hopping \(^7\text{Li}^+\). Here, both conductivity \(\sigma(\omega, T)\) and the spin relaxation \(R_1(\omega, T)\) are caused by the same Li ion motion so there must be a quantitative relationship between the two effects, which, however, has been difficult to derive for a glass. A recent surprise\(^1\) has been to find these two quantities yield time-correlation functions that differ by orders of magnitude and where \(\tau_{\text{cond}}\) is shorter.

Clearly, there are approximations and somewhat uncertain averages in the simple equations we have used for the poorly known disordered solids, and there may be formal inconsistencies in the way we combine percolation, random-walk, and effective-medium models. But, the fact that we can calculate a quantitative fit to \(\sigma(\omega, T)\) starting from only NMR \(R_1(\omega, T)\) data and limited structural information, shows our method does indeed give a useful picture of the physics involved. The good fit for the first composition we tried is unlikely to be incidental since our method also works\(^4\) for \((\text{Li}_2\text{O})_{0.4}+\text{B}_2\text{O}_3+\text{LiCl})_{0.6}\) and other glasses which have quite different distributions of barriers.

To be more clear we briefly repeat the three main steps in our calculations. Each step can be judged alone for model consistency and for fit to the experimental data:  

(i) We assume a Gaussian distribution \(Z_{\text{NMR}}\) of barriers \(E_a\), hop rates \(r = r_0 \exp(-E_a/k_BT)\) over each of the six nearest neighboring barriers, and sum the Bloembergen-Purcell-Pound relaxation contributions for each \(E_a\), which is permitted for fast spin diffusion. The parameters of \(Z_{\text{NMR}}\) were thus determined by the fit to the \(R_1(\omega, T)\) experimental data. We emphasize the attempt rate \(r_0\) cannot be fit arbitrarily as is often done, but must equal the oscillation frequency in the well, \(r_0 \approx (E_a/2m)\)^{1/2}/d.

(ii) We calculate \(\sigma_{\text{dc}}\) from

\[
\sigma_{\text{dc}}(T) = CP(e^2d^2/6k_BT\tau_{\text{av}}),
\]

where \(P = 0.25\) is the percolation fraction of the concentration \(C\) of mobile ions in a simple cubic lattice approximation of the disordered lattice, and \(\tau_{\text{av}}\) is the average time between random hops of average length \(d\) in \(P\). We assume

\[
\tau_{\text{av}}(T)=\frac{\int_0^{E_{\text{max}}} Z_{\text{NMR}}dE_a}{6r_d\int_0^{E_{\text{max}}} Z_{\text{NMR}}dE_a},
\]

where the denominator equals \(P\). The calculated \(\sigma_{\text{dc}}(T)\) can be checked against the experimental data.

We understand Hunt accepts the principle of percolation in this step, and he claims recognition for having suggested it previously. However, we cannot see that he has written the equivalent of our \(\tau_{\text{av}}\) in any of his papers, and he appears to have missed the point that \(\tau_{\text{av}}\) is considerably shorter than his \(1/(\omega_c)\) at the percolation limit. We showed\(^1\) that the calculated \(\tau_{\text{av}}\) is in approximate agreement with the measured \(\tau_{\text{cond}}\) (Kohlrausch-Williams-Watts) fit with a stretched exponential, and (2) thus explains the much shorter observed correlation time for \(\sigma\) than for \(R_1\), as we expect for the truncated distribution.

(iii) We calculated the frequency dependence of the conductivity from the continuous-time random-walk model derived by Dyre\(^5\) and others where...
1/[σ(ω, T) + iω] \sim \left( 1/[γ(E_{a}, T) + iω] \right). \tag{3}

Here two inputs are required. The limit σ_{av}(T) for calibration of the units, which is known from calculations (ii) or from measurements, and the current decay rate γ which has not been known a priori. We first used the analytical average \(^3\) of (3) for a rectangular distribution of E_{a} and obtained a good fit to the complex conductivity σ(ω, T) when the limit 1/γ_{min}(E_{max}, T) was set equal to \(\tau_{av}(T)\). The rectangular distribution is of course unphysical, but it seems to reproduce the observed frequency behavior in many ionic conductors. However, our finding that \(γ_{min}\) can be associated with 1/\(τ_{av}\) shows that 1/γ\(E_{a}, T\) is likely to be the analog of (2) averaged over \(Z_{\text{NMR}}(E_{a})\) up to \(E_{a}\). This percolation idea may be somewhat inconsistent in the effective-medium formula (3), but it did permit a numerical average of (3) over \(Z_{\text{NMR}}(E_{a})\) to \(E_{\text{max}}\), which indeed led to a good fit for σ(ω, T) and the related dielectric constant \(ε\).

The overall agreement from (i) to (iii) for several Li fast-ion conductors, where we have used no adjustable coefficients except trying broad tails on the Gaussian distribution and \(P\) values slightly higher than 0.25, shows that our model is indeed consistent despite the theoretical doubts.