

Comment on “Ionic Conduction in Glass: New Information on the Interrelation between the ‘Jonscher Behavior’ and the ‘Nearly Constant-Loss Behavior’ from Broadband Conductivity Spectra”

In a recent Letter [1], Roling, Martiny, and Murugavel (RMM) report on the nearly constant loss (NCL) contribution to the conductivity spectra of various ionic conducting glasses. They start by stating that isothermal conductivity spectra are usually well described in the literature [2] by the sum of a Jonscher expression and the term $A\nu$ corresponding to the NCL, i.e.,

$$\sigma'(\nu) = \sigma_{dc}[1 + (\nu/\nu_J)^p] + A\nu. \quad (1)$$

To support their claim that both the Jonscher term and the NCL term are related to ionic hopping, they fit the experimental data of some ionic glasses to the expression

$$\sigma'(\nu) = \sigma_{dc}[1 + (\nu/\nu_J)^{0.7} + (\nu/\nu_{NCL})^{0.95}], \quad (2)$$

where ν_{NCL} is introduced as a characteristic frequency for the NCL term.

From the linear correlation between ν_J and ν_{NCL} , they conclude that the Jonscher term and the NCL term are closely interrelated.

In this Comment, we point out that this conclusion cannot be drawn unambiguously from the results of the analysis conducted in [1] using Eq. (2). The faults of their arguments are as follows.

(i) When ac conductivity data are represented by Eq. (1), it is widely accepted, and acknowledged in [1], that for a given glass composition both ν_J and σ_{dc} have an Arrhenius temperature dependence with the same activation energy, while A has a much weaker temperature dependence compared to σ_{dc} . Except for the small difference between the arbitrarily chosen value 0.95 for the exponent in Eq. (2) and 1.0 in Eq. (1), the two equations are effectively the same. Therefore $A \approx \sigma_{dc}/\nu_{NCL}$ and, from the near temperature independence of A , ν_{NCL} necessarily has about the same activation energy as σ_{dc} and ν_J . The fact that ν_J and ν_{NCL} , determined from Eq. (2), have the same activation energy is just a restatement of the experimentally observed weak temperature dependence of A . It cannot be used to prove unequivocally any relation of NCL to hopping motion of the mobile ions.

(ii) RMM force the fit the conductivity spectra of glasses with different compositions by Eq. (2) with two fixed exponents, 0.7 for the Jonscher term and 0.95 for the NCL term. From these fits, they find the *same* linear relation $\nu_{NCL} = B\nu_J$ holds for a constant B (see Fig. 4 of [1]) which is independent of chemical composition of the glasses. Now this supposedly general result of RMM can be rewritten as

$$\sigma'(\nu)/\sigma_{dc} = [1 + (\nu/\nu_J)^{0.7} + B^{-0.95}(\nu/\nu_J)^{0.95}], \quad (3)$$

which states that the normalized conductivity spectra, $\sigma'(\nu)/\sigma_{dc}$, of *all* glasses with mobile ions is a universal function of the scaled frequency, ν/ν_J . However, it has been shown by several groups [3–5] including a recent Letter [5], published by two of the authors of [1], that the shape of the conductivity spectra depends on the composition of the glass. Hence, conductivity spectra of glasses cannot be scaled to the universal function such as given by Eq. (3), and a *same* linear relation between $\log \nu_J$ and $\log \nu_{NCL}$, as proposed in [1], cannot be valid in general.

In a $\log \sigma' - \log \nu$ plot such as that used by RMM, it may appear that Eq. (3) is a reasonably good fit to the data. But on close examination of Fig. 1 in [1], the fits are actually poor quantitatively throughout the range $1 \leq \sigma'(\nu)/\sigma_{dc} \leq 10$. RMM did not specify the criterion for “good” fits to their data by their Eq. (2). The same data can be represented as $\log \varepsilon''$, where $\varepsilon'' = (\sigma' - \sigma_{dc})/2\pi\nu$ and the apparent good fit by RMM (Fig. 1) has to be judged as poor in the plot of $\log \varepsilon''$ versus $\log \nu$. Thus, one is obliged to say that the errors of ν_J are larger than half a decade, which seriously undermines the linear relation between ν_J and ν_{NCL} purported by Fig. 4 because the entire range in $\nu_J/\sigma_{dc}T$ covered by the data is only one decade. Therefore, RMM must provide and justify their criterion for obtaining good fits to the data, supply error estimates for ν_J , and show them in Fig. 4. Otherwise, Fig. 4 and the comparison with the RBM line have no scientific value.

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