Universal Approach for Scaling the ac Conductivity in Ionic Glasses

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In a recent Letter, Roling *et al.* [Phys. Rev. Lett. **78**, 2160 (1997)] proposed a novel scaling approach, requiring no arbitrary parameters, for the analysis of the ac conductivity resulting from ionic motion in glasses. However, this approach cannot be applied to alkali germanate glasses whose alkali content varies by more than a decade, since changes which occur in the ion hopping length that accompany the changing alkali content are not incorporated. Here, I show that these changes can be incorporated into a universally valid approach which successfully scales the ac conductivity of sodium germanate glasses as well as two additional ionic systems without the introduction of arbitrary parameters. [S0031-9007(99)09058-4]

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Scaling is an important feature in any data evaluation program. The ability to scale different data sets so as to collapse all to one common curve indicates the process can be separated into a common physical mechanism modified only by thermodynamic scales [1]. A prominent example of the usefulness of scaling concepts is found in the gas-liquid coexistence of many molecular fluids. It is well known that when the coexistence curves of different fluids are scaled by the density and temperature at the critical point, they collapse to a single universal curve [2,3]. Hence all these fluids, despite differing molecular interactions involved, exhibit an identical process of phase separation. In this example, the universality stems from the dominance of long range correlations which develop near the critical point and which behave similarly for different fluids regardless of the nature of short range interactions [1,3].

Recently, renewed interest has developed regarding the scaling observed in the frequency dependence of the ionic conductivity of ion-containing glasses [4–6]. For these materials the ac conductivity, spanning frequencies from mHz to GHz, is generally well approximated by [7]

$$\sigma(f) = \sigma_0[1 + (f/f_0)^n] + Af\,. \tag{1}$$

The first term in Eq. (1) results from the relaxation of dissociated ions (usually cations) in the glass matrix. At low frequencies, long range diffusion of these cations results in the frequency independent (dc) conduction σ_0. With increasing frequency, the conductivity increases approximately as a power law whose exponent is often observed [8] near $n = \frac{2}{3}$. The last term in Eq. (1) represents an additional contribution to the conductivity due to processes that are believed to be unrelated to the cation motion [9,10]. This contribution has been referred [11] to as the "near constant loss" (NCL) as its nearly linear frequency dependence implies a frequency independent dielectric loss. Unlike the ionic contribution which exhibits a strong, approximately Arrhenius temperature dependence, the NCL contribution is only weakly temperature dependent and values of the prefactor are typically observed [12,13] around 10^{-12} sec/Ω m.

In regimes where the NCL contribution can be neglected, the ac conductivity then follows a scaling law of the form

$$\frac{\sigma}{\sigma_0} = F\left(\frac{f}{f_0}\right); \qquad F(x) \approx 1 + x^n, \tag{2}$$

where f_0 is a characteristic, but arbitrarily determined, frequency. This scaling has been well documented in the literature [6,14]. In a recent series of publications, Roling and co-workers [4,5] have proposed an improved form of the scaling law in which the arbitrary frequency f_0 is instead expressed in terms of directly accessible quantities such as the dc conductivity, the temperature, and the concentration of mobile charge carriers. In their examination of a series of alkali borate glasses $(\mathrm{Na_2O})_x(\mathrm{B_2O_3})_{1-x}$, they showed that for a given composition (i.e., fixed x), $\sigma(f)$ measured at different temperatures could be scaled according to Eq. (2) with $f_0 = \sigma_0 T$. However, when attempting to scale $\sigma(f)$ spectra obtained from glasses containing different alkali concentrations, they concluded that this characteristic frequency needed to be modified to $f_0 = \sigma_0 T/x$, so as to incorporate changes in the cation number density. This second version of the characteristic frequency did indeed collapse the sodium borate spectra for $0.1 < x < 0.3$ to a common scaling curve. The success of these expressions for the characteristic frequency are remarkable given that the dc conductivity varies by several decades over the temperature and alkali concentration ranges investigated.

In this Letter, I examine the Roling scaling approach for a similar glass system, $(\mathrm{Na_2O})_x(\mathrm{GeO_2})_{1-x}$, but for a substantially wider range of cation concentration ($0.003 < x < 0.1$). Over this range, it is observed that the characteristic frequency $f_0 = \sigma_0 T/x$, proposed by Roling *et al.* [4], fails to collapse the spectra to a common curve. It is suggested that this failure stems from a neglect of changes occurring in the length scale of cation diffusion which may accompany the changing alkali concentration. Instead, it is shown that these length changes can be correctly incorporated by choosing the characteristic frequency, $f_0 = \sigma_0/\Delta\varepsilon$, where $\Delta\varepsilon$ is the observed increase in the dielectric permittivity due to ionic relaxation.

Experimental.—Glasses with $x = 0.1$, 0.03, 0.01, and 0.003 were prepared by melting high purity (>99.99%) GeO_2 and Na_2CO_3 in a platinum crucible at temperatures between 1200 and 1400 °C. Impedance samples were obtained by rapid quenching of the melt onto a brass plate to form glass disks approximately 1 mm in thickness. After annealing, platinum electrodes were deposited on opposite faces. Measurements of the complex impedance were obtained over a frequency range from 1 Hz to 1 MHz for several temperatures using a commercial (Schlumberger 1260) impedance analyzer.

Results.—For the purposes of the present discussion, one individual spectrum was selected from the temperature series of each of the four compositions studied. These were selected such that each exhibited a similar balance of dc and power law behavior within the available frequency window of the spectrometer. Consequently, all exhibited roughly the same σ_0 (3×10^{-7} S/m) and f_0 (3 kHz). In all instances, $\sigma(f)$ remained at least a decade larger than that of the NCL contribution.

These four spectra are presented in Fig. 1 scaled with $f_0 = \sigma_0 T/x$. In contrast to the findings of Roling *et al.* for sodium borate glasses over a narrower composition range, this scaling approach is unsuccessful over the more substantial composition range of the present sodium germanate glasses. A similar finding has recently been reported by Jain and Krishnaswami [15] who interpret this failure as the result of increasing encroachment of the NCL into $\sigma(f)$ with decreasing alkali concentration.

Instead, I contend that this failure is a result of neglecting the possibility that the distance over which the cations move in a given diffusion step may increase with decreasing cation concentration. The diffusion of cations through the glass matrix occurs by random hopping between charge-compensating anionic sites located throughout the lattice. The conduction can be related to this diffusion through the Nernst-Einstein relation

$$\sigma_0 = \frac{\gamma N q^2 d^2}{6kT} H_R f_H \,, \tag{3}$$

where N is the cation density (proportional to x), γ is the fraction of cations which are mobile, q is the charge of the cation, d is the distance traversed in a single hop, and f_H is the rate at which these hops occur. H_R is the Haven ratio which accounts for possible cross correlation in the diffusion. For low alkali contents, these cross correlations can be neglected ($H_R = 1$) and the hopping rate can be expressed as

$$f_H = \left(\frac{6k}{q^2}\right)\left(\frac{\sigma_0 T}{N}\right)\frac{1}{\gamma d^2} \,. \tag{4}$$

Here it is evident that the second term in parentheses is just the characteristic frequency $f_0 = \sigma_0 T/x$ proposed by Roling *et al.* If the hopping distance and the mobile fraction of carriers remains constant, then one expects the Roling scaling alone to be successful. Indeed, for the narrow range of their investigation ($0.1 < x < 0.3$), the variation in γd^2 may not be significant. However, it is probable that d would increase with decreasing cation concentration, perhaps increasing with the average separation between anionic sites [6], $d \approx x^{-1/3}$. Consequently, inclusion of the factor d^2 would favor $f_0 = \sigma_0 T/x^a$, where a is less than unity.

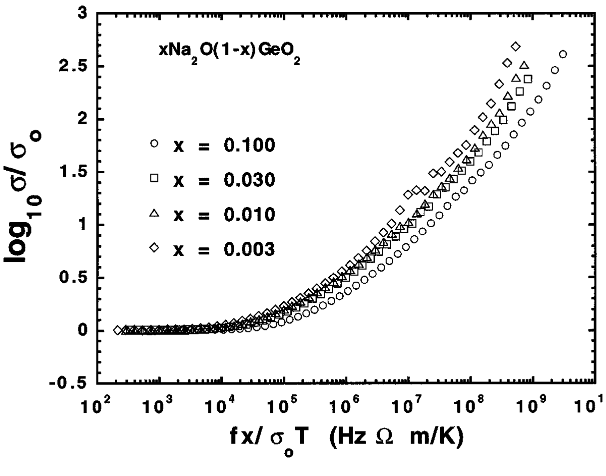

FIG. 1. The ac conductivity in $(Na_2O)_x(GeO_2)_{1-x}$ glasses scaled in the manner proposed by Roling and co-workers.

In Eq. (4) the cation concentration enters into the characteristic frequency both as a bulk number density as well as through the hopping length. This hopping length cannot be *a priori* determined from the measured $\sigma(f)$. However, this dilemma can be circumvented by making use of the dielectric permittivity $\varepsilon(f)$, which is also dependent upon the quantity γd^2 and which is obtained together with $\sigma(f)$ in measurements of the complex impedance. The frequency dependent permittivity is shown in Fig. 2. With decreasing frequency $\varepsilon(f)$ increases from the unrelaxed baseline (ε_∞) to the fully relaxed level ε_s. The permittivity change $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is a direct consequence of the relaxation of hopping cations. Since the hop of the cation between anionic sites is analogous to the rotation of a permanent dipole, the Debye model [16] offers a suitable approximation of the permittivity change,

$$\Delta\varepsilon = \frac{\gamma N (qd)^2}{3\varepsilon_0 kT} \,, \tag{5}$$

where the quantity in parentheses is the effective dipole moment of the hopping cation. The quantity γd^2 determined from Eq. (5) is shown in the inset in Fig. 2 and indeed increases with decreasing x, roughly like $x^{-2/3}$.

Since both σ_0 [Eq. (3)] and $\Delta\varepsilon$ [Eq. (5)] contain a similar dependence upon γd^2, this unknown quantity can

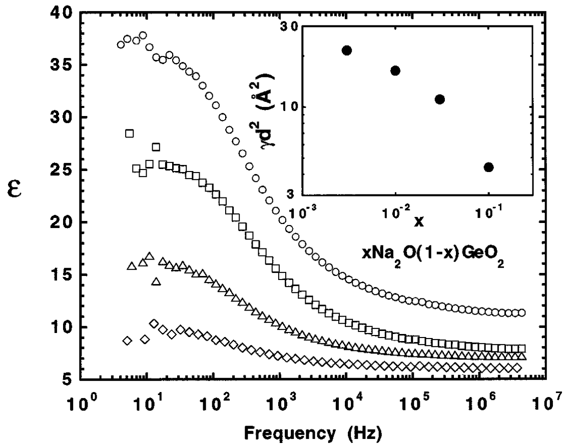

FIG. 2. The ac permittivity in $(Na_2O)_x(GeO_2)_{1-x}$ glasses showing variation of $\Delta\varepsilon$ with alkali content. Symbols are defined in Fig. 1. The inset shows the increase in γd^2 (see text) with decreasing alkali concentration.

be reduced away by simply choosing the characteristic frequency $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$, so that the scaling law becomes

$$\frac{\sigma}{\sigma_0} = F\left(\frac{f\varepsilon_0\Delta\varepsilon}{\sigma_0}\right). \tag{6}$$

As shown in Fig. 3, the present conductivity spectra can be successfully scaled in accordance with Eq. (6).

In an effort to evaluate the generality of this finding, the scaling is also attempted for two additional examples taken from the literature: the ionic melt [17] $0.4Ca(NO_3)_2$-$0.6KNO_3$ and the thioborate glass system [18] $(K_2S)_x \times (B_2S_3)_{1-x}$. Results are provided in Figs. 4 and 5, respectively. For the ionic melt, an attempt to scale the spectra using $f_0 = \sigma_0 T$ was unsuccessful. The reason appears to be that, despite the fixed composition of the melt, $\Delta\varepsilon$ increases with increasing temperature indicating that the quantity γd^2 does not remain fixed. For the potassium thioborate series, spanning a composition range similar to that of the sodium germanate series, similar increases in γd^2 with decreasing alkali content were observed and scaling by $f_0 = \sigma_0 T/x$ was inadequate. Scaling could be attained, however, using $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$.

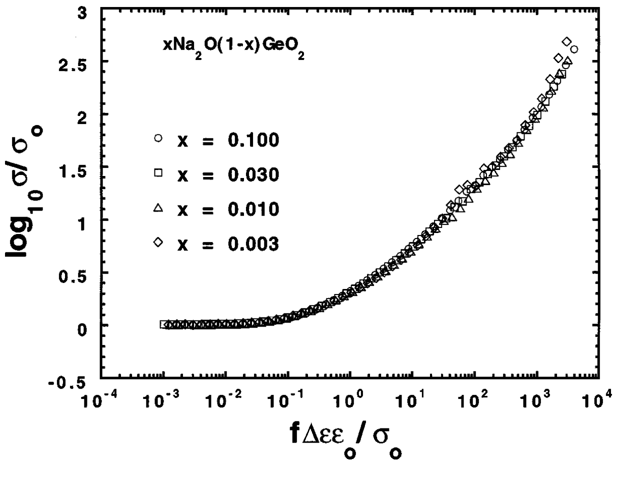

FIG. 3. The ac conductivity in $(Na_2O)_x(GeO_2)_{1-x}$ glasses scaled using $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$.

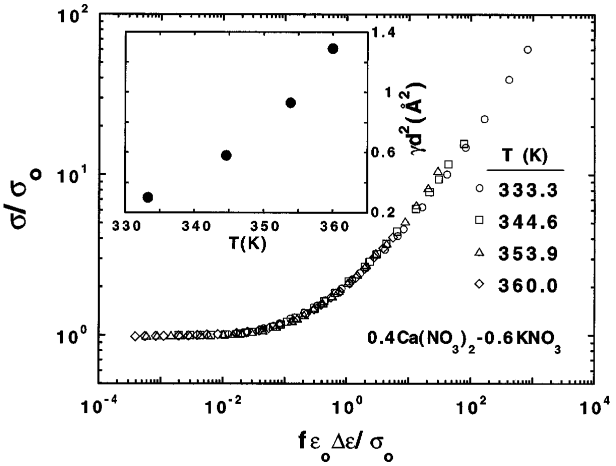

FIG. 4. The ac conductivity in $0.4Ca(NO_3)_2$-$0.6KNO_3$ (Ref. [17]) at four temperatures scaled using $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$. The inset shows the temperature dependence of γd^2.

Curiously, the characteristic frequency $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$ is similar to an empirical relation seen to hold between σ_0, $\Delta\varepsilon$, and the frequency of maximum dielectric loss, known by some as the Barton-Nakajima-Namikawa relation [19,20]. However, this characteristic frequency may have a more fundamental origin. Consider the relaxation of fluctuating free space charge in the glass [16]. This space charge ρ_{cat} could be envisioned as thermally driven deviations from local charge neutrality due to displacements of the cations. From the Maxwell equations,

$$j_{cat} + \frac{\partial}{\partial t}D_{cat} = \nabla \times H \tag{7}$$

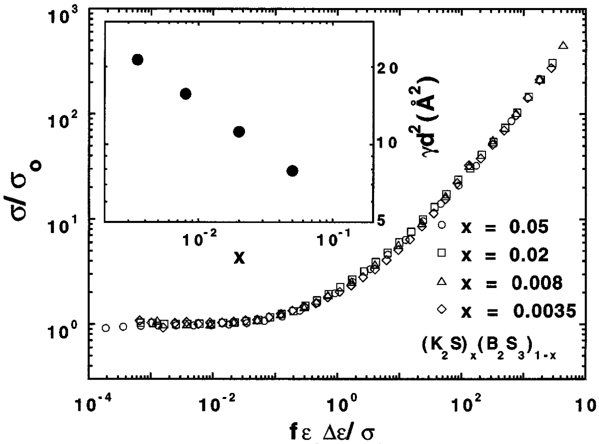

FIG. 5. The ac conductivity in $(K_2S)_x(B_2S_3)_{1-x}$ (Ref. [18]) at four compositions scaled using $f_0 = \sigma_0/\varepsilon_0\Delta\varepsilon$. The inset shows the variation of γd^2 with alkali content.

and

$$\nabla \cdot D_{\text{cat}} = \rho_{\text{cat}} .$$

The current density j_{cat} can be approximated using Ohm's law $(j_{\text{cat}} = \sigma_0 E)$, and upon taking the divergence of Eq. (7), obtains

$$\sigma_0 \nabla \cdot E = -\frac{\partial \rho_{\text{cat}}}{\partial t} .$$

Finally, upon substituting for the electric field using $D_{\text{cat}} = \varepsilon_0 \Delta \varepsilon E$,

$$\frac{\partial \rho_{\text{cat}}}{\partial t} = -\left(\frac{\sigma_0}{\varepsilon_0 \Delta \varepsilon}\right) \rho_{\text{cat}} .$$

Thus, local fluctuations of the space charge decay with a characteristic rate that is identical to that required to scale the ac conductivity.

In summary, scaling is an important feature of the ac conductivity in ionic glasses. Although the approach proposed by Roling and co-workers captures much of the temperature and composition dependence of the characteristic scaling frequency, it requires revision to incorporate variations that may also occur in the length scale for cation diffusion. This length scale dependence can be incorporated in a natural manner by choosing a scaling frequency constructed from aspects of both the dc conductivity and the permittivity change.

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