PHYSICAL REVIEW E **90**, 062315 (2014)

Invariance of conductivity relaxation under pressure and temperature variations at constant conductivity relaxation time in $0.4Ca(NO_3)_2$-$0.6KNO_3$

Z. Wojnarowska,[1,2,*] K. L. Ngai,[3,4] and M. Paluch[1,2]
[1]*Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland*
[2]*Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland*
[3]*CNR-IPCF, Largo B. Pontecorvo 3, I-56127 Pisa, Italy*
[4]*Dipartimento di Fisica, Università di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy*
(Received 30 September 2014; published 29 December 2014)

The article reports the dependence of the conductivity relaxation on temperature T and pressure P in the canonical ionic glass former $0.4Ca(NO_3)_2$-$0.6KNO_3$ (CKN). At constant conductivity relaxation time τ_σ, the entire conductivity relaxation spectra obtained at widely different combinations of T and P superpose almost perfectly, and thus it is the ion-ion interaction but not thermodynamics that determines the frequency dispersion. Moreover, on vitrifying CKN by either elevating P or decreasing T, changes of P or T dependence of τ_σ at the glass transition pressure P_g and temperature T_g are observed to occur at the same value, i.e., $\tau_\sigma(P_g) = \tau_\sigma(T_g)$, indicating that the relation between τ_σ and the structural relaxation time τ_α is also independent of P and T.

DOI: 10.1103/PhysRevE.90.062315 PACS number(s): 64.70.pj, 72.80.−r, 77.22.−d

The salt mixtures of $Ca(N0_3)_2$ with $KN0_3$ are excellent glass-forming systems. Widely studied is the one with composition $0.4Ca(NO_3)_2$-$0.6KNO_3$ (CKN). Studies on structural relaxation and glass transition using various techniques include ultrasonics [1,2], viscosity [3], mechanical [4] neutron scattering [5], light scattering [6–8], dielectric and conductivity relaxation [9,10], other optical techniques [11], and molecular dynamics simulations [12,13].

CKN is also an ionically conducting material, and the dynamics of ions from conductivity relaxation measurements have been an active research subject. The conductivity relaxation has relaxation time, τ_σ, practically the same as the structural α relaxation time, τ_α, at temperatures above ~400 K, but becomes increasingly shorter than τ_α as temperature T is lowered towards the glass transition temperature T_g, while the frequency dispersion narrows monotonically. The conductivity relaxation correlation function,

$$\phi_\sigma(t) = \exp[-(t/\tau_\sigma)^{\beta_\sigma}], \tag{1}$$

used to fit the frequency dispersion, has the fractional exponent $\beta_\sigma \equiv (1 - n_\sigma)$ increasing with decreasing T [3,14]. The conductivity relaxation in CKN had been used to test predictions of theory and model [15].

The structural α relaxation and conductivity relaxation of CKN have many properties that are general for glass formers and ionic conductors, respectively. In recent years advances in the study of dynamics of glass formers have benefited from the introduction of pressure P as the thermodynamic variable in addition to T. The facts obtained from the combined effects of P and T is helpful as well as necessary in the search of the basic physics governing the structural α relaxation and glass transition. Among several effects found is the invariance of the frequency dispersion of the α relaxation to widely different combination of P and T while keeping τ_α constant [16]. If the Kohlrausch function,

$$\phi_\alpha(t) = \exp[-(t/\tau_a)^{1-n_a}], \tag{2}$$

is used to characterize the dispersion, the effect can be restated as invariance of $\beta_\alpha \equiv (1 - n_\alpha)$ or n_α at constant τ_α. In some glass-forming systems where the secondary β relaxation belonging to a special class [called the Johari-Goldstein (JG) β relaxation] [17] appears together with the α relaxation, the frequency dispersion of the α relaxation as well as the β relaxation time, τ_β, are invariant to variations of P and T that keep τ_α constant [16,18–20]. In many glass formers, τ_β is too close to τ_α, making the JG β relaxation not resolved, and instead showing up in the susceptibility spectra is an excess wing on the high-frequency flank of the α relaxation. Even in this case the entire spectrum consisting of the α-loss peak and the excess wing is unchanged on varying P and T when τ_α is held constant [15]. The effect has far reaching implications. First, the α dispersion or n_α at any fixed τ_α does not depend on thermodynamic factors such as volume and entropy, but instead on the many-body nature of the α relaxation governed by the interaction and its potential. Second, we have coinvariance of τ_α, n_α, and τ_β for any fixed τ_α. As shown before [16–20], the coinvariance is a consequence of the coupling model (CM) relations,

$$\tau_a = [t_c{}^{-n_\alpha}\tau_0]^{1/(1-n_\alpha)} \quad \text{and} \quad \tau_0 \approx \tau_\beta \tag{3}$$

where τ_0 is the primitive relaxation time, and t_c is a constant.

In this article, we present experimental data from measurements of conductivity relaxation in CKN at ambient and elevated pressures. The results show that the same effects discussed above are found in the conductivity relaxation of CKN. The electric modulus spectrum obtained at isothermal conditions at elevated pressure superposes almost perfectly at all frequencies with the one measured at ambient pressure, provided the conductivity relaxation time τ_σ is the same. Moreover, the ratio, τ_α/τ_σ, is the same at glass transition independent of whether it occurs isobarically at T_g on varying T or isothermally at P_g on varying P. These properties indicate that, at any fixed value of τ_σ, the frequency dispersion of the conductivity relaxation as well as the decoupling of the conductivity relaxation from the structural relaxation are not determined by thermodynamic factors.

---

[*] zaneta.wojnarowska@us.edu.pl

1539-3755/2014/90(6)/062315(5)

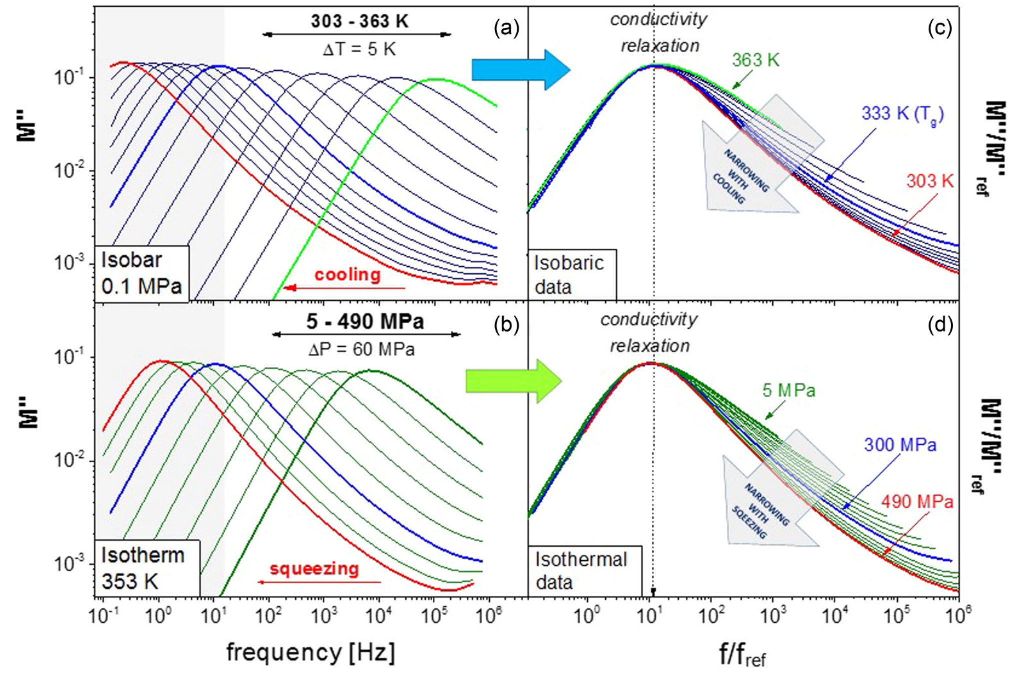

FIG. 1. (Color online) The dielectric loss modulus $M''(f)$ spectra from conductivity relaxation of CKN at various temperatures (a) and pressures (b) in the liquid and glassy states. Note that the well-pronounced conductivity relaxation peak observed in the dielectric spectra, called σ relaxation, is related to the translational mobility of ions. The conductivity relaxation time estimated from the frequency corresponding to the M'' maximum: $\tau_\sigma = 1/2\pi f_{\max}$ can be also defined as $\tau_\sigma = \varepsilon_\infty \varepsilon_0/\sigma$. (c, d) The superimposed dielectric spectra of CKN taken at ambient pressure ($P = 0.1$ MPa) and several different temperatures and at constant temperature ($T = 353$ K) at several different pressures, respectively.

The ambient pressure dielectric spectra of CKN were taken from Ref. [21], and the high-pressure data were measured by a Novocontrol Alpha analyzer at constant temperature (353 K) over broad frequency and pressure ranges. The high-pressure experiments were performed in a Unipress system with a custom flat parallel capacitor. A detailed description of the high-pressure equipment can be found in Ref. [22]. Measurements made are presented in terms of frequency-dependent complex electric modulus, $M^*(f) = M'(f) + iM''(f)$. Shown in Fig. 1(a) are the imaginary part $M''(f)$ from isobaric measurements at ambient pressure over a range of temperature from above to below T_g. Presented in Fig. 1(b) are examples of isothermal data of $M''(f)$ at $T = 353$ K and P ranging from 5 to 490 MPa in step increases of 60 MPa. By inspection of Fig. 1(c) it is evident that the $M''(f)$ loss peak narrows on lowering temperature or increasing τ_σ, more significantly above the calorimetric $T_g = 333 \pm 2$ K [3,23], and less so when near or in the glassy state. The trend on lowering T is reflected by the increase of $\beta_\sigma(T) \equiv [1 - n_\sigma(T)]$, acquired from fits of the spectra to the Fourier transform of the Kohlrausch function, as shown in Fig. 2, where $\beta_\sigma(T)$ is plotted against $\log\tau_\sigma(T)$. The same behavior of $M''(f)$ can be seen on increasing P in Fig. 1(d). The narrowing of the dispersion with increase of P is also presented as the increase of $\beta_\sigma(P)$ with increasing $\log\tau_\sigma(P)$ in Fig. 2. Within the uncertainties in fitting the loss modulus data to determine $\beta_\sigma(T)$ and $\beta_\sigma(P)$, the data in Fig. 2 can be considered as evidence of invariance of the frequency dispersion, or β_σ, to changes of P and T while maintaining τ_σ constant. In other words, neither temperature nor pressure determines the time correlation function of the ion conductivity relaxation, $\phi_\sigma(t) = \exp[-(t/\tau_\sigma)^{\beta_\sigma}]$. The result implies that it is the ion-ion interaction potential that controls the time dependence of the correlation function. However, this does not mean T and P play no role in the ion dynamics. They

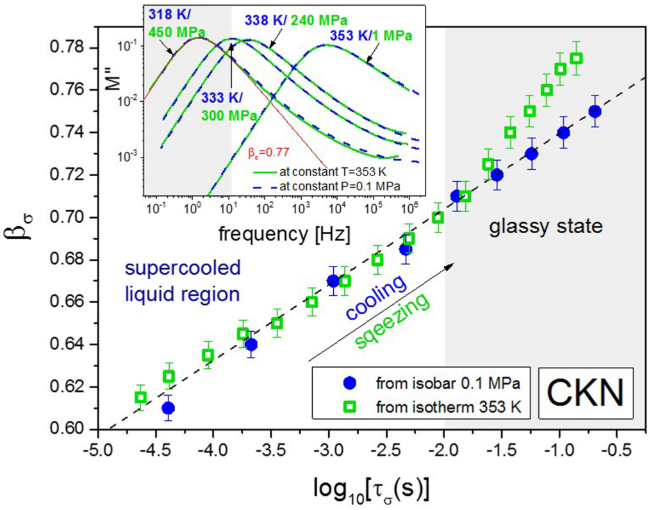

FIG. 2. (Color online) Plot of β_σ vs $\log\tau_\sigma$. Circles and squares are obtained from fitting the isobaric and isothermal $M''(f)$ loss peaks in Figs. 1(a) and 1(b), respectively. The inset presents the comparison of dielectric spectra recorded at different temperature and pressure conditions and at the same conductivity relaxation time. Solid red line is the fit to the KWW function with $\beta = 0.77$.

have an influence on the dependences of τ_σ on P and T, which will be considered later, after completing the discussion on the frequency dispersion of $M''(f)$.

The inset to Fig. 2 shows examples of the almost exact correspondence of the $M''(f)$ from isothermal and isobaric measurements over the entire frequency range. The loss peak described by the Fourier transform of $\phi_\sigma(t)$ covers only part of the entire dispersion. In analogy to the dielectric loss peak of structural α relaxation, this part is called the conductivity α relaxation loss peak, and the remaining part on the high-frequency side not accounted for is called the excess wing. Although not universally accepted, the excess wing originates from the Johari-Goldstein (JG) β relaxation, which is not resolved. Again in analogy to JG β relaxation in dipolar glass formers [24], the excess loss on the high-frequency flank of the α-loss peak of $M''(f)$ in CKN, not accounted for by the Kohlrausch fit, is the unresolved secondary β conductivity relaxation with relaxation time $\tau_{\sigma\beta}$. The almost perfect superposition of the isothermal and isobaric $M''(f)$ with the same peak frequency suggests that not only the conductivity relaxation α loss but also the excess wing or the unresolved β conductivity relaxation is invariant to changes of thermodynamic condition, above and below T_g or P_g. The slight deviation from superposition in the glassy state at high frequencies is due to physical aging during performance of the high-pressure measurement. Hence, there is coinvariance of τ_σ, β_σ, and $\tau_{\sigma\beta}$ to variations of P and T that keep either τ_σ or $\tau_{\sigma\beta}$ constant. The frequency dispersion of $M''(f)$ of the α conductivity relaxation in the room-temperature ionic liquid, 1-methyl-3-trimethylsilylmethylimidazolium tetrafluoroborate, is broader than that of CKN [25]. A smaller $\beta_\sigma = 0.57$ is needed to fit $M''(f)$ of this ionic liquid as compared with $\beta_\sigma = 0.77$ for CKN. According to the CM relation for ionic conductivity relaxation [15,19,25],

$$\tau_\sigma = [(t_{\sigma c})^{-n_\sigma}\tau_{\sigma 0}]^{1/(1-n_\sigma)} \quad \text{and} \quad \tau_{\sigma 0} \approx \tau_{\sigma\beta} \tag{4}$$

where $\tau_{\sigma 0}$ is the primitive conductivity relaxation time and $t_{\sigma c}$ is typically about 1 ps; the ratio $\tau_\sigma/\tau_{\sigma\beta}$ is much larger for a smaller $\beta_\sigma \equiv (1-n_\sigma)$ value of 0.57 of the ionic liquid than 0.77 of CKN. Consequently, the β conductivity relaxation is well resolved from the α relaxation in the ionic liquid. In Ref. [25] we found not only good agreement between the experimental value of $\tau_{\sigma\beta}$ and $\tau_{\sigma 0}$ calculated by Eq. (4), but also direct experimental evidence of coinvariance of τ_σ, β_σ, and $\tau_{\sigma\beta}$ to variations of P and T, while keeping either τ_σ or $\tau_{\sigma\beta}$ constant. The analogue of this property in nonionic glass formers, i.e., coinvariance of τ_α, β_α, and τ_β to variations of P and T that keep either τ_α or τ_β constant, is even more widespread [16–20] and found in glass formers with a broad range of β_α values. This general property shared by structural and conductivity relaxation is remarkable. We accentuate this shared property in Fig. 3 by choosing in particular the nonionic glass former, cresolphthalein-dimethylether (KDE), which has almost the same frequency dispersion of its dielectric loss, $\varepsilon''(f)$ as that of $M''(f)$ of CKN, i.e., $n_\sigma = n_\alpha = 0.23$. Data of $\varepsilon''(f)/\varepsilon''_{\max}$ from KDE [16] were taken at two combinations of T and P, ($T = 325$ K and $P = 0.1$ MPa) and ($T = 363$ K and $P = 137$ MPa). The $M''(f)/M''_{\max}$ data of CKN were obtained at $T = 318$ K and $P = 0.1$ MPa and $T = 353$ K and $P = 450$ MPa. Indicated by the arrows, the primitive frequencies, $f_{\sigma 0} = 1/(2\pi\tau_{\sigma 0})$ and $f_0 = 1/(2\pi\tau_0)$, are too close to the peak frequency, and this is the reason why the β relaxation is not resolved.

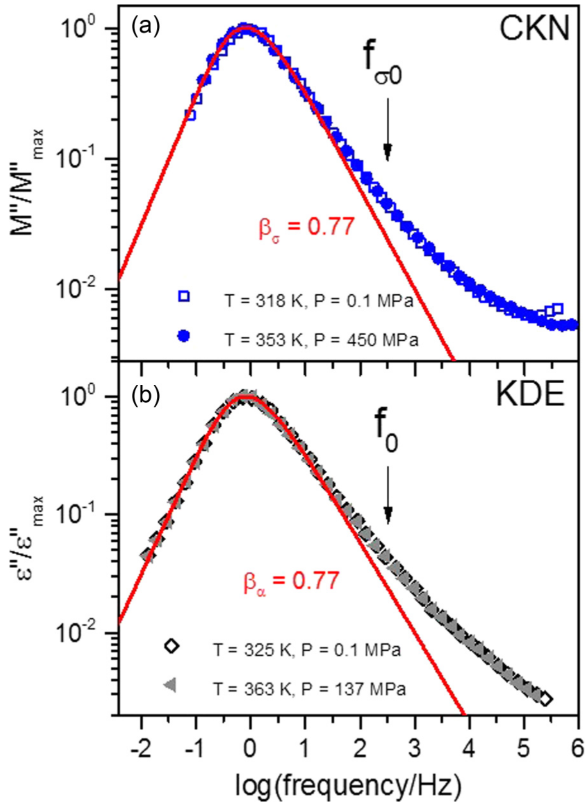

FIG. 3. (Color online) $M''(f)$ spectra of CKN (a) and $\varepsilon''(f)$ spectra of KDE (b) recorded at different temperature and pressure conditions while maintaining the relaxation time constant. A small horizontal shift of 0.05 decade to lower frequencies of the $\varepsilon''(f)$ data is applied to have its maximum at the same frequency as $M''(f)$ of CKN. Solid lines are the fits to the KWW function with β_σ and $\beta_\alpha = 0.77$. The arrow indicates the primitive relaxation frequencies, $f_{\sigma 0}$ and $f_{\alpha 0}$ calculated by Eqs. (3) and (4) of the coupling model [15–17].

Presented in Fig. 4 are the isothermal and isobaric τ_σ. The change of τ_σ in T and P dependencies in the two panels are due to glass transition. The broken line indicates that τ_σ has the same value at glass transition. Thus, the ratio, τ_α/τ_σ is the same at glass transition independent of whether it occurs isobarically at T_g on varying T or isothermally at P_g on varying P. This indicates that the decoupling of the conductivity relaxation from the structural relaxation is also independent of the thermodynamic factors. It is also worth noting that the behavior of $\tau_\sigma(P)$ observed for CKN differs markedly from that found for protic ionic conductors, where the characteristic kink of the τ_σ-P curve moves toward shorter conductivity relaxation times with increasing pressure [26–29]. Naturally, the mechanism of decoupling between τ_σ and τ_α in CKN [14] is not the same as fast proton hopping from the Grotthuss mechanism as postulated for protic ionic glasses.

Returning to the role of P and T in determining τ_σ and $\tau_{\sigma\beta}$, we bring back the molecular dynamics simulations of CKN by Ribeiro *et al.* [13] They calculated at various

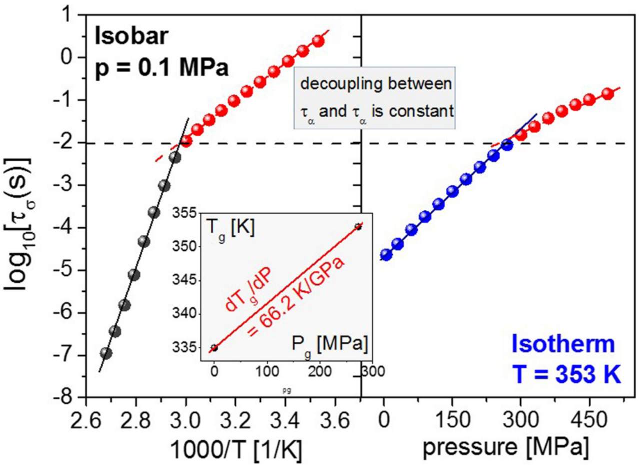

FIG. 4. (Color online) Isobaric and isothermal dielectric measurements of conductivity relaxation time of CKN. The inset presents the pressure dependence of the T_g temperature for CKN. The value of $dT_g/dP = 60$ K/GPa determined from conductance measurements presented in Ref. [23] is consistent with our own measurements.

P and T the incoherent scattering function, $F_s(\boldsymbol{k},t) = \langle \exp\{-i\boldsymbol{k}\cdot[\boldsymbol{r}_i(t)-\boldsymbol{r}_i(0)]\}\rangle$, where $k = 2.0\,\mathring{\mathrm{A}}^{-1}$ corresponding to the main peak of the static structure factor $S(k)$ and $\boldsymbol{r}_i(t)$ is the coordinate of ion i at time t. The stretched exponential function, $\phi_k(t) = \exp[-(t/\tau_k)^{\beta_k}]$, was used to fit $F_s(\boldsymbol{k},t)$ for each P as functions of T. Combined with the T dependence of the density ρ at each P also obtained, all the results of $\tau_{\mathrm{ion}}(P,T)$ for the anions can be described by a single function of ρ^γ/T with $\gamma = 1.8 \pm 0.1$. In addition, they obtained the diffusion coefficient, $D(P,T)$, from the long-time limit of the mean squared displacement, $\langle |r_i(t) - \mathbf{r}_i(0)|^2\rangle$, of the anion, as well as the reorientation relaxation time, $\tau_r(P,T)$, of anions from the correlation function $C_r(t) = \langle \boldsymbol{u}_i(t)\cdot\boldsymbol{u}_i(0)\rangle$, where $\boldsymbol{u}_i$ is an unit vector on the C_3 axis of $NO_3{}^-$. They found D and τ_r are also functions of the same product variable, ρ^γ/T, with a common value $\gamma = 1.8 \pm 0.1$, and the same as for τ_k, although the functions themselves, $D(\rho^\gamma/T)$, $\tau_r(\rho^\gamma/T)$, and $\tau_{\mathrm{ion}}(\rho^\gamma/T)$ are all different. Since cross terms in the correlation function of conductivity relaxation is usually negligible, $D(\rho^\gamma/T)$ is proportional to conductivity and hence inversely proportional to τ_σ. From this, we can infer that τ_σ obtained from our conductivity relaxation experiment also is the function, $\tau_{\sigma\alpha}(\rho^\gamma/T)$, with $\gamma = 1.8 \pm 0.1$. The fact that $D(\rho^\gamma/T)$ or $\tau_{\sigma\alpha}(\rho^\gamma/T)$, $\tau_r(\rho^\gamma/T)$, and $\tau_{\mathrm{ion}}(\rho^\gamma/T)$ are all different functions of the variable ρ^γ/T with the same γ is intriguing, and a possible rationalization has been mentioned by Ribeiro *et al.* [13] and given in Ref. [30].

Furthermore, the invariance of the entire $M''(f)$ spectrum (i.e., the α-loss peak and the excess wing or the unresolved β conductivity relaxation) to variations of P and T at constant τ_σ, implies the invariance of the ratio $\tau_\sigma/\tau_{\sigma\beta}$, and hence $\tau_{\sigma\beta}$ is also a function of ρ^γ/T for the same γ. Such dependence on ρ^γ/T of the structural α relaxation time, τ_α, and JG β relaxation time, τ_β, for the same γ is a general property of nonionic glass formers [30]. Because the JG β relaxation precedes the α relaxation in time, from causality it follows that the dependences of τ_α and τ_β on ρ^γ/T, for the same γ, originates from τ_β. The same reasoning applied to the present case of conductivity relaxation in CKN suggests that the dependences of τ_σ and $\tau_{\sigma\beta}$ on ρ^γ/T, for the same γ, originates from $\tau_{\sigma\beta}$. In either structural or conductivity relaxation, the dependence of τ_β or $\tau_{\sigma\beta}$ on ρ^γ/T is passed onto τ_α or τ_σ as time increased and is magnified by many-body (cooperative) effects associated with the structural or the conductivity α relaxation.

The effective interaction potential $U(r)$ between Ca^{2+}, and oxygen atoms of $NO_3{}^-$ is the sum of an attraction term from Coulomb interaction, and another term proportional to r^{-p} to account for repulsion at short distance. The best fit to $U(r)$ gives the repulsive potential exponent $p = 4.7$. The dependence on ρ^γ/T came from approximating the intermolecular potential by a repulsive inverse power law, r^{-p}, with the weaker attractive forces treated as a spatially uniform background term [31], where r is the intermolecular distance. In this approximation, all reduced dynamical quantities of the liquid [32] can be presented as a function of ρ^γ/T with $\gamma = p/3$. Applying this approximation, Rebeiro *et al.* used the value of $p = 4.7$ of the repulsive potential and arrive at $\gamma = p/3 = 1.5$, which is close to $\gamma = 1.8$ obtained from thermodynamic scaling of D, τ_k, and τ_r of CKN. The scaling exponent γ is a material specific constant whose magnitude is related to the steepness of the repulsive part of $U(r)$, evaluated around the distance of closest approach between particles, which was verified by simulations of Lennard-Jones systems [33]. Such local interactions that determines the value of γ explains why the local JG β relaxation in nonionic glass formers, and the β conductivity relaxation discussed herein, have the ρ^γ/T dependence [30].

In summary, in the classical inorganic glass former and ionic conductor, CKN, we found the entire frequency dispersion of the conductivity relaxation in invariant to changes of thermodynamic conditions while the conductivity relaxation time $\tau_{\sigma\alpha}$ is kept constant. This result indicates that the frequency dispersion is determined by the many-body dynamics governed by the ion-ion interaction but not the thermodynamic factors. The relation between τ_σ and the structural relaxation time τ_α is unchanged at glass transition whether effected isothermally or isobarically. Simulations had found that $\tau_{\sigma\alpha}$ is a function of ρ^γ/T with γ approximately equal to $p/3$, where p is the exponent of the repulsive part of the intermolecular potential proportional to r^{-p}. Assuming that the excess wing is an unresolved conductivity β relaxation with relaxation time, $\tau_{\sigma\beta}$, the ratio $\tau_\sigma/\tau_{\sigma\beta}$ is also invariant to change of P and T at constant value of either τ_σ or $\tau_{\sigma\beta}$, and hence $\tau_{\sigma\beta}$ is also a function of ρ^γ/T with the same γ as $\tau_{\sigma\alpha}$. Causality suggests that the dependence on ρ^γ/T originates at $\tau_{\sigma\beta}$ and is inherited by $\tau_{\sigma\alpha}$. All the findings of the conductivity relaxation dynamics have exact analogues in the structural α relaxation and JG β relaxation of nonionic glass formers. The perfect analogy of the two entirely different processes indicates their dynamics are governed by the same physics based on the intermolecular or interionic potential.

Z.W. and M. P. are deeply grateful for the financial support by the National Science Centre within the framework of the Maestro2 project (Grant No. DEC-2012/04/A/ST3/00337). Z.W. acknowledges financial assistance from FNP START (2014).

[1] R. Weiler, R. Bose, and P. B. Macedo, J. Chem. Phys. **53**, 1258 (1970).

[2] G. M. Glover and A. J. Matheson, Trans. Faraday Soc. **67**, 1960 (1971).

[3] F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, J. Phys. Chem. **78**, 639 (1974).

[4] H. G. K. Sundar and C. A. Angell, in *Collected Papers of the XIVth International Congress on Glass, New Delhi, 1985* (Indian Ceramic Society, Calcutta, 1986), Vol. II, pp. 161–168.

[5] F. Mezei and M. Russina, J. Phys.: Condens. Matter **11**, A341 (1999).

[6] C. A. Angell and L. M. Torell, J. Chem. Phys. **78**, 937 (1983).

[7] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, Phys. Rev. A **45**, 3867 (1992).

[8] E. A. Pavlatou, A. K. Rizos, G. N. Papatheodorou, and G. Fytas, J. Chem. Phys. **94**, 224 (1991).

[9] P. Lunkenheimer, A. Pimenov, and A. Loidl, Phys. Rev. Lett. **78**, 2995 (1997).

[10] A. Pimenov, P. Lunkenheimer, H. Rall, R. Kohlhaas, A. Loidl, and R. Böhmer, Phys. Rev. E **54**, 676 (1996).

[11] L.-T. Cheng, Y.-X. Yan, and K. A. Nelson, J. Chem. Phys. **91**, 6052 (1989).

[12] G. F. Signorini, J.-L. Barrat, and M. L. Klein, J. Chem. Phys. **92**, 1294 (1990).

[13] M. C. C. Ribeiro, T. Scopigno, and G. Ruocco, J. Chem. Phys. **135**, 164510 (2011).

[14] Z. Wojnarowska, K. Kołodziejczyk, K. J. Paluch, L. Tajber, K. Grzybowska, K. L. Ngai, and M. Paluch, Phys. Chem. Chem. Phys. **15**, 9205 (2013).

[15] K. L. Ngai, J. Phys.: Condens. Matter **15**, S1107 (2003).

[16] K. L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, and C. M. Roland, J. Phys. Chem. B **109**, 17356 (2005).

[17] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).

[18] M. Mierzwa, S. Pawlus, M. Paluch, E Kaminska, and K. L. Ngai, J. Chem. Phys. **128**, 044512 (2008); K. Kessairi, S. Capaccioli, D. Prevosto, M. Lucchesi, S. Sharifi, and P. A. Rolla, J. Phys. Chem B **112**, 4470 (2008).

[19] S. Capaccioli, M. Paluch, D. Prevosto, L.-M. Wang, and K. L. Ngai, J. Phys. Chem. Lett. **3**, 735 (2012).

[20] G. Floudas, M. Paluch, A. Grzybowski, and K. L. Ngai, *Molecular Dynamics of Glass-Forming Systems—Effect of Pressure* (Springer, Berlin, 2011).

[21] M. Paluch, Z. Wojnarowska, and S. Hensel-Bielowka, Phys. Rev. Lett. **110**, 015702 (2013).

[22] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).

[23] C. A. Angell, L. J. Pollard, and W. Strauss, J. Chem. Phys. **50**, 2694 (1969).

[24] S. Hensel-Bielowka and M. Paluch, Phys. Rev. Lett. **89**, 025704 (2002).

[25] G. Jarosz, M. Mierzwa, J. Ziolo, M. Paluch, H. Shirota, and K. L. Ngai, J. Phys. Chem. B **115**, 12709 (2011).

[26] Z. Wojnarowska, C. M. Roland, A. Swiety-Pospiech, K. Grzybowska, and M. Paluch, Phys. Rev. Lett. **108**, 015701 (2012).

[27] Z. Wojnarowska, Y. Wang, J. Pionteck, K. Grzybowska, A. P. Sokolov, and M. Paluch, Phys. Rev. Lett. **111**, 225703 (2013).

[28] A. Swiety-Pospiech, Z. Wojnarowska, S. Hensel-Bielowka, J. Pionteck, and M. Paluch, J. Chem. Phys. **138**, 204502 (2013).

[29] A. Swiety-Pospiech, Z. Wojnarowska, J. Pionteck, S. Pawlus, A. Grzybowski, S. Hensel-Bielowka, K. Grzybowska, A. Szulc, and M. Paluch, J. Chem. Phys. **136**, 224501 (2012).

[30] K. L. Ngai, J. Habasaki, D. Prevosto, S. Capaccioli, and M. Paluch, J. Chem. Phys. **137**, 034511 (2012).

[31] W. G. Hoover and M. Ross, Contemp. Phys. **12**, 339 (1971).

[32] Y. Hiwatari, H. Matsuda, T. Ogawa, N. Ogita, and A. Ueda, Prog. Theor. Phys. **52**, 1105 (1974).

[33] D. Coslovich and C. M. Roland, J. Phys. Chem. B **112**, 1329 (2008).