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Heterogeneous Dynamics of Prototypical Ionic Glass CKN Monitored by Physical Aging

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In this Letter, we investigate the time evolution of the conductivity relaxation process in a prototypical ionic glass former, $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN), undergoing physical aging. It is demonstrated that the heterogeneous nature of molecular dynamics is manifested by an increase in the slope of the high frequency wing of the conductivity relaxation peak as the sample is annealed below the glass transition temperature. This finding is also confirmed for other ionic glass formers. Additionally, we analyze the kinetics of the change in the ionic conductivity in glassy CKN to probe its structural relaxation.

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A proper description of time evolution of the macroscopic properties of glasses is quite complex due to the physical aging process [1–5] that depends not only on the structural relaxation rate but also on the thermal history experienced by the glass [6]. Additional complexity arises when the heterogeneous nature of molecular dynamics is also taken into account [7,8]. It is hypothesized that glasses and supercooled liquids consist of distinct subensembles of molecules with enhanced or reduced mobility with respect to the average relaxation rate [9–20]. Thus, the existence of slow and fast subensembles in the glassy state should also result in distinct aging rates for these different regions in the system. As a consequence of this dynamical heterogeneity, one may expect that the spectral shape of the response function of a structural (α) relaxation process should vary as a function of aging time.

Testing this scenario experimentally requires one to measure the entire structural relaxation process in the frequency domain during aging below the glass transition temperature. However, this is a rather challenging task because the α-relaxation process is too slow to be monitored in an experimentally accessible frequency range. Moreover, even if some modern spectroscopy techniques (like broadband dielectric spectroscopy) enable one to perform measurements at frequencies as low as 10^{-5} Hz [21], one has to face another problem. The time required to acquire each experimental point of a relaxation curve in the lowest frequency range is usually comparable to, or even longer than, the characteristic aging time. This may lead to an uncontrolled distortion of the spectral shape of a measured response function. For that reason, most dielectric aging experiments are limited to studies of the time evolution of dielectric loss only in a higher frequency range [22,23]—high enough to avoid this problem.

In this Letter, we provide experimental evidence that the heterogeneous nature of molecular dynamics in glass-forming liquids is reflected in the behavior of the spectral shape of the relaxation function during physical aging. In order to realize this task we carried out dielectric aging experiments in the prototypical ionic glass former $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN), measuring the conductivity relaxation process that mimics, to some extent, the structural relaxation process. Since the conductivity relaxation time, τ_σ, at T_g is almost four decades faster than the α-relaxation time, τ_α, it was also possible to monitor directly the change of τ_σ during aging. The conductivity relaxation spectra of CKN were measured using a Novocontrol Alpha analyzer. The CKN sample was prepared according to the procedure described in Ref. [24].

Figure 1(a) depicts the loss component of the complex electric modulus, M^*, measured during cooling of the sample from 363 to 303 K at every 5 K. The relaxation

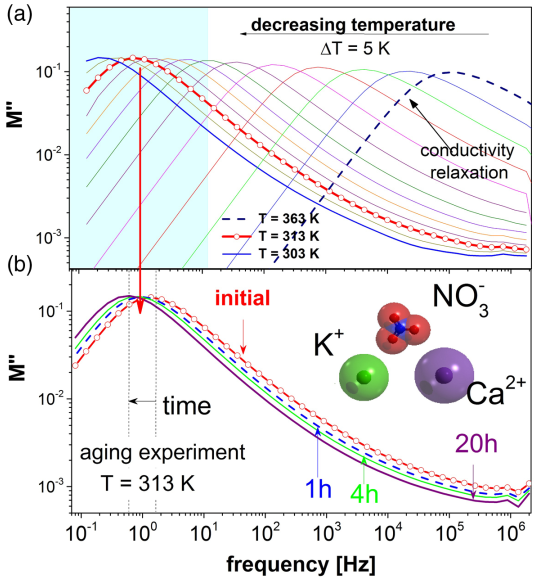

FIG. 1 (color online). (a) The dielectric loss modulus spectra due to conductivity relaxation of CKN at various temperatures in the liquid and glassy states. (b) The shift of the conductivity peak during physical aging at a temperature 313 K.

peak observed in the dielectric spectra is due to ion motion. A close inspection of the data shows that the changes of the frequency position of the conductivity relaxation peak maximum are less pronounced in the low temperature range. This behavior is a manifestation of the liquid-glass transition that takes place at $T_g = 335$ K. Note that at this temperature the maximum of the $M''(f)$ occurs at about 10 Hz—about four decades faster than the structural relaxation rate. Thus, it is still possible to observe the maximum of this mode in the measurement frequency window even at temperatures as low as 30° below T_g. The dielectric aging measurements were performed at six different temperatures: 333, 323, 318, 313, 308, and 303 K. For each measurement the sample was first annealed for 10 min at $T = 353$ K. After that, it was rapidly (10–15 K/min) quenched to the desired temperature, and next dielectric spectra in frequency range 10^{-1}–10^{6} Hz were recorded at every 15 min for approximately 20 hr. Because of the physical aging, the conductivity relaxation peak moves towards lower frequencies (see lower panel in Fig. 1), and consequently the characteristic relaxation rate becomes slower. This change of the M'' peak position during aging was previously observed at 329 K by R. When *et al.* [25].

Figure 2(a) presents two dielectric loss modulus spectra measured immediately after rapid cooling from 353 to 303 and 308 K. As can be seen in Fig. 2(b), all relaxation curves have identical shapes immediately after the quench. However, when we include on the same plot the relaxation curve recorded after annealing at 308 K for 20 hr, significant differences become evident. It is apparent from the comparison of data in Figs. 2(a) and 2(b) that the slope of the high frequency wing of $M''(f)$ becomes steeper during aging. The fit function with $\beta_{\mathrm{KWW}} = 0.71$ well describes all the initial spectra. However, close inspection of Fig. 2(b) reveals that it is too broad to describe the final spectrum of 308 K [open circles in Fig. 2(b)]. The narrowing of the high frequency side of the relaxation peak is due to the fact that faster (high frequency) modes in the distribution of relaxation times progress toward equilibrium faster than the modes at lower frequency. This observation supports the existence of the heterogeneous nature of relaxation dynamics of CKN glass.

The question that should be addressed is whether such type of behavior observed for CKN is unique. To answer this question we additionally carried out aging experiments in three other ionic liquids, i.e., mixture of ammonium phosphate and 85wt % phosphoric acid (of $NH_4H_2PO_4$ mole fraction = 0.035, wt% = 28.1%), [BMIM][PF_6] and procaine hydrochloride, representing different types of ionic materials, both protic and aprotic, organic and inorganic. The common feature of all the chosen samples is the characteristic change of the temperature dependence of the ionic relaxation times at T_g which correspond to τ_σ of order 10^{-1} s. Because of this we were again able to observe the whole conductivity relaxation peak during aging. In the insets of Figs. 3(a) and 3(b) we showed the temperature dependence of the σ-relaxation times, with a clearly visible kink in the T_g region. As can be seen in each case, we observe very clear narrowing of the right-hand side of the

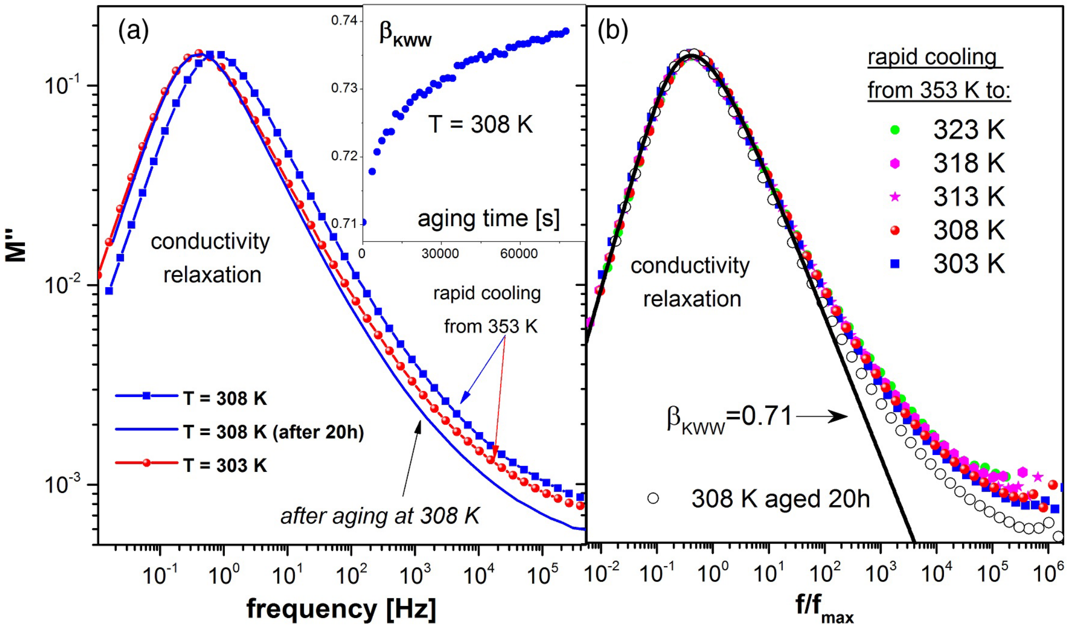

FIG. 2 (color online). (a) Two M'' spectra measured at 303 and 308 K, both recorded after rapid cooling from $T = 353$ K; and the final spectrum recorded during the physical aging at 308 K (after 20 h). Inset: evolution of β_{KWW} parameter during aging at 308 K. (b) Superposition of all M'' spectra recorded at the beginning of isothermal aging measurements depicted together with a fully aged spectrum at 308 K. The solid line is the Kohlrausch function with $\beta_{\mathrm{KWW}} = 0.71$.

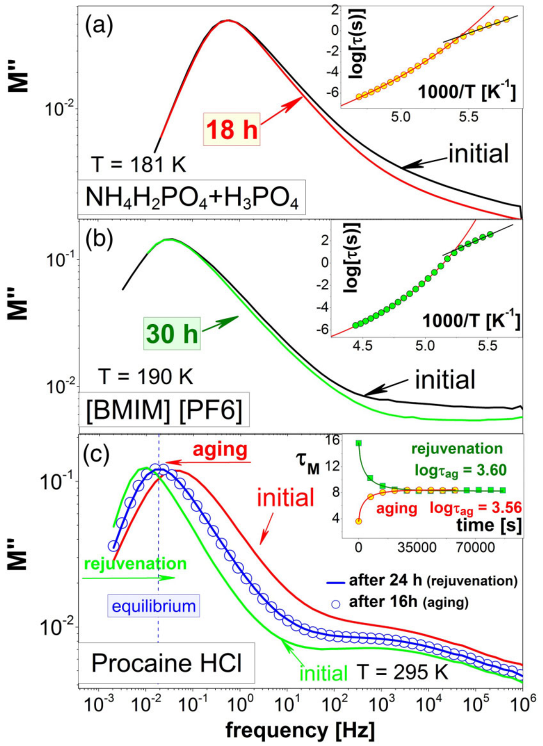

FIG. 3 (color online). Comparison of the shape of the rapidly quenched and aged modulus spectra of three different ionic liquids. (a)–(b) insets: logτ_σ(1000/T) dependences. In (c) inset: comparison of the changes of the τ_M during physical aging and rejuvenation experiments is presented.

spectrum. This result encouraged us to test whether the effect of narrowing of the spectra during aging is reversible. To this end we carried out two different experiments in procaine HCl. The first, aging experiment, was performed in a common manner with a rapid jump to aging temperature of 295 K. In the other measurement cycle, the sample was first quenched to $T = 291$ K and after equilibration the temperature was raised to the temperature of 295 K. As can be seen in Fig. 3(c) the process of rejuvenation takes place. However, not only does the position of the peak change but also the shape changes. This time it is broadening to the equilibrium value. It is worth noting that the final value of the β_{KWW} is the same as that obtained in a regular aging experiment. Our results indicate that the change of the modulus peak shape during aging and the same heterogeneous nature of the physical aging process are probably universal features of the ionic glasses.

Apart from monitoring the changing spectral shape with aging time, we are also able to examine the aging time evolution of τ_σ. The experimentally determined time dependence of τ_σ (defined as $1/2\pi f_{\max}$) at different aging temperatures are plotted in Fig. 4(a) and were fitted by the stretched exponential function [26,27]

$$\tau_\sigma = A \exp\left[-\left(\frac{t}{\tau_{\mathrm{age}}}\right)^{\beta_{\mathrm{age}}}\right] + \tau_{\infty}, \qquad (1)$$

in which A, β_{age}, τ_{age}, and τ_∞ are constants. As shown in Fig. 4(a), this function describes the experimental data well. From this analysis, we determined values of the stretched exponential parameter, β_{age}, [see Fig. 4(b)]. On the same figure we also plot the exponent β_{KWW} from the Kohlrausch-Williams–Watts function $\varphi(t) = \exp[-(t/\tau_\sigma)^{\beta_{\mathrm{KWW}}}]$ used to fit the conductivity relaxation peaks. The values of the Kohlrausch exponent, being in perfect agreement with the ones previously reported by A. Pimenov *et al.* [24], are much larger on average than the values of β_{age} obtained from analysis of the aging data by Eq. (1). In some papers [23,25] this disagreement is explained by the fact that Eq. (1) does not account for the fact that τ_{age} changes during aging. However, the stretching parameter β_{age} coincides reasonably well with β_{KWW} determined on the basis of the enthalpy relaxation measurements [28] [see Fig. 4(b)]. The enthalpy relaxation experiments were carried out to probe the structural relaxation process. On the other hand, in the case of CKN, the conductivity in the vicinity of T_g is strongly decoupled from the α relaxation, which is visible in Fig. 5. Thus, the β_{KWW} of the σ process does not need to be equal to the β_{KWW} of the structural relaxation. Taking into account the good correspondence between values of β_{KWW} and β_{age}, one can conclude that the aging dynamics of CKN is governed by the structural relaxation process. The same conclusion can be drawn from the analysis presented in Refs. [23,25]. The relaxation time obtained by the authors with use of the equation accounting for nonlinearity of the structural relaxation perfectly fits to the structural relaxation times from mechanical spectroscopy and not to the dielectric σ-relaxation times. We conducted a similar analysis with the use of Eq. (1) for the procaine HCl sample. In the inset of Fig. 3(c) we present the change of the σ-relaxation time observed during aging and rejuvenation processes at 295 K. It can be seen also that τ_{age} obtained in both experiments gave the same value, and both processes are well described by means of the mentioned equation.

As already mentioned, the analysis of the aging data from Fig. 4(a) in terms of Eq. (1) allows us to determine the characteristic aging time, τ_{age}. In Fig. 5, the Arrhenius plot of τ_{age} is shown. Additionally, in Fig. 5 the values of τ_σ determined for the CKN sample measured using two different experimental procedures are plotted. In one case the relaxation data were obtained during the slow cooling process, whereas in the other case the sample rapidly quenched in the liquid nitrogen (~ 100 K/min) was measured during heating from a glassy to a supercooled liquid state. For comparison, in Fig. 5 we also present the conductivity relaxation times as well as average shear relaxation times—τ_α, previously reported by other authors [24,29].

A closer look at the τ_σ data in Fig. 5 reveals that the activation energy (E_σ) of $\tau_\sigma(T)$ in the glassy state depends on the thermal history of the sample. A smaller value of E_σ

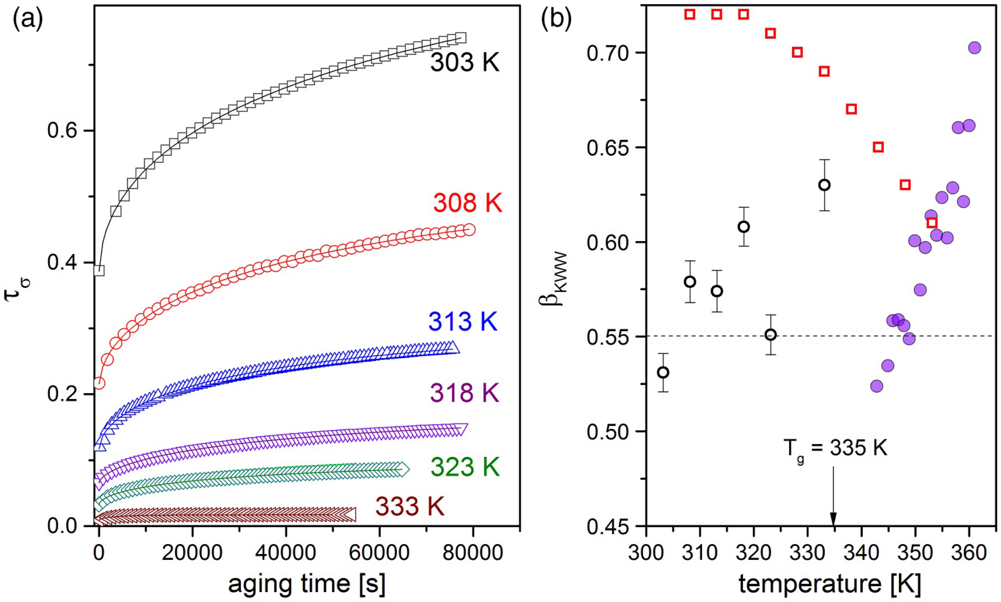

FIG. 4 (color online). (a) Change in τ_σ observed during physical aging at the indicated temperatures. Solid lines are fits by means of Eq. (1). (b) Temperature dependence of β_{KWW} parameter. Open circles are the values of β_{age} obtained from analysis of the aging data by Eq. (1). Closed circles are β_{KWW} parameters determined based on the enthalpy relaxation measurements presented in Ref. [28]. Open squares present the values of β_{KWW} determined from fitting of KWW function to the dc-conductivity relaxation peaks measured in glassy and supercooled liquid states.

can be obtained for the rapidly quenched CKN ($E_\sigma = 84 \pm 1$ kJ/mol), while a larger value is achieved if the temperature of the sample is slowly lowered, and the spectra are collected just during cooling ($E_\sigma = 105 \pm 2$ kJ/mol). In this context, it is interesting to note that the activation energy of $\tau_{\mathrm{age}}(T)$ is similar to that found for $\tau_\sigma(T)$ in the quenched sample. This implies that there is no decoupling of the temperature dependence of $\tau_{\mathrm{age}}(T)$ and $\tau_\sigma(T)$ below T_g, which is completely opposite to what is observed above T_g. In fact, in the supercooled liquid state, the two temperature dependences, $\tau_\alpha(T)$ and $\tau_\sigma(T)$, are strongly decoupled. This phenomenon is often described using the fractional Debye-Stokes-Einstein (fDSE) equation, i.e., $\tau_\sigma \tau_\alpha^{-s} = \mathrm{const}$ [30–33].

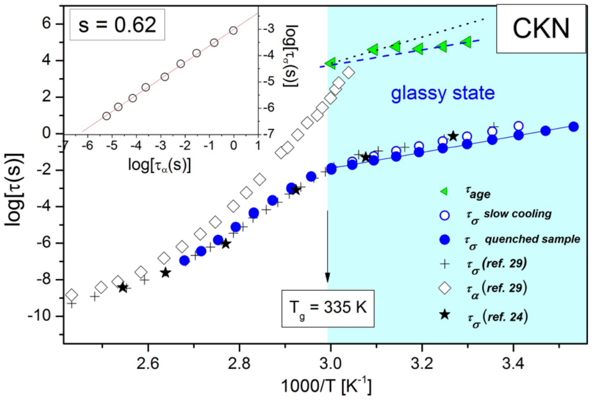

FIG. 5 (color online). Conductivity relaxation times for CKN obtained after rapid cooling of the molten salt (filled circles) and slow cooling of the melt (open circles). Solid triangles are the structural relaxation times extracted from the change in τ_σ during physical aging. Additionally, $\tau_\sigma(T)$ and $\tau_\alpha(T)$ presented in Refs. [24,29] are depicted. Solid and dashed lines are the Arrhenius fits to the τ_σ and τ_{age}, respectively. Dotted line is the Arrhenius fit with the activation energy following from the equation $E_\alpha = s^{-1*}E_\sigma$. Inset: τ_σ vs. τ_α in a double logarithmic scale. Parameter $s = 0.62$ is the exponent in the fDSE equation.

As shown in the inset of Fig. 5, the data confirm validity of the fDSE equation. From the simple linear regression analysis we found that the slope of the solid line, which defines the fractional exponent s, is equal to 0.62. In the case when the decoupling phenomenon observed above T_g was maintained also in the glassy state, the temperature dependence of $\tau_\alpha(T)$ should have a larger activation energy (see dotted line in Fig. 5). Taking into account the general definition of activation energy, $E = R(d\ln\tau/dT^{-1})$, and the fDSE equation, it can be easily derived that $E_\alpha = s^{-1*}E_\sigma$.

In summary, the changes in the conductivity relaxation process observed during isothermal aging of the ionic glasses provide strong experimental evidence of the heterogeneous nature of deeply supercooled liquids. We observe a narrowing of the relaxation dispersion, specific to higher frequencies, that is a consequence of dynamic fluctuations in the structure with rates that are different in different regions of the sample. This observation is possible because the conductivity relaxation, that mimics, to some extent, the structural relaxation, is almost four decades faster than the α process. Additionally, the changes in the ion conductivity during physical aging enable us to probe the structural dynamics in the glassy state of CKN.

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