

Neutron Spin-Echo Study of Dynamic Correlations near the Liquid-Glass Transition

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(Received 22 October 1986)

Neutron spin-echo measurements have been performed on the ionic system $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ around the glass transition temperature T_0 , in order to determine the time dependence of the density correlation function $\phi_q(t)$, which plays a central role in recent theories. Above T_0 the results reveal that $\phi_q(t)$ contains two distinct "slow" components, the slower of which (a) has a stretched exponential form $\exp[-(t/\tau)^\beta]$, (b) shows a slowing down as T approaches T_0 which scales with the Stokes-Einstein diffusion constant, and (c) tends to become the nonergodic fraction of the structure factor at T_0 .

PACS numbers: 64.70.-p

Considerable progress has recently been made in the understanding of the fundamental nature of the liquid-glass transition.¹⁻⁴ Theories considering nonlinear density fluctuations in a simple compressible high-density liquid were able to predict a transition from an ergodic to a nonergodic state, which shows many qualitative features observed in liquid-glass transitions in real systems. The quantity of central interest for the description of phenomena related to the transition is the density-correlation function $\phi_q(t)$, where q is the wave number and t the time. The nonergodic glass phase is characterized by a finite value of $\phi_q(t)$ at $t \rightarrow \infty$, in quite the same way as has been proposed for spin-glasses.⁵ In the ergodic state on the liquid side of the transition $\phi_q(t)$ relaxes to zero in a finite time. More generally, since the glass transition is widely considered as a transition of dynamic origin, the entire nature of the phenomenon is expected to be revealed in depth by the behavior of this correlation function $\phi_q(t)$. Indeed, theoretically predicted general properties of $\phi_q(t)$ have been analyzed by now in great detail.^{6,7} On the experimental side, neutron spin-echo (NSE) spectroscopy⁸ allows the direct observation of the so-called intermediate scattering function $S(q,t)$ which is nearly identical to $\phi_q(t)$ for coherent scattering. [Actually $S(q,t)$ corresponds to the density correlation function weighted by the neutron-scattering amplitudes of the nuclei.] The NSE method proved to be particularly successful in our studying the dynamics in spin-glasses, in particular, in identifying a tendency towards nonergodicity and in revealing the unusual nonexponential time dependence in the spin relaxation.⁹ This latter feature of the relaxation in random systems also received considerable attention in recent years^{10,11} and glasses as random systems are also of primary interest in this respect.

With these motivations in mind, we have performed NSE experiments in order to explore the behavior of the

density correlation function $\phi_q(t)$ in the vicinity of the glass transition in a typical glass-forming system $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ at q values close to the first peak in the structure factor $S(q)$, a q range which is expected to play the dominant role in the transition mechanism.^{2,3}

We had to choose for this study a glass-former system which has very little tendency to crystallization above the phenomenological glass temperature T_G , since neutron-scattering scans last for several hours. At the same time we wanted to avoid network glasses, which are systems very far from simple model liquids considered in theories. Our choice, the mixed ionic glass $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$, is a very stable glass, which has been extensively studied and characterized by bulk measurements.¹²⁻¹⁵ The transition temperature T_0 , defined as the temperature where the viscosity appears to diverge, is about 50 °C, and $T_G \approx 60$ °C. The material is easily obtained by heating of the mixture of components to ~ 400 °C for about 12 h.¹⁶ As it is strongly hygroscopic, the experiments have been performed in a vacuum furnace. We have verified in a series of separate x-ray tests that no detectable crystallization occurs on the time scale and temperature cycling involved in the neutron experiments.

The measurements have been performed with the IN11 NSE spectrometer¹⁷ at Institut Laue-Langevin (ILL) in Grenoble. The incoming neutron beam had an average wavelength of 5.2 Å with a FWHM spread of 18%. Therefore we actually probed the intermediate scattering function $S(q,t)$ averaged over a q range of 18% FWHM, with a center of gravity of 1.7 \AA^{-1} , close to the first maximum in the liquid structure factor $S(q) \equiv S(q,t=0)$. Theories predict⁶ little q dependence in the behavior of the normalized quantity $s(q,t) = S(q,t)/S(q)$, which is directly measured in NSE. More precisely, in the actual experiment most of the high-energy ($\hbar\omega > 4$ meV) phononlike contributions

to $S(q)$ were not detected because of the limited bandwidth of the neutron-detection assembly. These contributions are expected to be small and slowly varying with temperature in any case, and with much of them outside the detection band, they will be considered as negligible. Thus in this experiment we are basically concerned with processes slow compared with the Enskog atomic-collision time, which is expected to be of the order of 10^{-14} s.

The NSE spectra obtained at various temperatures are shown in Fig. 1. We started at room temperature with a sample kept at this temperature for about a week before the experiment. The room-temperature spectrum (open circles) consists of a component with 5% of the total intensity, which relaxes to zero on a time scale shorter than 4×10^{-11} s, the lower edge of our time window. (As mentioned above, some of this contribution could be phononlike.) The remaining 95% of the structure factor is long lived and it actually corresponds to the arrested glass structure. This is the $t \rightarrow \infty$ limit nonergodic fraction of $S(q)$. On heating of the sample up to 73°C , i.e., well above T_0 , this spectrum did not change appreciably. On further gradual heating some crystallization became apparent at 110°C ; thus the other spectra in Fig. 1 were obtained on cooling from low-viscosity liquid state at 230°C directly to the temperature of the measurement (indicated in the figure in degrees centigrade) with a rate of $1^\circ\text{C}/\text{min}$. Between two of these scans the sample was kept at 230°C for about half an hour, and subsequently no crystallization occurred during the measurements at the temperatures indicated, including 110°C . Thus the tendency for crystallization showed a hysteresis.

The spectra in Fig. 1 show a dramatic slowing down of the relaxation of the structure factor with decreasing temperature. It is reasonable to compare this slowing

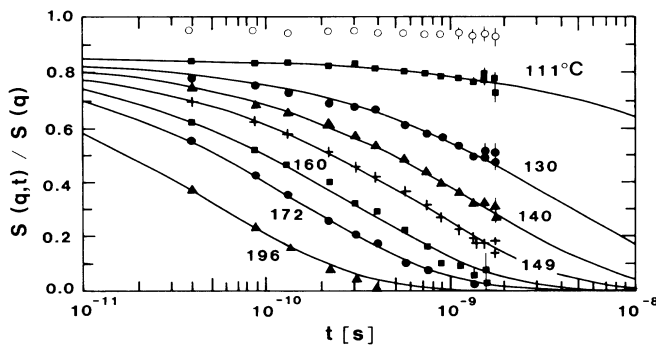


FIG. 1. The time-dependent dynamic structure factor of the $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ ionic glass system at various temperatures, as directly observed by NSE spectroscopy ($q \approx 1.7 \text{ \AA}^{-1}$). The open circles are room-temperature data; for the other spectra the temperature is indicated in degrees celsius. The solid lines represent Eqs. (1) and (2) evaluated for the given temperatures with parameters obtained by fitting of the scaled plot in Fig. 2, as described in the text.

down to the decrease of the Stokes-Einstein diffusion constant $D = kT/6\pi\eta R$, where η is the viscosity (known from Ref. 13) and R is the unknown effective radius of the diffusing object. Indeed, replotting the data in Fig. 1 (with the exception of those at room temperature) as a function of a scaled time t/τ , where τ is proportional to $1/D$, we obtain a unique curve $f(t/\tau)$ as shown in Fig. 2. This common curve can be reproduced by a stretched exponential (the so-called Kohlrausch law):

$$s(q,t) = f(t/\tau) = Ae^{-(t/\tau)^\beta}, \quad (1)$$

where $\beta \approx 0.58$ and $A \approx 0.84$. This value of A means that there is a component to $s(q,t)$ with a 16% weight, which relaxes faster than the 4×10^{-11} -s lower limit of observation. Furthermore, tentatively identifying τ with the characteristic diffusion time at our wave number, i.e.,

$$\tau^{-1} = Dq^2 = kTq^2/6\pi\eta R, \quad (2)$$

we find $R = 0.75 \text{ \AA}^{-1}$, which is reasonably close to atomic radii.

It has to be stressed, however, that the excellent fit of all data by Eqs. (1) and (2), as clearly apparent on Figs. 1 and 2, might also be partially accidental. Forgetting about this common fit for all temperatures we can at least state in any case that (a) the slowing down scales with the diffusion coefficient (i.e., $\tau \propto D^{-1}$) between 140°C and 196°C (limits included); (b) the line shape is a stretched exponential with $\beta \approx 0.6$ between 149°C and 172°C ; and (c) the amplitude of the observed slowly relaxing component is about 0.8–0.85 between 111°C and 140°C . (Note that the averaging over the 18% neutron-wavelength band used in the experiment could not modify the relaxation line shapes beyond a fraction of the size of the points in the figures.)

Let us examine these findings in view of recent theories.^{2-4,6,7} (In doing this we have to keep in mind,

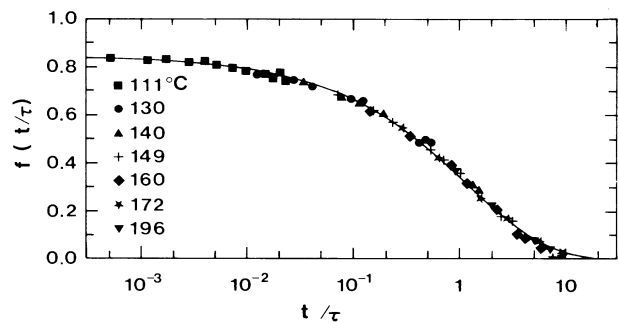


FIG. 2. The same data as in Fig. 1 plotted against the scaled time variable t/τ , where τ was calculated from Eq. (2). The solid line represents Eq. (1) with the best choice of parameters A , β , and the position of the $t/\tau = 1$ point on the abscissa. Overlapping data points have only been plotted for one of the temperatures.

however, that these theories have not been worked out as yet for real glasses of complex composition and therefore we can only expect qualitative agreements.) Maybe the most fundamental theoretical prediction is the two-stage relaxation of the density correlation function $\phi_q(t) \sim s(q,t)$ above T_0 :

(a) A slower ("quasielastic") component with a relaxation rate proportional to the diffusion constant and with a temperature-independent amplitude f_q^c . This component becomes arrested at the critical point T_0 , where the viscosity diverges (D vanishes) and therefore it becomes the nonergodic fraction of the structure factor, with f_q^c being the value of the nonergodicity parameter f_q at T_0 . (Below T_0 , f_q increases towards unity.) f_q^c is not a universal parameter of the theory. The simplest models give $f_q^c = 0.5$, although somewhat higher values were also obtained.^{4,18}

(b) A faster relaxing "scaling" contribution with a weight of $1 - f_q^c$ and power-law behavior $(t/t_c)^{0.4}$, where the characteristic frequency $\omega_c = t_c^{-1}$ goes to zero in a critical fashion as T approaches T_0 .

Our results provide experimental evidence for the existence of these two components. Our estimate for $f_q^c \approx 0.84$ is substantially higher than the theoretical values obtained in simplified models. At room temperature we have $f_q \approx 0.95$ (or somewhat higher, if phonon-like scattering was not fully negligible). The initial stability of the spectra on heating is also understandable. The density is believed to be the control parameter, which drives the transition and determines the dynamics. Thus with the room-temperature structure frozen in below 110°C , where crystallization started, the main feature of the dynamics, the value of the nonergodicity parameter f_q , also remained at its room-temperature value. (In addition, this observation confirms the negligible role of phononlike scattering in the temperature dependence of the spectra, as assumed above.)

The simplest mode-coupling approximation predicted³ an exponential decay (Lorentzian energy line shape) for the quasielastic component we have analyzed. This behavior has also been experimentally established in liquid metals,¹⁹ in contrast to the present case. It is encouraging that in more recent, refined numerical computations⁷ a roughly stretched-exponential line shape has been obtained, although with $\beta \approx 0.8$. It is furthermore well known that many bulk relaxation phenomena in various glasses could be well described by the Kohlrausch law with β values between 0 and 1. [For example, macroscopic mechanical relaxation data in $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ at 172°C can be described²⁰ by a Kohlrausch law with $\beta \approx 0.8$. This is different from the value $\beta \approx 0.6$ that we find for the relaxation of $\phi_q(t)$, but we do not expect any simple relation between the two experiments.]

It is interesting to observe that the simplest model explanation of nonexponential relaxation dynamics, i.e., the assumption of a constant distribution of Arrhenius ac-

tivation barriers $F(E)$,

$$s(q,t) \propto \int F(E) \exp(-t/\tau_0 e^{E/kT}) dE, \quad (3)$$

does not work in this case. Equation (3) has been found to describe *both* the time *and* the temperature dependence in a variety of relaxation phenomena, including spin-glasses⁹ above the freezing temperature T_f . Trying to fit our present data, however, we would have to assume unrealistically small values ($\sim 10^{-21}$ s) for τ_0 . By arbitrarily replacing the Arrhenius law $\tau_0 \exp(E/kT)$ in Eq. (3) by the Vogel-Fulcher law $\tau_0 \exp[E/k(T - T^*)]$ (where T^* is a constant) we could bring τ_0 close to the correct 10^{-13} -s range, but the fit would not work with a single barrier distribution $F(E)$ for several temperatures. Thus, we conclude that we have to do with a more complicated case of nonexponential relaxation than the simple fixed-energy-landscape model of Eq. (3). This means that strong interactions between subsequent relaxational states have to be assumed, such as in the correlated-states scheme of Ref. 10, or the hierarchically constrained relaxation hypothesis introduced in Ref. 11. Such complex mechanisms are, of course, naturally built in (and eventually hidden) in the *ab initio* calculations of the detailed, explicit theories.^{6,7,18} It is worth mentioning that Eq. (3) also breaks down in spin-glasses in the vicinity of T_f .

Beyond providing evidence for its existence with a relative weight of about 16%, i.e., less than the conjectured 50%, our data give little information on the faster ("scaling") contribution to $\phi_q(t)$. Numerical calculations indicated³ that it should occur on a time scale of 100–1000 times the Enskog collision time ($\sim 10^{-14}$ s), unless we are very close to a sharp transition. The present experiment also indicates that it is situated between $\sim 2 \times 10^{-13}$ s (i.e., the cutoff energy of the detection system) and the 4×10^{-11} -s edge of our experimental window. This range can be explored by a neutron spectrometer of lesser resolution than NSE.

To conclude, we have to stress the complexity of the behavior of real glasses in contrast to the simplified models in the calculations performed so far. For example, the viscosity of our sample material can be well parametrized¹³ in terms of the empirical Vogel-Fulcher law $\eta = (5.8 \times 10^3 \text{ P}) \exp[670/(T - 327)]$, where T is the temperature in kelvins. In contrast, the mode-coupling theories^{2,3} predict a power law $\eta \propto (T - T_0)^{-\alpha}$ with $\alpha \approx 1.8$. In the temperature range 130°C – 180°C this law can roughly describe η —however, with an unreasonable value to $T_0 \approx 120^\circ\text{C}$. On the other hand, a power law with $\alpha \approx 4.2$ gives a reasonable fit from 100°C upward, with $T_0 \approx 90^\circ\text{C}$ this time. Thus a more probing comparison to theory of the present results would certainly require a better understanding of the behavior of the viscosity.

In sum, we have experimentally established in the ion-

ic glass $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ that above the glass transition temperature T_0 the dynamic behavior of the density-density correlation function $\phi_q(t)$ reveals two distinct relaxation steps. One of them occurs in the time interval 2×10^{-13} – 4×10^{-11} s, and the other at longer times. This latter, slower process has a stretched-exponential time dependence with $\beta \approx 0.6$ and it shows a dramatic slowing down as T approaches T_0 . The slowing down scales with the Stokes-Einstein diffusion constant and thus it tends to become at T_0 the nonergodic (arrested) part of the structure factor $f_q^c = \phi_q(t \rightarrow \infty)$. This relaxation step accounts for about 84% of $\phi_q(t=0)$, independently of the temperature, which implies that at the transition temperature the structure factor only becomes partially arrested. These findings are in qualitative agreement with predictions of most recent nonlinear theories.

Our results call for two obvious extensions of the present experiments: (a) a study of the faster-relaxing component of $\phi_q(t)$ in the 10^{-12} – 10^{-11} -s time domain, and (b) investigation of the q dependence of the observed behavior. We plan to continue our work in these directions.

The authors are indebted for stimulating discussions with Professor Bosse, Professor Geszti, Professor Götze, Professor Ramaswamy, and Professor Sjölander.

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