

Experimental Evidence for Fast Heterogeneous Collective Structural Relaxation in a Supercooled Liquid near the Glass Transition

M. Russina and F. Mezei

*Los Alamos National Laboratory, MS H805, Los Alamos, New Mexico 87545
and Hahn-Meitner-Institute, Glienicker Strasse 100, 14109 Berlin, Germany*

R. Lechner, S. Longeville, and B. Urban

Hahn-Meitner-Institute, Glienicker Strasse 100, 14109 Berlin, Germany

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We have extended the exploration of microscopic dynamics of supercooled liquids to small wave numbers Q corresponding to the scale of intermediate range order, by developing a new experimental approach for precise data correction for multiple scattering noise in inelastic coherent neutron scattering. Our results in supercooled $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ reveal the first direct experimental evidence, after a decade of controversy, that the so-called picosecond process around the glass transition corresponds to a predicted first, faster stage of the structural relaxation. In addition, they show that this process takes the spatial form of fast heterogeneous collective flow of correlated groups of atoms.

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The similarity between the structure of glasses and liquids gives reason to assume that the mechanism driving the glass transition lies in dramatic changes of the microscopic dynamics. Inelastic neutron scattering experiments played a uniquely important role in the past decades in unraveling this dynamics. The results have revealed, quite surprisingly, that beyond the expected phononlike and local vibrations and the so-called α process, i.e., the main bulk structural relaxation that reflects the viscosity governed flow, an additional dynamic process occurs in the supercooled liquid state [1,2]. This additional process with strongly temperature dependent intensity appears on the picosecond time scale around the glass transition temperature and indistinguishably merges with the main structural relaxation on approaching the equilibrium melting temperature. The physical origin of this process (which we refer to for the purpose of the present discussion as the “picosecond process”) is the subject of a decade old controversy. Mode coupling theories (MCT) [3,4] predicted the existence of a fast step in the structural relaxation (usually called “ β ” or “fast β ” relaxation). Others suggested that the picosecond process is of a vibrational nature either due to the emergence of additional soft excitations [5] or to the relaxation of modes contributing to the so-called boson peak [6,7].

The answer to the question about the nature of the picosecond process lies in information on the spatial character of the corresponding atomic motion, which is reflected in the wave number Q dependence of the dynamic structure factor $S(Q, \omega)$. In a number of recent studies the model assumption

$$S(Q, \omega) = A(\omega)Q^2S(Q) + B(\omega)Q^2 \quad (1)$$

has been used [5,8], where $S(Q)$ represents the static structure factor and $A(\omega)$ and $B(\omega)$ have been identified with the spectra of propagating phononlike (or in phase) and

local (or random phase) vibrational excitations, respectively. This approach was found to describe well the experimental data in several glass forming liquids with similar structure factors as in Fig. 1, but often with clear, unexpected deviations for $Q < 1 \text{ \AA}^{-1}$. Atomic motions at these small wave numbers correspond to the domain of the intermediate range order (IRO), i.e., to the length scale of several times the nearest neighbor atomic distances, and they are expected to best reveal the features of *collective* phenomena, which ultimately determine the global behavior. Unfortunately, due to neutron scattering experimental difficulties, namely, to the weakness of the signal compared to the strong spurious multiple scattering

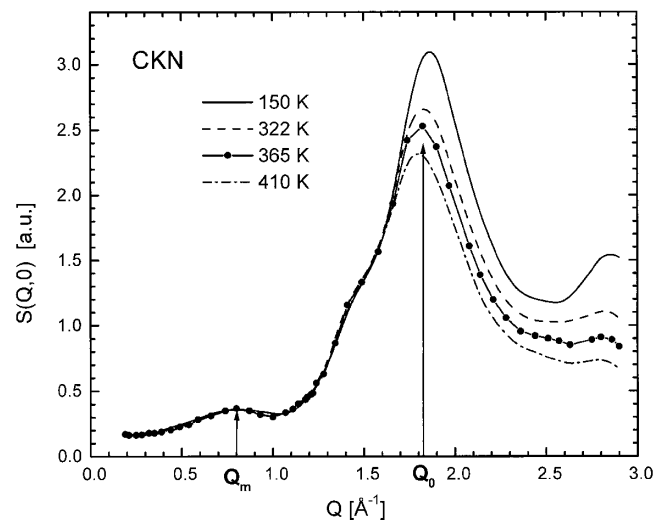


FIG. 1. Measured elastic structure factor in CKN at two temperatures in each of the glass and liquid phases. The glass transition temperature T_g is 333 K. The individual data points are shown only for one temperature.

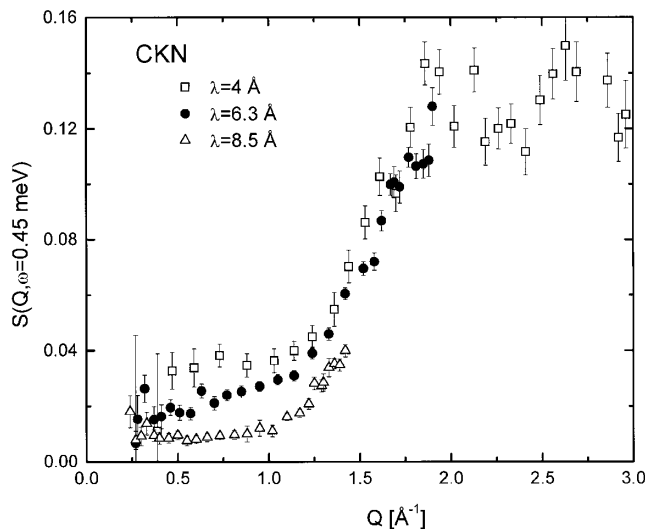


FIG. 2. Comparison of the apparent dynamic structure factors as measured with different incoming neutron wavelengths for the raw data only corrected for background and sample absorption. The marked differences below 1.5 \AA^{-1} are due to the strong increase of multiple scattering contributions with decreasing wavelengths. Below 4.6 \AA wavelength Bragg scattering on aluminum parts of the cryofurnace also participates in multiple scattering events.

noise (Fig. 2), the dynamics on this length scale could not be explored now.

In this Letter we present the first experimental evidence for collective fast atomic motion in a supercooled liquid that cannot be attributed to vibrations. We arrived at this result by analyzing the dynamics in an extended Q range, in particular, at the wave numbers corresponding to the length scale of the IRO. In order to open up this range for neutron scattering investigations we have developed a new, model independent experimental approach to high precision data correction for multiple scattering contributions. Using this powerful new tool we were able to uncover the nature of the picosecond process [1,2] and show that this process is due to a first step of structural relaxation as was predicted by numbers of theories [3,4,9,10]. In view of the spatially extended character we have observed for this motion we conclude in addition that this process is heterogeneous and corresponds to the correlated motion of groups of atoms of the type recently predicted by molecular dynamic simulation (“strings”) [11,12].

For our experiments we choose the well studied fragile class glass $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN), which mainly scatters neutrons coherently; thus the scattered intensity delivers information on the *correlated motion of atoms*. The IRO manifests itself in a so-called prepeak in the structure factor $S(Q)$ at $Q_m \cong 0.8 \text{ \AA}^{-1}$, while the main peak around $Q_0 \cong 1.83 \text{ \AA}^{-1}$ corresponds to the short range order (or to the distances between the nearest atomic neighbors); cf. Fig. 1. In our experiments on the time-of-flight spectrometer NEAT at Hahn-Meitner-Institut, Berlin, three wavelengths of incident neutrons ($\lambda = 8.5, 6.3,$ and 4 \AA)

have been used in order to reliably cover the $0.3\text{--}2.7 \text{ \AA}^{-1}$ range of Q . The raw data were corrected for scattering on the empty sample cell and normalized to vanadium.

Figure 2 clearly illustrates the difficulty of obtaining reliable inelastic spectra at $Q < 1 \text{ \AA}^{-1}$. The signal in this range is very small and therefore one has to work with reasonable sample volume, which leads to high multiple scattering contributions. Under customary experimental conditions (i.e., using a single incoming neutron wavelength of about 5 \AA in order to cover the required Q range of about $0.4\text{--}2.2 \text{ \AA}^{-1}$) in our 3 mm thick flat slab sample one has around $Q \cong 0.8 \text{ \AA}^{-1}$ an order of magnitude more multiple scattering (MS) noise than signal. (This noise is dominated by the combination of one inelastic and one elastic scattering event, both close to the backward direction, and it is very strong in the angular range of single scattering at small Q 's.) Such a huge spurious contribution cannot be reliably corrected for, and this is why this Q range has not been accessible up to now for neutron inelastic scattering study. The use of a set of incident neutron wavelengths is one key of our novel high, precision method for multiple scattering correction and allows us (a) to cover the necessary range of Q and (b) to vary the multiple scattering contribution to the spectra. At our longest wavelength the accessible range of Q is $\leq 1.5 \text{ \AA}^{-1}$, which means in view of Figs. 1 and 2 that the leading MS contribution is reduced by more than an order of magnitude compared to the data at $\lambda = 6.3 \text{ \AA}$. Combining the data taken at different wavelengths we can reliably establish the ideal single scattering function in a wide range of Q with the help of a detailed Monte Carlo simulation of all scattering processes in the sample. Information at small Q 's primarily comes from data taken at the longest wavelength and little affected by MS, while the short incoming wavelength data deliver information in the range of higher Q 's. The good agreement we have always found after self-consistent, iterative MS correction between the overlapping portions of data taken at different wavelengths (cf. Fig. 4) benchmarks the validity of our approach, which also takes into account self-screening of and absorption in the sample. More experimental details are given elsewhere [13].

We have utilized this novel approach to explore the nature of the picosecond process, whose appearance is illustrated in Fig. 3. Here the spectra are normalized to the Bose phonon population factor in order to remove the trivial harmonic temperature dependence. The slight hump around $\omega \cong 3 \text{ meV}$ in the glass phase is the *first neutron scattering observation of the so-called boson peak in CKN*, which becomes more pronounced in light scattering spectra [14]. Dramatic deviations from harmonic temperature dependence appear in the supercooled liquid phase where the growth of the spectrum can be described at $\omega < 3 \text{ meV}$ by a power law $\omega^{-\alpha}$ with $\alpha \approx 0.7$. Such a self-similar line shape has been predicted for the MCT β process and this actual value of the exponent was found to be consistent

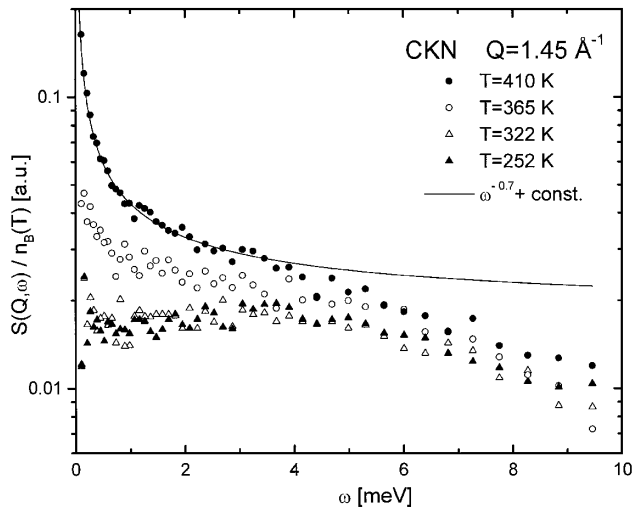


FIG. 3. Temperature dependence of the dynamic structure factor in CKN at a given Q value. The dramatic anharmonic increase of the spectral intensity above T_g corresponds to the appearance of the so-called picosecond process.

with the scaling features proposed by this theory [15]. Figure 4 shows the Q dependence of the dynamical structure factor at 410 K and $\omega = 0.45$ meV (in actual fact the integral between $\omega = 0.35$ and 0.55 meV), i.e., well on the time scale of the picosecond processes. We also found very similar variation with Q in two other energy groups around 0.27 and 1 meV, respectively. The data at 322 K could be well described by the vibrational model Eq. (1), and the dashed line in Fig. 4 represents a fit to these data scaled to 410 K by assuming the degree of deviation from harmonic temperature dependence observed at $\omega > 3$ meV in Fig. 3 (i.e., 30% more than that given by the Bose factor n_B). On our extended Q range 0.3 – 2.5 \AA^{-1} it becomes obvious that at 410 K $S(Q, \omega)$ cannot be described by the common vibrational model of Eq. (1): The signal in the Q range of the IRO is not compatible with a factor Q^2 . We actually find that the additional signal above the quasi-harmonic vibrational contribution extrapolated from 322 K (dashed line) is roughly proportional to $S(Q)$, which leads to the modified model

$$S(Q, \omega) = A(\omega)Q^2S(Q) + B(\omega)Q^2 + C(\omega)h(Q)S(Q). \quad (2)$$

The last term dominates the dynamics at values of Q corresponding to the intermediate range order. The function $h(Q)$ is included here to take into account deviations of this additional contribution from exact proportionality to $S(Q)$. Random flow of volumes with large enough dimension D , so that in the Q range of interest $Q > \pi/D$, would lead to $h = 1$ if the static atomic short and medium range order are rigidly maintained in the flow. Thus $h(Q)$ can be regarded as a measure of deviation from structural rigidity. For $Q \ll \pi/D$ this contribution too drops rapidly to zero, in a fashion similar to Eq. (1). Numerical MCT calculations on various model systems (hard

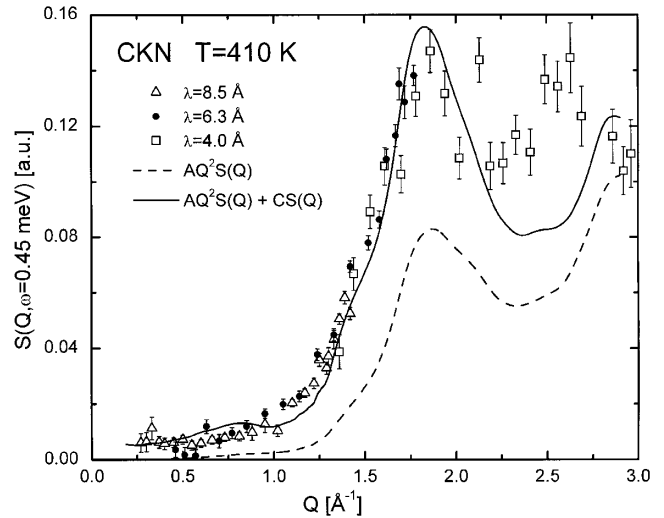


FIG. 4. Wave number dependence of the dynamic structure factor at constant energy in CKN in the supercooled liquid phase. For comparison, the dashed line represents the extrapolation to this temperature of the vibrational model Eq. (1) found to well describe (actually with $B = 0$) the dynamic structure factor in the glass phase at 322 K. The continuous line was obtained by adding an additional term $CS(Q)$, as introduced in Eq. (2) with $h(Q) = 1$. Although many approximate fits are possible using Eq. (2) with different A and B combinations, at the low- Q end of the spectra these terms in Q^2 remain always much too small compared to the data points.

sphere, Lennard-Jones) found that $h(Q)$ oscillates around 1 with a tendency of displaying minima at the maxima of $S(Q)$ [16].

In our case shown in Fig. 4 the relevant Q range extends to 0.3 – 0.4 \AA^{-1} on the lower end so the essential part of the distribution of D has to reach 8 – 10 \AA or more. The function $h(Q)$ shows a minimum around Q_m , which corresponds to the MCT expectation [16] and it also correlates with the strong de Gennes–type narrowing in the structural α relaxation previously observed just in the same Q range [17]. Thus the geometrical nature of our processes described by the last term in Eq. (2) must imply *collective, correlated quasirigid* displacement of a rather large number of neighboring atoms. This takes place at times short compared to the α relaxation and with amplitudes of the displacement large compared to the vibrational motions corresponding to the first two terms in Eq. (2). Such a motion in a liquid can exist only in the form of *heterogeneous, random fast flow* of chunks of matter. The strong increase of the intensity on heating (Fig. 3) indicates the increasing probability of the number of particles that participate in this process at a given time. One can argue that the much slower viscous flow—giving rise to the large α -relaxation signal involving atoms which undergo only small displacements on a time scale shorter than the α -relaxation times—is facilitated by these rapid collective displacements of parts of the matter, the same way as activated jumps of single atoms determine self-diffusion in solids. The slow α -relaxation of the bulk reflects the

complete loss of correlation of the particle positions over long periods of time, a consequence of the frequent fast flow motion events as well as of diffusion of individual atoms. Comparing the energy integrated intensity of the picosecond process to that of the quasielastic line, whose energy width is governed by the viscosity and corresponds to the usual nanosecond time scale at 410 K, we found that only a fraction of the matter (no more than 5%–15% at 410 K) participates in the heterogeneous flow at any given time. *Cooperative heterogeneous motion* of strings of atoms, on a time scale long compared to atomic vibrations and short compared to the bulk of structural relaxation (α process), has been revealed in recent molecular dynamics simulations of glass forming Lennard-Jones supercooled liquids [11,12]. The space and time behavior of this string-type collective motion is consistent with the nature of the picosecond process we have experimentally established. It is also remarkable that the existence near the glass transition of such a first, fast structural relaxation step with power law spectral line shape was predicted by MCT a long time ago, without revealing geometrical details on the atomic scale, of course [3,4].

Previous neutron scattering studies, which could access only a much smaller range of Q , tentatively identified the picosecond process in other samples with extra vibrational modes, in contrast to a fast step of structural relaxation. The signs of deviations from model (1), nevertheless visible in both fragile [5] and strong [8] supercooled liquids, may suggest that these conclusions were affected by the limitations of the Q range explored in those experiments and those samples too may in reality rather behave like ours.

In summary, our observations identify the so-called picosecond process near the glass transition (which was discovered more than a decade ago) with a first, fast stage of structural relaxation and we rule out the proposed interpretation in terms of local and/or propagating vibrations. This result solves a long-standing fundamental controversy in the study of the glass transition. In addition we have also shown that this fast relaxation process corresponds to heterogeneous, fast flow of chunks of matter on an order(s) of

magnitude shorter time scale than that of the main, slow α -relaxation process. Our experimental findings support mode coupling theoretical and molecular dynamics computational predictions.

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- [1] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987).
 - [2] W. Knaak, F. Mezei, and B. Farago, Europhys. Lett. **7**, 529 (1988).
 - [3] W. Götze, Z. Phys. B **60**, 195 (1985).
 - [4] L. Götze and W. Sjögren, Rep. Prog. Phys. **55**, 242 (1992).
 - [5] U. Buchenau, A. Wischniewski, D. Richter, and B. Frick, Phys. Rev. Lett. **77**, 4035 (1996).
 - [6] S. Kojima and V. Novikov, Phys. Rev. B **54**, 222 (1996).
 - [7] A. Sokolov, J. Phys. Condens. Matter **11**, A213 (1999).
 - [8] D. Engberg, A. Wischniewski, U. Buchenau, L. Börjesson, A. J. Dianoux, A. P. Sokolov, and L. M. Torell, Phys. Rev. B **58**, 9087 (1998).
 - [9] K. L. Ngai, C. M. Roland, and G. N. Greaves, J. Non.-Cryst. Solids **182**, 172 (1995).
 - [10] K. L. Ngai, J. Phys. Condens. Matter **11**, A119 (1999).
 - [11] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **80**, 2338 (1998).
 - [12] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).
 - [13] F. Mezei and M. Russina, J. Phys. Condens. Matter **11**, A341 (1999); M. Russina and F. Mezei, in *Neutrons and Numerical Methods*, edited by M. R. Johnson, G. J. Kearley, and H. G. Büttner, AIP Conf. Proc. No. 479 (AIP, New York, 1999), p. 47.
 - [14] A. P. Sokolov, E. Rossler, A. Kisliuk, and D. Quitmann, Phys. Rev. Lett. **71**, 2062 (1993).
 - [15] F. Mezei, in *Static and Dynamic Properties of Liquids*, edited by M. Davidovic and A. K. Soper (Springer-Verlag, Heidelberg, 1989), p. 100.
 - [16] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984); J. Bengtzelius, Phys. Rev. A **34**, 5059 (1986).
 - [17] F. Mezei, W. Knaak, and B. Farago, Phys. Scr. **T19**, 363 (1987).