

## Ergodicity breaking in strong and network-forming glassy systems

S. Caponi,<sup>1,2</sup> M. Zanatta,<sup>1</sup> A. Fontana,<sup>1,2</sup> L. E. Bove,<sup>3</sup> L. Orsingher,<sup>1,2</sup> F. Natali,<sup>4</sup> C. Petrillo,<sup>2,5</sup> and F. Sacchetti<sup>2,5</sup><sup>1</sup>*Dipartimento di Fisica, Università di Trento, I-38050 Povo Trento, Italy*<sup>2</sup>*Research Center SOFT-INFM-CNR, Università di Roma "La Sapienza," I-00185 Roma, Italy*<sup>3</sup>*Département Physique des Milieux Denses, CNRS-IMPMC, Université Paris 6, F-75015 Paris, France*<sup>4</sup>*INFM-OGG, c/o ILL, 6 rue Jules Horowitz, F-38042 Grenoble Cedex 9, France and CRS-SOFT, c/o ILL, 6 rue Jules Horowitz, F-38042 Grenoble Cedex 9, France*<sup>5</sup>*Dipartimento di Fisica, Università di Perugia, I-06100 Perugia, Italy*

(Received 24 September 2008; revised manuscript received 27 March 2009; published 4 May 2009)

The temperature dependence of the nonergodicity factor of vitreous GeO<sub>2</sub>,  $f_q(T)$ , as deduced from elastic and quasielastic neutron scattering experiments, is analyzed. The data are collected in a wide range of temperatures from the glassy phase, up to the glass-transition temperature, and well into the undercooled liquid state. Notwithstanding the investigated system is classified as prototype of strong glass, it is found that the temperature and the  $q$  behavior of  $f_q(T)$  follow some of the predictions of mode coupling theory. The experimental data support the hypothesis of the existence of an ergodic to nonergodic transition also in network-forming glassy systems.

DOI: 10.1103/PhysRevB.79.172201

PACS number(s): 64.70.kj, 61.05.F–, 61.43.Fs

On cooling a liquid below the melting point avoiding crystallization, its viscosity increases and its molecular motion is slowed down. Below the glass-transition temperature,  $T_g$ , no more molecular rearrangements typical of a liquid occur: the system, becoming a glass, is completely arrested at least on the observation time scale. The structural ( $\alpha$ ) relaxation process describes the dynamical arrest. Its characteristic time  $\tau_\alpha$  exhibits a strong temperature dependence, usually mirrored by that of the static transport coefficients, such as the shear viscosity,  $\tau_\alpha \propto \eta$ . In the glassy state, only secondary relaxation processes,  $\beta$ , remain activated. They are attributed to local reorientational motions.

Great effort has been devoted to understand the glass-transition phenomenology:<sup>1</sup> on the experimental side, universal scaling law has been found to isolate the common features of this process.<sup>2–5</sup> From theoretical side, several different microscopic pictures have been proposed to universally describe the dynamical arrest characterizing the glass transition.<sup>6–10</sup> Up to now, the mode coupling theory (MCT) is the only approach which provides a self-consistent treatment of the particle dynamics. Thanks to the introduction of a nonlinear microscopic equation of motion, it allows to calculate the time evolution of  $\Phi_q(t)$ , the normalized density autocorrelation function at momentum transfer  $q$ . The glass transition is approached by a dynamical instability, which occurs at some temperature,  $T_c$ , above  $T_g$ . The transition from ergodic (high temperature) to nonergodic (low temperature) state takes place at this temperature.<sup>7</sup> From the microscopic point of view,  $T_c$  corresponds to a critical density from which each particle is trapped in the cage made by its neighbors. In this picture, only the rattling motion of the particles blocked inside the cages is permitted: this motion is the microscopic origin of the  $\beta$  relaxation.<sup>7</sup>

In recent years, a considerable amount of work has been done to extend and solve the MCT equations for systems much more complex than simple liquids with spherically symmetric interactions for which the theory was originally formulated.<sup>11–15</sup> Some universal features, largely independent from the particular system one is analyzing, were fore-

seen. For instance, in a temperature region close to  $T_c$ , a cusplike behavior of the long time limit of the density correlator,  $\Phi_q(t) \rightarrow_{t \rightarrow \infty} f_q(T)$  is predicted. In fact, in a liquid  $f_q(T)$  is equal to zero, indicating that at long enough times, a given particle can leave the transient cage made by its nearest neighbors. Crossing  $T_c$ , no more molecular rearrangement occurs and  $f_q(T)$  changes discontinuously assuming a finite value. In this sense  $f_q(T)$  is usually considered as an indicator of the ergodic to nonergodic transition.<sup>7</sup>

The inelastic neutron scattering (INS) and inelastic x-ray scattering (IXS) experiments provide a good mean to study the temperature evolution of  $f_q(T)$  in a wide  $q$  range. From an experimental point of view,  $\Phi_q(t)$  and  $f_q(T)$  are accessible measuring the intermediate scattering function,  $F(q, t)$ . In a supercooled liquid,  $\Phi_q(t)$  is expected to go to zero exhibiting a two-step decay related to the  $\beta$  and  $\alpha$  relaxations. On cooling the sample, the structural rearrangements became slower and slower, and the decay of  $\Phi_q(t)$  related to the  $\alpha$  relaxation is shifted to longer and longer times. When the temperature is low enough and the  $\alpha$  relaxation is frozen, the characteristic time of its decay is no more measurable and, for long times,  $\Phi_q(t)$  assumes a finite value:  $f_q(T)$ . Alternatively, the plateau value separating the  $\beta$  relaxation from the  $\alpha$  one, sited at longer times, can be determined in the frequency space by measuring the dynamic structure factor,  $S(q, \omega)$ . When the characteristic time of the  $\alpha$  process is shifted to so long time that  $1/\tau_\alpha$  is inside the frequency interval defined by the instrumental resolution function, the evolution of the  $\alpha$  process can be directly monitored by measuring the elastic scattering intensity. Under this condition,  $f_q(T)$  is determined by the ratio of the elastic to the total scattered intensity, that is,  $f_q(T) = S_{el}(q, \omega=0)_T / S(q)_T$ . Up to now, the experimental studies performed by INS (Refs. 16–18) and more recently also by IXS (Refs. 19 and 20) were carried out mainly on glass formers without directional bonds which show high fragility. Recently, both theoretical and simulation studies<sup>11–13</sup> and experimental data<sup>21,22</sup> have suggested that the MCT can describe the behavior of  $f_q(T)$  also in systems with a spatial organization of the molecules.

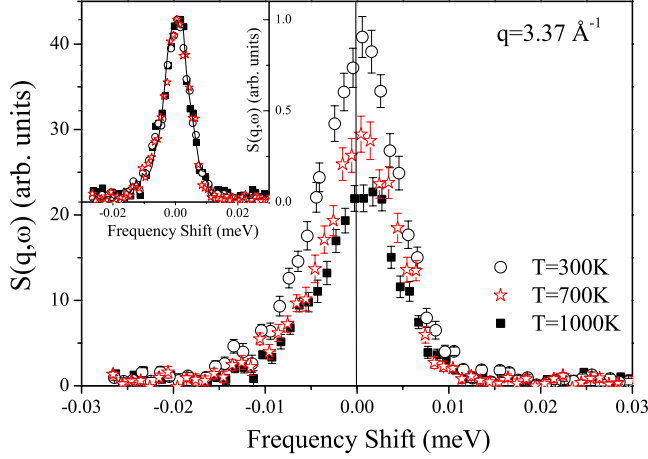


FIG. 1. (Color online) Quasielastic scattering measurements at  $q=3.37 \text{ \AA}^{-1}$  are reported for selected temperatures, 300 K (circles), 750 K (stars), and 1000 K (squares). In the inset the normalized spectra are reported together with the instrumental resolution measured by a vanadium scan (full line). The spectra are identical to the instrumental resolution which, due to the experimental setup, is somewhat asymmetric.

The aim of the present work is to experimentally test which MCT predictions, if any, are valid also in a network-forming liquid. For this purpose, we choose as prototype system the vitreous germania,  $v\text{-GeO}_2$ : it is one of the strongest glasses  $m_{\text{GeO}_2}=20$  (Ref. 23) and it exhibits a rather low glass-transition temperature easily accessible by the experiments ( $T_g \approx 800 \text{ K}$ ). The samples were obtained by melt-quench process of the germanium (IV) oxide crystalline powder purchase by Aldrich (purity greater than 99.998%). The system has been investigated by neutron scattering experiments.

Elastic and quasielastic measurements were performed on the thermal backscattering spectrometer IN13 at the Institut Laue-Langevin (ILL, Grenoble, France). The total elastic intensity,  $S_{\text{el}}(q, \omega=0, T)$ , was measured as a function of temperature from 20 to 1100 K. Quasielastic spectra were collected at significant temperatures in the energy range  $[-0.026; 0.03] \text{ meV}$  with an energy resolution  $\Delta\omega=9 \text{ } \mu\text{eV}$ .

The measurements of the static structure factor,  $S(q)$ , were performed at the diffractometer 7C2 located on the hot source of the reactor Orphée of the Laboratoire Leon Brillouin (LLB, Saclay, France). The incident wavelength  $\lambda=0.729 \text{ \AA}$  was chosen to access a wide  $q$  range between  $0.4$  and  $15 \text{ \AA}^{-1}$  and to minimize the inelasticity corrections. The  $S(q)$  was investigated in the temperature range from room temperature to the liquid phase. The two sets of data were reduced using Monte Carlo simulation to estimate the multiple scattering, the cell contribution, and the transmission coefficients.<sup>24</sup>

In Fig. 1, where the quasielastic spectra are reported for selected temperatures, the decreasing intensity underlines the temperature effect of the atom motion. In the inset of Fig. 1 we report the same spectra, normalized at the maximum intensity. No changes in the quasielastic line shape are observed in the whole explored temperature range, indicating that there are no detectable thermally activated processes at

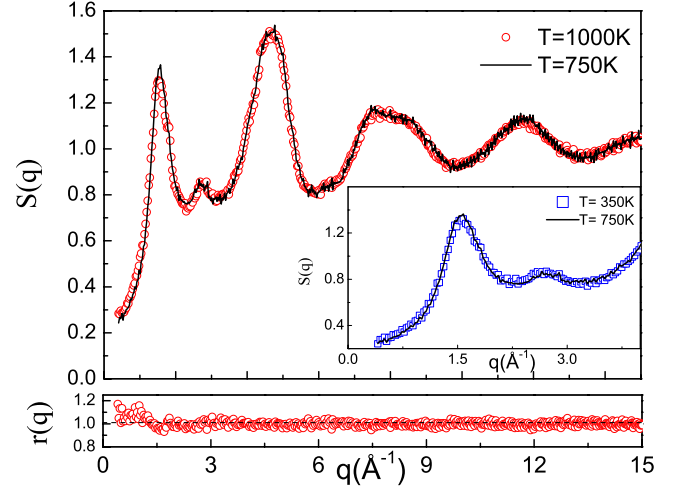


FIG. 2. (Color online) Static structure factor  $S(q)$  measured at the two relevant temperatures  $T=750 \text{ K}$  (line, upper panel) and  $T=1000 \text{ K}$  (circles, upper panel). The ratio  $r(Q) = \frac{S(Q)_{T=1000 \text{ K}}}{S(Q)_{T=750 \text{ K}}}$  is also reported (circles, lower panel). The dashed line in the lower panel is a horizontal guide for the eyes. The errors bars are of the same size as the symbols. In the inset the low  $q$  part of  $S(q)$  is measured at  $T=350 \text{ K}$  (squares) and  $T=750 \text{ K}$  (line).

least within the width of the experimental resolution. Therefore the  $\alpha$  relaxation process is always inside the elastic peak and the relation  $\Delta\omega\tau_\alpha(T) \gg 1$  is always fulfilled. As mentioned before, under this condition the  $f_q(T)$  can be analyzed according to the previous description. In particular, considering that  $f_q(T \rightarrow 0)=1$ ,  $f_q(T)$  is obtained as<sup>18</sup>

$$\frac{S_{\text{el}}(q, \omega=0)_T}{S_{\text{el}}(q, \omega=0)_{T=0}} = f_q(T) \frac{S(q)_T}{S(q)_{T=0}}. \quad (1)$$

In this way each data set is normalized by its low temperature measurement, thus canceling all instrumental normalization constants. Since our low temperature datum in the elastic scan is  $20 \text{ K}$ , we linearly extrapolate the  $S(q, \omega=0)_{T=20 \text{ K}}$  to  $S(q, \omega=0)_{T=0 \text{ K}}$ . Room temperature is the lowest temperature where the static structure factor was measured. Since the diffraction pattern does not show any significant change from room temperature up to  $750 \text{ K}$  (as shown in the inset of Fig. 2), we safely approximate  $S(q)_{T=0 \text{ K}}$  to  $S(q)_{T=350 \text{ K}}$ . Smooth temperature evolution is found in the  $S(q)$  for temperatures greater than  $750 \text{ K}$ . In Fig. 2,  $S(q)$  is presented at two significant temperatures (before the glass transition  $T=750 \text{ K}$  and in the liquid state  $T=1000 \text{ K}$ ) together with the ratio,  $r(q)$ , between the two spectra.  $r(q)$  is almost constant in the whole range apart at very low  $q$ , where slight differences are present.

The  $f_q(T)$  values, obtained by Eq. (1), are reported in Fig. 3 as a function of temperature for three selected wave vector transfers,  $q$ . The data follow the same trend: in the low temperature region, the temperature dependence of  $f_q(T)$  follows a linear behavior; at a certain temperature, independently from the analyzed  $q$  value, a sudden slope variation occurs. In the highest temperature range and in the whole investigated liquid phase,  $f_q(T)$  becomes almost temperature inde-

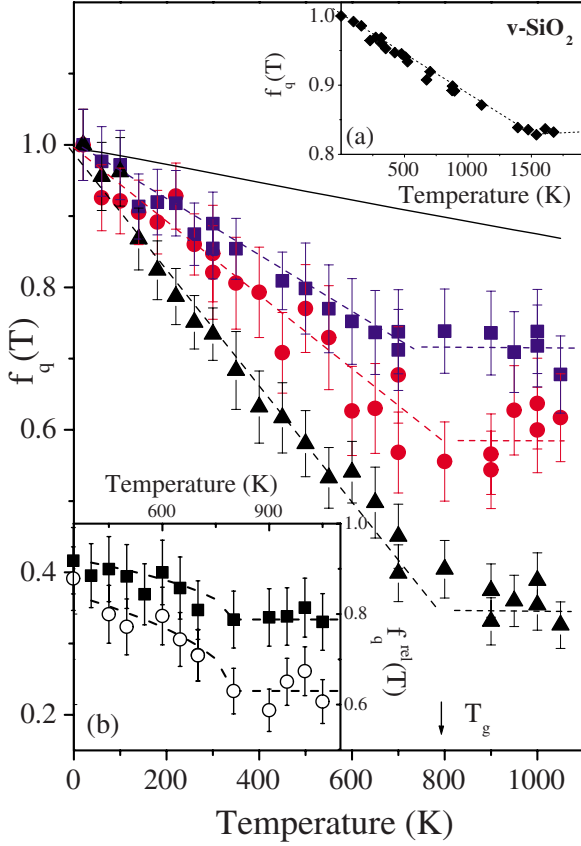


FIG. 3. (Color online) Temperature dependence of  $f_q(T)$  measured in  $v\text{-GeO}_2$  at  $q=0.77 \text{ \AA}^{-1}$  (circles),  $q=1.37 \text{ \AA}^{-1}$  (squares), and  $q=3.40 \text{ \AA}^{-1}$  (triangles). The dashed lines are reported as guides for the eyes. The continuous line is the evaluation of  $f_q^{\text{vibr}}(T)$  at  $q=1.37 \text{ \AA}^{-1}$ . In the inset (a)  $f_q(T)$  is reported for the  $v\text{-SiO}_2$  (Ref. 25). In the inset (b)  $f_q^{\text{rel}}(T)$  is reported for  $q=2.93 \text{ \AA}^{-1}$  (circles) and  $q=3.40 \text{ \AA}^{-1}$  (squares); the dashed lines are the best fits obtained using the square-root function predicted by the MCT.

pendent. Interestingly, a very similar temperature dependence is also found in  $v\text{-SiO}_2$  reported in the inset (a) of Fig. 3.<sup>25</sup>

The measured  $f_q(T)$  can be assumed as the superposition of the vibrational and relaxational contributions,<sup>18</sup>

$$f_q(T) = f_q^{\text{rel}}(T)f_q^{\text{vibr}}(T). \quad (2)$$

The pure vibrational contribution  $f_q^{\text{vibr}}(T) = e^{-1/3q^2\langle u^2 \rangle}$  can be calculated in harmonic approximation through the mean square displacements,  $\langle u^2 \rangle$ ,

$$\langle u^2 \rangle = \frac{3\hbar}{2M} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \coth(\hbar\omega/2k_B T), \quad (3)$$

where  $M$  is the average mass of the atoms constituting the  $\text{GeO}_2$  molecular units and the density of states,  $g(\nu)$ , is taken by Ref. 26. As expected,  $f_q^{\text{vibr}}(T)$  (reported as full line in the main panel of Fig. 3 for  $q=1.37 \text{ \AA}^{-1}$ ) shows a linear temperature dependence; consequently the break in  $f_q(T)$  has to be fully ascribed to the relaxational contribution. As previously described, in the framework of MCT,  $f_q^{\text{rel}}(T)$  is expected to display a cusp behavior in the region close to the

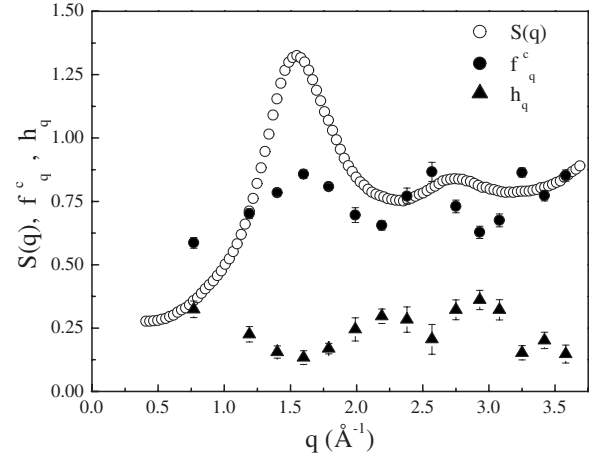


FIG. 4. Wave-vector dependence of  $f_q^c$  (dots) and  $h_q$  (triangles), compared with  $S(q)$  measured at  $T=900 \text{ K}$  (circles).

critical temperature,  $T_c$ , which should be located above  $T_g$ . The theory foresees that close to  $T_c$  the following relationship holds:

$$f_q^{\text{rel}}(T) = \begin{cases} f_q^c + h_q[(T_c - T)/T_c]^\beta, & T < T_c \\ f_q^c, & T > T_c, \end{cases} \quad (4)$$

where  $\beta=0.5$  is expected and  $f_q^c$  and  $h_q$  are positive quantities depending only on  $q$ .<sup>7</sup> In order to apply this relation the static structure factor,  $S(q)$ , must depend smoothly on temperature: this guarantees that any change in the temperature behavior is not related to a structural rearrangement, but it has a dynamical origin. This condition is fulfilled by our data as clearly shown in Fig. 2.

$f_q^{\text{rel}}(T)$  obtained from Eqs. (2) and (3) is reported, for two selected  $q$  values, in the inset (b) of Fig. 3, where the best fits obtained using the square-root function predicted by the MCT according Eq. (4) are also shown. From the fit, the obtained value of the critical temperature  $T_c$  comes out to be  $q$  independent within experimental error,  $T_c = (800 \pm 100) \text{ K}$ , while  $f_q^c$  and  $h_q$  are strongly  $q$  dependent. The large error in the evaluation of  $T_c$  is due to the scattering of the data and to the lacking of measurements in the region close to  $T_c$ .

As foreseen by MCT, the presented data suggest the existence of a break in the trend of  $f_q(T)$  versus temperature and it is located near  $T_g$ . Since in strong glasses it is expected to largely exceed  $T_g$ ,<sup>27</sup> it might not straightforward to identify the temperature of the break as  $T_c$  defined in Eq. (4). However it is evident that a transition occurs and that the system starts to anomalously change its dynamics at a certain temperature where no structural changes are present. It is quite interesting to observe that the same behavior is observed also in  $v\text{-SiO}_2$  where  $T_c$  is expected to be much higher than the temperature where the break occurs, i.e.,  $1500 \text{ K}$ . The inconsistency between the expected and the obtained value of the critical temperature is not yet clearly explained. This aspect deserves further investigations and, at the same time, suggests a new direction of investigation.

A further test to analyze the results is represented by the  $q$

dependence of  $f_q^c$  and  $h_q$  that, in the present case, are reported in Fig. 4 together with the static structure factor,  $S(q)$ . The values of  $f_q^c$  follow in phase the oscillations of  $S(q)$ , while those of  $h_q$  are in antiphase. This behavior, in agreement with MCT calculations for simple liquids, has been experimentally observed in different glass-forming systems.<sup>8</sup> Here, the ability of  $f_q^c$  and  $h_q$  to oscillate in phase and in antiphase, respectively, with the main feature of  $S(q)$  is again verified also in liquid with a spatial organization of the molecules.

Our results confirm that the MCT is able to qualitatively describe some universal aspects of the glass transition that is shared both by simple liquids and by liquids with a local order. Even though the temperature, at which the ergodicity breaking occurs, is astonishingly close to  $T_g$ , its presence is

clearly visible in both  $v\text{-GeO}_2$  and  $v\text{-SiO}_2$ . The existence of the ergodicity breaking in network-forming glassy systems has been previously formulated analyzing the results on  $\text{B}_2\text{O}_3$  (Ref. 28) and on two phosphate glasses.<sup>29</sup> However, in those cases,  $f_q(T)$  does not show a well-defined discontinuity in its temperature dependence like we found in the present case. Our findings suggest that the description of the dynamical arrest made in the MCT scenario might be extended to a wider class of materials, such as network-forming systems.

We acknowledge U. Buchenau for providing us the silica data. We thank ILL for technical and financial support. The experiment at LLB was supported by the European Commission under the Sixth Framework Programme (Contract No. RII3-CT-2003-505925).

- <sup>1</sup>A. Fontana, P. Verrocchio, and G. Viliani, *Philos. Mag.* **87**, 355 (2007).
- <sup>2</sup>T. Scopigno, G. Ruocco, F. Sette, and G. Monaco, *Science* **302**, 849 (2003).
- <sup>3</sup>U. Buchenau and A. Wischnewski, *Phys. Rev. B* **70**, 092201 (2004).
- <sup>4</sup>U. Buchenau and R. Zorn, *Europhys. Lett.* **18**, 523 (1992).
- <sup>5</sup>L. Larini, A. Ottochian, C. De Michele, and D. Leporini, *Nat. Phys.* **4**, 42 (2008).
- <sup>6</sup>M. H. Cohen and G. S. Grest, *Phys. Rev. B* **20**, 1077 (1979).
- <sup>7</sup>W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Lesvesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991); W. Götze and M. R. Mayr, *Phys. Rev. E* **61**, 587 (2000); W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
- <sup>8</sup>W. Götze, *J. Phys.: Condens. Matter* **11**, A1 (1999).
- <sup>9</sup>D. Kivelson *et al.*, *Physica A* **219**, 27 (1995); P. Viot, G. Tarjus, and D. Kivelson, *J. Chem. Phys.* **112**, 10368 (2000).
- <sup>10</sup>P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).
- <sup>11</sup>F. Sciortino and W. Kob, *Phys. Rev. Lett.* **86**, 648 (2001).
- <sup>12</sup>L. Fabbian, A. Latz, R. Schilling, F. Sciortino, P. Tartaglia, and C. Theis, *Phys. Rev. E* **60**, 5768 (1999).
- <sup>13</sup>J. Horbach and W. Kob, *Phys. Rev. B* **60**, 3169 (1999).
- <sup>14</sup>R. Schilling and T. Scheidsteger, *Phys. Rev. E* **56**, 2932 (1997).
- <sup>15</sup>T. Franosch, M. Fuchs, W. Gotze, M. R. Mayr, and A. P. Singh, *Phys. Rev. E* **56**, 5659 (1997).
- <sup>16</sup>E. Kartini, M. F. Collins, B. Collier, F. Mezei, and E. C. Svensson, *Phys. Rev. B* **54**, 6292 (1996).
- <sup>17</sup>B. Frick, B. Farago, and D. Richter, *Phys. Rev. Lett.* **64**, 2921 (1990).
- <sup>18</sup>E. Bartsch, F. Fujara, J. F. Legrand, W. Petry, H. Sillescu, and J. Wuttke, *Phys. Rev. E* **52**, 738 (1995).
- <sup>19</sup>D. Fioretto, M. Mattarelli, C. Masciovecchio, G. Monaco, G. Ruocco, and F. Sette, *Phys. Rev. B* **65**, 224205 (2002).
- <sup>20</sup>G. Monaco, C. Masciovecchio, G. Ruocco, and F. Sette, *Phys. Rev. Lett.* **80**, 2161 (1998).
- <sup>21</sup>L. Comez, S. Corezzi, G. Monaco, R. Verbeni, and D. Fioretto, *Phys. Rev. Lett.* **94**, 155702 (2005).
- <sup>22</sup>S. Corezzi, L. Comez, G. Monaco, R. Verbeni, and D. Fioretto, *Phys. Rev. Lett.* **96**, 255702 (2006).
- <sup>23</sup>R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
- <sup>24</sup>C. Petrillo and F. Sacchetti, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **46**, 440 (1990); **48**, 508 (1992).
- <sup>25</sup>These measurements were collected using the IN6 spectrometer installed at ILL, with  $q \sim 2.6 \text{ \AA}^{-1}$ . A. Wischnewski (unpublished).
- <sup>26</sup>E. Fabiani, U. Buchenau, and A. Fontana, *J. Chem. Phys.* **128**, 244507 (2008).
- <sup>27</sup>V. N. Novikov, E. Rossler, V. K. Malinovsky, and N. V. Surovtsev, *Europhys. Lett.* **35**, 289 (1996).
- <sup>28</sup>A. Brodin, L. Börjesson, D. Engberg, L. M. Torell, and A. P. Sokolov, *Phys. Rev. B* **53**, 11511 (1996); D. Sidebottom, R. Bergman, L. Börjesson, and L. M. Torell, *Phys. Rev. Lett.* **71**, 2260 (1993); D. Engberg *et al.*, *Europhys. Lett.* **47**, 213 (1999).
- <sup>29</sup>S. Caponi *et al.*, *J. Non-Cryst. Solids* **352**, 4577 (2006).