

Slow dynamics in glycerol: collective de Gennes narrowing and independent angstrom motion

Makina Saito¹ · Yasuhiro Kobayashi¹ · Ryo Masuda¹ ·
Masayuki Kurokuzu¹ · Shinji Kitao¹ · Yoshitaka Yoda² ·
Makoto Seto¹

© Springer International Publishing Switzerland 2016

Abstract The slow dynamics of microscopic density correlations in supercooled glycerol was studied by time-domain interferometry using ⁵⁷Fe-nuclear resonant scattering gamma rays of synchrotron radiation. The dependence of the relaxation time at 250 K on the momentum transfer q is maximum near the first peak of the static structure factor $S(q)$ at $q \sim 15 \text{ nm}^{-1}$. The q -dependent behavior of the relaxation time known as de Gennes narrowing was confirmed in glycerol. Conversely, de Gennes narrowing around the second and third peaks of $S(q)$ at $q \sim 26 \text{ nm}^{-1}$ and 54 nm^{-1} was not detected. The q dependence of the relaxation time was found to follow a power-law equation with power-law index of 1.9(2) in the q region well above the first peak of $S(q)$ up to $\sim 60 \text{ nm}^{-1}$, which corresponds to angstrom scale, within experimental error. This suggests that in the angstrom-scale dynamics of supercooled glycerol, independent motions dominate over collective motion.

Keywords De Gennes narrowing · Glycerol · Nuclear resonant scattering · Time-domain interferometry

1 Introduction

The study of microscopic dynamics of supercooled glass formers is critical to understanding the nature of glass transition [1, 2]. In particular, the diffusional relaxation process known

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2015), Hamburg, Germany, 13-18 September 2015*

✉ Makina Saito
msaito@rri.kyoto-u.ac.jp

¹ Research Reactor Institute, Kyoto University, Osaka 590-0494, Japan

² Japan Synchrotron Radiation Research Institute, Sayo, Hyogo, 679-5198 Japan

as α process has been considered to be closely related to the glass transition. In fragile glass formers, the α -relaxation time increases with cooling following the Vogel–Fulcher–Tammann law. This divergence is attributed to the growth of the cooperative rearrangement region (CRR), where molecules move cooperatively. Therefore, it is expected that the motional collectivity of the α process is developed with decreasing temperature. Conversely, another process known as the slow β process (Johari–Goldstein process) seems to branch from the α process with cooling in the relaxation map and can be observed even in the glass state [3]. The slow β process seems to be a local activation process; however, the origin is not fully understood. Understanding the hierarchy dynamics with structural assignment of the origin is a key to understand the glass transition mechanism. Quasi-elastic scattering measurements give the relaxation time of the microscopic structures specifying the spatial scale of the structure to be studied. The spatial scale is selected by setting the detection angle of the scattered beam to the corresponding angle. The momentum transfer q is related to the spatial scale l of the scatterer as $q \sim 2\pi/l$. Then, the energy broadening of the scattered beam due to the diffusion in the sample is studied at the selected angle. The broadening relates to the relaxation time of the microscopic scatterer, and the dependence of the relaxation time on q shows the microscopic dynamical picture in detail. Half a century ago, de Gennes predicted that the q dependence of the α -relaxation time of the collective motion shows the maximum at around the first peak of the static structure factor $S(q)$ [4]. The configuration of a molecular pair with distance related to the first peak of $S(q)$ is more stable than other similar configurations with slightly different distances. This is a simple explanation of the q behavior, which is known as de Gennes narrowing. This phenomenon has been actually observed in liquids [5–7]. However, the observations covered a limited temperature region near the melting point. This is partly because of the limitations in q and time accessibilities by conventional methods, such as the neutron spin echo (NSE) method. Clearly, it is challenging to study if motional coherency enhanced by cooling modifies the shape of de Gennes narrowing in deeply supercooled liquids. Therefore, the q behavior of the relaxation time in the relatively deeply supercooled state requires to be studied. Another interesting task is to understand the microscopic behavior of supercooled liquids from the molecular (sub nm) to the atomic (angstrom) scales, which have never been fully accessed in the time scale of 100 ns.

NSE method enables us to observe the collective motion at time scales shorter than nanoseconds. In addition, the Rayleigh scattering of Mössbauer radiation (RSMR), which is a quasi-elastic scattering method that uses the gamma rays from a radioactive isotope (RI), has been used to study the microscopic slow dynamics [8]. In this method, gamma rays from the first excited state of ^{57}Fe nuclei, whose energy is 14.4 keV (the momentum is 73 nm^{-1}) with natural energy width of 4.67 neV, is typically used as the probe photon of the quasi-elastic scattering. Thus, the microscopic dynamics of time scales in the order of 100 ns, which is a unique time scale and not easily accessed by other quasi-elastic scattering methods, can be studied. However, the RSMR requires very long times (e.g., one week) because the RI sources emit gamma rays uniformly in all directions and only the quasi-directive gamma rays passing through a slit can be used. Therefore, studies such as the q dependence of the relaxation time have been hardly performed. Time-domain interferometry (TDI) using the nuclear resonant scattering (NRS) gamma rays of synchrotron radiation (SR) is the time-domain analogue of the RSMR based on SR source [9–11]. Because coherently emitted gamma rays in the forward direction inherit the directionality characteristic of SR, the TDI method allows for more efficient quasi-elastic scattering experiment. Using

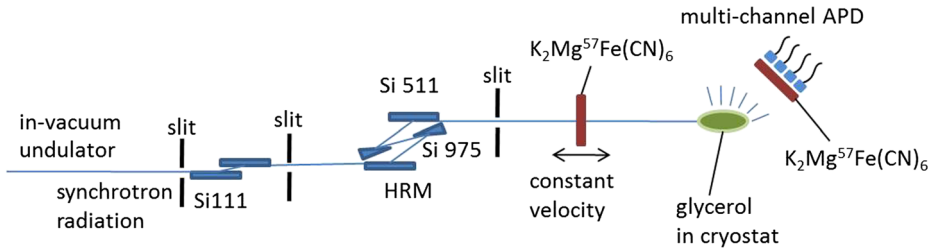


Fig. 1 TDI experimental setup using NRS gamma rays from the first nuclear excited state of ^{57}Fe at BL09XU in SPring-8. See main text for details

TDI, we studied the microscopic dynamics in glycerol and the slow dynamics in the 100 ns region up to $q \sim 60 \text{ nm}^{-1}$. The q value of 60 nm^{-1} corresponds to the angstrom scale suggesting that atomic dynamics could be observed in the nanosecond time scale.

2 Experiment

The TDI experiments were performed at the NRS beamline (BL09XU) of SPring-8 in Japan. The TDI experimental setup is shown in Fig. 1. The energy width of the incident radiation was set at $\sim 3.5 \text{ meV}$ at the excitation energy of the first nuclear excited state of ^{57}Fe using a high-resolution monochromator (HRM) comprising asymmetric Si (511) and Si (975) channel-cut crystals. The measurements at q below 41 nm^{-1} and above 48 nm^{-1} were performed at different beam times. The storage ring was operated in the several-bunch timing mode (1/7-filling + several 5-bunch mode with bunch interval of 684.3 ns for q below 41 nm^{-1} and 1/14-filling + several 12-bunch mode with bunch interval of 342 ns for q above 48 nm^{-1}). Upstream and downstream from the sample, $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ plates, whose ^{57}Fe density is 1.0 mg/cm^2 , were placed. The upstream $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ plate was driven using a velocity transducer with constant velocity of ~ 15 and 20 mm/s , respectively, for the measurements at q below 41 nm^{-1} and above 48 nm^{-1} . Conversely, the downstream $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ plate was kept stable. Spectroscopic grade glycerol was purchased from Sigma-Aldrich and used for the experiment. The temperature of the sample was controlled by a He-flow cryostat. A multielement Si-avalanche photodiode (APD) detector was used for counting the NRS gamma rays. Time spectra were simultaneously measured at four scattering angles by one APD detector. The microscopic relaxations of glycerol are reflected on the time spectrum of the NRS gamma rays as the disappearance of the quantum beat pattern caused by the interference between the gamma rays from the upstream and downstream $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ plates. The time dependence of the disappearance is related to the intermediate scattering function $F(q, t)$. The TDI time spectra were measured at 250 K at 19 q points between 10 and 58 nm^{-1} . This temperature is well below the melting point of $\sim 291 \text{ K}$ and above the glass transition temperature T_g of $\sim 184 \text{ K}$. Typical TDI time spectra are shown in Fig. 2. Least squares fittings were performed using the equations available elsewhere [10, 11]. The Kohlrausch–Williams–Watts (KWW) function $\exp\left\{-\left(t/\tau\right)^{\beta_{\text{KWW}}}\right\}$ was used as the relaxation function with a fixed stretching parameter β_{KWW} of 0.7 for glycerol at approximately 250 K [13], where τ is the relaxation time and t is time. A small change in

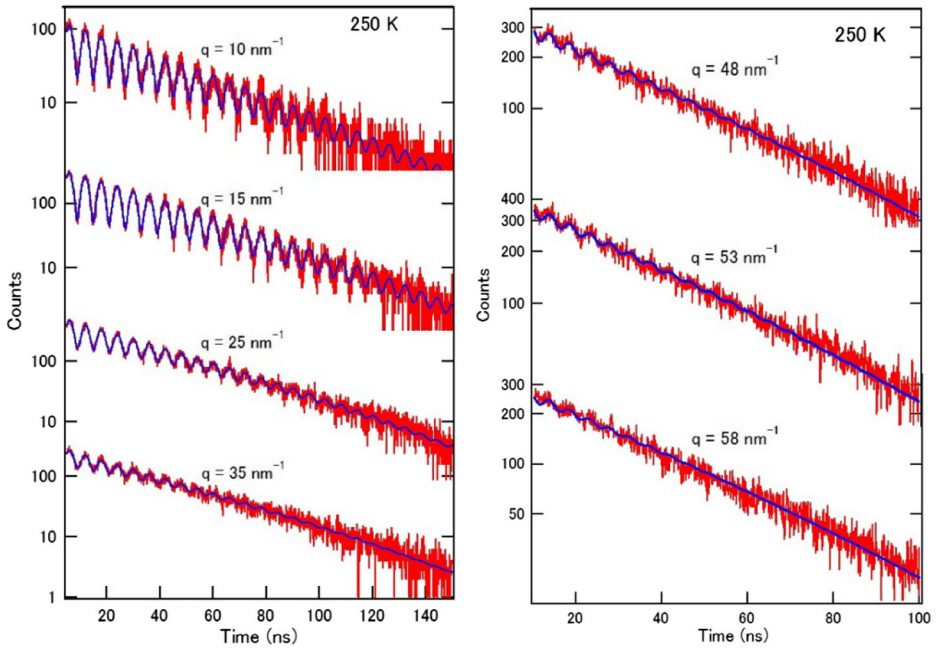


Fig. 2 Typical TDI time spectra and fitting curves at several q at 250 K for glycerol

β_{KWW} hardly affects the results. From the obtained τ , the mean relaxation time is calculated according to $\langle\tau\rangle = \tau\Gamma(1/\beta_{\text{KWW}})/\beta_{\text{KWW}}$, where Γ is the gamma function [14].

3 Results and discussion

In Fig. 3, we show the q dependence of the scattering intensity data $I(q)$ and the q dependence of $\langle\tau\rangle$ at 250 K. The $S(q)$ data obtained at 250 K from a previous study [15] considering our q resolution is also shown. Three peaks were observed at $q \sim 15, 26,$ and 54 nm^{-1} in both $S(q)$ and $I(q)$ data. The first peak at $\sim 15 \text{ nm}^{-1}$ is related to the intermolecular correlation, whereas the other peaks are related to the intramolecular correlation. First, we focus on the origin of the detected relaxations. In *o*-terphenyl and polybutadiene, it has been observed that the relaxation times obtained at the first peak of $S(q)$ and higher q start to decouple with cooling at a certain temperature $T_{\alpha\beta}$ because of the emergence of the slow β process [16–18]. Well above $T_{\alpha\beta}$, the diffusional α process causes the relaxation of both intermolecular and local correlations. Conversely, well below $T_{\alpha\beta}$, the relaxation of local correlations is mainly caused by the slow β process because its relaxation time is much shorter than the relaxation time of the α process. The existence of the slow β process in glycerol is controversial [19]. $T_{\alpha\beta}$ of glycerol is, if it exists, expected to be around the dynamical crossover temperature $T_c \sim 228 \text{ K}$ from the empirical relation $T_c \sim 1.2T_g$ [20]. Because the temperature of 250 K is well above the estimated T_c and $T_{\alpha\beta}$ and the relaxation time in Fig. 3 shows smooth q dependence in the entire q region, the relaxation observed at higher q than the first peak of $S(q)$ is attributed to the α process at this temperature.

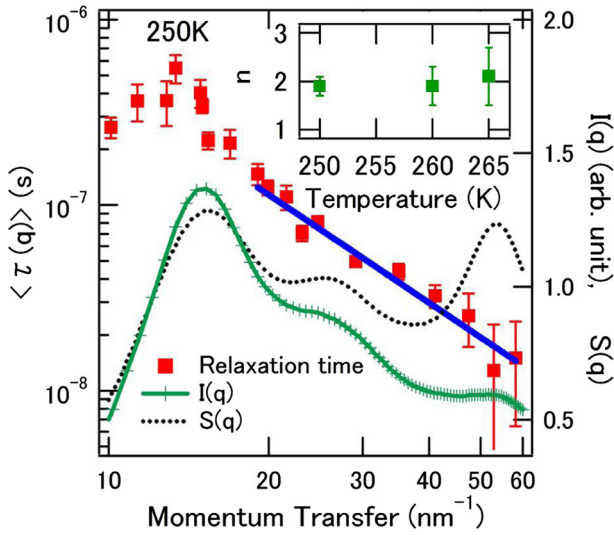


Fig. 3 q dependence of the mean relaxation time $\langle \tau \rangle$ at 250 K. The solid line with the plus symbols and the bold line represent the q dependence of the scattering intensity $I(q)$ and the static structure factor $S(q)$ at 250 K [15], respectively. The solid line denotes fitting to $\langle \tau(q) \rangle$ by a power-law equation in the q region above 20 nm^{-1} . The inset shows the temperature dependence of the power-law index n [23]

Next, we consider the q dependence of $\langle \tau \rangle$. In Fig. 3, $\langle \tau(q) \rangle$ is maximum around the first peak of $S(q)$. de Gennes narrowing is assumed as the origin. However, there is no general formula to express de Gennes narrowing. In the simplest monoatomic liquids, $\langle \tau(q) \rangle$ is expressed as $\langle \tau(q) \rangle \propto S(q) \langle \tau_{inc}(q) \rangle$ [21]. $\langle \tau_{inc}(q) \rangle$ is the incoherent relaxation time, which is related to independent motion, and is fit with a power-law equation ($\langle \tau_{inc}(q) \rangle \propto q^{-n}$, where n is the power-law index) [21]. We replot the $\langle \tau(q) \rangle / S(q)$ in Fig. 4 and show the result of the least squares fit with the power-law equation (bold line). We first consider the q region around the first peak of $S(q)$. $\langle \tau(q) \rangle / S(q)$ roughly follows the power-law equation even at 250 K. Therefore, the $\langle \tau(q) \rangle$ behavior is attributed to de Gennes narrowing. However, the fit deviates around the first peak of $S(q)$. This deviation is partly caused by the lack of coincidence of the first peak position of $S(q)$ and the maximum relaxation time also seen in polybutadiene [6]. Thus, clearly, a more detailed model is required. In the high q region around 40 nm^{-1} , $\langle \tau(q) \rangle / S(q)$ also clearly deviates from the fitting curve. This suggests that the assumed relation $\langle \tau(q) \rangle \propto S(q) q^{-n}$ is not correct in the high q region. Using another model, we consider the microscopic dynamics at the q region higher than the first peak of $S(q)$. In this q region and at relatively higher temperatures, the q dependences of the coherent and incoherent relaxation times can be well described by a power-law equation [22]. Even in deeply supercooled *o*-terphenyl near the decoupling temperature, a power-law equation well describes the q dependence of the relaxation time [17] so that $\langle \tau(q) \rangle$ itself is proportional to $\langle \tau_{inc}(q) \rangle \propto q^{-n}$. The fitting results in Fig. 3 well describe the measured relaxation times $\langle \tau(q) \rangle$ from 20 to 60 nm^{-1} with power-law index of $1.9(2)$. This n value is close to the values of $1.9(4)$ and $2.1(6)$ reported for 260 K and 265 K , respectively [23]. In the inset of Fig. 3, we plot the temperature dependence of n , and it is seen that the q dependence of $\langle \tau \rangle$ follows the relation $\langle \tau(q) \rangle \propto q^{-n}$ at 250 K , where n is around 2 . In *o*-terphenyl case, the large $n \sim 3$ observed in the q region well above the first peak of $S(q)$ (from $\sim 20 \text{ nm}^{-1}$ to $\sim 50 \text{ nm}^{-1}$) at 265 K suggesting change in the dynamical behavior

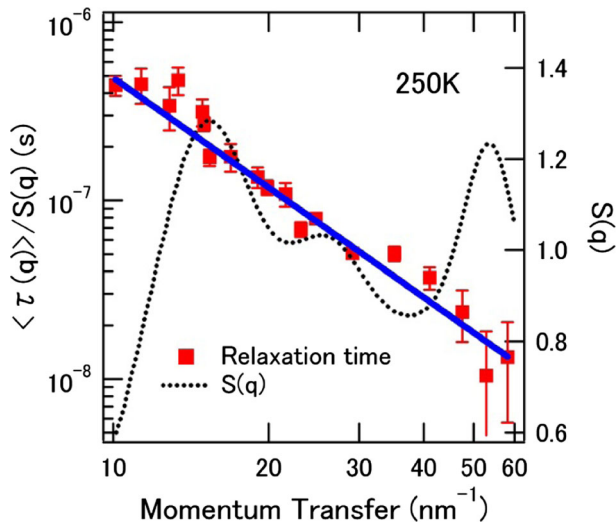


Fig. 4 q dependence of the mean relaxation time $\langle \tau \rangle$ at 250 K, where $\langle \tau(q) \rangle$ is normalized by the static structure factor $S(q)$ at 250 K. The dashed line represents $S(q)$. The solid line shows the fitting to $\langle \tau(q) \rangle$, by assuming power-law q dependence in the entire q region

from liquid-like ($n \sim 2$) to glass-like ($n > 2$) in the deeply supercooled state [17]. At 250 K, relatively near T_g , the local motion in glycerol still shows liquid-like behavior.

de Gennes narrowing was not detected at the second and third peaks of $S(q)$, and we need to consider the reason. It is expected to be observed if molecules prefer particular conformations and the coherent scattering originating from such local structures is sufficiently intense compared with contributions from other structures. Regarding the local structure of glycerol, hydrogen bonding is the dominant interaction and the distance between oxygen atoms, which is sensitive to the gamma rays (X-rays), is 0.24–0.32 nm. The hydrogen bond is a good candidate for the origin of the de Gennes narrowing at the q region of 20–26 nm^{-1} . However, locally, there are many local structures of various length scales and the switching of the hydrogen bond can trigger the relaxation of these structures by inducing conformation changes. Therefore, de Gennes narrowing is presumably hidden by many other relaxations and too weak to be observed at the high- q region. Similar conclusions have been reached for polybutadiene [6]. As a result, $\langle \tau(q) \rangle$ is dominated by the independent motion in the q region without clear maximum. This situation at the high- q region is different from that at the first peak of $S(q)$, where there is an almost unique intermolecular length scale.

The dynamics in the order of nanoseconds in the q region up to $\sim 60 \text{ nm}^{-1}$ has not been studied to date because it is too slow for many methods, e.g., inelastic neutron, NSE or X-ray scattering methods at the q range. In this study, the angstrom-scale dynamics was found to follow the power-law q behavior even at 250 K with $n \sim 2$ in the case of glycerol using gamma rays with angstrom wavelength and neV-energy resolution. Problems to be addressed in the future are (i) the change in the shape of de Gennes narrowing near T_g because of the increase in the CRR size, (ii) the slow β process in glycerol, and (iii) the q -dependent behavior at the high- q region in deeply supercooled glycerol to understand the angstrom-scale dynamics in glycerol.

4 Conclusions

In the time region around 100 ns, the microscopic relaxation time of a supercooled liquid was obtained up to $\sim 60 \text{ nm}^{-1}$, which corresponds to the angstrom scale. As a result, de Gennes narrowing was confirmed in glycerol around the first peak of the static structure factor $S(q)$ at 250 K. However, it was not observed around the second and third peaks of $S(q)$. Instead, in the q region well above the first peak of $S(q)$, the q dependence of the relaxation time was found to follow a power-law equation with a power-law index of 1.9(2). This suggests that independent motion is dominant compared with the collective motion in the angstrom-scale dynamics of supercooled liquids.

Acknowledgments We thank S. Kishimoto (High-Energy Accelerator Research Organization) for developing the detectors. We are also grateful to Prof. T. Kanaya (High-Energy Accelerator Research Organization) for reading the manuscript and constructive comments. The experiment was performed with the approval of the Japan Synchrotron Radiation Research Institute (proposal No. 2012B146, 2013A14457, and 2014B1061). This work was supported by JSPS KAKENHI (Grant-in-Aid for Scientific Research (S)) Grant Number 24221005 and JSPS KAKENHI (Grant-in-Aid for Young Scientists (B)) Grant Number 15K17736.

References

1. Ediger, M.D., Angell, C.A., Nagel, S.R.: Supercooled liquids and glasses. *J. Phys. Chem.* **100**, 13200 (1996)
2. Debenedetti, P.G.: *Metastable liquids* (princeton university press princeton (1996)
3. Johari, G.P., Goldstein, M.: Viscous liquids and the glass transition. II. secondary relaxations in glasses of rigid molecules. *J. Chem. Phys.* **53**, 2372 (1970)
4. De Gennes, P.G.: Liquid dynamics and inelastic scattering of neutrons. *Phys. A* **25**, 825 (1959)
5. Richter, D., Frick, B., Farago, B.: Neutron-spin-echo investigation on the dynamics of polubutadiene near the glass transition. *Phys. Rev. Lett.* **61**, 2465 (1988)
6. Kanaya, T., Kakurai, K., Tsukushi, I., Inoue, R., Watanabe, H., Nishi, M., Nakajima, K., Takemura, K., Furuya, H.: Thermal neutron spin-echo studies on dynamics of a glass-forming polymer in a high Q range. *J. Phys. Soc. Jpn.* **74**, 3236 (2005)
7. Inui, M., Hosokawa, S., Matsuda, K., Tsutsui, S., Baron, A.Q.R.: Collective dynamics and de Gennes narrowing in polymeric liquid Se: high-resolution inelastic x-ray scattering. *Phys. Rev. B* **77**, 224201 (2008)
8. Champeney, D.C., Woodhams, F.W.D.: Investigation of molecular motions in supercooled liquids by Mossbauer scattering. *J. Phys. B* **1**, 620 (1968)
9. Baron, A.Q., Franz, H., Meyer, A., Ruffer, R., Chumakov, A.I., Burkel, E., Petry, W.: Quasielastic scattering of synchrotron radiation by time domain interferometry. *Phys. Rev. Lett.* **79**, 2823 (1997)
10. Smirnov, G.V., van Buerck, U., Franz, H., Asthalter, T., Leupold, O., Schreier, E., Petry, W.: Nuclear γ resonance time-domain interferometry: quantum beat and radioactive coupling regimes compared in revealing quasielastic scattering. *Phys. Rev. B* **73**, 184126 (2006)
11. Saito, M., Seto, M., Kitao, S., Kobayashi, Y., Higashitaniguchi, S., Kurokuzu, M., Sugiyama, M., Yoda, Y.: Development of ^{151}Eu time-domain interferometry and its application for the study of slow dynamics in ionic liquid. *Appl. Phys. Exp.* **2**, 026502 (2009)
12. Saito, M., Seto, M., Kitao, S., Kobayashi, Y., Kurokuzu, M., Yoda, Y.: Small and large angle quasi-elastic scattering experiments by using nuclear resonant scattering on typical and amphiphilic liquid crystals. *J. Phys. Soc. Jpn.* **81**, 023001 (2012)
13. Lunkenheimer, P., Pimenov, A., Schiener, B., Böhmer, R., Loidl, A.: High-frequency dielectric spectroscopy on glycerol. *Europhys. Lett.* **33**, 611 (1996)
14. Tölle, A.: Neutron scattering studies of the model glass former ortho-terphenyl. *Rep. Prog. Phys.* **64**, 1473 (2001)
15. Soltwisch, M., Steffen, B.: The X-ray Structure Factor of Liquid Glycerol. *Z. Naturforsch.* **36 a**, 1045 (1981)
16. Richter, D., Zorn, R., Farago, B., Frick, B., Fetters, L.J.: Decoupling of time scales of motion in polybutadiene close to the glass transition. *Phys. Rev. Lett.* **68**, 71 (1992)

17. Saito, M., Kitao, S., Kobayashi, Y., Kurokuzu, M., Yoda, Y., Seto, M.: Slow processes in supercooled *o*-terphenyl: relaxation and decoupling. *Phys. Rev. Lett.* **109**, 115705 (2012)
18. Kanaya, T., Inoue, R., Saito, M., Seto, M., Yoda, Y.: Relaxation transition in glass-forming polybutadiene as revealed by nuclear resonance X-ray scattering. *J. Chem. Phys.* **140**, 144906 (2014)
19. Bauer, T.h., Lunkenheimer, P., Kastner, S., Loidl, A.: Nonlinear dielectric response at the excesswing of glass-forming liquids. *Phys. Rev. Lett.* **110**, 107603 (2013)
20. Novikov, V.N., Sokolov, A.P.: Universality of the dynamic crossover in glass-forming liquids: a “magic” relaxation time. *Phys. Rev. E* **67**, 031507 (2003)
21. Colmenero, J., Arbe, A., Coddens, G., Frick, B., Mijangos, C., Reinecke, H.: Crossover from independent to cooperative segmental dynamics in polymers: experimental realisation in poly(vinyl chloride). *Phys. Rev. Lett.* **78**, 1928 (1997)
22. Colmenero, J., Alvarez, F., Arbe, A.: Self-motion and the α relaxation in a simulated glass-forming polymer: Crossover from Gaussian to non-Gaussian dynamic behavior. *Phys. Rev. E* **65**, 041804 (2002)
23. Saito, M., Battistoni, A., Kitao, S., Kobayashi, Y., Kurokuzu, M., Yoda, Y., Seto, M.: Slow dynamics of supercooled liquid revealed by Rayleigh scattering of Mössbauer radiation method in time domain. *Hyperfine Interact.* **226**, 629 (2014)