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Long-range density fluctuations in orthoterphenyl as studied by means of ultrasmall-angle x-ray scattering

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The structure factor of a fragile glass-forming liquid orthoterphenyl was measured in the previously inaccessible intermediate q range between the conventional light scattering (LS) and small-angle x-ray scattering (SAXS) q ranges using the low-angle scattering beam line at the European Synchrotron Radiation Facility. At low q the structure factor exhibits an excess scattering and matches well the LS data. This excess scattering is due to long-range density fluctuations also observed in the isotropic component of scattered light. At high q the structure factor decays to a plateau corresponding to the isothermal compressibility in agreement with the conventional SAXS data. In the intermediate q range, the structure factor exhibits a power law q dependence which indicates that the excess scattering is due to fractal aggregates of denser domains.

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I. INTRODUCTION

Despite extensive experimental and theoretical studies the dynamics and structure of supercooled liquids is not well understood. One of the important questions in this field is concerned with the problem of spatial and dynamical heterogeneities in such liquids [1,2]. A large number of experimental studies clearly reveal the existence of dynamical heterogeneities. New experimental methods have been applied to this question, including multidimensional NMR [3,4] dielectric hole burning [5], time resolved optical spectroscopy [6], photo bleaching techniques [7], and forced Rayleigh scattering [8]. In addition, early concepts for the explanation of the liquid to glass transition are based on the existence of cooperatively rearranging regions (CRR) [9,10] and estimates of a characteristic length scale yield values of $2-3$ nm near T_g [10,11]. The same order of magnitude was found by spin diffusion NMR experiments [12]. Structural heterogeneities with that length scale have not been detected so far by means of static x-ray or neutron scattering experiments. However, detailed wide angle x-ray scattering studies of two glass-forming organic liquids (salol and propylene carbonate) [13,14] revealed temperature-dependent changes of the liquid structure factor in the range of $q \approx 0.7$ to 1.7 Å^{-1}, which means in the neighborhood of the main liquid peak at ~ 1.3 Å^{-1}. These observations support the model of heterophase fluctuations in glass-forming liquids [15–17], which has been proposed in order to explain the results of static and dynamic light scattering described below. Density fluctuations in glass-forming liquids and polymers have been observed several years ago [16,18–21] on a much longer length scale than the estimated range of the CRR's. By means of static light scattering measurements correlation lengths of the order of 100–300 nm have been detected. It is important to note that this long-range fluctuation gives rise to an ''ultraslow'' hydrodynamic mode with relaxation rates Γ_{us} proportional to q^2 (q is the scattering wave vector) and with values about 10^6 to 10^9 times smaller than those of the primary α-relaxation process. These features can be observed only in the isotropic component of the scattered light and are not present in the depolarized component. Therefore they have been assigned to density fluctuations. The light scattering experiments were carried out in the q range between 7×10^{-3} to 4×10^{-2} nm^{-1}. In addition, the density fluctuations were measured by conventional small-angle x-ray scattering (SAXS) covering a q range $q > 2\times10^{-1}$ nm^{-1}. In the case of orthoterphenyl (OTP) a q-independent intensity was observed up to $q \approx 2$ nm^{-1}. The absolute intensity value was found to be proportional to the isothermal compressibility β_T (see Fig. 6 in Ref. [16]), as is expected for the static structure factor $S(q)$ of a liquid in the limit $q \to 0$ [22]. The light scattering intensity in the temperature range between $T_g < T < T_g +$ about 100 K is, however, much higher than expected. Such an excess light scattering intensity $I_{exc}(q)$ was found for many glass-forming liquids and polymers [16,18–21]. Now the important questions arise whether the excess intensity is also observed by x-ray scattering in a q range $q < 2\times10^{-1}$ nm^{-1}, and what is the q dependence of the static x-ray structure factor $S(q)$ within the gap between the former light scattering and SAXS measurements. This intermediate q range between 2×10^{-2} and 2×10^{-1} nm^{-1} [ultrasmall-angle x-ray scattering (USAXS)] is now available at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The present paper reports the results obtained for OTP and concludes with a qualitative discussion of the origin of the long-range density fluctuations.

II. EXPERIMENTAL SETUP

The measurements were performed on beamline ID2 at the ESRF. The beamline is designed for small-angle x-ray scattering and is described in detail in [23]. The beamline was operated with a wavelength $\lambda = 1$ Å. A two-dimensional gas-filled detector was used. A flat-field correction was applied to the data to correct for any inhomogeneities in detection efficiency. The scattering intensities

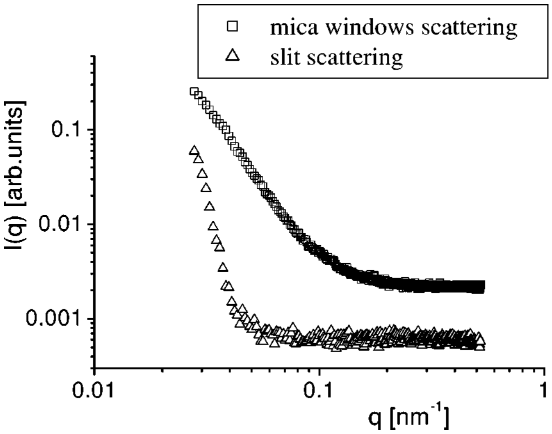

FIG. 1. Scattering due to slit scattering, △, and the added contributions of slit scattering and scattering by mica windows, □. Note: intensities are in logarithmic scale; units are the same as in Fig. 2.

measured were approximately converted to an absolute scale by comparison with a Lupolen standard sample and were normalized with respect to the illuminated sample area A, resulting in a dimensionless scattering cross section $I_A(q)$,

$$I_A(q)=\frac{1}{A}\frac{d\sigma}{d\Omega}. \tag{1}$$

The distance sample to detector was set to 10 m. In this configuration the resolution of the setup results in a smallest observable scattering vector $q_{min}=0.03\ \mathrm{nm}^{-1}$, about one order of magnitude lower than what is usually achieved with a setup mounted to a conventional x-ray tube. For measurements on weakly scattering samples as they are reported here, in addition the background scattering has to be reduced to a level weaker than the signal under investigation. For that reason a cross-shaped vacuum tube connection between the evacuated flight paths in front of and behind the sample was inserted. Samples are inserted from the top and connected through a flexible vacuum bellow at the bottom to a translation stage operating in the x and z direction. With this setup the necessary number of windows is reduced to two, holding the liquid sample in its place. Thin mica sheets ($d=20-30\ \mu$m) were used as windows, since this material exhibits very little scattering in the q range under investigation. Apart from the window the other main source of background scattering is the collimating slits themselves. Their contribution was reduced to a minimal level by careful alignment. The remaining slit scattering is strongly confined to the vertical and horizontal direction, according to the slit position, and is small along the diagonals of the detector area. Therefore, for the analysis only the data points collected in a sector covering $\pm 9°$ around the detector diagonals were used. The use of a two-dimensional detector yet has another advantage. Occasionally local damage on the window could be observed giving rise to a stronger, anisotropic scattering pattern. All measurements were checked for the absence of any such pattern and otherwise disregarded. In that way the complete background scattering could be reduced to a level below $I_A(q)\approx 0.5$, even at the lowest q values. Figure 1 shows the scattering due to slit scattering and the added contributions of slit scattering and scattering by a set of mica windows. With the short wavelength of $\lambda=1$ Å a sample of 10 mm thickness could be used, which again improves the signal to background ratio compared to a setup using a conventional copper x-ray tube. The transmission of the sample was 30%.

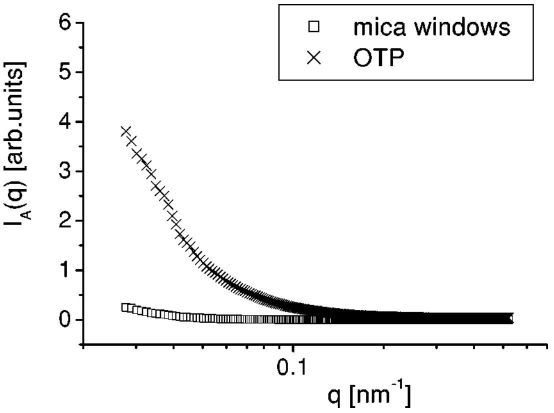

FIG. 2. Scattering due to long-range density fluctuations, ×, at a temperature of 293 K in comparison to the background contribution, □.

III. SAMPLES

Orthoterphenyl was purchased from FLUKA and purified by distillation. The sample holder consisted of a piece of stainless steel with a hole of 6 mm diameter, covered on both sides by a thin mica sheet and sealed with an O ring. It was filled at 80°C, which is above the melting temperature ($T_m=56°$C) of orthoterphenyl, and subsequently cooled to room temperature. Under these conditions crystallization is usually avoided. Occasionally crystallization, caused by heterogeneous nucleation occurred. If so, this could be easily observed, since a polycrystalline sample scatters light strongly giving rise to a white color. Also the small-angle x-ray scattering signal rises by about three orders of magnitude. Once crystallization sets in the sample is fully crystallized within some 10 min. The data presented here are taken from supercooled samples with no sign of crystallization present. Light scattering experiments were taken with an ALV (Langen, Germany) goniometer and an argon-ion laser with $\lambda=514$ nm. The scattering intensity was calibrated against a toluene standard sample.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the scattering caused by the long-range density fluctuations in comparison to the background scattering and demonstrates that the background has been reduced sufficiently to render the long-range density fluctuations visible. In the entire q range the background is at least by a factor of 10 weaker than the signal under investigation. Since the scattering from one set of mica windows to the next varies to some extent a background subtraction was not performed. Figure 3 shows the USAXS data in a double logarithmic representation together with the isotropic part of the scattering cross section as measured in a light scattering experiment. The x-ray data taken fill the gap between conventional small-angle x-ray scattering and light scattering ex-

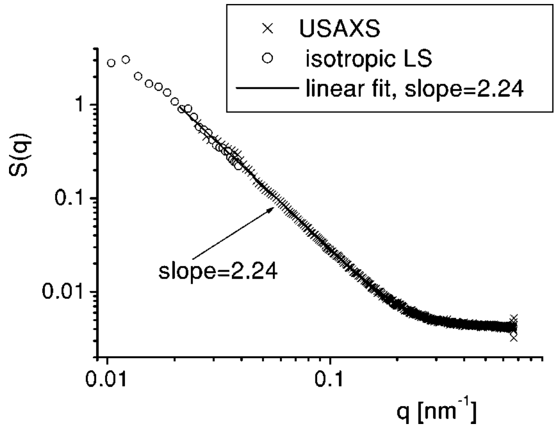

FIG. 3. USAXS scattering, ×, due to long-range density fluctuations on double logarithmic scale together with light scattering data, ○, both measured at a temperature of 293 K. In the intermediate q range $S(q)$ follows a power law.

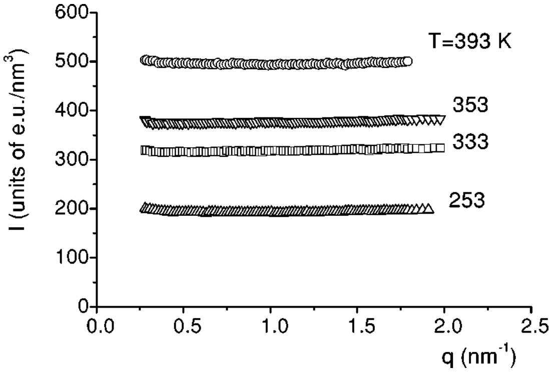

FIG. 4. Scattered intensities (in electron units/nm^3) of OTP measured by the Kratky Compact camera for different temperatures [25].

periments. Indeed the scattering signals observed with the two techniques are comparable. In order to compare the light scattering data with the scattered intensity of the USAXS experiment we introduce the static structure factor related to the Fourier transformed density fluctuation $\delta\rho(q)$ of a one-component liquid by

$$S(q)=\frac{1}{N}\langle\delta\rho(q)\delta\rho(-q)\rangle, \tag{2}$$

where N is the number of molecules in the scattering volume V. In static light scattering experiments (LS) the Rayleigh ratio $R(q)$ (in cm^{-1}) is used which is defined by

$$R(q)=\frac{I_s(q)}{I_0}\frac{d^2}{V}, \tag{3}$$

where d is the distance to the detector, and $I_S(q)$ and I_0 are the scattered and incident intensities, respectively. There is a simple relation between $R(q)$ and $S(q)$,

$$R(q)=\rho\frac{d\sigma}{d\Omega}S(q), \tag{4}$$

where ρ is the mean number density of molecules, and $d\sigma/d\Omega$ is the scattering cross section per molecule (in cm^2). Light scattering theory [24] yields

$$\frac{d\sigma}{d\Omega}=\frac{4\pi^2n^2}{\lambda^4}\left(\frac{\partial n}{\partial\rho}\right)^2, \tag{5}$$

where λ is the wavelength of the incident beam and n is the mean refractive index. In the case of x-ray scattering in the small-angle range, where the structure factor of the molecules is $F(q)\approx Z_m$, one obtains for the scattering cross section per molecule,

$$\frac{d\sigma}{d\Omega}=r_e^2Z_m^2, \tag{6}$$

where Z_m is the number of electrons in the molecule. r_e is the classical radius of the electron equal to 2.818 $\times10^{-13}$ cm. As it follows from statistical fluctuation theory [22] for a one-component liquid without long-range density fluctuations the limit of $S(q)$ for $q\rightarrow0$ is given by

$$\frac{\langle\delta N^2\rangle}{N}=\lim_{q\rightarrow0}S(q)=\rho k_BT\beta_T(T)\equiv S_0(T), \tag{7}$$

where β_T is the isothermal compressibility. In such cases where no q dependence of the scattered intensity is observed, the Rayleigh ratio of the scattered light is given by

$$R_0(T)=\frac{4\pi^2n^2}{\lambda^4}\rho\left(\frac{\partial n}{\partial\rho}\right)^2S_0(T). \tag{8}$$

Accordingly, for x-ray scattering we have

$$R_0(T)=r_e^2Z_m^2\rho S_0(T). \tag{9}$$

As was already mentioned, the SAXS intensities of OTP in the conventional q range (0.2 nm$^{-1}<q<2$ nm^{-1}) were found to be in good agreement with Eq. (9). Figure 4 shows the scattered intensities in this q range for OTP measured with a Kratky Compact camera [25]. The primary beam intensities were determined in absolute units by means of the moving slit method [26]. For room temperature S_0 (293 K) was determined to be 5.6×10^{-3} corresponding to an isothermal compressibility of $\beta_T\approx5.3\times10^{-4}$ MPa^{-1}, in a good agreement with the literature data [27]. In contrast, the light scattering intensity for $q<2\times10^{-2}$ nm^{-1} was much higher than expected from Eq. (8). In Figs. 2 and 3 it is shown that this strong excess intensity is also observed by ultrasmall-angle x-ray scattering.

Since the absolute values of the scattered x-ray intensities in the USAXS measurements are not very well defined, for experimental reasons we adjusted the tail ($q>0.4$ nm^{-1}) of the scattering curve by the values of $S_0(T)$ obtained from conventional SAXS measurements of OTP; see Fig. 4. The moving slit method yields more reliable absolute values than the Lupolen standard used for the USAXS measurements. (For adjustment the original USAXS values had to be shifted for 0.34 in the logarithmic scale.)

The USAXS scattering curve obtained from the adjusted $I_A(q)$ values matches well the structure factor $S(q)$ from the light scattering data in the overlapping q range; see Fig. 3.

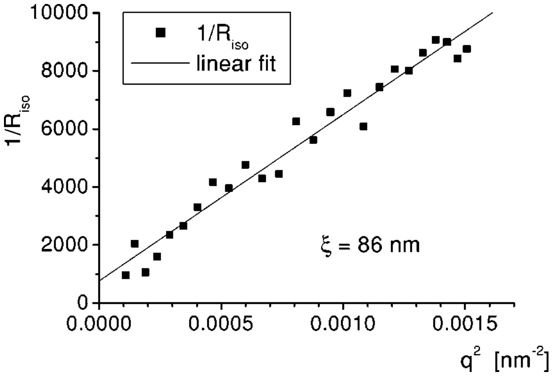

FIG. 5. Estimation of correlation length from light scattering data.

The structure factor $S(q)$ for the light scattering measurement was calculated from the measured Rayleigh ratio according to Eq. (4). The scattering cross section per molecule was determined by measurements of $n(T)$ and $\rho(T)$ and amounts for room temperature to $d\sigma/d\Omega = 4.33 \times 10^{-25}$ cm^2 using Eq. (5). As is shown in Fig. 3 the $S(q)$ values at $q < 0.2$ nm^{-1} for both light and x-ray scattering deviate significantly from the S_0 value expected for a simple liquid according to Eq. (7). The excess intensity is more than two orders of magnitude higher than the contribution from the isothermal compressibilitly. It must be caused by long-range density fluctuations. For x-ray scattering this conclusion is quite obvious, in the case of light scattering it is established by the fact that the depolarized scattered intensity in VH geometry does not show excess scattering.

In the intermediate q range between SAXS and LS the structure factor $S(q)$ follows a power law with a power close to -2. A best fit is obtained with a power of -2.2; see Fig. 3. This shows that the excess scattering signal is not caused by large objects of different density with a sharp interface, which would lead to the well known Porod behavior, $I(q) \propto q^{-4}$ for $qR >> 1$. Here R is a typical value for the size of the objects. Although formally a power law scattering can also be explained by single particle scattering assuming a broad, power law size distribution, we interpret the observed excess scattering as an indication for a structure factor reflecting the correlated fractal arrangement of regions of higher density. The correlation extends up to a certain length scale ξ, which can be estimated from the q dependence of the light scattering data. For small q they can be analyzed in terms of an Ornstein-Zernike approximation,

$$I(q) = \frac{I_0}{1 + q^2\xi^2}. \tag{10}$$

Figure 5 shows the light scattering data in a representation linearizing expression (10). The resulting length ξ is 86 nm, which can be regarded as an estimation of the correlation length even if the q exponent is -2.2 instead of -2.

The main objective of the present paper is the observation of the strong q dependence of $S(q)$ in the USAXS range in quantitative agreement with the light scattering data. A well developed theory for an explanation of the long-range density fluctuation is still missing. At present it is believed that those fluctuations are caused by the coexistance of local structures with energetically preferred configurations (''glassy clusters'') on one hand and ''fluidlike'' regions on the other hand [15,16]. The different dynamic states couple to the density fluctuations. During annealing at temperatures above T_g the glassy clusters aggregate and form extended secondary clusters with a fractal structure. In previous LS studies [16,18–21,28] it has been shown that the excess intensity $I(q)$ and the correlation length ξ depend strongly on the thermal history with characteristic equilibration times much longer than the α-process relation time. It may be mentioned that some recent results of molecular dynamics simulations qualitatively support the scenario described above. For Lennard-Jones liquids it has been shown that spatial correlations between the displacements of molecules become increasingly long ranged if the mode-coupling temperature T_c is approached [29]. Other simulations of monoatomic liquids revealed the growth and aggregation of clusters with icosahedral topology [30]. The number of icosahedral clusters increases with decreasing temperature. In recent simulation studies [31] of monoatomic systems the existence of two amorphous states was clearly shown. The average potential energies per atom differ for about 7%, where the energy of the more densely packed phase is about 1–2% higher than in the bcc crystalline state.

V. CONCLUSIONS

The structure factor of a fragile glass-forming liquid, OTP, has been measured in a previously inaccessible q range between the conventional LS and SAXS q ranges using the low-angle beamline at ESRF. At low q (overlapping with the LS q range) this structure factor exhibits an excess scattering consistent with the LS data. At high q (overlapping with the SAXS Kratky camera q range) this structure factor decays to a plateau defined by the isothermal compressibility, in agreement with the previous SAXS studies [16]. Thus the long-range density fluctuation in glass-forming liquids can be observed both in the isotropic component of scattered light and in the USAXS, provided the proper q range is covered. The power law q dependence of the scattered intensity in the intermediate q range indicates that the excess scattering is not due to large bulky dense regions but to fractal aggregates of denser domains.

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