Structural fluctuations in glass-forming liquids: Mössbauer spectroscopy on iron in glycerol

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Mössbauer absorption spectra of $^{57}Fe^{2+}$ dissolved in a glycerol-water mixture have been measured over a wide temperature range (80–275 K). In the supercooled liquid state the shapes of the spectra depend strongly on temperature. The Mössbauer spectra can be fit with jump diffusion with a Cole-Davidson distribution of fluctuation times. The results are in agreement with those obtained from dielectric and ultrasonic volume relaxations, proving that the α relaxation of viscous liquids is responsible for the line broadening of the spectra. From the temperature dependence of the integrated area of the Mössbauer spectrum a second dynamic process is inferred. Its activation energy of 31.4 kJ/mol is typical for the β relaxation.

INTRODUCTION

A supercooled liquid is obtained by rapid cooling of the liquid through the equilibrium freezing temperature, thereby avoiding nucleation into a crystal. The viscosity in this state increases drastically with decreasing temperature. A pronounced deviation from the Arrhenius law $\eta = \eta_0 \exp(E/k_B T)$ is found for the viscosity (and other transport coefficients).[1,2] A description of the temperature dependence which is valid over many orders of magnitude in η is given by the Vogel-Fulcher-Tammann-Hesse (VFTH)[3-5] equation

$$\eta = \eta_0 \exp[E/k_B(T - T_0)] \qquad (1)$$

or the expression[6-8]

$$\eta = \eta_0 \exp(T_0^2/T^2) . \qquad (2)$$

A glass is formed when the viscosity approaches such large values that the liquid behaves like a solid. The "glass transition" is usually defined to occur at the temperature T_g where the viscosity reaches 10^{13} Poise. Although appearing like a thermodynamic phase transition the glass transition may be a purely kinetic process.[2] The glass is in a nonequilibrium state and its properties depend on its thermal history.

The dynamic properties of supercooled liquids and glasses have been investigated by various experimental methods. In particular, measurements of the dielectric relaxation[9-15] and ultrasonic viscoelastic relaxation[12,16-18] provide detailed information about the time scales of the motions involved. The presence of a very broad absorption band extending over several decades in frequency is a fundamental property of viscous liquids. Actually such a band arises from two different processes, usually referred to as the α and β relaxations.

The α relaxation is the dominant process in the supercooled liquid. The temperature dependence of the peak position ω^α of the α band coincides with the one found for the viscosity;[9] the α process governs the viscous flow of the supercooled liquid, and cooperative rearrangements of large clusters of atoms and molecules are involved.[2] The β band is found at a higher frequency than the α band and is much weaker near T_g.[13,14] Usually it cannot be resolved from the α relaxation in the supercooled liquid state and thus is mainly studied in the glass region. The peak position ω^β follows the Arrhenius law, but the β relaxation times also show a broad distribution. The β process is presumably due to local movements of clusters of a few atoms.

Several investigations of supercooled liquids using Mössbauer spectroscopy have been performed.[19-25] The absorption spectra that were obtained with ^{57}Fe ions dissolved in the samples all exhibit the same qualitative features: broad diffusional lines are observed, the widths of which increase with increasing temperature, accompanied by a drastic apparent loss of integrated area of the spectra. The detailed interpretations, though, differ from author to author. The spectra were variously explained by continuous diffusion,[21] superpositions of continuous and single mode jump diffusion,[14] and combinations of diffusion and bound modes.[23-25]

The relaxation properties of supercooled liquids and glasses described above suggest a different interpretation. According to the fluctuation-dissipation theorem[26] the Mössbauer nucleus in the viscous liquid should be sensitive to fluctuations that correspond to the α relaxation found in dielectric and ultrasonic experiments. The presence of a broad spectrum of relaxation times implies that the usual treatment of the Mössbauer spectra of supercooled liquids in terms of a few Lorentzian lines is inappropriate.

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Thus we decided to revisit the Mössbauer effect in glycerol, a substance for which a large amount of complementary information from other investigations is available. The velocity window for the Mössbauer spectra was extended up to ± 60 mm/s in order to follow the broadening of the line over a significant temperature range. For the interpretation of the spectra we introduce a simple jump diffusion model with distributed fluctuation times consistent with the results obtained from relaxation experiments.

A DIFFUSION MODEL WITH DISTRIBUTED JUMP TIMES

In the high-temperature limit the transient response of a glass-forming liquid to an electrical or mechanical perturbation is exponential in time and is described by the conventional Debye relaxation. In contrast, the supercooled viscous liquid shows markedly nonexponential time dependence. The relaxation function $\phi_r(t)$ can generally be formulated with a weight distribution $g(\tau)$ of exponential relaxations:

$$\phi_r(t) = \int g(\tau) e^{-t/\tau} d(\ln \tau) \ . \tag{3}$$

In order to model the distribution of relaxation times various expressions have been introduced for the function $g(\tau)$. Their properties are discussed by Macdonald.[27] For the present study we use the Cole-Davidson distribution, allowing us to compare our data with results from dielectric relaxation and ultrasonic volume relaxation experiments previously analyzed in terms of this distribution.[12]

Davidson and Cole showed that their dielectric relaxation data on glycerol were in agreement with the following distribution function:[9]

$$g(\tau) = \begin{cases} \dfrac{\sin\beta\pi}{\pi} \left[\dfrac{\tau}{\tau_c - \tau} \right]^\beta \ , & \tau < \tau_c, \\[4mm] 0 \ , & \tau > \tau_c. \end{cases} \tag{4}$$

This distribution function increases monotonically from small times to a maximum time τ_c. The parameter β $(0 < \beta < 1)$ determines the width of the distribution. A Lorentzian corresponds to $\beta = 1$, i.e., to a single relaxation time. The distribution broadens with decreasing β. The Cole-Davidson distribution gives good agreement with relaxation data for a large number of glass-forming liquids including glycerol-water mixtures (unless the water content exceeds 30% mole fraction[15]).

We now calculate the Mössbauer spectrum for a simple jump diffusion model including a distribution of jump times according to Eq. (4). Let an atom rest at a given site for a time τ before jumping to another position in a time τ_1, with $\tau_1 \ll \tau$. We assume no correlations between one jump and the next. The incoherent scattering law $S(\mathbf{k}, \omega)$ can be calculated following the formalism given by Singwi and Sjölander:[28,29]

$$S(\mathbf{k}, \omega) = \frac{\tilde{p}(\omega)}{1 + \tilde{p}'(\omega) \tilde{h}(\mathbf{k})} + \text{c.c.} \tag{5}$$

The energy and momentum transfers are given by $\hbar\omega$ and $\hbar\mathbf{k}$, respectively. The Fourier transform of the probability $p(t)$ to stay at a given lattice site is $\tilde{p}(\omega)$ and the Fourier transform of the time derivative $p'(t)$ is denoted by $\tilde{p}'(\omega)$. The Fourier transform of the probability $h(\mathbf{r})$ to surmount a distance $\mathbf{r}$ when jumping is given by $\tilde{h}(\mathbf{k})$. We now introduce the Cole-Davidson distribution according to Eq. (4) and distinguish two different cases. (i) The probability $p(t)$ is taken as $e^{-t/\tau}$ with a distinct fluctuation time τ for every atom. We then assume a distribution of jump processes with the weight function $g(\tau)$ given by Eq. (4) and obtain

$$S(\mathbf{k}, \omega) = \frac{-\text{Im}(1 + i\omega\{\tau_c / [1 - \tilde{h}(\mathbf{k})]\})^{-\beta}}{\pi\omega} \ . \tag{6}$$

(ii) The fluctuation times are distributed for the different steps of each atom. Then both $p(t)$ and $p'(t)$ take the form of distributions of exponentials as given in Eq. (3) with $g(\tau)$ from Eq. (4). After performing the Fourier transform and inserting into Eq. (5) we arrive at the expression

$S(\mathbf{k}, \omega)$

$$= \frac{-\text{Im}(1 + i\omega\tau_c)^{-\beta}[1 - \tilde{h}(\mathbf{k})]/\pi\omega}{1 - 2\,\text{Re}(1 + i\omega\tau_c)^{-\beta}\tilde{h}(\mathbf{k}) + (1 + \omega^2\tau_c^2)^{-\beta}\tilde{h}^2(\mathbf{k})} \ . \tag{7}$$

Small jump distances cause a narrower line than large ones. While in case (i) the line narrows without changing its overall shape, in case (ii) both the width and shape of the line are influenced by the jump distance r. For large jump distances $(|r| \gtrsim \pi/|\mathbf{k}| = 0.43$ Å for ^{57}Fe) $\tilde{h}(\mathbf{k})$ approaches 0. Then both Eqs. (6) and (7) lead to the expression

$$S(\mathbf{k}, \omega) = \frac{-\text{Im}(1 + i\omega\tau_c)^{-\beta}}{\pi\omega} \ . \tag{8}$$

Using the thin-absorber approximation, the Mössbauer transmission spectrum $T(\omega)$ can be calculated by convoluting the absorption $A_0(\omega)$ in the absence of motion with the incoherent scattering law $S(\mathbf{k}_0, \omega)$,

$$T(\omega) = 1 - A_0(\omega) * S(\mathbf{k}_0, \omega) \ . \tag{9}$$

Here, $|\mathbf{k}_0| = 2\pi/\lambda$, wavelength $\lambda = 0.86$ Å for ^{57}Fe radiation.

EXPERIMENTAL

In the preparation of the samples, $FeCl_2$ was dissolved in water. Small amounts of hydrochloric acid were added to adjust the pH to 1.8 to prevent oxidation of the iron in the sample. Dry glycerol was added. The mixture was stirred for ten days at 70 °C to ensure homogeneity of the samples. Three glycerol-water solutions (water content 6.5 wt% $\cong 26.2\%$ mole fraction) were prepared differing in the iron content. Sample A was made from ^{57}Fe-enriched ferrous chloride to contain 0.84 mg/cm^2 ^{57}Fe. Sample B was also made from ^{57}Fe-enriched $FeCl_2$ but contained one-tenth as much ^{57}Fe. Sample C contained

the same amount of ^{57}Fe as sample B and the same total amount of iron as sample A. The solutions were encapsulated in air-tight sample holders and stored at 250 K until used. For the Mössbauer measurement a bath cryostat was employed which kept the temperature constant within ±0.5 K. The samples were cooled to 80 K at a rate of approximately 40 K/h. Subsequently, series of Mössbauer spectra were collected in appropriate temperature intervals. The experiments were done with a ^{57}Co Rh source mounted on an electromechanical driving system capable of source velocities as high as ±500 mm/s in a sinusoidal mode. The transmitted gamma-quanta were detected by a xenon-filled proportional counter. The data were stored in a multichannel analyzer in 2048 channels. Pulse-height spectra of the transmitted intensity were taken to determine the recoilless fraction.

RESULTS

To avoid large thickness corrections in the determination of the areas of the Mössbauer spectra, we took samples B and C for the experiments at temperatures below 240 K. The velocity window of the spectrometer was set to ±8 mm/s. The absorption areas were obtained from the spectra and corrected for the thickness effect according to the method of Lang.[30] Only minor corrections were necessary. The areas were set proportional to the Lamb-Mössbauer factor $f = \exp(-k_0^2 \langle x^2 \rangle)$. To obtain an absolute scaling, the mean-squared displacements were extrapolated to 0 K. The pedestal at 0 K was subtracted from the $\langle x^2 \rangle$ values. From the pedestal the iron con-

tent was calculated. Agreement within 2% to the known amount of iron in the sample shows the reliability of this scaling procedure which has often been used for the determination of $\langle x^2 \rangle$ values from protein samples.[31,32] The temperature dependence of the $\langle x^2 \rangle$ values is displayed in Fig. 1.

Mössbauer absorption spectra of sample A were measured between 250 and 275 K. A velocity window of ±60 mm/s was suitable for these temperatures. Some of the spectra are shown in Fig. 2. We performed least-squares fits using the Cole-Davidson function according to Eqs. (8) and (9). The quadrupole splitting is obscured by the strong diffusional broadening between 265 and 275 K. Therefore, we extrapolated this parameter from the temperature dependence observed at the lower temperatures. The Mössbauer absorption in the absence of diffusional motion $A_0(\omega)$ was taken as a Lorentzian of width 0.4 mm/s (FWHM) in accord with the low-temperature spectra of samples B and C. The convolution integral was evaluated numerically. In a first step, the spectra at six different temperatures were fitted according to the Cole-Davidson function [Eq. (8)], treating the line area A, limiting time τ_c, and the distribution width parameter β as free parameters. The results are given in Table I. Good agreement between theory and experimental data was obtained. From dielectric relaxation[11] and viscoelastic relaxation experiments[12] a fairly constant β parameter is expected between 220 and 270 K, increasing up to a value of 1 at higher temperatures. This parameter can be determined precisely only with measurements over several orders of magnitude in time (or energy). Unfor-
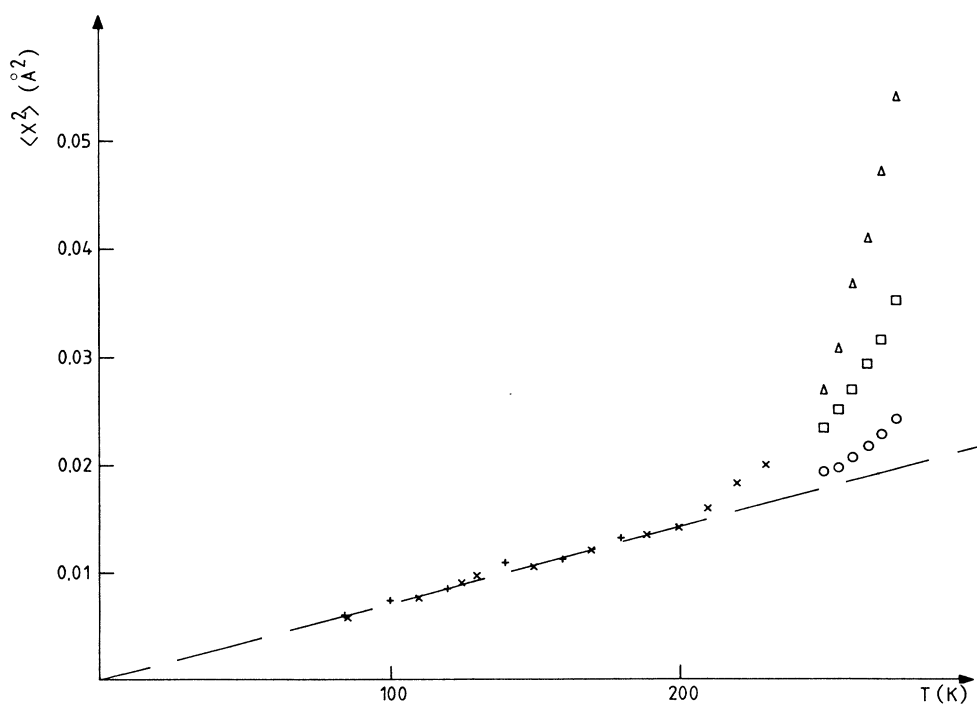

FIG. 1. Mean-squared displacements, $\langle x^2 \rangle$, for Fe^{2+} in glycerol-water as a function of temperature. Crosses (x): sample B, crosses (+): sample C. Triangles: sample A, $\langle x^2 \rangle$ was determined from the area of the narrow Lorentzian of a two-Lorentzian fit; squares: sample A, $\langle x^2 \rangle$ was determined from the sum of the areas of a two-Lorentzian fit; circles: sample A, $\langle x^2 \rangle$ was determined from the area of the Cole-Davidson function with $\beta = 0.28$ [Eqs. (8) and (9)].

TABLE I. Average relaxation times $\tau_{av} = \beta\tau_c$ and β parameters obtained from the Mössbauer spectra on glycerol.

$T(K)$	β	τ_{av}(ns) (β var.)	τ_{av}(ns) (β=0.28)	τ_{av}(ns) (β=0.32)
250	0.65	34.5	30.2	31.0
255	0.48	16.2	13.3	14.0
260	0.33	6.5	6.0	6.5
265	0.26	2.8	2.9	3.1
270	0.20	1.1	1.4	1.5
275	0.34	0.79	0.69	0.76

tunately, Mössbauer spectroscopy supplies information only in a narrow energy window. As a consequence the β values from the fits scatter considerably. For our fits we use a constant parameter β=0.28, which is the average of the four higher temperatures. The β values found for 250 and 255 K were excluded because they are markedly larger than the other four values and are suspect for two reasons: (i) the absorption is largest; distortions of the

lines are expected. (ii) The jumping distance is expected to be smallest; the assumption of large jumping distances and thus Eq. (8) may be invalid. In addition to β=0.28 we also fit our spectra with β=0.32 which is the value reported from ultrasonic volume relaxation.[12] Table I shows that the average relaxation times $\tau_{av} = \beta\tau_c$ are not very dependent on the choice of β. From the areas obtained with the Cole-Davidson function we calculated mean-squared displacements. They are shown in Fig. 1 together with $\langle x^2 \rangle$ values from fits to a sum of two Lorentzians with different widths. The data from sample A were normalized to the low-temperature data (samples B and C) so as to account for the different amounts of ^{57}Fe.

DISCUSSION AND CONCLUSIONS

Figures 1 and 2 display the typical temperature dependence of Mössbauer spectra from supercooled liquids. Above a certain temperature, a drastic apparent loss of area occurs in a narrow energy window. In addition, a strong diffusional broadening of the Mössbauer line is observed. The model applied to the spectra has to explain both of these features.

We first consider the line shapes. Figure 2 shows that the observed lines are well described by a diffusion model with distributed jump times. The average fluctuation times obtained from the fits of the Mössbauer spectra are compared with relaxation times from dielectric and ultrasonic volume relaxation in Fig. 3. The dielectric relax-
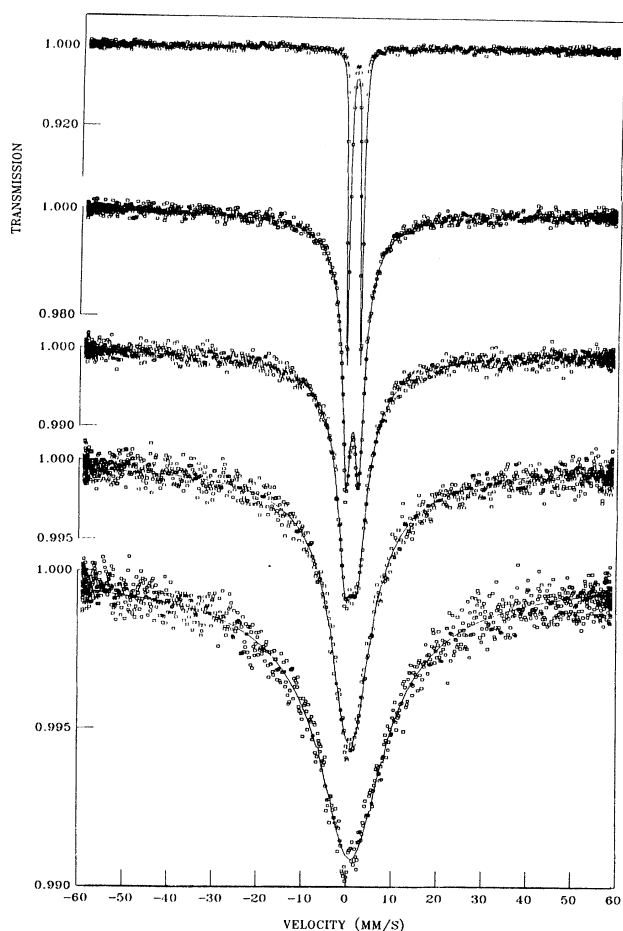

FIG. 2. Mössbauer spectra from Fe^{2+} in glycerol-water (sample A). From top to bottom: T=220, 260, 265, 270, and 275 K. The solid lines are obtained from least-squares fits of a Cole-Davidson distribution with β=0.28 [Eqs. (8) and (9)]. See the text for details.
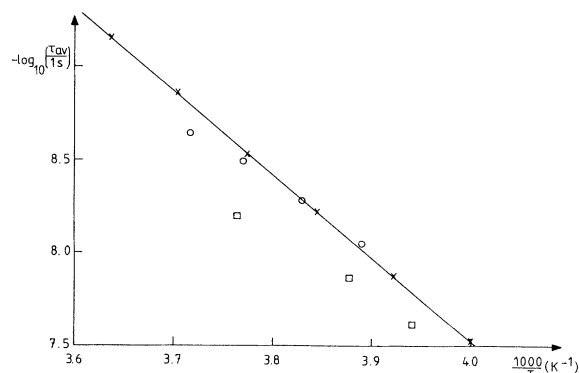

FIG. 3. Arrhenius plot of the average relaxation and fluctuation times, τ_{av}. Squares: dielectric relaxation (Ref. 10), circles: ultrasonic volume relaxation (Refs. 10 and 12), crosses: Mössbauer spectroscopy (see Table I, β=0.28).

ation data[10] are interpolated to the water content of our samples (26.2% mole fraction). From these data and the ratio τ_d/τ_v of the dielectric and volume average relaxation times,[12] volume relaxation times have also been calculated. A good agreement between volume—or structural—relaxation and Mössbauer effect relaxation times is found. The motion of the Mössbauer nuclei is thus closely coupled to the structural relaxation process. The dielectric times are larger by roughly a factor of 2. Assuming the structural relaxation to be the rate-determining step for the dielectric relaxation, the dielectric response is expected to be slower.[12] An Arrhenius fit to the Mössbauer data in Fig. 3, shown as a solid line, yields an activation energy $E = 88$ kJ/mol and a preexponential factor $A \cong 10^{26}$ s^{-1}. These values are characteristic for the α relaxation above T_g and imply that instead of the Arrhenius law a relation of the form of Eq. (1) or Eq. (2) should be used.

From the mean-squared displacements displayed in Fig. 1, one can distinguish two regions with distinctly different temperature dependences. Up to 200 K the $\langle x^2 \rangle$ values exhibit the linear dependence typical of harmonic solids. These data were obtained from samples B and C. While the content of ^{57}Fe in the two samples is similar, the total amount of iron differs by about a factor of 20. Nevertheless, in both cases the same slope of 7.1×10^{-5} Å^2/K occurs. Thus the thermal motions in the glycerol-water mixture are not very sensitive to small amounts of impurities. Above 200 K the mean-squared displacements significantly deviate from the linear temperature dependence as additional motions are thermally activated. While for samples B and C the $\langle x^2 \rangle$ values were calculated from the experimental spectral areas, those for sample A have been determined from the areas obtained from the fits. The $\langle x^2 \rangle$ values computed with the Cole-Davidson function are much lower than those of the Lorentzian fit, because the Cole-Davidson distribution is very broad and has more area away from the center of the spectrum. It is reasonable to assume that the harmonic thermal vibrations observed in the low-temperature region are also present at higher temperatures. If our jump model described the diffusional motions completely, the mean-squared displacements obtained from the fits would coincide with the extrapolation of the low-temperature behavior. Figure 1 shows, however, a small deviation. The deviation can be explained by assuming a second class of motions with higher frequencies. We calculated $\langle x^2 \rangle$ values by subtracting the contribution from the harmonic solid-state vibrations, i.e., the $\langle x_v^2 \rangle$ values represented by the dashed line in Fig. 1. Figure 4 shows an Arrhenius plot from which an activation energy of 31.4 kJ/mol is determined, a reasonable value for the β relaxation or secondary relaxation. According to Johari,[14] the β process should have an Arrhenius energy similar to the processes seen at high temperatures, where the viscosity of the liquid is several centipoises. Around 150 °C an Arrhenius energy of 32 kJ/mol has been reported for glycerol.[33] The β relaxation does not show up in the Mössbauer spectrum at lower temperatures, where it should produce quasielastic lines in the window of observation, because of the very
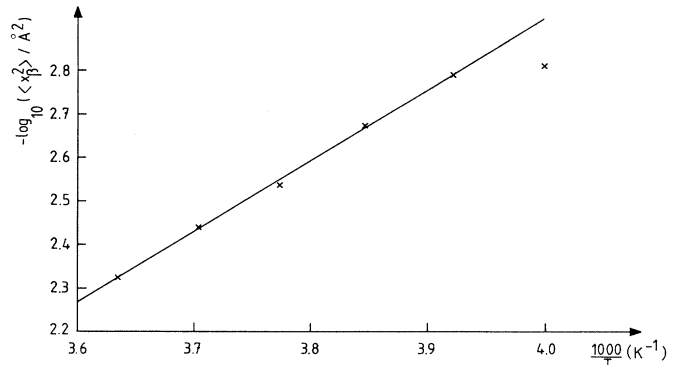

FIG. 4. Arrhenius plot of $\langle x_\beta^2 \rangle$, the contribution from the β process to the mean-squared displacements. Solid line: Least-squares fit to the data, the point at 250 K was excluded because the effective absorber thickness was too large.

small area associated with this process. For example, the extrapolation of the Arrhenius plot to 200 K gives a contribution of the β process to the mean-squared displacement $\langle x_\beta^2 \rangle$ of only 5×10^{-5} Å^2.

The present study shows that ^{57}Fe nuclei dissolved in supercooled liquids probe fluctuations corresponding to the well-known relaxation properties of these substances. Mössbauer experiments are performed on a linear energy scale. So a large velocity window is needed in order to discover the broad distribution in relaxation times. The Mössbauer effect has an intrinsic energy resolution Γ that is determined by the lifetime τ_N of the excited nuclear level. If the Mössbauer nucleus is subject to motions with characteristic times less than τ_N, the energy transfer is too small to be resolved against the intrinsic line shape of the sample in the absence of motion. If we deal with broad distributions of fluctuation times, the low-frequency part can still be covered in the narrow line, while high-frequency tails of the distribution already escape from the energy window. We actually observe such a behavior. Above 200 K there is a clear decrease in area in addition to the decrease due to thermal vibrations. Up to 250 K, however, the contribution of this distribution is too small to be extracted unambiguously. At temperatures between 250 and 275 K the dominant part of the distribution is well resolved in the velocity window. Above 275 K spectra are too difficult to measure because of the small intensities of the lines.

Similarities between glass-forming liquids and proteins have been stressed in recent papers.[34–37] In proteins, too, broad distributions of relaxation times are observed. Mössbauer spectra from proteins exhibit line broadenings that resemble those found in glycerol.[19] A paper discussing the glasslike behavior of proteins as seen by Mössbauer spectroscopy has been submitted.[38]

ACKNOWLEDGMENTS

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