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Fast dynamics of glass-forming glycerol

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The vibrational and relaxational dynamics of glycerol has been measured by incoherent neutron scattering for energy transfers from some 10 μeV to several 10 meV, and for temperatures from 4 to 413 K. On heating towards and above the glass transition, scattering from low-frequency vibrations shows an unspectacular increase that is consistent with ultrasonic data. We propose using the vibrational density of states for calculating the Fourier transformed time correlation function $S(q,t)$ without the cutoff usually imposed by the kinematics of neutron scattering. For high temperatures and low frequencies, structural relaxation is well described by the empirical Kohlrausch law. There is no extended crossover region between vibrations and structural relaxation.

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I. INTRODUCTION

On time scales of nanoseconds or longer, the glass transition is characterized by the freezing of structural relaxation. Microscopic investigations focus on the question of how relaxational motion decouples from vibrational modes on a picosecond scale. In a number of fragile liquids [1,2], this crossing over seems to be correctly described by the scaling laws of mode coupling theory [3,4]. Other crossover scenarios have been considered in recent studies of polymer dynamics [5–7].

In a Letter [8] we have reported on neutron and light scattering experiments in glycerol. The associated liquid glycerol [$C_3H_5(OH)_3$; $T_g = 185\,\mathrm{K}$, $T_m = 291\,\mathrm{K}$] with its ability to form multiple hydrogen bonds has been extensively studied as a model for a weak network that is intermediate between fragile and strong glass formers on an Angell plot [9].

Some of the most detailed predictions of mode coupling theory are based on an asymptotic expansion of the dynamic susceptibility around the minimum that separates structural relaxations on the low-frequency side from vibrational excitations at high frequencies. While the scaling behavior of glycerol in many respects resembles the mode coupling β relaxation, a more quantitative analysis made clear that asymptotic exponents violate constraints imposed by the theory.

In this paper, we present our neutron scattering experiment in more detail. We concentrate on the asymptotic regimes that were not considered in the Letter: vibrations on short time scales (Secs. III–V), and structural relaxation in the opposite limit of long times (Sec. VI). In both cases our data are in partial contradiction with results reported for other, mainly polymeric, glass formers.

II. SCATTERING EXPERIMENT

The neutron cross sections of our samples are dominated by incoherent scattering from hydrogen. Glycerol is a polyalcohol with three OH groups per molecule. Since we are not primarily interested in the dynamics of hydrogen bonds, we used a partially deuterated sample glycerol-D_3 ($C_3H_5(OD)_3$) so that incoherent scattering can be ascribed to self-correlations of atoms in the molecule's backbone. For comparison, a few scans were taken with the inverse sample glycerol-D_5 ($C_3D_5(OH)_3$). If not stated otherwise, displayed data are for glycerol-D_3. Partially deuterated glycerol was prepared by exchange of glycerol-D_0 and glycerol-D_8 with D_2O and H_2O, respectively. The material was distilled twice and then filled into sealed aluminum containers under argon atmosphere.

Neutron scattering experiments were performed on the time-of-flight spectrometer Mibémol at the reactor Orphée of the Laboratoire Léon Brillouin, CEN Saclay, France. Using cold neutrons with $\lambda = 8.5\,\text{Å}$ a resolution of $40 - 50\,\mu\mathrm{eV}$ [full width at half maximum (FWHM)] was achieved at detector angles 2θ ranging from 38° to 141°. The dynamic range will be discussed in more detail in Sec. IV (Fig. 5).

There were 51 groups of three ^{3}He detectors each, and neutrons were counted in 508 time channels. So we obtained huge raw data sets with low count rates per channel, and the first task was to condense the information into a reasonable number of data points. We retained 16 detector groups, covering intervals of 3°–6°. We regrouped as many time channels into a single data point as was necessary to keep the relative errors below a bound of typically 2×10^{-3}.

The conversion to $S(2\theta,\omega)$ and the subtraction of container and background scattering were straightforward. Spectra were normalized to glycerol-D_3 at 4 K; by comparison with a vanadium standard it was ensured that coherent contributions in glycerol-D_3 do not amount to more than 10%. In the other sample glycerol-D_5 there is an additional 30% elastic scattering in the neighborhood of the structure factor maximum (which is located at $q = 1.44\,\text{Å}^{-1}$ for glycerol-D_8).

Because of low count rates, we had to use relatively thick samples. The measured transmission was 77.5%. Hollow cylindrical sample geometry was chosen in order to keep self-absorption and unwanted scattering as isotropic as possible. Nevertheless, multiple scattering must be expected to present a major problem.

In our analysis of the vibrational behavior (Sec. III), we were guided by analogy with the case of *o*-terphenyl [10]: from a detailed Monte Carlo simulation the main effect of multiple scattering was found to be an isotropic redistribution of scattering intensity which does not alter spectral line shapes. As a first order correction we multiplied $S(2\theta,\omega)$ by the measured transmission.

It is less clear how multiple scattering affects relaxational spectra at higher temperatures. A simulation can be performed only if one succeeds in constructing a model $S(q,\omega)$ which reasonably extrapolates the measured data into a dynamic range which is not directly accessible by single scattering because of kinematic restrictions. So far, no attempts have been made in this direction.

Representative data, interpolated to a constant $q = 1.2\,\text{Å}^{-1}$, are shown in Fig. 1.

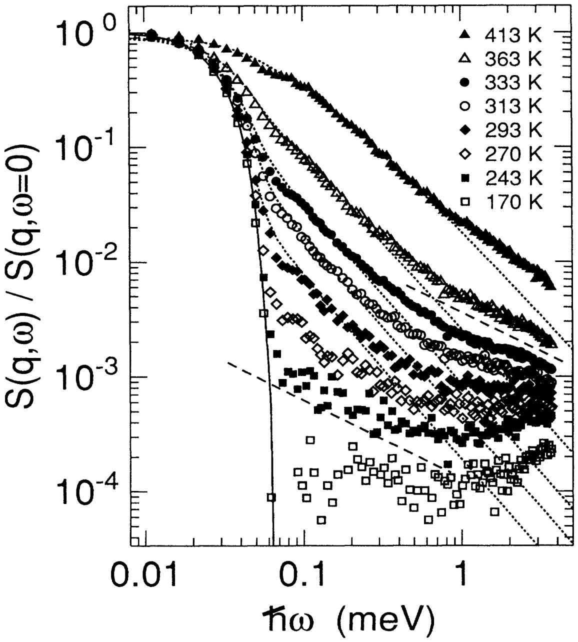

FIG. 1. Scattering law $S(q\omega)$ at $q = 1.2\,\text{Å}^{-1}$, for better presentation rescaled by $S(q,\omega{=}0)$. The measured resolution (solid line) is nearly ideal Gaussian. Note the exceptionally good signal-to-noise ratio of better than 10^{-4}. Dotted lines are Kohlrausch fits as discussed in Sec. VI. Above 333 K and below 243 K, the long dashes indicate the asymptotic slope ω^{a-1} (10) with $a = 0.32$ as found in the scaling analysis [8] referred to in Sec. V.

III. DENSITY OF VIBRATIONAL STATES

Incoherent neutron scattering from harmonic solids measures the density of vibrational states (DOS) $g(\omega)$. At finite values of q, however, $S(q\omega)$ is not simply proportional to $g(\omega)$ because in a significant number of all scattering events a neutron emits or absorbs more than one phonon. Quite different procedures for calculating $g(\omega)$ are in use

(i) In principle, the one-phonon cross section can be obtained by extrapolating $S(q\omega)$ to $q \to 0$.

(ii) After a Fourier transformation $\omega \to t$, the DOS is related to the scattering law by the simple relation

$$S(qt) = \exp\left[2W(qt) - 2W(q0)\right] \tag{1}$$

with the displacement correlation

$$2W(qt) = q^2 \left\langle u(0)u(t)\right\rangle = \frac{\alpha}{3}\int d\omega\, e^{-i\omega t}\frac{g(|\omega|)}{\beta}n(\omega)\,, \tag{2}$$

the Bose-Einstein occupation $n(\omega) = [\exp(\beta) - 1]^{-1}$, and the usual abbrevations

$$\alpha \equiv \frac{\hbar^2 q^2}{2Mk_BT} \quad \text{and} \quad \beta \equiv \frac{\hbar\omega}{k_BT}\,. \tag{3}$$

After calculating $S(qt)$, one can divide by the Fourier transform of the resolution function so that instrumental effects are deconvoluted. The backtransform of $\ln S(qt)$ is found to be numerically quite stable [11]. The procedure has the disadvantage that measured $S(2\theta,\omega)$ must be interpolated to constant q before a Fourier transform can be performed. As will be discussed in the next section, this inevitably restricts the accessible energy range, in our case to $\hbar\omega \lesssim 6\,\text{meV}$.

(iii) If $g(\omega)$ is represented by a simple mathematical model, multiphonon cross sections can be calculated analytically and then subtracted from the measured $S(2\theta,\omega)$ [12]. The accuracy of this method depends on the correct description of $g(\omega)$ by a few-parameter fit.

(iv) If the incoherent cross section is dominated by just one species of atom, the iterative procedure (iii) can be applied without intercalating a model fit: one can calculate the multiphonon corrections by numerical convolution of $g(\omega)$. This method which has been discussed in detail in our work on *o*-terphenyl [10] is found to be adequate for glycerol as well.

It has been observed in numerous experiments that inelastic scattering intensities are not proportional to $q^2 + O(q^4)$ as expected from (1) and (2) [10,12–15]. Deviations are ascribed to multiple scattering which redistributes intensity more or less uniformly in q [16]. For small q multiple scattering becomes dominant so that the extrapolation (i) is rather difficult to perform. In our iterative calculation (iv) we minimize the influence of multiple scattering by using data from large scattering angles only.

In Fig. 2, the resulting DOS is shown for both glycerol samples. A rather broad distribution of vibrational energies is found. A first maximum at 9 meV is followed by a second one at about 17 meV which might be attributed to internal motion of the carbon chain since it is seen only in glycerol-D$_3$. Above 20 meV, count rates are poor and the experimental data become less and less reliable. It appears that a significant number of modes lies even above 40 meV. If there were a need to study these excitations, one would have to use thermal instead of cold neutrons.

At small ω and in one-phonon approximation, the DOS is proportional to $\omega^2 S(q\omega)$. This means that low-energy modes which are measured with good precision appear with rather low weight in a plot of $g(\omega)$ vs ω. In the inset of Fig. 2 we therefore display $g(\omega)/\omega^2$. Again, there are significant differences between both samples. Most probably the additional scattering from glycerol-D$_5$ can be ascribed to fluctuations of the hydrogen bonds.

Many properties of a solid depend on its DOS. So we can relate our $g(\omega)$ to a number of other experiments.

(i) A first check of consistency can be made within the realm of neutron scattering. From (2), we see that the integral over $g(|\omega|)n(\omega)/\omega$ must reproduce the mean square displacement $\langle u^2(T)\rangle$. For a harmonic system, the displacement can be obtained from the elastic scattering intensity $S(q,\omega=0)=\exp(-q^2\langle u^2\rangle)$. In Fig. 3(a), we show $\langle u^2(T)\rangle$ as obtained on the backscattering spectrometer IN13 in the range $q = 3-5\,\text{Å}^{-1}$ [20]. Up to about 210 K, the data are well described by the harmonic model; at higher temperatures, quasielastic scattering becomes visible in the dynamic window of IN13 (FWHM of 10 μeV). It is found that the mean square displacement is surprisingly insensitive to differences in the isotopic composition.

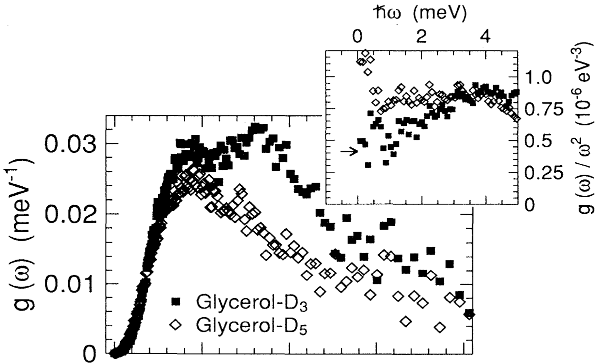

FIG. 2. Density of vibrational states $g(\omega)$ of the two partially deuterated glycerol samples at 120 K. To emphasize differences at small energies, the inset shows $g(\omega)/\omega^2$. The arrow marks the $\omega \to 0$ limit calculated from sound velocity data.

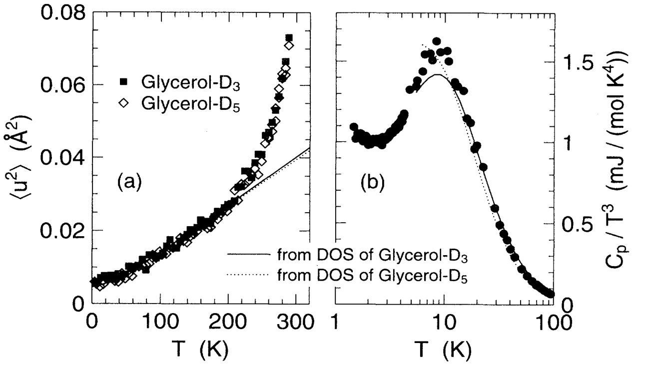

FIG. 3. (a) Mean square displacement $\langle u^2(T)\rangle$ of two glycerol isotopes derived from elastic scattering on the high-resolution spectrometer IN13 at $q = 3-5\,\text{Å}^{-1}$, compared to the harmonic behavior calculated from the DOS at 120 K. The offset $\langle u^2(0)\rangle$ was taken from the DOS of glycerol-D$_3$ and imposed on the other curves. (b) Specific heat of ordinary glycerol [17–19] shown as c_p/T^3, again compared to the behavior calculated from the DOS at 120 K.

(ii) Similarly, the specific heat can be calculated as an integral,

$$c_V(T) = k_B \int d\omega\, g(\omega)\, \frac{(\beta/2)^2}{\sinh^2(\beta/2)}\,. \tag{4}$$

This can be compared directly with $c_p(T)$ data measured in glycerol-D$_0$ [17–19,21]. As shown in Fig. 3(b), there is good agreement over a broad temperature range. Around and below the maximum at 9 K which is directly correlated with the "boson" maximum in $g(\omega)/\omega^2$ differences between glycerol-D$_3$ and glycerol-D$_5$ become sensible. At lower temperatures, the integral (4) is dominated by very-low-energy modes which cannot be experimentally resolved. In particular, there is no chance of reproducing the non-Debye behavior of $c_p(T)$ below 2 K, which in any case is generally assumed to be an anharmonic effect that cannot be described by (4).

(iii) Assuming a Debye behavior $g(\omega) = 9\omega^2/\omega_D^3$ at very low frequencies, one can compare ω_D with the experimentally determined longitudinal and transverse sound velocities $c_\parallel$ and $c_\perp$,

$$\frac{1}{\omega_D^3} = \frac{V}{18\pi^2 N}\left(\frac{1}{c_\parallel^3} + \frac{2}{c_\perp^3}\right). \tag{5}$$

In Figs. 2 and 4 we have marked with arrows the limiting values $g(\omega)/\omega^2 \to 9/\omega_D^3$ derived from ultrasound measurements [22,23]. At 120 K, this value is in good agreement with the DOS of glycerol-D$_3$ but not with the one of glycerol-D$_5$. This may be taken as a confirmation of our starting hypothesis that collective motion is studied best in the isotope glycerol-D$_3$. In other glasses

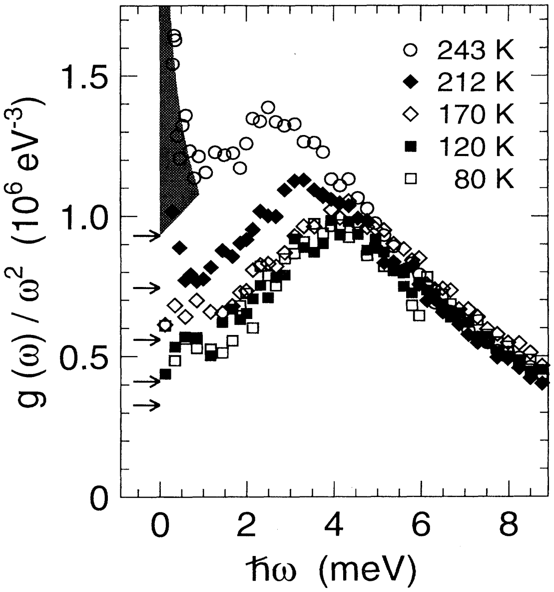

FIG. 4. Density of vibrational states of glycerol-D_3 from measurements at different temperatures below and above $T_g = 190\,\mathrm{K}$, plotted as $g(\omega)/\omega^2$. The arrows mark the limiting value $g(\omega)/\omega^2 \to 9/\omega_D^3$ as derived from ultrasonic data [22,23]. The shaded area indicates schematically the onset of quasielastic scattering in the 243 K spectra.

like silica or amorphous germanium similar agreement between the DOS, the specific heat, and the sound velocity has been found [24,25].

On this basis, we can now investigate how the DOS of glycerol-D_3 depends on temperature. In Fig. 4, $g(\omega)$ is found temperature invariant above 5 meV within the limits of experimental accuracy, whereas the density of low-energy modes already begins to increase significantly below T_g. On heating from 170 to 243 K this increase accelerates more and more. As a net effect, the maximum of $g(\omega)/\omega^2$ is shifting to lower frequencies. Of course, this does not necessarily imply that all excitations contained in the "boson peak" are shifting; our data rather indicate a qualitatively different behavior of modes below and above roughly 5 meV. A similar temperature evolution has been observed in many different glass formers [5,15]. An exception is presented by methanol, a hydrogen-bonded glass which is chemically quite similar to glycerol, but for which a strong temperature dependence of the DOS up to at least 30 meV has been reported [26].

Considering the temperature dependence of the low-frequency modes more closely we can distinguish two effects: a rather steady increase of the DOS between 0 and about 2.5 meV, and at 243 K a strong additional scattering below 1 meV. In our discussion of Fig. 1 in Sec. VI we will argue that the latter is quasielastic scattering from relaxational modes. An onset of this process is possibly observed even at 212 K. It is clear that a relaxational broadening of the elastic line is inconsistent with harmonic theory, and that it has to be excluded from the iterative calculation of multiphonon scattering. For temperatures above 243 K the quasielastic scattering increases so strongly that a reliable determination of $g(\omega)$ is no longer possible.

Discounting quasielastic scattering, the temperature evolution of $g(\omega)$ is in accord with the Debye frequency calculated from ultrasonic data. The sound velocities we use are high-frequency limiting values c_∞, i.e., their increase does not reflect structural relaxation but rather the regular thermal expansion and softening of a solid on heating. We therefore tend to interprete our data within quasiharmonic theory: even if the DOS is not invariable, at a given temperature the spectra can still be explained in terms of oscillations around local equilibrium positions.

A similar separation of quasiharmonic and relaxational contributions does possibly hold for other nonfragile glass formers as well. Available data, however, do rarely extend to sufficiently low-energy transfers so that a meaningful extrapolation $g(\omega \to 0)$ cannot be made.

IV. FOURIER TRANSFORM

The inelastic neutron scattering law is the Fourier transform (FT) of a time correlation function $S(qt)$. In certain experimental situations measured data are analyzed best by explicitly transforming them into the time domain: by Fourier deconvolution it is possible to remove instrumental resolution effects, and with some effort spectra from different instruments with overlapping dynamic ranges may be combined into one $S(qt)$ [10]. Numerical FT of quasielastic scattering data is particularly useful for a scaling analysis of the long-time decay of $S(qt)$ (Sec. VI).

Recently, time domain analysis has also been applied to time-of-flight data in the psec region [5,7]. From a technical point of view, there is no advantage in subjecting those data to a numerical FT, since the instrumental resolution has a negligible effect on vibrational spectra at THz frequencies [27]. On the other hand, the time law $S(qt)$ describing the decay of correlations is a very intuitive quantity, and theoretical modeling is often done in the time domain. A numerical FT of experimental data is by no means a trivial operation, and before proceeding to interpret the short-time behavior of $S(qt)$ in Sec. V, we have to consider the side effects of FT in some detail.

In glycerol and in any comparable substance, one observes significant contributions to $S(2\theta,\omega)$ up to several 10 meV. Unfortunately, this function is unphysical insofar as a constant detector angle 2θ does not correspond to a constant scattering vector q; in particular, $S(2\theta,t)$ is a completely meaningless quantity. Before calculating a FT, one has to interpolate the measured spectra to a scattering law $S(q\omega)$ at constant values of q. Furthermore, $S(qt)$ can be evaluated only if the frequency spectrum includes the elastic channel $\omega = 0$. As illustrated in Fig. 5, this imposes a severe restriction upon the accessible energy transfers ($\hbar\omega \lesssim 6\,\mathrm{meV}$ for 8.5 Å neutrons), and this in turn implies that in the FT a considerable

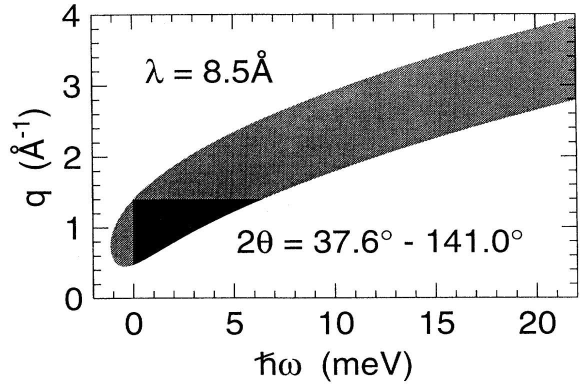

FIG. 5. Dynamic range of neutron scattering: the shaded area indicates the $q\omega$ region accessible by cold neutrons of given wavelength and for given detector angles. Only the black subregion is used when interpolated spectra $S(q\omega)$ are Fourier transformed.

part of $S(q\omega)$ is truncated.

Mathematically a truncation at ω_c may be described as a multiplication with the step function

$$H(\omega) = \begin{cases} 1 & \text{for } |\omega| \leq \omega_c \\ 0 & \text{else.} \end{cases} \tag{6}$$

Consequently, the numerically calculated $S(qt)$ is a convolution of the true time law with

$$H(t) = 2\omega_c \frac{\sin \omega_c t}{\omega_c t}\,. \tag{7}$$

This function has zeros at $t = j\pi/\omega_c$ with $j = \pm1, \pm2, \ldots$. A numerically computed FT bears therefore maximum information if it is evaluated with constant time steps $\Delta t = \pi/\omega_c$. This is just the spacing that is automatically imposed by fast FT algorithms [28].

If instead of using a fast FT algorithm $S(qt)$ is computed as a continuous curve in between the equidistant points $t_j = j\Delta t$, the FT behaves unpredictably. In the best case when the $S(qt_j)$ vary smoothly, it provides a reasonable interpolation; in the worst case when Δt is so large that there appears a step in $S(qt_j)$, the continuous FT produces ripples that do not reflect the true physics but are entirely due to the oscillatory function (7). Both cases are illustrated by examples in Fig. 6.

In our glycerol experiment $S(q\omega)$ is truncated at about 4 meV for $q = 1.2\,\text{Å}^{-1}$. This truncation effect is most apparent in $S(q, t=0)$, calculated as $2\int_0^\infty d\omega\, S(q\omega)$. At 212 K we find only $S(q, t=0) = 0.90$ instead of the exact value 1: about 10% of the scattering intensity is cut off, and the FT is not reliable below 1 psec [dashed line in Fig. 6(a)].

There is, however, an indirect way to construct a better approximation to the true correlation function $S(qt)$. Under the condition that the short-time behavior of our sample is correctly described by harmonic theory, we may calculate $S(qt)$ via Eqs. (1) and (2) from the measured DOS $g(\omega)$. We have performed the FT $g(\omega) \rightarrow W(qt)$ with different truncations frequencies, and we find that it is necessary to extend the Fourier integral to several 10 meV before it becomes approximately independent of ω_c. Three typical curves are shown in Fig. 6. By construction (1) all curves coincide at $t = 0$ where truncation effects in $2W(qt)$ and $2W(q0)$ cancel.

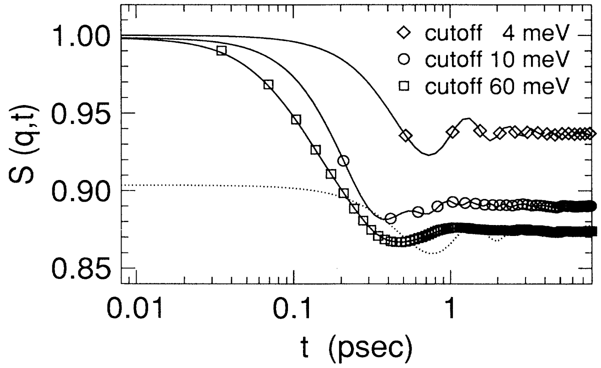

FIG. 6. Correlation function $S(qt)$ at $q = 1.2\,\text{Å}^{-1}$ and $T = 212\,\text{K}$, calculated from a scattering law $S(q\omega)$ that has been obtained either directly from measured $S(2\theta, \omega)$ (dashed line) or via $g(\omega)$ using Eqs. (1) and (2) (solid lines and symbols). The symbols are results of a fast Fourier transform; the lines are from continuous integration using the Filon FT algorithm. The reconstructed $S(q\omega)$ have been truncated at different frequencies $\hbar\omega_c$. This figure demonstrates that continuous FT of insufficient input data gives a wrong idea of the short-time behavior of $S(qt)$.

For comparison, the dashed line indicates the conventional $S(qt)$ as obtained from the direct FT of interpolated $S(q\omega)$ data. For times $t \gg 1\,\text{psec}$, this curve should

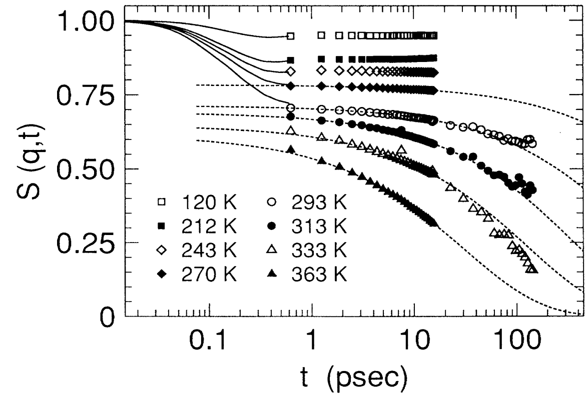

FIG. 7. Time correlation function $S(qt)$ of glycerol-D_3 at $q = 1.2\,\text{Å}^{-1}$. Points between 0.6 and 15 psec are obtained by fast FT of time-of-flight spectra from Mibémol. Additional points up to 150 psec are from a fragmentary backscattering experiment that was not considered further in our quantitative analysis. Dashed lines are Kohlrausch fits with $\beta = 0.58$. The solid lines represent $S(qt)$ as reconstructed from the DOS; see discussion in Sec. IV and Fig. 6.

coincide with $S(qt)$ calculated from the DOS. Due to multiple scattering, however, the phonon scattering does not follow the expected q^2 dependence. In order to achieve consistent results, we had to rescale q in (2) by a factor of nearly 2. It would be desirable to check this procedure by an appropriate multiple scattering simulation. In any case this rescaling concerns chiefly the amplitude of the decay steps of $S(qt)$ and not the characteristic time dependence. We are confident that $S(qt)$ calculated from $g(\omega)$ with truncation at $\hbar\omega = 60\,\mathrm{meV}$ represents a better approximation to the true correlation function $S(qt)$ than any other FT proposed so far. In Fig. 7 we have included curves that were obtained using the same procedure for temperatures from 120 to 293 K.

V. SHORT-TIME BEHAVIOR

Mode coupling theory [3,4] predicts that correlations in supercooled liquids decay in two steps. In a first step, the microscopic transient crosses over to a power law

$$S(qt) = f_q + (t/t_0)^{-a}\,, \quad a < 0.395\,. \tag{8}$$

Then in a second step, structural relaxations take $S(qt)$ from the plateau f_q to zero. In experiments on molecular glass formers, the power law (8) has been most difficult to verify because there is no clear-cut crossover from vibrations to the β-relaxation regime around f_q [2].

In our earlier work on *o*-terphenyl, we proposed [15] to separate both processes by deconvolution: we divided $S(qt)$ not just by the instrumental resolution but by the FT of rescaled low-temperature spectra. Using the same deconvolution ansatz, Colmenero *et al.* [5,7] report that several polymers show a crossover from a diffusional short-time transient

$$S(qt) \propto \exp(-t/t_D) \tag{9}$$

to the usual long-time stretched exponential [see Eq. (11) below]. The characteristic time t_D is of the order 10^{-11} for $q = 1$ or $1.5\,\text{Å}^{-1}$.

Figure 7 shows that correlations in glycerol do, indeed, decay in two steps. The second decay step will be discussed in Sec. VI. For low temperatures the first step which is not accessible by direct FT of $S(q\omega)$ has been calculated from the harmonic scattering law reconstructed from the DOS. Up to at least 290 K, the two steps in the decay of $S(qt)$ are well separated: the intermediate plateau is reached within less than 1 psec whereas the characteristic time τ in (11) is of the order of nanoseconds.

We have made no attempt to remove vibrational contributions by deconvolution [5,7,15]. As is clear from the above discussion, a naive FT of $S(q\omega)$ does not correctly describe the initial decay of $S(qt)$. On the other hand, our reconstruction of the full $S(qt)$ relies on the assumption of harmonic behavior and cannot be extended to higher temperatures. So neither of the FT's can be employed to deconvolute vibrational contributions from a more complicated scattering law. Consequently, there is not much interest in fitting the exponential (9) to our data; as far as reliable FT's can be constructed, they definitely do not follow (9).

The data analysis in Refs. [5] and [7] was motivated in part by the coupling approach of Ngai [29]. This ansatz predicts an Arrhenius behavior for t_D. No such temperature dependence can be found in glycerol. Instead, the short-term limit of $S(qt)$ is temperature independent in shape; only its amplitude increases roughly proportional to temperature. Of course nothing else was to be expected, since without performing any FT we had demonstrated before (Fig. 1 of Ref. [8]) that $S(2\theta,\omega)$ follows Bose scaling above 5 meV.

Similarly, for testing the mode coupling prediction (8) nothing can be gained by explicitly Fourier transforming the measured spectra. In our scaling analysis of susceptibility spectra $\omega S(q\omega)$ (Figs. 3 and 4 of Ref. [8]) we have shown that in a small frequency window the data are consistent with an asymptotic power law

$$S(q\omega) \propto \omega^{a-1}\,; \tag{10}$$

the exponent $a = 0.32$ was kept fixed according to a constraint of mode-coupling theory. As indicated in Fig. 1, a transient behavior (10) can also be recognized in $S(q\omega)$. On the other hand, the data set $S(qt)$ obtained by FT is far too incomplete to attempt a fit with (8).

VI. LONG-TIME BEHAVIOR

Structural relaxation in glycerol has been studied by an impressive variety of experimental techniques [23,30–39] over a wide range of frequencies and temperatures. Dielectric susceptibility alone has been measured over sixteen decades [40–43].

Experimental results are most often parametrized by empirical functions like the streched exponential of Kohlrausch-Williams-Watts,

$$S(qt) = A_q(T)\exp(-(t/\tau_q(T))^{\beta})\,, \tag{11}$$

or by similar functions in the frequency domain, even if precise measurements reveal systematic deviations [40]. In a first approximation, the data obey time-temperature superposition: while the relaxation time τ_q shows a rather strong temperature dependence, the line shape of the spectral response [in the case of (11) represented by a single parameter β] changes only slowly.

By neutron or light scattering we can follow structural relaxations to much shorter times than with any technique that measures a dynamic response directly as a function of time or frequency. The energy transfer in quasielastic neutron scattering is of the order of the instrumental resolution width. For an analysis of slow relaxation, it is therefore preferable to Fourier deconvolute measured spectra and analyze them in the time domain. We refer back to Fig. 7 for a display of $S(qt)$.

Since the dynamic window of individual spectra is restricted to about one-and-a-half decades, three-parameter fits (11) often yield inconsistent results or unacceptable error bars. Meaningful output can be obtained only if some constraints are imposed upon the parameters. As in previous neutron scattering studies of structural relaxation [44–48], we use time-temperature superposition, i.e., we assume a temperature-independent Kohlrausch exponent β. Preliminary fits indicate that the relaxation time follows the usual viscosity scaling

$$\tau_q(T) \propto \eta/T\,. \tag{12}$$

Under the assumption that this scaling holds over the whole temperature range, we obtain for each q one master curve $S(q,t/\tau(T))/A_q(T)$. Two such curves are shown in Fig. 8. With increasing temperature, the amplitudes $A_q(T)$ which have been chosen by minimizing the squared difference between rescaled spectra show a regular decrease as was previously observed in the Debye-Waller factor [20].

Fitting the master curves with (11) we obtain a slightly q-dependent exponent $\beta_q = 0.53 \pm 0.02$. However, our data set does not allow us to decide whether time-temperature superposition holds over the whole temperature range 270 − 413 K. If the highest temperature is excluded, limiting the fit to the 270 − 363 K data, a sensibly different $\beta_q = 0.58 \pm 0.02$ is obtained (Fig. 8). This deviation may illustrate the limitations of time-temperature scaling.

In fact, from dielectric loss measurements it is known that the temperature dependence of the Kohlrausch exponent is not negligible at all: for temperatures between 185 and 320 K, β was found to rise from about 0.62 to 0.85 [41,43]; another group [42] has reported values between 0.56 and 0.74. Furthermore, this comparison suggests strongly that the relaxational stretching in incoherent neutron scattering and in dielectric loss is not the same. From the overall frequency dependence of $\epsilon''(\omega)$ one actually has to conclude that dielectric spectroscopy in glycerol does not probe the same dynamics as neutron and light scattering [43].

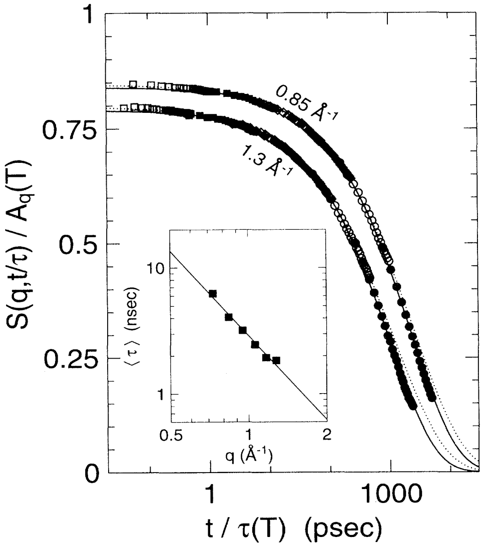

FIG. 8. Master curves $S(q\hat{t})/A_q$ vs rescaled time $\hat{t} = t/\tau(T)$. Different symbols correspond to temperatures from 270 to 413 K. The time scale $\tau(T) \propto \eta/T$ has been taken from viscocity measurements [22,54,55], with an arbitrary normalization $\tau(300\text{ K}) = 1$. From a Kohlrausch fit (solid lines), an exponent $\beta = 0.53$ is found; if the 413 K data are excluded (dotted lines), $\beta = 0.58$ is obtained. In the inset, the mean relaxation time $\langle\tau\rangle$ is plotted against q; the straight line is a power-law fit $\langle\tau\rangle \propto q^{-2.2}$.

The inset in Fig. 8 shows the average relaxation time

$$\langle\tau\rangle = \int dt\, S(qt) = \frac{\tau_{\mathrm{KWW}}}{\beta}\Gamma(1/\beta) \tag{13}$$

as a function of q. Results from both fits (including or excluding the 413 K data) coincide within the size of the symbols. The straight line is a power-law fit $\langle\tau\rangle \propto q^{-n}$ with $n = 2.2$. Of course the range of $0.7 - 1.3\,\text{Å}^{-1}$ is not sufficient to safely establish a scaling behavior in q. It can be stated, however, that our data contradict the relation $n = 2/\beta$ observed in a number of polymers [7,49,50]. It cannot be excluded that the power law is simply $\langle\tau\rangle \propto q^{-2}$, but it might also be speculated that there is a crossover between two asymptotic regimes, or that the true physics is even more complicated. Further experiments and improved multiple scattering simulations are needed to assess the apparently different q dependence of structural relaxation in molecular glass formers and their polymeric counterparts.

Before closing this section, let us consider briefly an alternative method of data analysis. Instead of converting experimental data into a deconvoluted time law $S(qt)$, it is possible to numerically Fourier transform the Kohlrausch function and to explicitly convolute it with the measured resolution function. Fits between 293 and 413 K (with fixed exponent $\beta = 0.58$) are shown in Fig. 1. For lower temperatures, the Kohlrausch function is so sharply peaked that the convolution with the instrumental resolution produced artificial spikes. The figure suggests nevertheless that there is quasielastic broadening down to 243 K, as anticipated in our discussion of Fig. 4 in Sec. III. A rough estimate of time scales indicates that this process is not ordinary structural relaxation. Its energy and temperature actually fall in the small subrange in which the susceptibility $\omega S(q\omega)$ was found to be consistent with the mode coupling β scaling [8].

From a technical point of view, Fig. 1 gives an impressive demonstration that the possibility to observe slow dynamics on a given instrument depends not so much on its nominal resolution, usually defined as the width at half the maximum, but rather on the signal-to-noise ratio and the sharpness of the resolution function at 10^{-2} or 10^{-4} the maximum value.

VII. CONCLUSIONS

Glycerol has proved once again to be a good model system for the study of the glass transition: the time correlation function decays in two distinct steps, and both asymptotic regimes follow comparatively simple laws with no remarkable anomalies.

For high temperatures and low frequencies, structural relaxation is well described by the Kohlrausch law. Time-temperature superposition is obeyed up to temperatures far above the melting point. In the low-temperature, high-frequency limit, inelastic spectra can be explained in terms of harmonic oscillations. The vibrational density of states is in good agreement with other experimental data.

For an intermediate regime (temperatures around T_g or above, energy below 5 meV) we have argued that the enhanced inelastic scattering might be explained by a rather unspectacular softening of collective modes. It is clear that this quasiharmonic ansatz as well as every other theory which starts from fluctuations around equilibrium positions must break down when long-ranged transport sets in. But it is a nontrivial result that quasiharmonic theory seems to hold nearly as long as there is no clearly distinguishable relaxational process.

In other words, the mode coupling β relaxation region is rather small, if it exists at all [8,51], and the crossing over from vibrations to relaxations occurs much faster in glycerol than in other molecular liquids. In this situation, we cannot expect to extract much additional knowledge about the molecular motion from the small subrange of $S(q\omega)$ that connects the two asymptotic regimes. Of course it would be nice to possess an interpolation formula fitting the whole scattering law. Buchenau *et al.* [6,7] have published a new model for the vibration-relaxation crossover which, however, cannot account for structural relaxation, and therefore does not fit polymer data [7, Fig. 11]. In the coupling model of Gochiyaev *et al.* [52,53], exponential relaxation is assumed, but more realistic functions like (11) could easily be included in their ansatz. Attempts to fit our spectra with this model remain inconclusive.

Overlooking the whole set of measured spectra, we have obtained a fairly complete and coherent picture of the ω dependence of $S(q\omega)$. The same does not hold for the q dependence. In Sec. III we have mentioned that inelastic intensities deviate from the expected q^2 behavior. This seems to be an experimental problem one can hope to resolve by the use of thinner samples and advanced multiple scattering corrections. There is a more interesting question about the characteristic time of structural relaxation. Even in the case of o-terphenyl where extensive experimental data are available [46], it is still unclear whether relaxation times scale with q^{-2} or $q^{-2/\beta}$ [50]. Our results for glycerol suggest that possibly neither simple law is correct. Further experiments over wider q ranges are needed to decide whether the q dependence reveals a significant, unexpected difference between low molecular weight and polymeric glass formers.

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