Neutron and Light Scattering Study of Supercooled Glycerol

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(Received 28 January 1994)

Relaxation dynamics was investigated in the hydrogen-bonded glass former glycerol using incoherent neutron scattering and depolarized light scattering. The neutron data have a q-independent form in the intermediate β-relaxation regime implying factorization of the q and ω dependences. Similar susceptibility spectra were obtained from both data sets qualitatively resembling the mode coupling theory scenario. Quantitative fits indicate apparent deviations of the exponents from mode coupling theory predictions suggesting that the influence of vibrational modes is severe in network glass formers.

PACS numbers: 64.70.Pf, 61.12.Ex, 78.35.+c

On supercooling a liquid towards the glass transition, the primary α relaxation slows down dramatically, whereas phononlike excitations continue to dominate at high frequencies. This evolution is described by mode coupling theory (MCT) [1], which in particular makes detailed predictions about density fluctuations at intermediate frequencies, designated as the β-relaxation region. The predicted power laws around the susceptibility minimum for temperatures above a critical (or crossover) temperature T_c have been observed in several fragile glass formers, supporting the essential validity of the MCT approach. Does MCT also apply to network materials where the formation and breaking of bonds may compete with mode coupling dynamics?

The primary experimental technique used to study supercooled liquid dynamics on a molecular length scale has been inelastic neutron scattering [2]. Recent depolarized light scattering spectra of several fragile glass formers [3] have revealed features similar to those found in neutron scattering experiments, but with much higher signal-to-noise levels, permitting the use of more refined data-analysis procedures [4]. These optical spectra have been interpreted as predominantly due to second-order scattering from density fluctuation modes, but it is unclear to what extent they also reflect orientational dynamics of anisotropic molecules. Do light scattering and neutron scattering actually probe the same dynamics in supercooled liquids?

We performed a parallel neutron and light scattering study of glycerol designed to address both of these questions. Glycerol [$C_3H_5(OH)_3$; $T_g = 185\,\mathrm{K}$, $T_m = 291\,\mathrm{K}$] is a hydrogen-bonded material which forms a weak H-bond network, making it intermediate between fragile and strong glass forming materials on an Angell plot [5]. The vibrational excitations [6] and α relaxation [7,8] in glycerol have been studied extensively by a variety of experimental techniques but very little is known about the intermediate frequency and temperature region where mode coupling effects might be expected. Very recently, Rössler *et al.* [9] reported a Raman scattering study of glycerol in this region. Also, dielectric measurements have been performed which extend up to 2×10^{10} Hz [8].

Neutron scattering was done at the time-of-flight spectrometer Mibémol of the Laboratoire Léon Brillouin. With cold neutrons of $\lambda = 8.5\,\text{Å}$, a resolution (FWHM) of 7 GHz was achieved. 57 detector rows at angles $16° \leq 2\theta \leq 141°$ covered elastic q from 0.2 to $1.4\,\text{Å}^{-1}$. We used partially deuterated glycerol $C_3H_5(OD)_3$ in order to concentrate on center-of-mass motion. Count rates were corrected to $S(2\theta, \omega)$ taking into account background and temperature-dependent container scattering. Care was taken to guarantee absolute intensity calibration: all runs from 4 to 333 K were measured in an uninterrupted series without removing the sample from the cryostat. By comparing to a vanadium standard we made sure coherent scattering was negligible so that data could be normalized to the 4 K run.

Depolarized light scattering was measured at City College with a Sandercock tandem interferometer and a Spex double monochromator Raman apparatus described previously [3]. In these experiments, normal glycerol (Aldrich) was used. By virtue of a depolarized 173° backscattering geometry, the transverse acoustic mode was suppressed within experimental precision; the small residual longitudinal acoustic line leaking through the polarizer was removed by subtracting the appropriately scaled polarized scattering. For each temperature, at least one Raman spectrum and four interferometric spectra of different spectral ranges were combined after removing the resolution-broadened elastic line.

In Fig. 1, spectra from the neutron and light scattering experiments are shown. The neutron spectra in Fig. 1(a) have been rescaled by the ratio of Bose factors $n(\omega, T_0)/n(\omega, T)$ for $T_0 = 170\,\mathrm{K}$ in order to test for harmonicity. Above 1.4 THz, all data fall roughly on the same curve. For lower temperatures (80 and 120 K, not shown in the plot) there are more pronounced deviations

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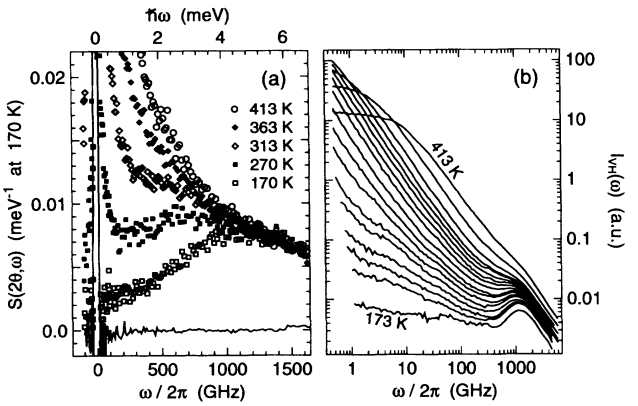

FIG. 1. (a) Neutron scattering spectra $S(2\theta,\omega)$ for $2\theta = 134°$ rescaled by the Bose factor ratio $n(\omega, 170\,\mathrm{K})/n(\omega, T)$ to test for harmonicity at high frequencies. The solid line shows the resolution function without rescaling. (b) Depolarized $\theta = 173°$ light scattering spectra $I_{VH}(\omega)$ for T = 413, 363, 333, 313 to 193 in steps of 10 K, and 173 K. In the THz region, the light scattering data obey Bose scaling as well; for clarity, they are not rescaled in the figure.

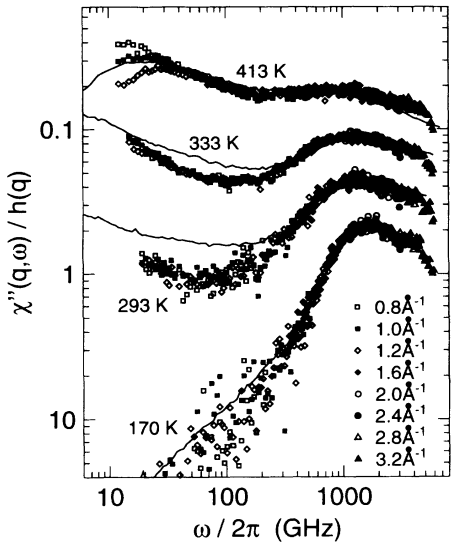

FIG. 2. Susceptibility spectra from neutron scattering, interpolated to constant q and rescaled to $\chi''_N(q,\omega)/h_N(q)$, for selected q at four different temperatures, compared to $\chi''_L(\omega)/h_L$ from light scattering (solid curves). The h_L are chosen arbitralily so that the neutron curves are matched in the boson-peak region.

which, however, are fully accounted for by processes involving two or more phonons. Thus the density of states is found to be temperature independent for $T < T_g$, favoring explanations of the boson peak in the glassy state as a harmonic vibrational effect due to structural disorder [10]. Above 1.4 THz, the density of states remains unchanged even for $T > T_g$. At lower frequencies, two things happen: the elastic line broadens into an α peak, and the gap between it and the boson peak fills up with another contribution, a fast secondary process whose appearance coincides with the anomalous decrease of elastic scattering observed earlier [11].

The light scattering data in Fig. 1(b) show qualitatively similar behavior. A log-log plot is needed to accommodate the large frequency and intensity ranges. The spectra are dominated by a quasielastic signal which increases dramatically with temperature. For the highest temperatures, a change in slope appears at low frequency; it corresponds to a susceptibility maximum and can be identified as the α-relaxation peak. In the THz region the spectrum exhibits the boson peak at low temperatures. At intermediate frequencies, the high-frequency α-relaxation wing shows a concave crossover corresponding to a susceptibility minimum.

The dynamic susceptibility $\chi''(q,\omega)$ was deduced from the neutron scattering (anti-Stokes) spectra and the light scattering (Stokes) spectra by $\chi''_N(q,\omega) = S(q,\omega)/n(\omega)$ and $\chi''_L(q,\omega) = I(q,-\omega)/[n(\omega)+1]$, respectively. MCT predicts that in the β-relaxation region the q and ω dependence of χ'' should factorize,

$$\chi''_{N,L}(q,\omega) = h_{N,L}(q)\chi''(\omega) \qquad (1)$$

and that the q-independent $\chi''(\omega)$ should obey the scaling law

$$\chi''(\omega) = |\sigma|^{1/2}\hat{\chi}''(\omega/\omega_\sigma), \qquad (2)$$

where $\sigma \propto (T - T_c)/T_c$ and $\omega_\sigma \propto |\sigma|^{1/2a}$. To test the factorization (1) for the case of neutron scattering, susceptibilities were interpolated to constant q and scaled to $\chi''_N(q,\omega)/h_N(q)$. In Fig. 2, the data for $0.8 \le q \le 3.2\,\mathrm{Å}^{-1}$ are shown to overlap within experimental error, with the clear exception of the α peak which is q dependent, consistent with MCT. The resulting $\chi''(\omega)$ can then be directly compared to $\chi''_L(q,\omega)/h_L(q)$ of light scattering (with $q = 4 \times 10^{-3}\,\mathrm{Å}^{-1}$). As shown in Fig. 2, there is qualitative agreement for the two sets of $\chi''(\omega)$ covering over three decades in frequency for all temperatures from 170 to 413 K. The design of our experiments, in particular the use of differently deuterated samples, does not allow us to draw any conclusions about the significance of quantitative differences.

In Fig. 3, we test the β-relaxation scaling law of Eq. (2) by plotting the $\chi''(\omega)$ spectra so that the minima coincide. The scaling range increases with decreasing T for both data sets, extending over nearly three decades at $T = 273\,\mathrm{K}$ ($0.02 < \omega/\omega_{\min} < 20$). Above T_c, the scaling function of MCT can be approximated by

$$\chi''(\omega) = \chi''_{\min}[b(\omega/\omega_{\min})^a + a(\omega_{\min}/\omega)^b]/(a+b), \qquad (3)$$

where a and b are subject to the constraint

$$\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b), \qquad (4)$$

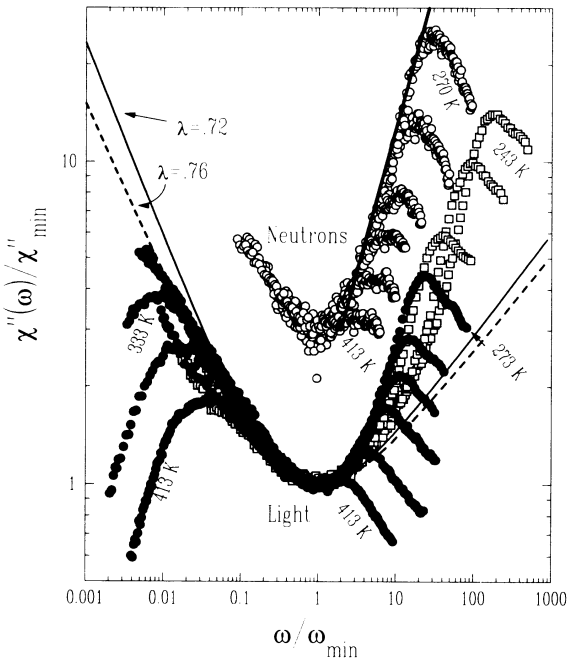

FIG. 3. Susceptibility spectra $\chi''(\omega)$ from the data of Fig. 1 scaled so that the minima coincide. For clarity the neutron data are shifted upward by a factor of 3. The solid and broken lines are MCT interpolations (3) for different values of λ (see text). Note that the light scattering data for $T = 243$ K to 263 K are shown by □. A line of slope 1 is shown through the high-frequency side of the neutron data.

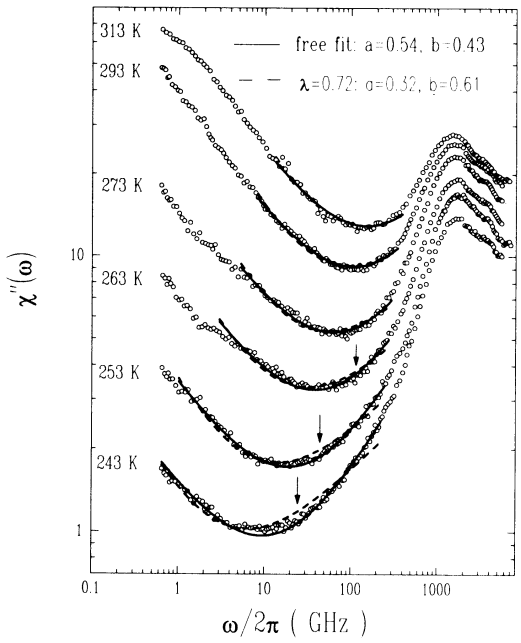

FIG. 4. $\chi''(\omega)$ spectra from light scattering with fits to the MCT interpolation, Eq. (3). The solid lines are global fits with unconstrained a and b which gave $a = 0.54$, $b = 0.43$. The dashed lines are global fits with a and b constrained by the λ equation (4) which gave $a = 0.32$, $b = 0.61$, $\lambda = 0.72$. The arrows on the three lowest-T curves indicate the end of the scaling region of the high-T data.

which implies $a < b$ and (if $b < 1$) $a < 0.395$. A free fit over the full scaling range of the 273–363 K data, however, gave values of a close to 1 (cf. the line of slope 1 in Fig. 3), corresponding to a "white noise" or "Debye density-of-states-like" behavior which leads up to the boson peak. For the high temperatures under consideration, the susceptibility minimum occurs between ω^{-b} and this ω^{+1} wing rather than between ω^{-b} and ω^{a} [12].

At $T < 273$ K, however, the high-frequency wing of the light scattering susceptibilities falls below the high-T scaling curve, with the 243 and 253 K curves suggesting a possible crossover towards the ω^{a} law of β relaxation. Including these temperatures, a much smaller common scaling range is obtained. In Fig. 4 we show fits to the light scattering spectra in this restricted range which was determined at each temperature from the scaling plot of Fig. 3. First, a free fit (a and b unconstrained but the same for all T) gave $a = 0.54$, $b = 0.43$; second, a constrained fit gave $a = 0.32$, $b = 0.61$, $\lambda = 0.72$ (and $\lambda = 0.75$ for the neutron data). At high temperatures, the two fits are indistinguishable, but at lower temperatures the constrained fit badly reproduces the positions of $\omega_{\min}$. It appears that the ω^{a} behavior, if there is any, is strongly perturbed by the ω^{+1} wing. The ω^{-b} wing of the α relaxation, on the other hand, is completely unaffected; for frequencies below $\omega_{\min}$, we obtain a very satisfactory fit with $\lambda = 0.76$, $b = 0.54$ (light scattering data, dashed line in Fig. 3).

The MCT scaling law (2) predicts that frequency and amplitude of the susceptibility minimum should exhibit a critical temperature dependence for $T > T_c$:

$$\omega_{\min} \propto (T - T_c)^{1/2a} \quad \text{and} \quad \chi_{\min} \propto (T - T_c)^{1/2} . \qquad (5)$$

To test these predictions we plotted in Fig. 5 $(\omega_{\min})^{2a}$ and $(\chi_{\min})^{2}$ versus T using exponents a as determined from the constrained susceptibility fits. For $(\omega_{\min})^{2a}$, we find an approximately linear T dependence, extrapolating to $T_c = 225 \pm 5$ K, or $\simeq 1.2T_g$ [13]. The amplitudes $\chi_{\min}$, however, deviate strongly from the predicted behavior. Finally, if viscosity [14] is compared to the MCT prediction $\eta \propto (T - T_c)^{-\gamma}$ with $\gamma = 1/2a + 1/2b$, the data extrapolate to a much higher $T_c \simeq 305$ K [15]. Thus a consistent T_c could not be obtained [16].

In summary, our parallel neutron and light scattering experiments revealed qualitatively similar spectra indicating that the two techniques very likely do probe the same dynamics. The neutron data exhibit the (q,ω) factorization predicted by MCT, and in a restricted scaling range both data sets show a scaling behavior which can be described, at least qualitatively, by Eq. (3). For frequencies above the minimum, however, $\chi''(\omega)$ increases much more steeply than the ω^{a} law of MCT predicts.

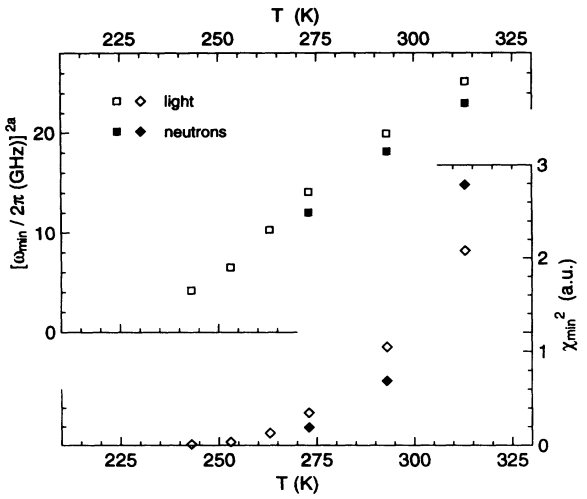

FIG. 5. $(\omega_{\min})^{2a}$ (top) and $(\chi_{\min})^2$ (bottom) vs T for the neutron and light scattering data (with $a_N = 0.35$, $a_L = 0.32$). The $\omega_{\min}$ and $\chi_{\min}$ values were taken from the unconstrained fits.

This may be related to the fact that the boson peak in glycerol, as in other network materials, is more pronounced than in fragile systems [17]; this suggests an increased strength of the microscopic dynamics, possibly enhanced by the network bonds, which extends to relatively low frequencies. Although our 243–263 K data indicate that there might be an intermediate β-relaxation regime in glycerol, the frequency and temperature range in which the ω^{-b}, ω^a crossover is not distorted are so small that the existence of such a scaling region cannot be safely established. We therefore conclude that although MCT may provide a partial description of supercooled liquid dynamics in intermediate glass formers, a more detailed description of the microscopic dynamics must be included to supply a quantitatively correct explanation of the experimental data. Our results illustrate that the agreement of existing MCT with observations in fragile glass formers [2–4] is highly nontrivial.

We thank W. Götze, C. Dreyfus, and S. Nagel for helpful discussions and suggestions. Research at Mainz and New York was assisted by the German BMFT and the U.S. NSF under Grants No. 03-Si2Mai and No. DMR-9014344, respectively. J.W. has been generously supported by the ILL, Grenoble. J.H. was supported by NIH grant GM08168. Laboratoire Léon Brillouin is laboratoire commun CEA-CNRS.

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