Fast Relaxation in a Fragile Liquid under Pressure

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(Received 5 June 1997)

The incoherent dynamic structure factor of orthoterphenyl is studied by quasielastic neutron scattering to 240 MPa. Tagged-particle correlations in the compressed liquid decay in two steps. The α-relaxation line shape is independent of pressure, and the relaxation time proportional to viscosity. A kink in the amplitude $f_Q(P)$ reveals the onset of β relaxation. The β-relaxation regime can be described by the mode-coupling scaling function; amplitudes and time scales allow a consistent determination of the critical pressure $P_c(T)$. α and β relaxation depend in the same way on the thermodynamic state; close to $P_c(T)$, this dependence can be parametrized by an effective coupling $\Gamma \propto nT^{-1/4}$. [S0031-9007(98)05550-1]

PACS numbers: 64.70.Pf, 61.25.Em, 62.50.+p, 61.12.–q

The glass transition can be induced by decreasing the temperature or by increasing the pressure. For practical reasons, most experimental investigations concentrate on temperature effects at ambient pressure $P_0 = 0.1$ MPa, although there is a clear interest in studying supercooled liquid dynamics in the full P, T parameter space. Variable pressure measurements have been decisive in demonstrating that density is not the only driving force behind the glass transition [1–3]. In the microscopic approach of mode-coupling theory [4], both pressure and temperature control the dynamics through variations of the static structure factor. Close to the dynamic crossover, the effect of these variations can be expressed through a single separation parameter which, however, is not given by density alone, as was confirmed by depolarized light scattering in the fragile liquid cumene [3].

Here we report on incoherent neutron scattering in the fragile van der Waals liquid orthoterphenyl (OTP, $T_g(P_0) = 243$ K) at variable pressure. As a function of temperature, the microscopic dynamics of OTP has been studied extensively by neutron scattering [5–7], light scattering [8,9], and molecular dynamics [10,11]. As a function of pressure, viscosity [12], photon correlation [13], dielectric loss [14], and specific heat [2,15] data are available for comparison. From the Debye-Waller factor [5,10] and from direct observation of fast β relaxation [6–9], a crossover was located at $T_c(P_0) = 290 \pm 5$ K [16].

OTP (Aldrich) was purified by repeated crystallization from liquid methanol and vacuum distillation. An Al7049.T6 high-pressure cell from the Institut Laue-Langevin (ILL) with a ratio of outer-to-inner diameter of 2 allowed us to attain up to 250 MPa at temperatures up to 335 K; helium was used to transmit the pressure.

The experiments were performed using backscattering (IN16) and time-of-flight (IN6) spectrometers of the ILL. Incident wavelengths 6.27 and 5.12 Å^{-1} gave resolutions (FWHM) of about 1 and 80 μeV, respectively. Vanadium was used to calibrate the detectors and to yield the resolution functions. The measured transmission of the empty pressure cell at P_0 was about 84%, that of the sample was about 88%. Self-shielding and multiple scattering turned out be negligible at large scattering angles. This was demonstrated by a comparison of spectra taken with and without the pressure cell at 290 K: the normalized intermediate scattering functions $S(Q, t)$ fall onto each other. Therefore we base our conclusions exclusively on high Q data ($\gtrsim 1$ Å^{-1}). On IN16 we measured isoviscous and isothermal (320 K) spectra as well as the isothermal (301 K) elastic intensity. On IN6 we monitored two different isotherms (316 and 324 K). Preliminary results from isochoric measurements have been reported in [17].

Before turning to the fast dynamics, we address the long-time limit of α relaxation; results on α relaxation will be needed as input in the analysis of β relaxation.

In a first survey, backscattering showed that the mean relaxation time follows the pressure dependence of viscosity. Then, the shape of α-relaxation spectra was determined in a couple of long running scans. At three points (P, T) with equal viscosity, the quasielastic spectra all coincide [Fig. 1(a)] which confirms that the microscopic relaxation time is proportional to the macroscopic viscosity η, and demonstrates that within experimental error the spectral distribution is independent of pressure. We deduce an average slope for isokinetic curves $(dT/dP)_\tau$ in the P, T plane of about 0.28 ± 0.01 K/MPa. Similar values were found for the pressure dependence of the glass transition temperature (dT_g/dP) [15], and for the α-relaxation time in photon correlation [13] and dielectric spectroscopy [14].

The invariance of the spectral shape is further illustrated by construction of a master curve. The intermediate scattering function $S(Q, t)$ is obtained by Fourier deconvolution of the measured $S(Q, \omega)$. Since the α-relaxation time is proportional to viscosity, reduced times can be defined via $\hat{t} = t\eta(P_0)/\eta(P)$. The rescaled $S(Q, \hat{t})$ coincide over two decades [Fig. 1(b)].

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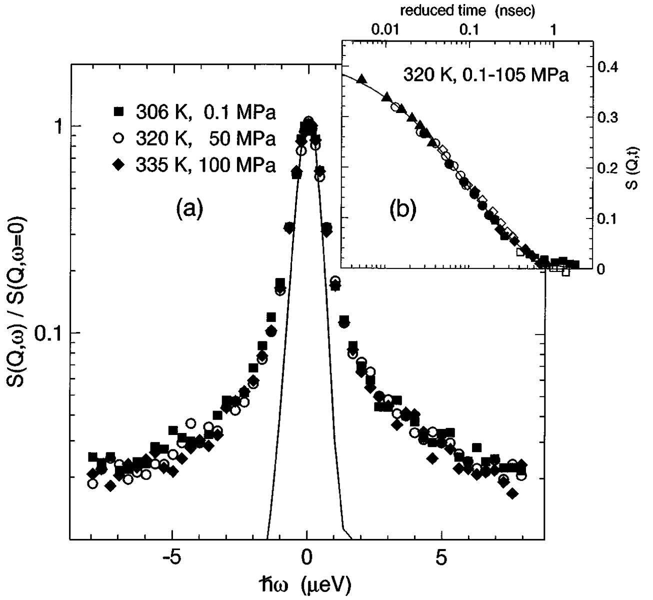

FIG. 1. (a) Spectra from IN16 at $Q = 1.8$ Å^{-1} for three combinations of temperature and pressure which lead to approximately the same viscosity. The spectra are scaled to their value at $\omega = 0$. The line represents the measured resolution function. (b) Master curve $S(Q, \hat{t})$ from isothermal (320 K) data constructed by rescaling times with viscosity. The solid line is a fit with the Kohlrausch function $f_Q \exp(-\hat{t}^\beta)$, with a stretching exponent $\beta = 0.6$.

Time-temperature-pressure superposition is well established by photon correlation and dielectric loss spectroscopy in OTP [13,14] as well as in other fragile liquids [18]; for a given time shift, the spectral line shape changes even less with pressure than with temperature [13,14]. Our measurements extend the validity of this scaling principle to a picosecond range, where contact can be made with fast molecular motion.

Via the total intensity of the elastic or quasielastic line, backscattering may reveal the presence of faster relaxation processes. In fact, the first manifestation of a dynamic transition at T_c was obtained from elastic scans [5]. Here, we monitored the pressure dependence of the elastic scattering $S(Q, \omega \simeq 0)$ at 301 K (Fig. 2). At high pressures, in the glassy phase, the elastic intensity is constant. This make the analysis even simpler than in temperature-dependent measurements, where the harmonic evolution of the Debye-Waller factor had to be taken into account. On releasing the pressure, as on increasing the temperature, an anomalous decrease of the elastic intensity indicates the onset of β relaxation. This decrease is observed first and most pronounced for large wave numbers. For the lowest pressures the elastic line begins to broaden, and its total intensity can no longer be determined from $S(Q, \omega \simeq 0)$. Instead, one has to take the integral over the full α line.

From the scaling analysis of isothermal α-relaxation spectra at 320 K [Fig. 1(b)], we find that, up to 105 MPa, the integrated α-relaxation amplitude f_Q does not depend on pressure. This allows us to extrapolate f_Q at 301 K from P_0 towards higher pressures, depicted as horizontal lines in Fig. 2. The intersection with the elastic intensities (vertical line) which turns out to be independent of Q permits the identification of a critical pressure $P_c \simeq 42$ MPa.

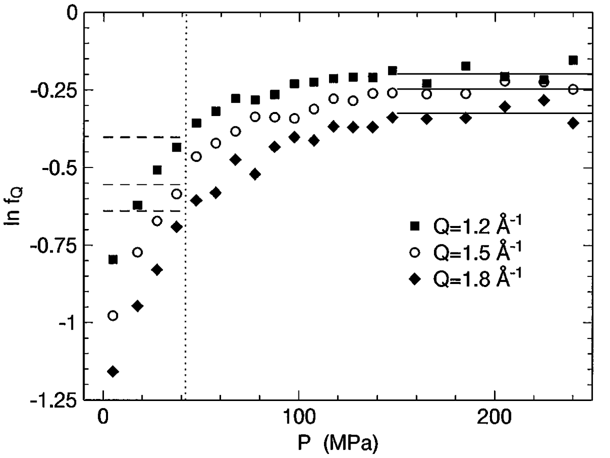

FIG. 2. Debye-Waller factor as a function of pressure at 301 K. Symbols show elastic scattering intensities: As long as there is no quasielastic broadening, they yield the Debye-Waller factor which is P independent in the glass (solid lines). Dashed horizontal lines indicate the integrated α intensity, measured at P_0 and shown to be P independent. The dotted vertical line indicates the critical pressure P_c.

On IN6 we access the β process directly. As the quasielastic broadening is of the same order as the instrument's resolution width, data are analyzed by Fourier deconvolution (Fig. 3). In our temperature-dependent experiments, spectra from different instruments were combined into an intermediate scattering function $S(Q, t)$ which covered three decades in time [6,7]; the fast β relaxation could be described by the mode-coupling prediction [19]

$$S(Q, t) = f_Q + H_Q g_\lambda(t/t_\sigma). \qquad (1)$$

The dynamic range of the present study does not allow an independent verification of (1); nevertheless, taking advantage of previous results, we can use (1) to extract the pressure dependence of H_Q and t_σ from IN6 data. Besides the shape parameter $\lambda = 0.77$, we input the Debye-Waller factor determined from a Kohlrausch fit to the long-time tail of low-pressure data. While the asymptotic law (1) does not cover the short-time dynamics below 1 psec, it consistently describes the bending of $S(Q, t)$ into and out of the intermediate plateau f_Q (Fig. 3).

Within mode-coupling theory, the α-relaxation amplitude f_Q, the β-relaxation amplitude H_Q, and the crossover time t_σ depend on the equilibrium structure factor $S(Q)$ which, in turn, is a regular function of parameters such as T and P. Close to the dynamic crossover, this dependence can be expressed through a linear separation parameter

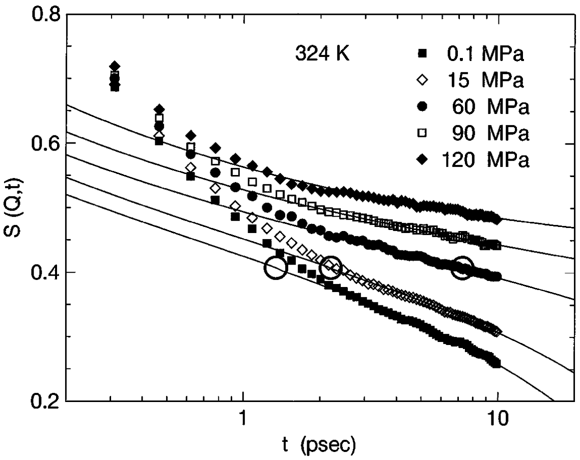

FIG. 3. Intermediate scattering function $S(Q,t)$ at $Q = 1.8$ Å^{-1} from IN6 in the β-relaxation regime for different pressures. Lines are fits with (1) with a fixed shape parameter $\lambda = 0.77$ and fixed plateau values f_Q (indicated by thick circles).

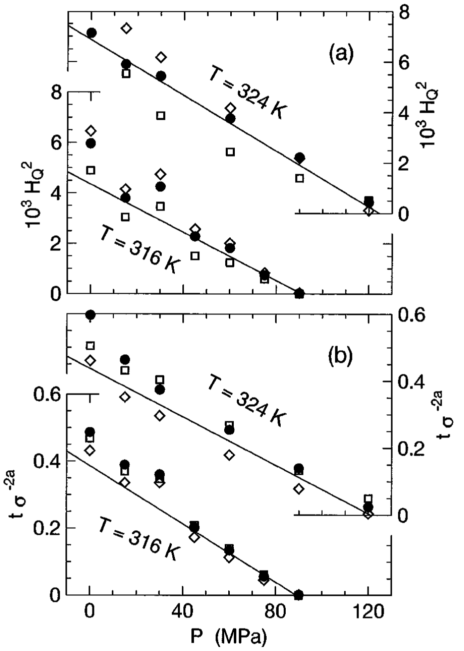

FIG. 4. β-relaxation amplitude and crossover time for two isotherms 316 and 324 K and three wave numbers $Q = 1.2$ (□), 1.5 (●), and 1.8 Å^{-1} (◇). The data are linearized as H_Q^2 and t_σ^{-2a} according to (2); lines are fits to Q averaged values.

[20], $\sigma \propto (T - T_c)/T_c$ in isochoric or $\sigma \propto (P_c - P)/P_c$ in isothermal experiments. On approaching the crossover from the liquid side, f_Q varies only weakly, whereas H_Q and t_σ are predicted to become singular:

$$H_Q \propto \sigma^{1/2} \quad \text{and} \quad t_\sigma \propto \sigma^{-1/2a}, \tag{2}$$

with a critical exponent $a = 0.295$ determined by λ.

In Figs. 4(a) and 4(b) these power laws are tested for two isotherms by plotting H_Q^2 and t_σ^{-2a} vs P. Asymptotically, linear behavior is observed, and extrapolation gives consistent estimates for P_c at 316 and 324 K. Away from the asymptotic limit, the data scatter considerably, similar to temperature-dependent experiments [6,7].

Together with T_c at ambient pressure and the value P_c(301 K) obtained from elastic scans, a total of four points of the dynamic phase boundary $P_c(T)$ is obtained. These points, summarized in Table I, fall onto a straight line with slope $dT_c/dP \simeq 0.28$ K/MPa which is in remarkable accord with the slope determined from α-relaxation, viscosity, and T_g data: The mode-coupling crossover line is parallel to lines of equal α response.

Lines of constant density, on the other hand, have slopes of about 0.70 K/MPa, which confirms [17] that temperature influences the dynamics not only via free volume. The same conclusion was reached by simulation of a Lennard-Jones system [21] and by light scattering in cumene [3]; it was suggested instead that at least the α dynamics can be parametrized by viscosity [3].

Our results imply that the dynamic crossover can still be characterized by one single separation parameter $\sigma(T,P)$ which, however, does not depend on density alone. Instead, it appears that density n and temperature T can be combined to an effective coupling $\Gamma \propto nT^{-1/4}$: Table I shows that Γ_c is constant within experimental error. Furthermore, constraint fits to $S(Q,t)$ confirm that the temperature and pressure dependence of amplitude and time scale can be described by the power laws (2) in conjunction with just one separation parameter $\sigma = (\Gamma - \Gamma_c)/\Gamma_c$.

A coefficient $\Gamma \propto nT^{-1/4}$ is known to characterize equilibrium properties of a dense soft-sphere fluid with repulsive core potentials of the Lennard-Jones r^{-12} type [22]. In a supercooled liquid, we are actually in a high-density regime, where the static structure factor $S(Q)$ is sensitive only to the repulsive part of the potential [22,23]. In simulations of binary soft-sphere [24] and Lennard-Jones [25] systems, the glass transition was found to occur at constant Γ_c.

It was not expected that these results would apply literally in a complex molecular liquidlike OTP. In fact, the comparison with a Lennard-Jones liquid can be made almost quantitative. To this end, we need the two parameters of the 6-12 potential: A van der

TABLE I. Critical pressure P_c and corresponding density n_c [28] as function of temperature. The product $\Gamma_c = n\sigma^3(\epsilon/T)^{1/4}$ is found to be constant (its errors are estimated from $\Delta T_c = \pm 3$ K at 290 K and $\Delta P_c = \pm 5$ MPa). The choice of $\sigma = 7.6$ Å and $\epsilon = 600$ K is explained in the text.

T (K)	P_c (MPa)	n_c (nm^{-3})	Γ_c
290	0.1	2.840	1.495(4)
301	42(3)	2.875	1.499(6)
316	90(7)	2.906	1.497(5)
324	123(7)	2.931	1.501(9)

Waals diameter $\sigma = 7.6$ Å, estimated from structural information [26], is in good accord with the recently observed prepeak in the static structure factor at $Q \simeq 0.85\text{--}0.9$ Å^{-1} [7,27], and a potential depth $\epsilon = 600$ K has been determined by calibrating a three-site OTP model to experimental density and diffusivity [10]. Using this input, we obtain $\Gamma_c = 1.50$ (Table I) which is closer to the Lennard-Jones result $\Gamma_c^{\text{LJ}} \simeq 1.25$ [21,25] than one could reasonably expect.

In conclusion, our experiments give a consistent picture of microscopic dynamics in the T-P plane.

Time-temperature-pressure superposition, known from Hz–MHz spectroscopy, describes structural α relaxation down to the picosecond range, where macroscopic properties of the material evolve from their microscopic dynamics. Spectral line shapes observed by incoherent neutron scattering are invariant, the mean relaxation time is proportional to the viscosity, and states of equal kinetic are connected by the same slope dT/dP, regardless of the time scale.

Fast β relaxation is detected from the α-relaxation amplitude; its full spectral shape is observed by time-of-flight spectroscopy. Just as in variable temperature measurements, the data are fully compatible with mode-coupling predictions; they allow the unambigous and consistent determination of a dynamic crossover line $P_c(T)$. This line is parallel to the lines of equal viscosity: α and β relaxation are driven by the same parameter.

At least in a certain neighborhood of $P_c(T)$ this parameter is linear in the effective coupling $\Gamma \propto nT^{-1/4}$ which in turn depends ultimately on the molecules' short-range interaction.

We gratefully acknowledge stimulating discussions with C. Alba-Simionesco, G. Diezemann, W. Kob, and W. Petry. We thank A. Doerk for help during sample preparation, K. Schug for communicating to us results prior to publication, and W. Götze and W. Kob for valuable comments on the manuscript. Special thanks to L. Melesi for the great support with the pressure equipment. Financial support by German BMBF under 03FU4DOR4 and 03PE4TUM9 is appreciated.

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