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Light scattering studies of high-frequency relaxation processes in organic glass formers

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Abstract. We describe recent light scattering measurements performed on two small molecules, metatoluidine and salol, and one polymer, 1-4 *cis-trans* polybutadiene, in their undercooled phase. For the small molecules, the α -relaxation times deduced from the isotropic and anisotropic spectra are different and we propose, through different experiments, that the latter spectra are related to the reorientation motion of the molecules, the dynamics of which follows some of the MCT predictions. For polybutadiene, a broad and rather flat spectrum dominates the anisotropic spectrum, while the damping of the acoustic phonons is possibly due to their coupling to intra-chain conformation motions.

1. Introduction; mode-coupling theory results

In its general sense, the mode-coupling theory (MCT) of the liquid state is a theory in which the entire dynamics of the system is described in terms of two-‘particle’ correlation functions. For its application to the problem of the liquid–glass transition, up to now, two more approximations have been made:

- (i) the ‘particles’ are shapeless, and interact via two-body potentials;
- (ii) the only relevant correlation functions are

$$\phi_q(t) = \langle \rho_q(0)\rho_q(t) \rangle / \langle |\rho_q|^2 \rangle \quad (1)$$

where $\rho_q(t)$ is the Fourier transform of the microscopic density function; $\phi_q(t)$ thus describes the dynamics of the density fluctuations at wave vector q .

The ideal version of MCT [1] predicts an ergodic-to-nonergodic transition at some temperature T_c where all the density fluctuations start freezing and specific predictions concerning their dynamics can be made for the vicinity of T_c : defining $\chi_q''(\omega) = \omega \text{Im} \phi_q(\omega)$, where $\phi_q(\omega)$ is the Laplace transform of $\phi_q(t)$, the characteristic dynamics of $\chi_q''(\omega)$ extends, in the temperature range $0 < (T - T_c)/T_c = \varepsilon(T) \ll 1$, over many decades and exhibits three different frequency domains.

(i) A high-frequency (typically around 1 THz) maximum which describes the single-mode, temperature-independent, dynamics.

(ii) A β -fast-relaxation region where $\chi_q''(\omega)$ exhibits a q -independent minimum at ω_{\min} . In this region, the dynamics may be approximately described by

$$\chi_q''(\omega) = \chi_q^{\min} \left[b \left(\frac{\omega}{\omega_{\min}} \right)^a + a \left(\frac{\omega}{\omega_{\min}} \right)^{-b} \right] / (a + b) \quad (2)$$

where $\omega_{\min} \sim (T - T_c)^{1/2a}$, a and b being positive, temperature- and wave-vector-independent numbers, mutually related.

(iii) An α - (or structural) relaxation regime which exists at still lower frequencies, where $\phi_q(\omega)$ is approximately the Laplace transform of a stretched exponential:

$$\tilde{\phi}_q(t) = \exp[-(t/\tau_q^\alpha)^{\beta_q}] \quad (3)$$

with

$$\tau_q^\alpha \sim \tau_q^0 (T - T_c)^{-\gamma} \quad \gamma = \frac{1}{2a} + \frac{1}{2b} \quad \beta_q > b. \quad (4)$$

Close to T_c , $\omega_{\min} \tau_q^\alpha$ diverges as $(T - T_c)^{-1/2b}$, and one can show that equation (2) describes a dynamics which, for $1 \ll \omega_{\min} t \ll \omega_{\min} \tau_q^\alpha$, may be expressed as

$$\phi_q(t) = f_c - h_q t^b \quad (5)$$

where h_q is a positive number.

The very important point is that the whole dynamics of $\phi_q(t)$ results from a single equation of motion for each mode, each equation depending on the entire set $\{\phi_q(t)\}$ and on parameters smoothly varying with temperature. The self-consistency of these equations makes the theory very attractive, which explains why, although no fragile glass former actually fulfils the basic condition of shapeless particles, many experiments have been aimed at testing whether this theory fits with experimental results.

2. Light scattering tests of MCT in fragile molecular liquids

Many of the fragile glass-former liquids are in fact molecular liquids, and though the basic approximation of shapeless particles is certainly never fulfilled for such liquids, their dynamical spectra have been frequently taken as test cases for the theory. In the last five years, light scattering techniques have been widely used for such studies because they can produce, over a large frequency range, spectra with a high signal/noise ratio, and a good resolution.

One of these methods consists in combining tandem Pérot–Fabry and Raman techniques to obtain DLS spectra in the 0.3 GHz–4 THz region. Those spectra, plotted as $\chi''_{DLS}(\omega) = \omega I_{DLS}(\omega)$, do indeed show, for small-‘molecule’ glass formers, the three spectral features recalled above, and their analysis in terms of the MCT predictions has provided coherent results for a , b and T_c , with $\beta_q > b$. This is the case, for instance, for salol [2], OTP [3] and metatoluidine [4], and is exemplified, for the latter material, in the two panels of figure 1. The corresponding α -relaxation times will be referred to as $\tau_{VH}(T)$.

Another method consists in measuring, in a backscattering geometry, the isotropic spectrum $I_{iso}(\omega) = I_{VV}(\omega) - \frac{4}{3}I_{VH}(\omega)$ (where $I_{VV}(\omega)$ and $I_{VH}(\omega)$ are respectively the polarized and depolarized light scattering intensities at frequency ω in the 1 GHz–20 GHz domain, where the Brillouin lines are located). Analysing the full spectrum as the result of the interaction of a weakly damped acoustic phonon with an α -relaxation process (taken as the Laplace transform of equation (3)—or rather of its Cole–Davidson analogue) provides a second relaxation time, $\tau_{VV}(T)$. Though this $\tau_{VV}(T)$ rapidly increases with decreasing temperature, as does $\tau_{VH}(T)$, the former is noticeably shorter than $\tau_{VH}(T)$, with a factor of $\sim 1/20$ for salol [5], or $1/4$ for metatoluidine [4].

The longitudinal phonon mostly interacts with the relaxation process responsible for the dynamical bulk viscosity, as will be shown in the next section, and $\tau_{VV}(T)$ should be identified with the τ_q^α of equation (3). Conversely the α -relaxation seen in the DLS experiment should be related to another mechanism which we need now to discuss.

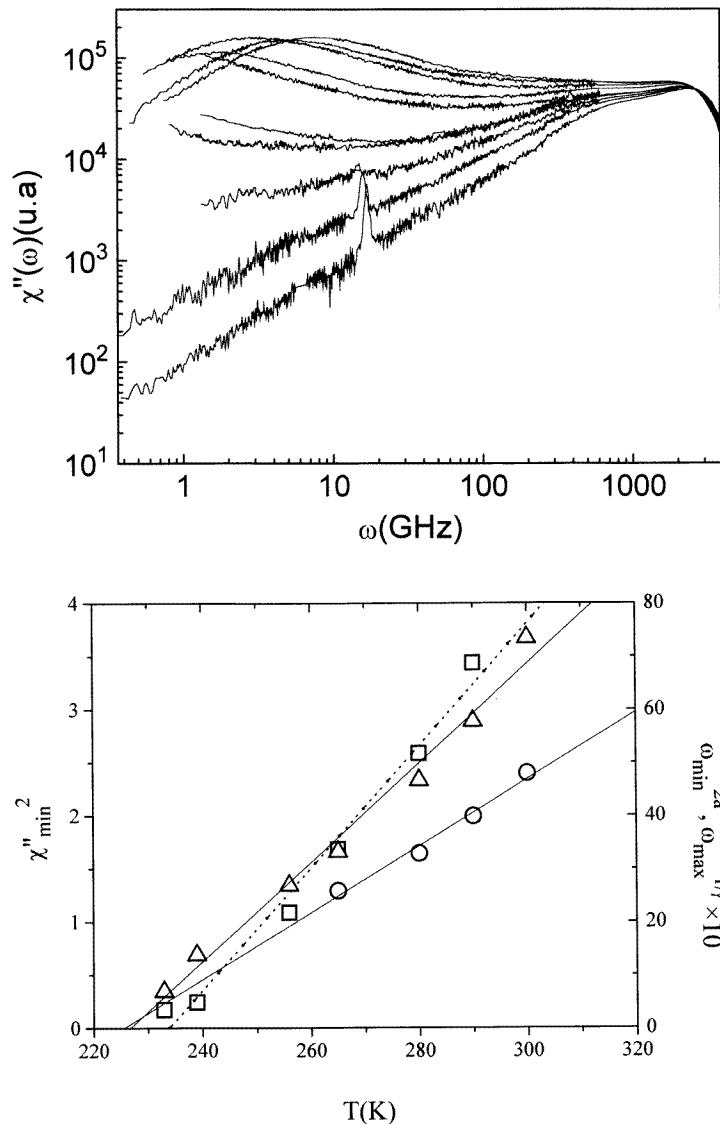


Figure 1. Metatoluidine. Top panel: susceptibility spectra; the temperatures are (from top to bottom) 300, 290, 280, 266, 256, 239, 233, 223, 213 and 193 K. Bottom panel: the temperature dependence, above T_c , of χ''_{\min}^2 (squares), ω_{\min}^{2a} (triangles), and $\omega_{\max}^{1/\gamma}$ multiplied by 10 (circles). The lines are linear fits to the data points with $T_c = 234, 226$ and 225 K, respectively.

As the broad-band spectra have a depolarization ratio $I_{VH}(\omega)/I_{VV}(\omega) = 0.75$ over the whole frequency range above the Brillouin lines, the corresponding spectra have been attributed either to a DID mechanism [2], or to the rotational dynamics of molecules with anisotropic polarizability tensors. The integrated intensities of a spectrum solely due to the DID mechanism and of the ‘iso’ spectrum both depend only on the isotropic part of the polarizability tensors, and on quantities which may be approximately computed or found in the literature. The integrated intensity of a spectrum due to the rotational

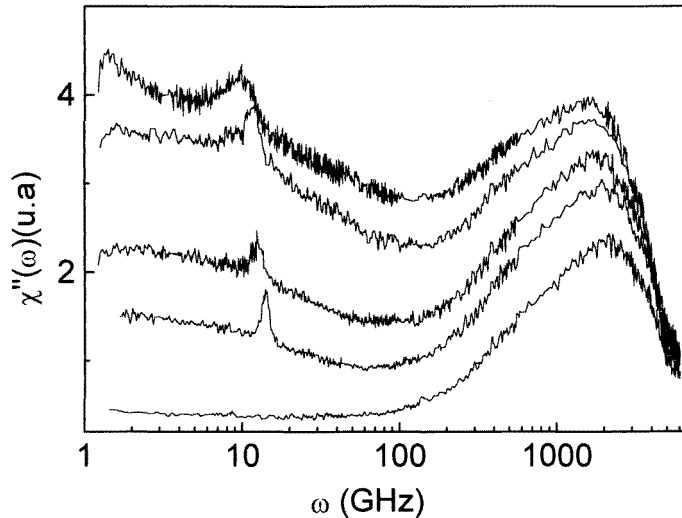


Figure 2. Polybutadiene. Susceptibility spectra; the temperatures are (from top to bottom) 293, 273, 253, 233 and 213 K.

dynamics of independent molecules can also be computed if the polarizability tensor is known. Thus direct measurement of the ratio of the integrated intensities of the DLS and of the ‘iso’ spectra may decide on which scattering mechanism is responsible for the DLS spectrum. In the case of salol [6], the experimental ratio is larger by a factor of 7 than the expected value for a DID mechanism, which suggests that, for this glass-forming liquid, broad-band spectroscopy probes the orientational dynamics of the molecules, and that the latter follows the MCT predictions originally established for the density fluctuation dynamics; its characteristic α -relaxation time, $\tau_{VH}(T)$, which is noticeably longer than τ_q^α , is the relaxation time of the reorientational fluctuations, which adds a slow dynamics to the dynamical shear viscosity as these two quantities are strongly coupled in molecular liquids formed of anisotropic molecules [7].

Nevertheless, in the DLS experiments of such molecular liquids, the integrated intensity of the spectral feature related to the α -relaxation process is a very large fraction of the total integrated intensity. It is then difficult to decide whether the high-frequency peak is also detected through the motion of the anisotropic part of the polarizability tensor (and probes another part of the orientational dynamics), or by a DID mechanism, related to a second dynamical variable which probes another type of motion, the minimum in $\chi_q''(\omega)$ resulting from the overlap between those two spectra.

Therefore, some of us have recently [8] used a femtosecond spectroscopy technique in order to look at this problem from a time domain point of view. In such an experiment (see e.g. [9]), one creates an index of refraction anisotropy in the liquid, through a very intense femtosecond, linearly polarized, light beam. This optical anisotropy is created both through a very weak electrostriction effect and a strong optical Kerr effect. The decay of this optical anisotropy is then probed by a delayed pulse which—from the preceding remark—essentially detects the orientational dynamics of the molecules. Because one performs a pulsed experiment, the signal turns out [9] to be proportional to the square of the time derivative of $\phi_q(t)$ (for $q = 0$), and, due to parasitic effects, it can be analysed, within the MCT scheme, only for $\omega_{mint} \gg 1$. The signal is thus sensitive to the t^b and the

stretched-exponential parts of $\phi_q(t)$ (equations (3) and (5)). Such an experiment has been performed between 290 °C and 333 °C on salol for which $\tau_{VV}(T)$ is much smaller than $\tau_{VH}(T)$ and $T_c \sim 265$ °C. Fixing β to the value obtained in the DLS experiment, the measured relaxation times, τ , agree with the DLS ones, at each temperature, proving the identity with the α -process measured by DLS. The important point is that the mean value of b also agrees with the value deduced from the analysis of $\chi''(\omega)$ by equation (2), proving that it is very doubtful that, in the region of the minimum of this function, the DLS spectra are sums of two different scattering processes.

Though this experiment still needs to be extended down to temperatures closer to T_c , this result is a strong indication that the orientational correlation functions related to the anisotropic part of the molecular polarizability follow some of the MCT predictions, i.e., exhibit the same type of two-step dynamics. The origins of such a result need to be explored from a theoretical point of view because it could be the simple consequence of a harmless linear coupling of the variables describing the orientation of the polarizability tensor to the density dynamics but, conversely, it could indicate that in such systems these orientational variables play, in the liquid–glass transition, a more important role than originally anticipated.

3. Light scattering by 1-4 *cis-trans* polybutadiene

Polymers are also fragile glass-former liquids, and the first inelastic neutron experiments, performed, in particular, on 1-4 *cis-trans* polybutadiene [10], led to the proposal that their dynamics would also follow the MCT predictions. Some of us [11] have performed the same type of DLS light scattering and Brillouin scattering experiments as described in section 2 on a similar sample with $M_w \sim 7700$. Though the susceptibility spectra display qualitatively the same high-frequency peak and intermediary minimum as in the case of figure 1, figure 2 shows that there are very important differences: the region of the minimum cannot be fitted with equation (2), nor is the low-frequency maximum reached, even at the highest temperature (325 K) compatible with the stability of our sample, for which the glass transition takes place at $T_g = 177$ K. Similarly, though the ‘iso’ spectra show a strong coupling with an α -relaxation mechanism, the latter cannot be related, except at the highest temperatures ($T > 280$ K), to the relaxation times deduced from viscosity measurements. At lower temperature, the Brillouin scattering relaxation times are much shorter than the viscosity relaxation times and are apparently governed by an activation energy mechanism. This second relaxation mechanism, which totally dominates the acoustic phonon damping at those low temperatures, could be due to a coupling of the acoustic phonons to some intra-chain conformational changes already seen by some molecular dynamics calculations [12], and not to their coupling to interchain motions, the polymeric analogue of a coupling to density fluctuations in the ‘small-molecule’ case.

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