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Pressure and temperature variation of the depolarized light scattering spectra of the fragile glass-former liquid salol

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Abstract. The pressure and temperature dependences of the depolarized light scattering spectra of salol have been measured at isobaric condition $P = 1$ bar for T between 328 and 393 K, and at isothermal condition $T = 343$ K for P between 1 and 625 bar, *i.e.* outside the metastable liquid region. The experimental results for both the α- and β-relaxations can be well described by the Mode Coupling Theory. The independence of the power-law parameters a, and consequently b and γ, from the thermodynamic variables T and P is demonstrated.The critical temperature T_c at 1 bar and the critical pressure P_c at $T = 343$ K have been determined from the normal liquid state.

PACS. 64.70.Pf Glass transitions – 07.35.+k High-pressure apparatus and techniques; shock tubes; diamond anvil cells – 78.35.+c Brillouin and Rayleigh scattering; other light scattering

1 Introduction

The study of the glass-transition dynamical properties in "fragile" glass formers is of great interest and it has received considerable attention in recent years. The transition can take place either by isobarically decreasing the temperature or by isothermally increasing the pressure of the liquid. Both types of experiments can be used in order to derive information on the behavior of the relevant parameters and to compare experimental results with theoretical models.

Several experimental spectroscopic methods have been used in order to extract dynamical information in liquid glass formers. However, only few experiments have dealt with measurements where pressure is varied at constant temperature. This is mainly due to the relative difficulty in performing spectroscopic experiments at pressures sufficiently high to observe the variation of the relevant parameters of the glass transition. Nevertheless, measurements in function of pressure are of interest not only to study the peculiarities of the glass formation along two different paths, *i.e.* the isothermal and the isobaric ones, but also to assess the validity of theoretical predictions such as the Mode Coupling Theory (MCT) [1].

Spectroscopic studies in function of pressure have been performed in few systems by means of dielectric relaxation [2], in cumene by depolarized light scattering [3], in orthoterphenyl by neutron scattering [4], and in PMMA by X-ray scattering [5].

Depolarized light scattering measurements on cumene showed the validity of the MCT models of α- and β-relaxations for the description of the spectra both in the supercooled and in the superpressed states, and density was also recognized not to be the only parameter driving the transition. The measurements in orthoterphenyl showed the consistency of the neutron data with MCT, allowing to extract the behavior of the critical cross-over parameter $P_\mathrm{c}(T)$ (critical pressure).

Here, we report depolarized light scattering spectra measurements of liquid salol ($C_{13}H_{10}O_3$, $T_\mathrm{m} = 315$ K) performed in thermodynamic states above the melting line [6], *i.e.* outside either the supercooled or the superpressed regions, both at constant pressure and variable temperatures (CP), and at constant temperature and variable pressures (CT).

Salol has been intensively studied as a function of temperature, mostly in the undercooled state, with different experimental techniques like depolarized light scattering [7–9], Brillouin scattering [10], impulsive stimulated light scattering [11], optical Kerr effect spectroscopy [12], and neutron scattering [13], however no measurement as a function of pressure has been reported.

We discuss our results using the ideal MCT in order to show the validity of this model and the derivation of the critical parameters solely from the normal liquid behaviour. Although MCT is considered applicable, in the form we use, only in the "vicinity" of the "critical transition", we experimentally find that also the normal liquid state can be considered "close enough" in this case.

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2 The experiment

The experimental measurements of depolarized light scattering spectra were performed at the four different temperatures 328, 343, 363, 393 K and at a pressure of 1 bar in the CP mode, and at the five different pressures 1, 125, 375, 500, 625 bar and at $T = 343$ K in the CT mode. Temperature was measured with an accuracy of 0.5 K by means of thermocouples inserted in the body of the scattering cell, while pressure was measured with an accuracy of 0.6 bar using a standard piezoelectric gauge connected to the pressure generating gas circuit. A thermostatized optical quartz cell was used to contain the sample in the CP mode, while a thermostatized high pressure cell with three optical windows sustaining up to 3 000 bar, designed in our laboratory, was used in the CT mode. Helium gas was chosen to transmit the pressure to the sample through a high pressure circuit, the sample being confined inside the light-scattering cell. The desired pressures were generated in the helium by means of compression and pressure intensification. The salol sample was obtained from Merck (99% purity), and was further distilled several times. The depolarized light-scattering spectra were measured in the CP case at 180° scattering angle, while in the CT case a 90° geometry was used to reduce stray light. The spectra were excited with an ion argon laser at a wavelength of 4 880 Å and with 200 mW of incoming power. The scattered light was analysed by means of a high resolution Raman double monochromator SOPRA DMDP 2 000 with a maximum frequency resolution of 1 GHz. The spectra were recorded by photon counting, over frequency shifts between −30 GHz and 4 000 GHz. For the high resolution measurements at lower frequencies, the SOPRA spectrometer was used in the double-pass double monochromator configuration. For low resolution at high frequencies the single-pass configuration was preferred to increase the signal intensity. For each thermodynamic point various runs were recorded for several hours and then summed to obtain the final spectra with better statistics.

3 Results and analysis

In order to discuss and analyze our depolarized light-scattering measurements we refer for convenience to the susceptibility spectra $\chi''(\omega)$ which are defined as the intensity spectra divided by the Bose factor, *i.e.* $\chi''(\omega) = I_{VH}(\omega)/(n(\omega)+1)$, where $I_{VH}(\omega)$ is the measured scattered intensity, $\omega = 2\pi\nu$ is the angular frequency shift, and $n(\omega)$ is the Bose-Einstein distribution.

Figure 1 shows the susceptibility spectra for both the CP and CT cases. The spectra were arbitrarily shifted vertically for the sake of clarity.

From Figures 1a, b we note the usual behaviour of the maximum of the α-relaxation. It shifts with temperature in the CP case, while for the CT case the stray light contamination in the first few points of the spectra up to 1 GHz prevents this to show up clearly. Moreover, also the shape of the β-relaxation shows the expected behaviour and a minimum starts to develop at the lowest temperature and at the highest pressure.

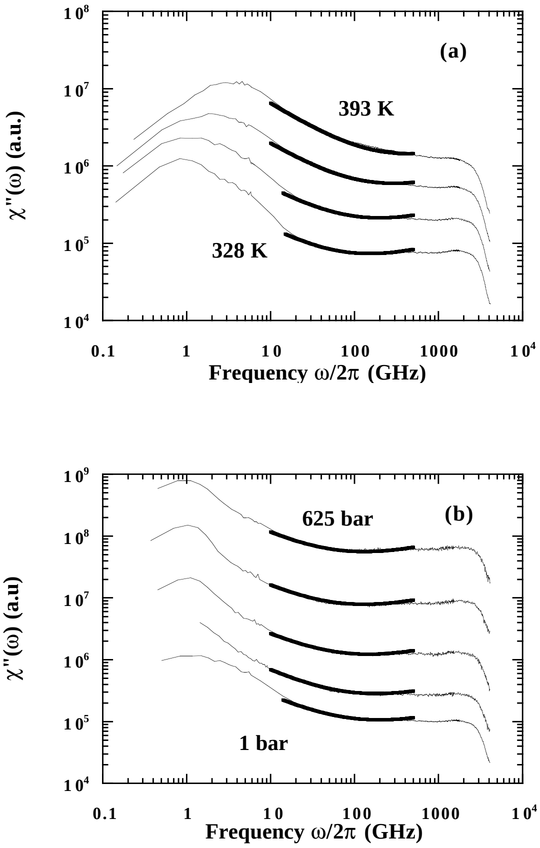

Fig. 1. (a) Susceptibility spectra from CP measurements at 1 bar. The temperatures are from top to bottom: 393, 363, 343 and 328 K. (b) Susceptibility spectra from CT measurements at 343 K. The pressures are from top to bottom: 625, 500, 375, 125 and 1 bar.

We analyze the spectral data within the framework of MCT [1]. We also discuss our CT data with respect to the pressure variable, as in [4], rather than using the density variable as in [3], because to our knowledge there is no equation of state for salol in this region. Anyway, since for liquids over a small pressure range, as in the present case, pressure and density are almost linearly related, the analysis of the data should give the same result with either variable.

We start with the α-relaxation. In this case it is well known that the Kohlrausch stretched exponential function $\phi(t) = A\exp(t/\tau_\alpha)^{\beta_\mathrm{K}}$ is a good approximation to the solution of the MCT equation. However, this function does not have an analytical Laplace transform. Thus, in order to analyze our data, we use as it is often done the Cole-Davidson expression [14]. This is known to approximate very well the Laplace transform of the stretched exponential. It is given by:

$$\chi_\mathrm{CD}(\omega) = \frac{\chi_0}{(1+\mathrm{i}\omega\tau_\mathrm{CD})^{\beta_\mathrm{CD}}}, \qquad (1)$$

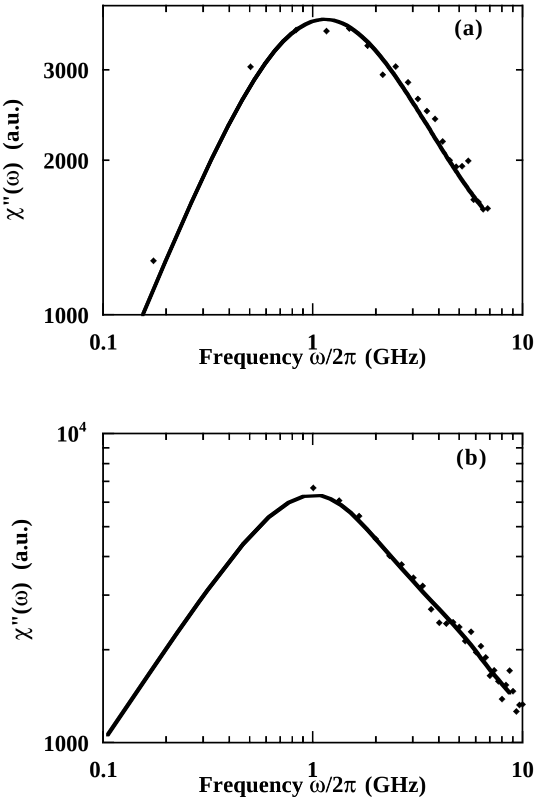

Fig. 2. Fit of $\chi''(\omega)$ in the α region for $T = 343$ K and $P = 1$ bar (a) and $T = 343$ K and $P = 375$ bar (b) using equation (1).

where the $\tau_{\rm CD}$ and $\beta_{\rm CD}$ are related to τ_α and $\beta_{\rm K}$ by [14]:

$$\beta_{\rm CD} = \frac{\beta_{\rm K} - 0.316}{0.683} \qquad 0.6 \le \beta_{\rm CD} < 1, \tag{2}$$

$$\beta_{\rm CD} = \frac{\beta_{\rm K} - 0.144}{0.970} \qquad 0.2 \le \beta_{\rm CD} < 0.6, \tag{3}$$

$$\tau_{\rm CD} = \frac{\tau_{\rm K}}{1.184\beta_{\rm K} - 0.184}\,. \tag{4}$$

We fitted, both in the CP and in the CT cases the part of our experimental spectra related to the α-relaxation with the imaginary part $\chi''(\omega)$ of the Cole-Davidson function convoluted with the experimental resolution function of our apparatus in order to derive $\tau_{\rm CD}$ and $\beta_{\rm CD}$ and then obtain τ_α and $\beta_{\rm K}$ for the Kohlrausch function. A typical fit of our experimental $\chi''(\omega)$ in the α region is given in Figures 2a, b for $P = 1$ bar and 375 bar, respectively, at the temperature $T = 343$ K.

In the CP case, the data between 0.2 and 10 GHz were used for the fitting of the α-relaxation, while in the CT case, owing to stray light contamination, we used only the spectra between 1 and 10 GHz, as reported in Figure 2, for all the data at 1, 375, 500 and 625 bar. Here we considered only the data up to 10 GHz, since in this range contamination of the high frequency behaviour could not be observed within the precision of our fit. From the previous analysis we found the values $\beta_{\rm K}$ for each temperature and pressure and then evaluated the average value and standard deviation, obtaining $\beta_{\rm K} = 0.84 \pm 0.02$ from the CP spectra and $\beta_{\rm K} = 0.84 \pm 0.03$ from the CT spectra. Within our experimental errors, there is thus no significant temperature and pressure dependence of the stretching parameter. Moreover, this parameter does not increase with either the increase of the temperature or the decrease of the pressure towards the diffusion limit in our normal liquid case, as already reported in other experiments [15,16].

From the temperature behaviour of $\tau_\alpha \propto (T - T_{\rm c})^{-\gamma}$ we obtained, by means of a least square fit procedure, $\gamma = 2.2 \pm 0.2$ and $T_{\rm c} = 255 \pm 10$ K, while for the CT case assuming for the pressure a similar behaviour $\tau_\alpha \propto (P_{\rm c} - P)^{-\gamma}$ with $\gamma = 2.2 \pm 0.2$, we obtain $P_{\rm c} = 2\,400 \pm 200$ bar. We note that the useful spectral range in the CT case is not sufficiently large to give a precise value of γ. Therefore, we decided to assume for γ the value extracted from the CP case to derive the critical pressure. The errors for γ and for the critical parameters were evaluated from the least square fit. The values derived for $T_{\rm c}$ and γ are in very good agreement with previous results [7].

We now focus our attention on the β-relaxation region. Here MCT gives the interpolation formula:

$$\chi''(\omega) \propto b(\omega/\omega_{\rm min})^a + a(\omega_{\rm min}/\omega)^b, \tag{5}$$

which describes with very good approximation the susceptibility $\chi''(\omega)$ in the region of the minimum, which is usually more evident in the supercooled state. We verified that in our case, in the frequency region of the minimum, equation (5) differs from the correct expression, calculated from tabulated expansion coefficients [17] by less than 1 per cent. Therefore, we assume that the expression (5) can be used to analyze the spectra in the normal liquid phase and to derive the relevant parameters. We performed the fit to the CP and CT spectra in the region between 15 GHz and 450 GHz, which is about that which can be defined by a scaling plot of the measured spectra. This has been done by means of the interpolation formula (5), with the three free parameters a, b and $\omega_{\rm min}$, with constraints for a and b given by the relation [1]:

$$\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b), \tag{6}$$

where λ is the exponent parameter and Γ is the Euler Γ function.

Figure 1 shows the result of the fit for both CP and CT. From the least square fitting procedure we derived values of a and evaluated the average value and standard deviation for the CP and CT measurements separately. This gives $a = 0.329 \pm 0.003$, and $a = 0.325 \pm 0.002$, respectively. These two values show that, within our experimental errors, a can be considered as independent from the thermodynamic variables T and P. This independence is known from previous work in the case of variable temperature. Here we show that this is also valid for the variable pressure case in salol, as already found for cumene

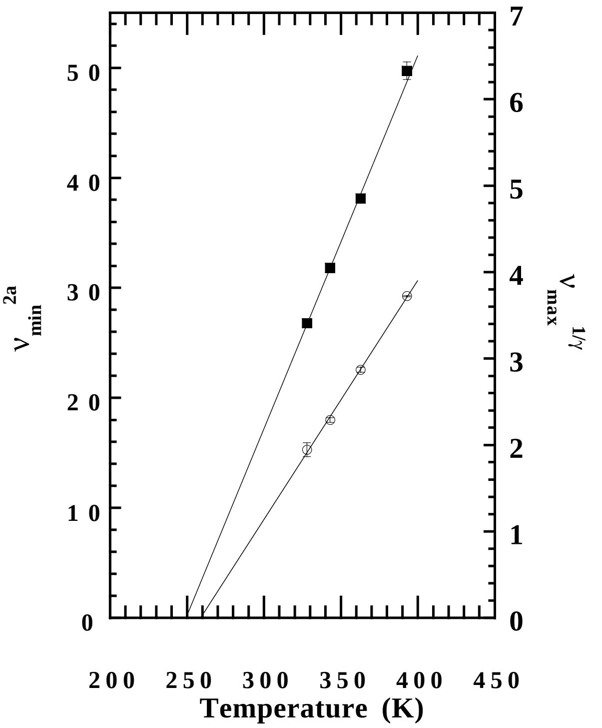

Fig. 3. Temperature dependence of ν_{min}^{2a} (full squares) and $\nu_{\mathrm{max}}^{1/\gamma}$ (empty circles) where ν_{min} and ν_{max} are in GHz.

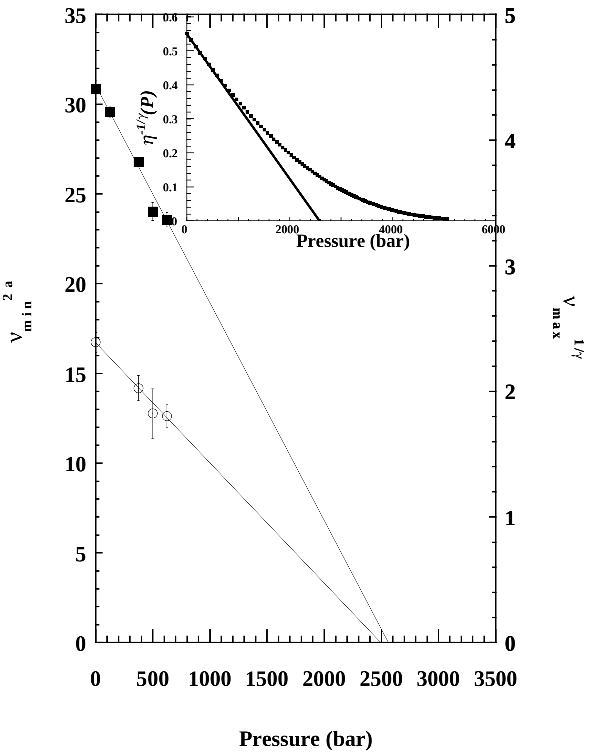

Fig. 4. Pressure dependence of ν_{min}^{2a} (full squares) and $\nu_{\mathrm{max}}^{1/\gamma}$ (empty circle) with ν_{min} and ν_{max} in GHz. The inset shows $\eta^{-1/\gamma}(P)$, where η is in cpoise.

in reference [3]. We derive our final experimental value for a by taking the average of the previous two values with the standard deviation, which gives $a = 0.327 \pm 0.005$, *i.e.* exactly the one previously derived for salol [7].

We now derive the experimental value of b from (6). This gives $b = 0.641 \pm 0.02$. The two values a and b lead to a value for γ, using $\gamma = 1/2a + 1/2b$. This gives $\gamma = 2.31 \pm 0.05$, in good agreement with the value derived independently from the α-relaxation in our spectra. The MCT also gives for ω_{min} the power law behaviour $(T - T_{\mathrm{c}})^{1/2a}$ in the CP case, and $(P - P_{\mathrm{c}})^{1/2a}$ in the CP case. Figure 3 shows our ν_{min}^{2a} as a function of T in the CP case, where $\nu_{\mathrm{min}} = \omega_{\mathrm{min}}/2\pi$, together with the $\nu_{\mathrm{max}}^{1/\gamma}$ obtained from the α-relaxation analysis, where $\nu_{\mathrm{max}} = \omega_{\mathrm{max}}/2\pi$.

Both quantities show the linear behaviour predicted by MCT, and both extrapolate to a common $T_{\mathrm{c}} = 254 \pm 20$ K, in good agreement with a previous value [7]. Figure 4 shows ν_{min}^{2a} and $\nu_{\mathrm{max}}^{1/\gamma}$ as a function of P in the CT case. Here we used for γ the value 2.31 ± 0.05. The linear fit to these data extrapolates to value $P_{\mathrm{c}} = 2\,550 \pm 250$ bar for the β-relaxation and $P_{\mathrm{c}} = 2\,500 \pm 200$ bar for the α-relaxation.

In this figure, the pressure dependence of the quantity $\eta(P)^{-1/\gamma}$ is reported in the inset. The viscosity $\eta(P)$ is obtained from references [18,19], while the γ is the one derived from the above analysis, *i.e.* $\gamma = 2.31 \pm 0.05$. One sees that for $\eta(P)^{-1/\gamma}$ the low pressure data show a linear behavior which extrapolates to $P_{\mathrm{c}} \sim 2780$ bar. The P_{c} values in the three cases are in good agreement.

4 Conclusions

We reported experimental depolarized light-scattering spectra of salol in the normal liquid state performed under isothermal and isobaric conditions. In particular, we measured the α- and β-relaxation behaviors as a function of pressure. The measurements show that MCT can usefully be applied also in thermodynamic states which could be considered far from the glass transition, *i.e.* outside the metastable state region, indicating that the mode-coupling mechanism, which eventually drives the glass formation process, and the α- and β-relaxation processes are here already well present in the normal liquid phase. This has not been stressed up to now, even though this was already found in several experiments [3,20]. It leads to the experimentally supported conclusion that the MCT $\chi''(\omega)$, can interpret very well the behaviour of the depolarized spectra also away from the strictly defined "critical region" or the vicinity of the critical point.

In particular, we demonstrated the independence of the parameters, a, b and γ in salol from the thermodynamic variables P and T, as it was done in reference [3] for cumene. This is an important fact, and a further support for the use of MCT. We also found the critical pressure $P_{\mathrm{c}} \sim 2\,500$ bar at $T = 343$ K.

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