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Hypersonic relaxation in liquid methanol

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Abstract. The hypersonic velocity and sound attenuation for liquid CD_3OD , CH_3OH and $\text{CD}_3\text{OD}/6\% \text{D}_2\text{O}$ are reported for a temperature range of 190 K–300 K. The results, measured from Brillouin–Mandelstam scattering, indicate the presence of at least one viscous relaxation phenomenon, for which the relaxation time is evaluated. The non-Arrhenius behaviour of the latter magnitudes evidences the appearance at low temperatures of a second relaxational mechanism.

1. Introduction

Brillouin scattering of light has long been recognized as a powerful technique for the investigation of the spectrum of longitudinal density fluctuation in viscous liquids [1–4]. The measured spectrum is characterized by a central, unshifted part and two sidepeaks attributed to the propagating sound waves in the medium. Although some details remain to be explained, the overall spectral features are now well understood [3], thus allowing the measurement of relevant magnitudes such as sound velocity and attenuation.

This paper reports the measurements of sound velocity and absorption of methanol (CD_3OD and CH_3OH) as well as a methanol–water mixture. The relevance of the alcohol and alcohol–water systems stems from their rather different behaviour compared with that of water; thus they serve as a reference system free from the thermodynamic anomalies exhibited by liquid water.

The present experiments were motivated by the need to relate data obtained by means of neutron inelastic spectroscopy to those obtainable in the thermodynamic limit. A collective excitation has been found in neutron triple-axis spectroscopy studies [5] and it was observed that, contrary to what, in principle, was expected from the knowledge of the temperature behaviour of the Brillouin linewidth [4], the lifetime of the excitation seemed to increase monotonically when the temperature was decreased. Therefore, there was a need to obtain reliable measurements of sound attenuation and velocity at relatively low temperatures since no data had, to our knowledge, been reported from ultrasonic or hypersonic (light-scattering) sources. On the other hand, the methanol–

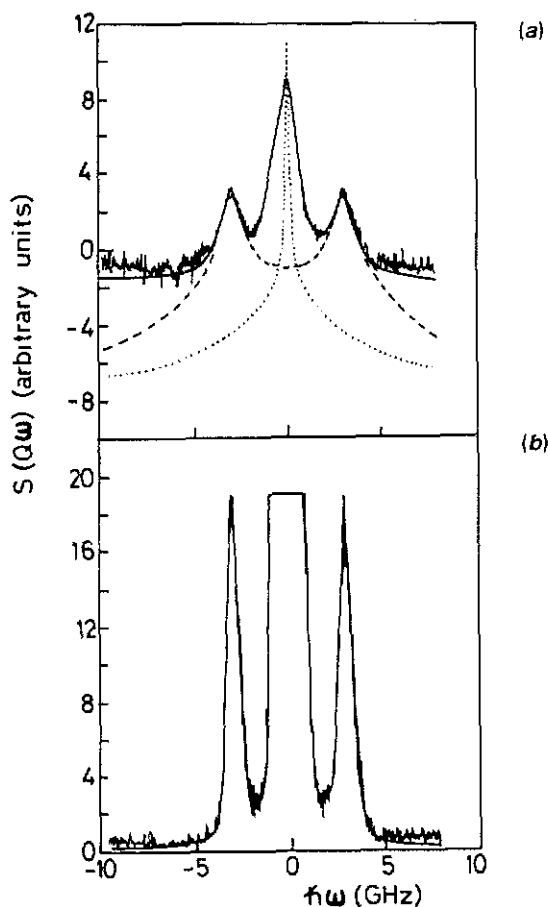


Figure 1. Brillouin-Mandelstam spectra of deuteromethanol at $T = 200$ K. (a) The $S(Q, \omega)$ dynamic structure factor is shown on a logarithmic scale as well as the Rayleigh and Brillouin components. (b) The fitted spectrum and the original intensity are shown on an expanded (linear) scale.

water mixture was chosen in order to explore the effect of small amounts of water on the supercooling properties of the alcohol.

2. Experimental details

The measurements were performed using a triple-pass Fabry-Perot set-up with a free spectral range of 44.26 GHz. Light from a single-mode Ar^+ laser ($\lambda = 4880 \text{ \AA}$) with an output power of about 0.1 W was used as the incident radiation, and the scattering at right angles was analyzed after collimation through a $500 \mu\text{m}$ pin hole. The overall finesse was about 60 and the instrumental resolution was measured introducing the attenuated direct beam into the cavity. Such a procedure resulted in an instrumental profile which approximated a cubic Lorentzian [6], and the fitted curve was then used as the slit function to be folded with the model scattering law. The sample holder consisted of a metallic cylinder with quartz windows at right angles, able to fit into a continuous flux cryostat with optical access which allows a temperature control of about 0.1 K within the range 100–300 K. An example of the measured spectral shapes is given in figure 1.

The data regarding refraction indices as well as some transport properties were taken from standard reference tables [7].

The parasitic light arising from the cryostat and cell quartz windows made an intensity analysis of the different spectral components extremely difficult, although such a contribution was undetectable in the frequency range of the Brillouin lines. As a consequence no information about the Landau-Placzek ratio could be derived from the present results.

3. Data analysis

The first step in the analysis consisted in the measurement of the position of the maxima of the Brillouin peaks by means of a fit in terms of a sum of three Lorentzian functions to the whole spectrum. Such a model-free approach evidenced the fact that the measured velocities were substantially higher than their ultrasonic (adiabatic) counterparts.

In order to ascertain the nature of such a deviation, a fit in terms of a model that includes both thermal and viscous relaxation effects was then carried out [1]. Such a model can be written in terms of four Lorentzian functions encompassing two central components (Rayleigh and Mountain modes) and a Brillouin doublet [1]:

$$\begin{aligned}
 S(Q, \omega) = I_R \frac{D_T Q^2}{(\omega^2 + D_T Q^2)^2} + I_B \left(\frac{\Delta \omega}{(\omega - \omega_B)^2 + \Delta \omega^2} - \frac{\Delta \omega(\omega - \omega_B)}{\omega_B [(\omega - \omega_B)^2 + \Delta \omega^2]} \right. \\
 \left. + \frac{\Delta \omega}{(\omega + \omega_B)^2 + \Delta \omega^2} + \frac{\Delta \omega(\omega + \omega_B)}{\omega_B [(\omega + \omega_B)^2 + \Delta \omega^2]} \right) \\
 + I_M \frac{2c_{s0}/\tau_{th}}{[\omega^2 + (c_{s0}/\tau_{th})^2]^2} \quad (1)
 \end{aligned}$$

where I_R , I_B and I_M represent the intensities of the Rayleigh, Brillouin and Mountain components respectively, the momentum transfer was $Q = 0.002 \text{ \AA}^{-1}$ in this study, D_T is the thermal diffusivity, ω_B is the Brillouin frequency shift, and the Brillouin linewidth is given by $\Delta \omega = (Q^2/2\rho)(\eta_L(T, \omega) + C(T))$, where ρ represents the equilibrium density, $\eta_L(T, \omega)$ a frequency-dependent longitudinal viscosity and $C(T)$ comprises the terms giving rise to thermal conduction. The last term of equation (1) represents a contribution due to thermal relaxation with a linewidth governed by the inverse of the thermal relaxation time τ_{th} ; c_{s0} represents a quantity defined in terms of the ratios of the adiabatic and hypersonic velocities and was left as a free parameter.

The analysis was thus performed in terms of the model $S(Q, \omega)$ function which was convolved with the experimental slit function to give an intensity distribution which was compared with the experimental intensities. A standard optimization scheme similar to one previously used [8] was followed in order to compute the final parameter values.

4. Results and discussion

The measured sound velocities and attenuation coefficients for the three samples are shown in figures 2 and 3. On qualitative grounds, it can be seen from figure 2 that the temperature behaviour follows 'S'-shaped curves in the three cases. Low-frequency sound (ultrasonic data) is approached in the case of hydrogenated methanol at tem-

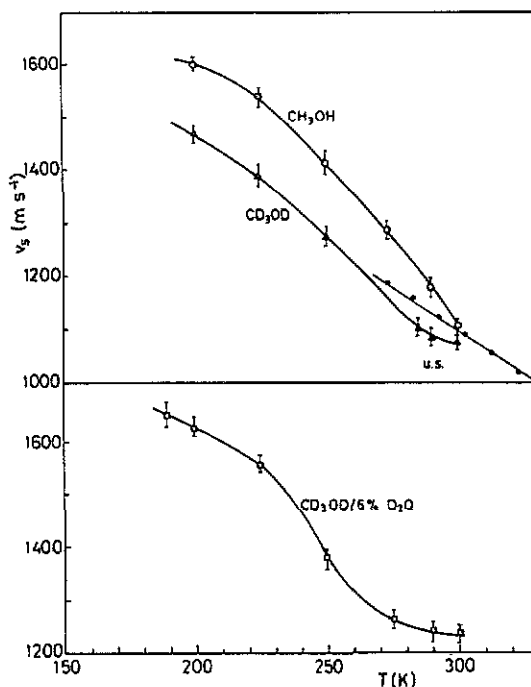


Figure 2. Hypersonic velocities for the three samples. The low-frequency (ultrasonic) data have been taken from [17].

peratures around 290 K. In order to rationalize the observed difference in the velocities between the deuterated and the hydrogenated compound, a simple scaling law of the form [9]

$$v^* = v(M/\varepsilon)^{1/2}$$

was considered, where the reduced velocity (v^*) was obtained from the observed quantity (v), the molecular mass (M) and the depth of the minimum of the intermolecular potential (ε).

The ratio of velocities of the two isotopic species could then be used as evidence of the different intermolecular potentials of the two species. In fact, the velocities cannot be explained by the mass difference alone, and an estimation of the ratio of the potential parameters for both species gives $\varepsilon_{\text{H}}/\varepsilon_{\text{D}} = 1.068$. Once this difference is taken into account, the two curves of figure 2(a) can be reproduced (within error bars) using the masses as the other scaling parameter.

A rather distinctive behaviour can be seen for the deuteromethanol–6% heavy water mixture where, apart from the well known hardening of the sound mode upon addition of water [10], a more pronounced bending is displayed, with an inflection point in the temperature dependence of the velocity curve which basically coincides with the maximum of the sound attenuation versus temperature curve.

The temperature dependence of the velocity shows a dispersion of about 45% in the temperature range explored. In all the cases analyzed the thermal component (Mountain mode) seems to be best represented by a nearly flat background which is difficult to separate from the electronic (dark current) contribution.

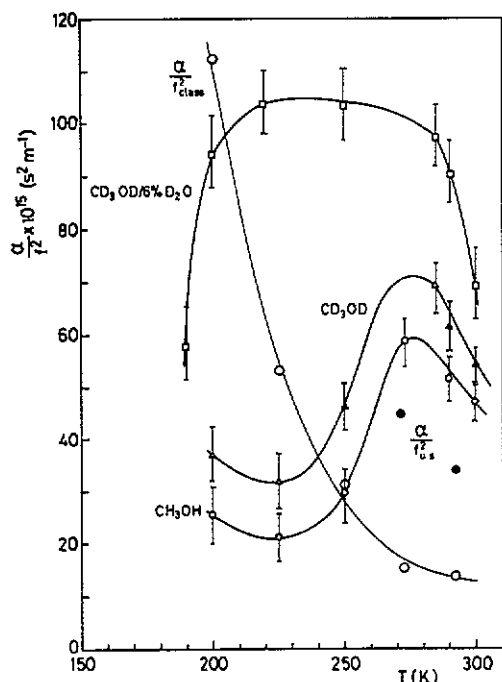


Figure 3. Sound attenuation versus temperature. The ultrasonic data were taken from [17]. The classical (or Stokes) attenuation coefficients have been computed from values of the shear viscosity given in [14].

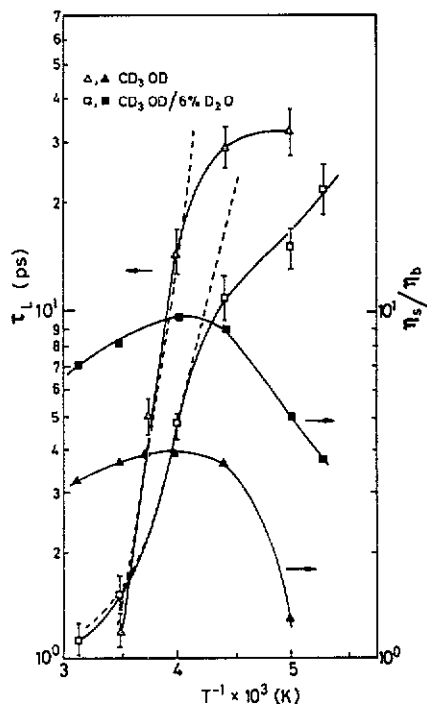


Figure 4. Temperature dependences of the relaxation time and of the ratio of bulk to shear viscosities. The approximations in terms of the Vogel-Fulcher-Tammann law are depicted by broken curves.

As a consequence, it seems clear that the positive dispersion of the sound velocity observed in the present experiment cannot be attributed to thermal mechanisms as is known to be the case in other molecular liquids [11], but is instead dominated by structural relaxation effects. The contribution of thermal mechanisms to the velocity dispersion as well as its frequency dependence can be easily estimated from [12, 13]

$$v_{th}^2 = \gamma B_T (1 + w^2/x^2) / (1 + \gamma w^2/x^2)$$

with $x = v_0^2 \rho C_p \lambda^{-1}$ where γ is the ratio of specific heats, v_0 the adiabatic sound velocity, C_p the specific heat at constant pressure, λ the thermal conductivity and B_T the bulk modulus.

A calculation using tabulated values for methanol at 298 K gives an estimate for x of the order of $1.12 \times 10^{13} \text{ rad s}^{-1}$ which sets the order of w^2/x^2 to 10^{-5} —so it can be safely disregarded. On the other hand, the absence of a noticeable contribution from the Mountain mode can be rationalized if the high vibrational frequencies of these molecules and the relatively low temperatures of these measurements are taken into account. In fact, the lowest-lying vibrational mode observed in the liquid phase corresponds to the CO stretch with a characteristic frequency of 1020 cm^{-1} , well above the energy available for thermal excitation which at the highest temperature is about 200 cm^{-1} .

Table 1. Transport properties for deuteromethanol.

T (K)	200	225	273	293
λ/c_p^a	1.04	0.98	0.87	0.83
$C_{th}(T)^b$	3.13	2.96	2.62	2.48
$\eta_s(T)^c$	4.58	2.56	0.89	0.63
$\eta_b(T, \omega)^c$	5.95	9.21	3.31	2.09
$\tau_L(T, \omega)^d$	32.0	29.1	2.80	0.76

^a 10^{-4} kg m⁻¹ s⁻¹.^c 10^{-3} N s m⁻².^b 10^{-5} N s m⁻².^d 10^{-12} s.

On the other hand, the sound attenuation coefficient shows a rather complicated behaviour with temperature. Above 250 K the measured attenuations are well above the value predicted for the 'classical' attenuation coefficient, thus indicating the presence of 'structural relaxation' processes. Below the above-mentioned temperature, the attenuation coefficients rapidly decrease below those computed for their classical counterpart which is usually interpreted as an indication of the appearance at those temperatures of a viscous relaxation process.

In order to analyse the data we have employed the classical form of the viscoelastic theory assuming the existence of only one significant relaxation time for the longitudinal viscosity. Under such conditions the hypersonic velocity and sound attenuation can be written as [12, 13]

$$v_s^2(T, \omega) = \{K_1(T) + \eta_L(T, \omega)[\omega^2 \tau_L(T, \omega)/(1 + \omega^2 \tau_L^2(T, \omega))]\}/\rho(T) \quad (2)$$

with

$$K_1(T) = v_0^2(T)\rho(T)$$

$$(\alpha/f^2)(T, \omega) = (2\pi^2/\rho(T)v_s^3(T, \omega))[\eta_L(T, \omega)/(1 + \omega^2 \tau_L^2(T, \omega))] + C \quad (3)$$

where $\tau_L(T, \omega)$ is a relaxation time for the longitudinal viscosity, $v_s(T, \omega)$ represents the sound dispersion, $\alpha(T, \omega)$ the sound attenuation at frequency f and the rest of the symbols have already been defined.

Assuming that the low-frequency sound velocity depends linearly on the temperature, the data obtained from ultrasound sources were extrapolated to cover the whole range of temperatures and thus the elastic modulus $K_1(T)$ was calculated.

Using equations (2) and (3), values for the relaxation time and frequency-dependent longitudinal viscosity are calculated from

$$\eta_L(T, \omega) = (\frac{1}{3}\eta_s(T) + \eta_b(T, \omega) + C_{th}(T)) \quad (4)$$

with $C_{th}(T) = (\gamma - 1)\lambda/c_p$ where the shear viscosities are assumed to have negligible frequency dependences, $\eta_b(T, \omega)$ represent the frequency-dependent bulk viscosity, and the symbols γ and λ retain their usual meanings. The contribution due to thermal conduction was evaluated from tabulated data and some results are summarized in table 1 along with some values for the relevant transport properties.

Taking the tabulated values for the shear viscosity we have computed the relaxation times as well as the ratio between bulk and shear viscosities for both deuterated methanol and the methanol-6% water mixture. The results for the temperature dependences of both quantities are shown in figure 4.

As can be seen, the relaxation times in both cases deviate from simple Arrhenius behaviour, as could be expected from the strong non-Arrhenius behaviour of the shear viscosity [14]. The onset for the observed deviation seems to be located at about 250 K for CD₃OD and 225 K for the mixture. Such behaviour is correlated with the decrease in the ratio of viscosities which drops from a mean value of about 3.5 for the temperature range of 225 K–300 K to about 1.3 at the lowest temperature for the alcohol, and from 8.6 to about 3.2 in the mixture.

The ratios of bulk to shear viscosity for methanol can be related to that of 3.2 reported for the alcohol at room temperature [13]. No such comparison was possible for the mixture due to the lack of reported data.

In summary, a high-frequency relaxation process has been detected from the analysis of Brillouin–Mandelstam spectra of these liquids which show characteristic times within the range $(0.5\text{--}33) \times 10^{-12}$ s for the alcohol and within the range $(1.8\text{--}22) \times 10^{-12}$ s for the mixture. The strong deviations from an Arrhenius behaviour seem to indicate the onset of a relaxation process at low temperatures. The measured velocity of sound at $T = 200$ K is well below the frequency of the excitation found for deuteromethanol from an inelastic neutron scattering study ($v = 2450$ m s⁻¹). The value of the relaxation time found for the longitudinal viscosity of CD₃OD at 200 K is 33×10^{-12} s, which is two orders of magnitude larger than that derived from inelastic neutron scattering [5].

Such a difference indicates the rather different nature of the collective phenomena sampled by the two techniques.

An attempt was made to analyze the temperature dependence of the relaxation times in terms of a phenomenological law of the Vogel–Fulcher–Tammann (VFT) form [15]:

$$\tau_L(T, \omega) = \tau_0(\omega) \exp[B/(T - T_0)]$$

where τ_0 , B and T_0 were taken as free parameters.

Such a function can explain the temperature dependence of the relaxation times for the methanol–water mixture. However, only the data corresponding to the temperature range 225 K–300 K can be fitted to such a function in the alcohol case.

Although the estimates have been derived from a rather small number of observations, the data for the deuterated compound deviate significantly from the predicted exponential behaviour especially in the low-temperature region.

The estimates of the parameters τ_0 and T_0 were 0.11×10^{-12} s and 168 K respectively, for the deuterated alcohol and 0.5×10^{-12} s and 150 K for the mixture. The estimated values for the temperatures T_0 are close to the glass transition temperatures and this can be interpreted as evidence that above 225 K the structural relaxation follows the universal VFT form [15], whereas a second relaxational mechanism becomes predominant at temperatures below that point.

5. Conclusion

Although no substantial deviations from purely Debye behaviour have been found in dielectric relaxation studies at temperatures in the range 270 K–300 K [16], the low-temperature liquids show clear evidence of sound velocity dispersion.

The hypersonic velocities found in methanol (CH₃OH, CD₃OD) and a methanol–water mixture have been interpreted in terms of a relaxational mode arising from purely viscous effects. The difference in longitudinal viscosities and velocities of the two isotopic

species can be well accounted for in terms of a simplified scaling law based upon the principle of corresponding states.

The presence of such positive dispersion at this length scale seems to suggest that the observed excitation found in neutron spectroscopy could be a continuation at larger wavevectors of the structural relaxational effects observed here.

Acknowledgments

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