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The dynamic glass transition of a ‘fragile’ molecular liquid in the megahertz domain*

M Cutroni†, P Migliardo†, A Piccolo† and C Alba-Simionesco‡

† Dipartimento di Fisica, Università di Messina and INFN, PO Box 55, 98166 S Agata, Messina, Italy

‡ CPMA URA 1104, CNRS, Université de Paris-Sud, 91405 Orsay Cédex, France

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Abstract. We have performed measurements of acoustic attenuation and sound velocity at ultrasonic frequencies in a molecular liquid (*m*-fluoroaniline) across its calorimetric glass transition T_g . This liquid offers the opportunity to observe its dynamical response continuously over an extended temperature domain where no crystallization is to be feared. The temperature dependence of the longitudinal moduli components $M'(T)$ and $M''(T)$ were derived and analysed with the Cole–Davidson and the Kohlrausch–Williams–Watts functions where a Vogel–Fulcher–Tarran expression and a power law were employed to link the main relaxation time to the temperature. The experimental behaviour of this molecular liquid is related to its ‘fragile’ character.

1. Introduction

The classic interpretation of the glass transition [1] of a supercooled liquid is focused on the remarkable increase of the viscosity when the temperature decreases towards T_g ; in other words, it supposes a divergent relaxation time at a temperature below T_g when overcrossing the experimental time scale. The liquid–glass transition observed in laboratory, therefore, is clearly a kinetic process, and this fact implies that the glass transition temperature T_g is defined relative to the probing frequency of a given technique crossing the main structural relaxation time. This phenomenon of ‘crossover’ is directly connected to the manifestation of resonances, or α -peaks, in the relevant dynamic susceptibilities; the static susceptibilities show, in correspondence, well marked ‘jumps’. So, for the frequencies involved in calorimetric equipments (10^{-2} – 10^{-3} Hz), T_g corresponds to the well known point where thermodynamic properties such as heat capacity C_p , expansivity α_p and compressibility κ_T show a sudden change from liquid-like to solid-like values [2]. The primary (or α) relaxation, hence, is strictly related to the problem of the glass transition. This explains the great amount of experimental effort (involving a wide variety of techniques such as specific heat [3], dielectric [4] and mechanic [5] relaxation, light scattering [6], and neutron scattering) made to study the relaxation properties approaching T_g .

At this point it must be remarked that while all systems behave with recurrent characteristics suggesting an underlying universality of the phenomenon, it is true that, in some respects, these characteristics appear to be rather system dependent [7]. Angell’s classification of glass-forming liquids between two extreme limits called ‘strong’ and

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'fragile' is both useful and explanatory of this specificity [8]. Reanalysing early studies on this subject matter [9, 10], he noticed that for 'strong' liquids (SiO_2 , GeO_2 , BeF_2 , etc) the viscosity (and related relaxation times of large-scale flow processes) has an Arrhenius behaviour and the relaxation function is fundamentally exponential. On the other hand, the most common resulting characteristics of the 'fragile' liquids, of which a molecular representative example is *o*-terphenyl, are the strong departure from Arrhenius behaviour of the viscosity, describing rather a Vogel–Fulcher–Tamman (VFT) behaviour, and a strongly non-Debye character of the response function.

This work deals with an ultrasonic study of the primary relaxation in a 'fragile' molecular liquid: *m*-fluoroaniline. When the dynamic response of a viscoelastic system is measured by means of a mechanical experiment, the commonly derived quantities are the real and imaginary parts of the longitudinal (or shear) modulus $M^* = M' + M''$ [11]. This is the convenient dynamic susceptibility describing the response of a system to an alternating acoustic strain.

Two phenomenological relaxation functions are mainly used to represent almost all the experimental data (dielectric, mechanic, light scattering spectroscopy, etc) relevant to the α -relaxation: the Cole–Davidson (CD) function [12]

$$M^*(\omega, T) = M_\infty(T) - M_r(T)/[1 + i\omega\tau_{\text{CD}}(T)]^{\beta_{\text{CD}}} \quad (1)$$

(rewritten in mechanical formalism) and the Kohlrausch–Williams–Watts (KWW) function [13, 14] defined in the time domain

$$\frac{M(t, T) - M_0(T)}{M_r(T)} = \Phi(t, T) = \exp\{-[t/\tau_{\text{WW}}(T)]^{\beta_{\text{WW}}}\} \quad (2)$$

and related to M^* by one-sided Fourier transformation

$$M^*(\omega, T) = M_\infty(T) - M_r(T) \int dt \left\{ -\frac{d}{dt} [\Phi(t, T)] \right\} \exp(-i\omega t) \quad (3)$$

where $M_r = M_\infty - M_0$ is the relaxation strength i.e. the difference between the high- and low-frequency limiting M' values. These two functions represent simply phenomenological expressions that have been developed primarily to distinguish Debye and non-Debye relaxation; nowadays, no concrete models exist from which the parameter β_{CD} (or β_{WW}) can be derived from microscopic quantities. The reason for their popularity remains essentially in their universal character being able to describe the dynamic behaviour of very different and complex glass-forming systems including polymers, metallic glasses, van der Waals liquids, H-bonded liquids etc.

We have applied these functions, introducing the temperature dependence of the main relaxation time in terms of the (VFT) relation

$$\tau = \tau_0 \exp[B/(T - T_0)] \quad (4)$$

or in terms of a power law

$$\tau = \tau_0 (T/T_c - 1)^{-\gamma} \quad (5)$$

as predicted from the more recent fluctuating hydrodynamics of mode coupling theory (MCT) [15]. Theories assuming the validity of equation (4) or of equation (5) constitute two entirely

different approaches to the problem of the glass transition and contribute to distinguish two temperature domains in the supercooled regime of a liquid; the latter, based on a model of a molecule trapped in the cage formed by its neighbouring molecules, describes qualitatively all the properties of a liquid down to a temperature T_c , above T_g , at an experimental viscosity of about 10 P. The freezing in of the density fluctuations defined by the MCT (and the consequent breaking of ergodicity) is restored by other activated processes not taken into account in the primary version of the theory, but to date, MCT is the only available theory for the study of the particular properties of a supercooled liquid. The former description keeps in mind a possible thermodynamic underlying phase transition and attributes some significance to a temperature T_0 , now below T_g , where the relaxation time may diverge. For 'fragile' liquids T_0 usually falls very close to T_g ($T_g/T_0 \sim 1.2$) so that they offer the remarkable possibility of observing at least the early stages of the equilibrium phenomenon.

Ultrasonic investigation is usually drawn in the temperature domain since the available experimental frequency range is generally insufficient to trace out the whole relaxation region. On the other hand, one of the best approaches for understanding this dynamic transition is varying the experimental temperature in a range across T_g . Among the liquids, because of some peculiar physical features, *m*-fluoroaniline is a good representative example for this study.

2. Experimental set-up

The sample holder, a cylindrical cell of copper (ensuring a good thermal exchange) was filled with the liquid sample and a quartz transducer was immersed in it. The diameter and the height dimension were suitable to collect with a standard pulse-echo method the ultrasonic attenuation data as well as the sound velocity. The sample holder was built to realize different acoustic path lengths and permits measurements when the liquid becomes solid going through the glass transition temperature. A cryotip assembly (Oxford Instruments) was used to go down to 140 K; the temperature stability and the resolution were better than 0.1 K. The detection of acoustic behaviour in the liquid and glassy *m*-fluoroaniline was possible because molecular *m*-fluoroaniline has the property that it never crystallizes. Therefore, one may obtain the vitrified liquid sample at the low cooling rate of the cryotip assembly ($\sim 4 \text{ K min}^{-1}$) and, at the same time, may study step by step its behaviour down to the low-temperature end of the liquid state. The calorimetric T_g of *m*-fluoroaniline lies at about $T = 173 \text{ K}$ (defined by differential scanning calorimetry (DSC) at 10 K min^{-1}) [16].

3. Results

The attenuation α and the velocity v of longitudinal and shear acoustic waves have been determined as functions of temperature and at fixed ultrasonic frequencies (5, 10, and 30 MHz). In figure 1 the experimental results obtained exploring the temperature range 140–300 K for the longitudinal case are shown. The data of acoustic absorption indicate typical relaxation behaviour: all the curves exhibit a very high-loss asymmetric peak. The large value of acoustic absorption in the relaxation region prevents us from acquiring exactly the temperature maximum location of the peak (about 200 K), which shifts towards higher temperatures when the frequency increases. The variation of the sound velocity reflects the absorption data. No frequency dispersion appears at low and high temperatures, where it

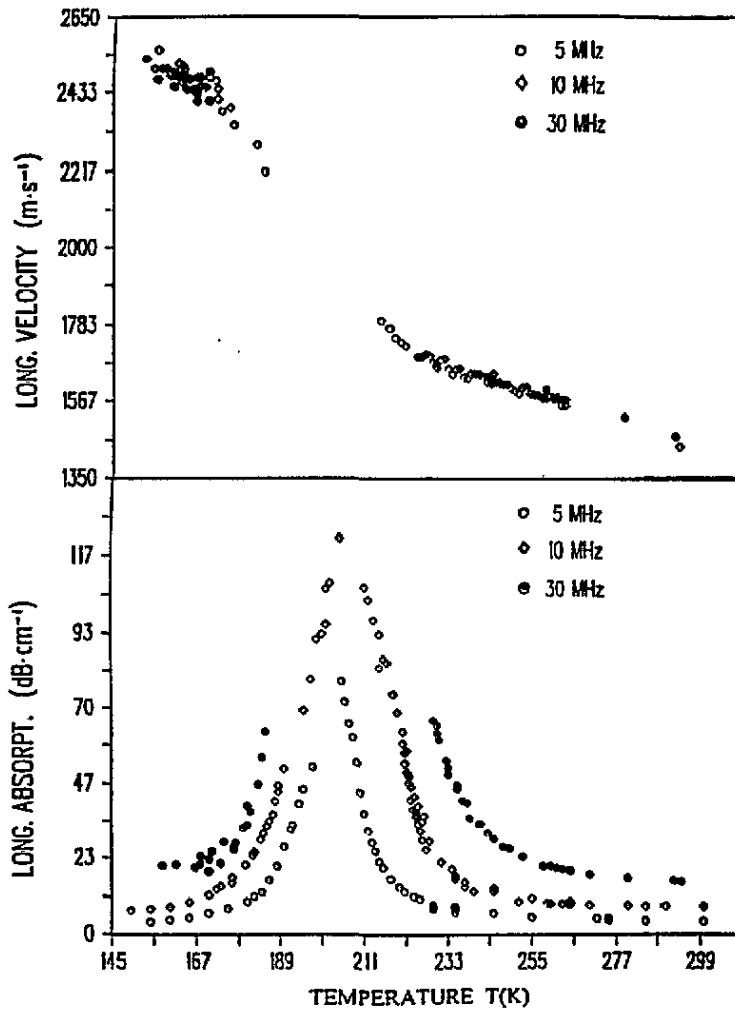


Figure 1. The temperature dependence of the longitudinal acoustic attenuation and the longitudinal sound velocity at various frequencies in *m*-fluoroaniline.

follows a slow linear temperature dependence and, in the relaxation region, a well marked change from liquid-like to solid-like values.

The temperature dependence of α and v for longitudinal wave propagation enables us to calculate the temperature dependence of the real and imaginary parts of the longitudinal modulus $M^* = M' + iM''$. It is well known, in fact, that the one-dimensional wave equation for the propagation of a longitudinal sound wave in the x direction is [17]

$$\rho \partial^2 u / \partial t^2 = M^* \partial^2 u / \partial x^2 \quad (6)$$

where ρ is the density. This equation can be solved assuming for the solution a sinusoidal damped plane wave

$$u = u_0 \exp[i\omega(t - x/v_1^*)] \quad (7)$$

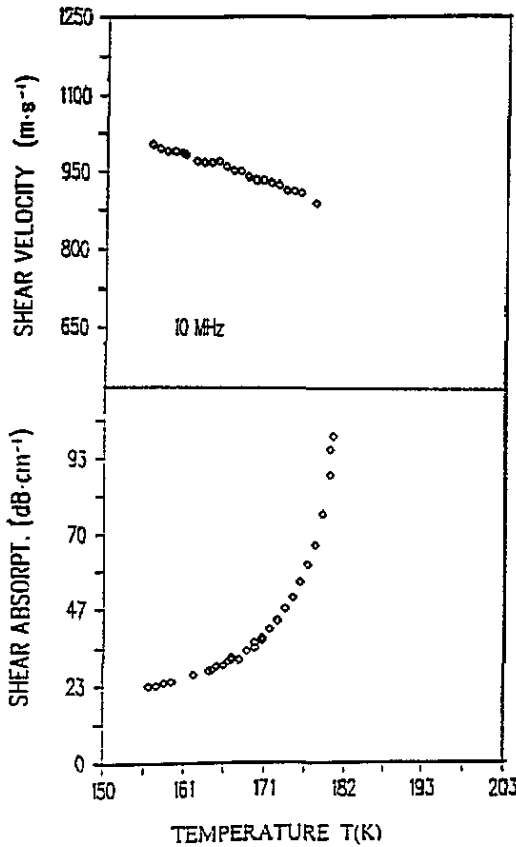


Figure 2. The temperature dependence of the shear acoustic attenuation and of the shear sound velocity at 10 MHz in *m*-fluoroaniline.

and

$$1/v_1^* = 1/v_1 - i(\alpha/\omega) \quad (8)$$

where α and v_1 are, respectively, the absorption coefficient and the phase velocity. Substituting equations (7) and (8) into the wave equation, one obtains (in the limit $\alpha v/\omega \ll 1$, well confirmed by our data)

$$M' = \rho v_1^2 \quad M'' = 2\rho\alpha v_1^3/\omega. \quad (9)$$

Thus, the two observable parameters α and v , which are measured in a wave propagation experiment, are related to the values of the two primary response functions $M'_\omega(T)$ and $M''_\omega(T)$. The curves extracted via equations (9) (subtracting a constant background from the experimental α values) have been analysed in the framework of linear viscoelasticity employing equations (1) and (3) as response functions incorporating the expressions (4) and (5) for $\tau(T)$ (with ω constant).

The density [18] of *m*-fluoroaniline has been extracted from thermal expansion data and fitted at atmospheric pressure as

$$\rho = 1.43 - 9.49 \times 10^{-4}T \text{ (K)}. \quad (10)$$

This relation has been employed to extrapolate the density values down to the glass transition temperature (173 K).

The shear-wave propagation was possible only in a limited temperature range close to T_g where the liquid begins to exhibit an effective shear rigidity. In this region it was possible to measure absorption and velocity with the usual echo-pulse technique (see figure 2).

4. Discussion

Assuming the same temperature dependence for M_∞ and M_0 , we have introduced in equation (1) a constant M_r (T independent) and a linear law for $M_\infty(T)$: $M_\infty(T) = C - D[T - 150 \text{ (K)}]$. In table 1 the results of an independent multiparameter fit using the CD function are reported. In figure 3 a comparison of the CD and KWW functions for the $M'(T)$ fit is also illustrated; the analysis with the last function was performed employing equation (3) in the series form reported in [19]. To extract an approximate value of the β_{WW} parameter from β_{CD} we have used the simple relation $\beta_{\text{WW}} = 0.97\beta_{\text{CD}} + 0.144$ [19]. The result of this conversion, $\beta_{\text{WW}} \simeq 0.37$, is slightly higher than the value $\beta_{\text{WW}} = 0.33$ obtained in the KWW fit (although they are within experimental error of each other). These low values suggest that in this (supercooled) liquid structural changes are correlated to highly cooperative viscous flow processes.

Table 1. Values of the parameters for the calculation of $M'(T)$ and $M''(T)$ employing the CD function (1) together with equations (4) and (5). Values are: M_r , $\text{dyn cm}^{-2} \times 10^{-10}$; C , $\text{dyn cm}^{-2} \times 10^{-10}$; D , $\text{dyn cm}^{-2} \text{ K}^{-1} \times 10^{-10}$.

VFT			
τ_0 ($\text{s} \times 10^{15}$)	B (K)	T_0 (K)	β_{CD}
6 ± 3	909 ± 10	140 ± 3	0.23 ± 0.03
Power law			
τ_0 ($\text{s} \times 10^{-12}$)	T_c (K)	γ	β_{CD}
2.2	156 ± 5	9.1 ± 0.5	0.33 ± 0.03
M_r	C	D	
3.4 ± 0.2	8.2 ± 0.1	0.017 ± 0.001	

The relaxation functions examined represent a good approximation of the dynamic behaviour of this system: the relaxation is found to be considerably stretched and this is in agreement with the hypothesis of correlation between the degree of fragility of a given system and the non-exponential extent of its temporal decay together with non-Arrhenius behaviour.

A temperature-independent β works fairly well in our fits and the same set of parameters has been found in the $M''(T)$ curves at both 5 and 10 MHz. This circumstance seems to suggest that the time-temperature superposition principle (thermorheological simplicity) is valid in the transformation region. It must be remarked, nevertheless, that because of the intrinsic roughness of ultrasonic investigations the set of available probe frequencies is too limited to exclude a gradual crossover to exponential relaxation at higher frequencies/temperatures. It is generally observed, in almost all cases, that the departure from exponentiality is temperature dependent and tends to vanish at high temperatures. In particular, systems exhibiting a stronger temperature dependence of β are those of greater fragility, a circumstance also predicted by Ngai and Rendell [20] in their coupling model and by percolation theories.

The computations performed with the VFT law have provided a value of $T_0 \simeq 140$ K lying about 30 K below the calorimetric glass-transition temperature. Because no crystal data exist for *m*-fluoroaniline we have made reference to the Kauzmann temperature estimated for a series of similar molecular liquids of comparable (high) fragility, such as *m*-fluorotoluene, *m*-xylene and *o*-terphenyl [16]. They have essentially the same structural

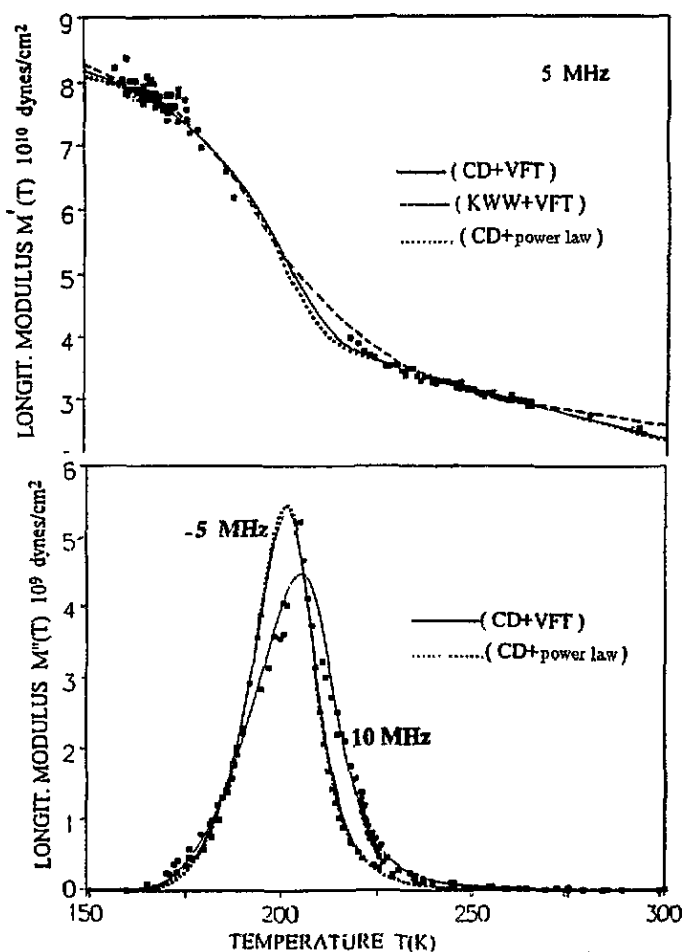


Figure 3. A comparison between the experimental data (blocks) and the CD fit with the VFT relation (solid line) and with a power law (dotted line) for the imaginary and real parts of the longitudinal modulus. The dashed line is a kww fit with $\beta = 0.33$.

shape but different strengths of intermolecular interaction, based on a systematic change of substituents on disubstituted benzene ring compounds. The fragility of *m*-fluoroaniline (and of the other liquids considered) can be correlated to its aromatic character (the absence of strong directional bonds), to its low liquid range index $T_b/T_g \approx 2.65$ (empirical rule: the higher the boiling point T_b to T_g ratio the stronger the liquid is [21]) and to the substantial change in the heat capacity at the glass transition $\Delta C_p \approx 82 \text{ J mol}^{-1} \text{ K}^{-1}$. These data are consistent with the quite low value of the fragility parameter $D \approx 6.5$ (obtained from our fits rewriting the VFT law in the modified form $\tau = \tau_0 \exp[DT_0/(T - T_0)]$) which locates *m*-fluoroaniline on the extreme right-hand side of the pattern illustrated in figure 4.

The value $T_g/T_0 \approx 1.23$ found for *m*-fluoroaniline is very close to the ratios T_g/T_K of the other liquids considered (see the legend of figure 4) and is nearly equal to that predicted by the Adam-Gibbs equation in VFT form for liquids of high fragility. This circumstance has induced us to analyse our results in the approach of the Adam-Gibbs theory. So, we have considered the well known expression [20]

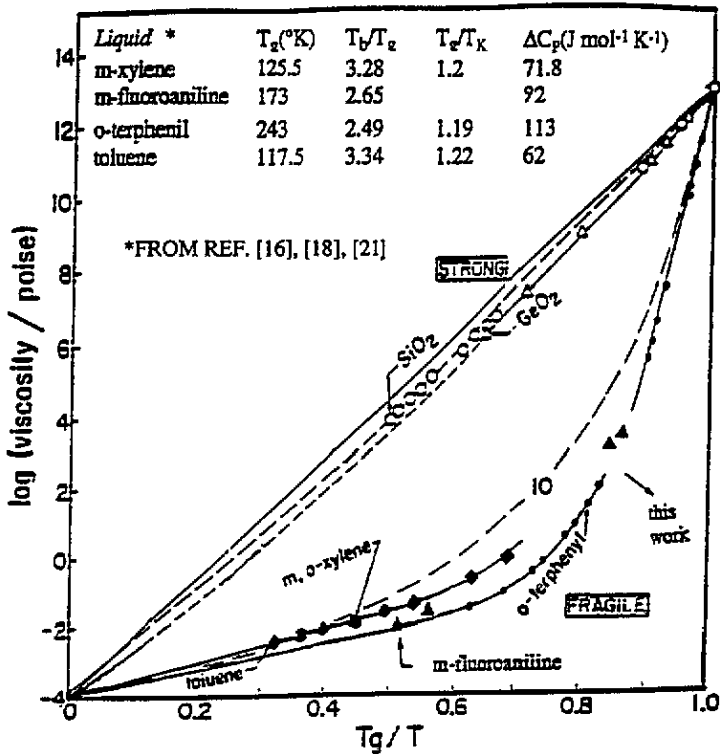


Figure 4. The variation with temperature of the viscosity of some liquids of various fragilities in a T_g -scaled Arrhenius plot. Here T_g is the calorimetric value. The legend gives T_g , T_b/T_g , T_g/T_K and ΔC_p values for each case.

$$D = s_c^* \Delta\mu / \Delta C_p (T_g) k_B T_g \quad (11)$$

in which the fragility parameter D is expressed in terms of the free-energy barrier $\Delta\mu$ crossed by a cooperatively rearranging region (CRR) and of the excess specific heat ΔC_p defined as the difference $C_p(\text{liquid}) - C_p(\text{glass})$ and where $s_c^* = k_B \ln 2$ would be approximately the same for all glass-forming liquids. Substituting the value $D \simeq 6.5$ in equation (11) we have found $\Delta\mu \simeq 32 \text{ kcal mol}^{-1}$ for *m*-fluoroaniline. This value is comparable with the activation energies for viscous flow near T_g of many glass-forming liquids.

The lack of experimental points in the relaxation region for the shear-wave investigation prevent us from making fits with theoretical curves so we have calculated in the available temperature range the internal friction Q^{-1} for both longitudinal and shear data (see figure 5). It is well known that this quantity gives a measure of the fraction of energy $\Delta W/W$ dissipated in heat in each acoustic cycle due to viscoelastic behaviour [22]:

$$Q^{-1} = M''/M' = 2\alpha v/\omega. \quad (12)$$

From the observed trend one could argue that shear and longitudinal processes begin to give different contributions for $T > T_g$. This is not surprising, reflecting that different stresses probe different aspects of molecular motion. A shear deformation involves exclusively shape changes while a longitudinal deformation is also accompanied by volume changes.

Evidently, the volume (or structural) relaxation effects, due to the compressional component of the longitudinal wave, become important as the system gains liquid-like degrees of freedom crossing the transformation region. Meister and co-workers [17] have pointed out that this phenomenon become relevant in those liquids where there is association among the molecules and, in particular, hydrogen bonding (as in *m*-fluoroaniline).

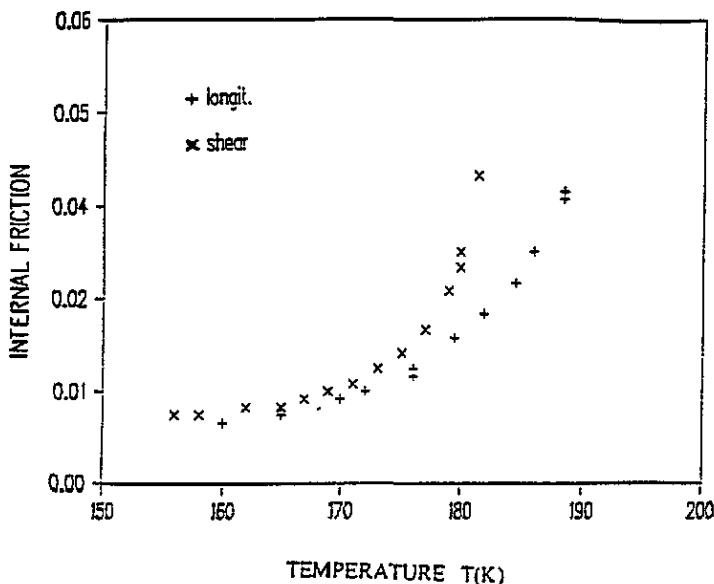


Figure 5. A comparison between the internal frictions calculated for the longitudinal and the shear-wave propagation at 10 MHz.

Supposing that τ_s and τ_l (the mean shear and longitudinal relaxation times) are similar in magnitude, we have calculated the viscosity of *m*-fluoroaniline at the temperatures of the two α -peak resonances ($\omega\tau = 1$) via the Maxwell relation $\eta = G_\infty\tau_s$ (assuming $\tau_s \simeq \tau_l$). For a typical value of the limiting high-frequency shear modulus G_∞ of 10^{10} dyne cm^{-2} we have found η ($T \simeq 200$ K) $\simeq 2 \times 10^3$ P and η ($T \simeq 205$ K) $\simeq 10^3$ P. These two points are shown in figure 4 together with the experimental data found for *m*-fluoroaniline at high temperatures. They appear in good agreement with the general trend followed by the other fragile liquids reported.

The glass transition defined by specific-heat spectroscopy corresponds to the temperature at which the enthalpy relaxation time reaches 100–200 s. Our fits reveal, after correction by the factors modulus/compliance $M_\infty/M_0 \sim 2$ and isothermal/adiabatic $C_{p0}/C_{p\infty} \sim 1.9$ (the quantity that compares directly to the specific heat is the compliance, not the modulus, and the propagation of sound is an adiabatic process), a mean longitudinal relaxation time (τ) = $\beta_{\text{CD}}\tau_{\text{CD}}$ [19] of about 10^{-2} s, so it would seem that in this molecular liquid longitudinal and enthalpic relaxation modes are decoupled near T_g with the mechanical relaxation processes occurring on a time scale shorter than that of relaxation under a thermal stress. This is not a new observation. Indeed, while most strong and intermediate liquids reach viscosities close to 10^{13} P at the calorimetric T_g , many molecular liquids (mostly fragile in character like *o*-terphenyl) have viscosities as low as 10^{10} P at T_g , implying a shear relaxation time τ_s of about 10^{-1} – 10^{-2} s. Accordingly [23], for these systems of high

fragility breaking of ergodicity must be more than just shear viscosity slow-down and the common rule of defining the glass transition temperature at an isoviscous point ($\eta \simeq 10^{13}$ P) is no longer applicable. Although the experimental basis is quite exiguous, it seems that this decoupling of relaxation modes affects principally very fragile systems and does not occur in the cases of intermediate and strong liquids.

We consider now the results obtained in the power-law fits. Analogously to that found by Jeong and co-workers in their ultrasonic investigation on glycerol [24], our computations reveal an unusual large value of the γ exponent. The value found for glycerol is $\gamma = 12.5$ whereas our value for *m*-fluoroaniline is of about 9.1 ± 0.5 . In accordance with these authors we may conclude that the region of power-law behaviour occurs at much higher temperatures and lower viscosities than those normally associated with the glass transition. In this region of a wide variety of fluid systems (benzene, aniline, toluene, etc) it is found that the exponent γ lies in the range between 1.5 and 2.3 [25]. In contrast we have employed a power law to fit our data in a very wide range of viscosity extending from T_g to high temperatures. Further, a value of T_c falling below T_g is not predicted by MCT. For these reasons, we cannot make a reliable comparison between our experimental findings and the statements of MCT even if a power-law form for $\tau(T)$ were able to cover the whole temperature range explored.

On the other hand, it must be noted that the time-temperature superposition principle for the α -peak (found in our case) is an important prediction of MCT.

5. Conclusions

The mechanic relaxation dynamics of the 'fragile' *m*-fluoroaniline has been studied in detail in the supercooled state. It is dominated by the appearance of a primary (α -) relaxation process whose stretched character is consistent with the long observed correlation between fragility and departure from Debye relaxation.

Further, data obtained from our fits provide values for fragility parameters that are comparable with those for other similar molecular liquids, suggesting that their common dynamic behaviour could arise from their isostructurally.

However, no reliable predictions of fragility from structural characteristics seem possible at this time, although Angell pointed out that this connection could lie in the stability of short- and medium-range order.

With regard to the stretching of the α -relaxation we have found thermorheological simplicity for our system. Because of the very limited frequency range accessible by ultrasonic investigations, however, the test of this property needs techniques with wider frequency spectral windows such as dielectric relaxation. In addition, this probe could allow us to examine in more detail the possible decoupling of several relaxation processes, which seems to influence the molecular dynamics of this system in the highly viscous supercooled state.

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