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Anharmonic properties of fragile and strong liquids: temperature dependence of the mode Grüneisen parameter

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Abstract. Brillouin spectroscopy, dilatometry and calorimetry results have been used to investigate the temperature anomaly of the mode and thermal Grüneisen parameters around the glass transition of the fragile liquid poly(vinyl acetate). These results are compared with those of the strong liquids C₁₇H₃₆, C₂₄H₅₀ and 4-cyano-4-6-alkylbiphenyl.

1. Introduction

Recently, it has been postulated that the thermal glass transition of poly(vinyl acetate) (PVAC) exhibits an underlying phase transition from the equilibrium liquid to the non-ergodic glassy state at an 'ideal' glass transition temperature T_{gs} [1, 2]. This interpretation was derived from the temperature and time dependences of the longitudinal elastic susceptibility c_{11} measured by time-domain Brillouin spectroscopy (TDBS) [1–4]. Taking into account that the glass transition in canonical glasses affects predominantly their mechanical properties, one could argue that these properties couple to the susceptibility of the hypothetical order parameter. In fact, the glass transition was evidenced by a sharp but small exciting kink in the sound frequency–temperature curve, yielding almost no hint of the existence of the order parameter in question. In addition this kink depends to a certain extent on the thermal history of the sample (see e.g. [4, 5]).

This situation is somewhat similar to that found around the freezing temperatures of spin glasses and quadrupolar glasses. In the case of spin glasses [6] and quadrupolar glasses [7] the linear order parameter susceptibilities just show a cusp whereas the non-linear susceptibilities have been found to diverge in the vicinity of the freezing temperature T_g . These latter facts stimulated us to study non-linear elastic properties around the glass transition of canonical glasses.

Usually non-linear elastic properties are not easy to measure (see, e.g. [8]); this especially holds true for the glass transition zone of canonical glasses. A quantity which reflects non-linear elastic properties on the one hand [9] and which can be determined rather easily is the longitudinal-mode Grüneisen parameter (LMGP) [10]. In an isotropic solid the LMGP relates the sound frequency of a longitudinally polarized sound mode of a given wavevector \mathbf{q} to its mass density ρ [9–11]. It is anticipated that the concept of the LMGP can be extended to acoustic waves propagating in liquids, that within a given

phase the LMGP [9] varies only slightly with temperature and that the LMGP of a liquid still reflects the anharmonic mechanical properties of the materials [9–15]. Drastic changes in the LMGP are believed to be representative of drastic changes in the average molecular interaction potential of an amorphous material. To our knowledge there exist no theoretical predictions for the temperature behaviour of the LMGP at the glass transition of canonical glasses.

For the determination of the temperature dependence of the LMGP within liquids and glasses, Brillouin spectroscopy (BS) is an experimental method of particular interest because it measures the mechanical properties of the glass former in a completely non-destructive manner and without mechanically contacting the sample [3, 4, 16]. Moreover, in temperature regimes where hypersonic relaxations are absent, BS yields the possibility of estimating the volume expansion coefficient via the determination of the refractive index of the material [3, 4]. In glass formers this condition is fulfilled even some 10 K above T_g because BS measures the instantaneous elastic response in the ‘slow-motion regime’ in the sense that $\tau_s v / \Lambda \gg 1$ holds (where Λ is the acoustic wavelength, τ_s the structural relaxation time and v the sound velocity).

There exist only a few investigations on the temperature dependence of the LMGP at the glass transition [3, 4, 12] of polymers. Brody *et al* [12] investigated polystyrene by BS and reported at T_g a small step in the LMGP. In [3, 4] the observed discontinuity in the LMGP of polystyrene at the glass transition temperature T_g was found to be 4.3 which is larger by a factor of 3.6 than that reported in [12]. This illustrates the difficulties of determining reliable data of LMGP, but at least the tendency of the LMGP discontinuity was the same; the LMGP, i.e. the anharmonicity, was always larger above T_g than below T_g .

Taking PVAC as a model system for an ‘ideal’ glass former [1, 2] we want to elucidate the behaviour of the LMGP in the glass transition zone. We shall confirm the existence of a step-like anomaly of the LMGP within the glass transition regime and we shall relate its temperature position as well as its magnitude to the heating or cooling rate dependences of the density, the sound velocity, the volume expansion coefficient, and the temperature derivative of the sound velocity. We shall show that the temperature dependence of the LMGP of the fragile and strong liquids under study differ from each other.

2. Experimental details

The PVAC under study is an atactic polymer with a molecular weight $M_w = 91 \text{ kg mol}^{-1}$. From the raw material we prepared a plate-like sample of 1 mm thickness and of diameter 12 mm. From earlier Brillouin measurements around the glass transition of polystyrene and poly(methyl methacrylate) [3, 17] we knew that every mechanical constraint imposed from outside the sample, especially every sticking of the sample to the sample holder, affects seriously the mechanical and thermal properties at the glass transition. Therefore the sample plate was well annealed in an oven under vacuum. Moreover, in order to get a stress-free sample with the optical quality of the relevant surfaces, we pressed the sample between two plates of silicone rubber having surfaces of optical quality. The sample disc was put into a special cuvette having inner dimensions slightly larger ($10 \mu\text{m}$) than the sample itself. In order to avoid any sticking of the samples to the sample holder we used partially polymerized silicone rubber as an immersion liquid which provided the condition of constant external pressure during all thermal treatments and measurements. The degree of polymerization was chosen in such a way that the molecules of the immersion liquid could not cause the PVAC sample to swell. Prior to the Brillouin measurements the sample was aged within its sample holder at T_g for several months. The optical sample quality was

tested with an optical polarizing microscope and with a laser beam. We found no hints of swelling due to penetration of the partially polymerized silicone rubber.

$C_{17}H_{36}$ (Aldrich), $C_{24}H_{50}$ (Aldrich) and 4-cyano-4'-alkylbiphenyl (6CB) (Merck) were contained in suitable glass cuvettes.

The Brillouin measurements were made either on stepwise heating or stepwise cooling. They have been performed with a five-pass Fabry–Perot spectrometer [4, 18] using the 90A and 90R scattering geometries [4]. The simultaneous application of both scattering arrangements allows the determination of the refractive index of the sample [4, 19–21]. In order to obtain the required long-time stability the temperature of the spectrometer including the spectrometer control was stabilized to better than 0.1 K. Moreover, the spectrometer control (including the temperature control of the sample, the data collection procedure and the evaluation of the data) has been completely automated, yielding immediately the final Brillouin data after each measurement. The samples were positioned within a home-made top-loading thermostat. The temperature control was maintained with a PID controller (ITC-4, Oxford Instruments) using a rhodium–iron resistor. In order to reduce temperature fluctuations of the sample below 0.03 K we controlled even the temperature of the outer body of the thermostat. The temperatures of the samples were measured with a thin chromel–alumel thermocouple positioned within the sample slightly above the scattering volume. In order to control the influence of local heating of the sample by the laser beam we made Brillouin measurements as a function of the laser power. The Brillouin measurements usually were performed with an incident laser power of 10 mW .

3. Results and discussion

In an isotropic solid the LMGP $\gamma_L(\mathbf{q})$ relates the sound frequency $f_L(\mathbf{q})$ of a longitudinally polarized sound mode of a given wavevector \mathbf{q} to its mass density ρ [11]:

$$\gamma_L(\mathbf{q}) = \frac{\partial \{\ln[f_L(\mathbf{q})]\}}{\partial (\ln \rho)}. \quad (1)$$

There are two ways to evaluate the LMGP $\gamma_L(\mathbf{q})$ from experimental data. Either the change in specific volume occurs at constant pressure or it occurs at constant temperature. In the former case, equation (1) can be treated using the temperature as a common parameter for both the hypersonic frequency and the specific volume.

Then, equation 1 can be rewritten as

$$\gamma_L(\mathbf{q}, T) = \frac{\rho(T)}{f_L^{90A}(\mathbf{q}, T)} \left. \frac{\partial f_L^{90A}(\mathbf{q}, T)}{\partial \rho(T)} \right|_P = \left. \frac{\delta_L(\mathbf{q}, T)}{\alpha(T)} \right|_P \quad (2)$$

where

$$\alpha(T)|_P = - \left. \frac{1}{\rho} \frac{\partial \rho}{\partial T} \right|_P$$

is the volume expansion coefficient and

$$\delta_L(\mathbf{q}, T)|_P = - \left. \frac{1}{f_L^{90A}(\mathbf{q}, T)} \frac{\partial f_L^{90A}(\mathbf{q}, T)}{\partial T} \right|_P$$

corresponds to the relative temperature derivative of the sound frequency f_L^{90A} . The determination of the LMGP reduces therefore to the determination of $\delta_L(\mathbf{q}, T)$ and $\alpha(T)$. In the immediate glass transition zone there may eventually exist sound frequency relaxations in the time domain which could yield ambiguous $\gamma_L(\mathbf{q})$ -values. Therefore, we exclude preventively all data in the temperature range between the ‘ideal’ glass transition temperature

at 295 K and the definite end of the relaxation to the liquid equilibrium at 310 K (shaded regime in figure 1) from our discussions.

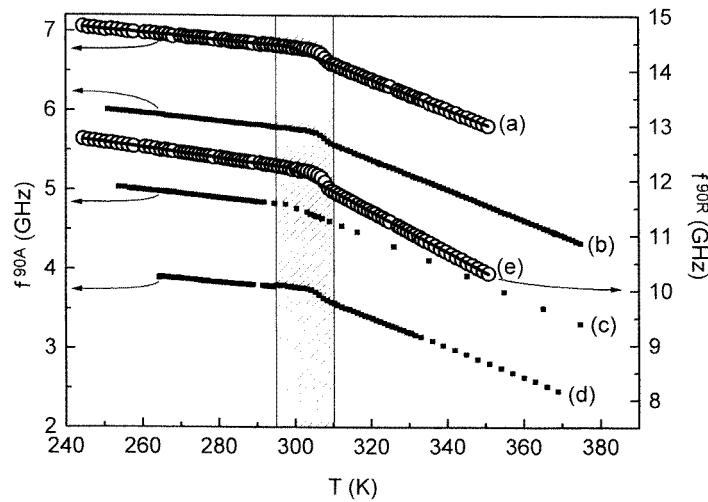


Figure 1. Hypersonic frequencies of PVAC as a function of temperature: curves (a) and (e), f^{90A} and f^{90R} on heating of a well annealed sample (straight lines, linear fits to the frequency data outside the shaded regime); curve (c) f^{90A} measured on cooling using TDBS (see [1, 2]); curve (b), f^{90A} in a subsequent heating run; curve (d), f^{90A} in a stepwise heating run of a quenched sample using TDBS (see [1, 2]). Curves (b), (c) and (d) are shifted by -1 GHz, -2 GHz, and -3 GHz, respectively.

3.1. Determination of $\delta_L(q, T)$ of poly(vinyl acetate)

The determination of $\delta_L(q, T)$ is based on the sound frequency curves $f^{90A}(T)$ (the index L is omitted in the further discussion) given in figure 1. These sound frequency curves have been measured under different conditions and reflect different thermal histories. Curve (c) was measured on cooling using TDBS as explained in [1, 2]. The data collection time was adapted to the relaxation time at every temperature jump. The corresponding f^{90A} data are almost fully relaxed [1, 2]. Curve (b) was obtained during the subsequent heating run (stepwise heating) for several days. Prior to the measurement of curve (d) the sample was strongly quenched. Subsequently TDBS measurements were performed on stepwise heating of the sample. At about 295 K the sample started to relax towards the equilibrium liquid. Although we gave no time for full equilibration at 295 K, the sound frequency curve showed the typical over-heating effect of a well annealed sample on further heating. Curves (a) and (e) were measured simultaneously using the 90A and the 90R scattering geometry at the same time [4, 19–21]. Prior to the Brillouin experiments the sample was annealed at about 300 K for several months. These curves contain linear fit curves which were obtained after omitting the immediate transition interval between the ‘ideal’ glass transition temperature at 295 K and the definite end of the relaxation to the liquid equilibrium at 310 K (shaded regime in figure 1).

In fact, all high- and all low-temperature branches of the sound frequency curves (a)–(d) have, independently of the thermal history of the samples, almost the same temperature derivative, respectively (see table 1). On the other hand, as expected, the glass transition

temperature depends significantly on thermal history of the material. Table 1 also contains $\delta(q, T)$ -values at the border of the immediate transition interval. Again, these values are almost independent on the sample history.

3.2. The determination of $\alpha(T)$ of poly(vinyl acetate)

The finding of reliable $\alpha(T)$ data is somewhat more difficult. We have found data in the papers of Kovacs [22] and Aklonis and Kovacs [23]. These data seemed to us of high quality. Moreover, the PVAC used in [22, 23] showed a T_g close to ours, indicating that the molecular weight of the material was similar to that used in this work. In [22, 23] the rate dependence of the volumetric data of PVAC was also studied around the glass transition. According to the specific volume measurements in [22, 23] the glass transition temperature T_g depends on the thermal history of the sample but, outside the immediate transition zone, the volume expansion coefficient (table 1) is invariant under the change in heating or cooling conditions.

Alternatively, the volume expansion coefficients above and below T_g can be estimated exclusively from curves (a) and (e) in figure 1. As discussed in section 2, this can be done using simultaneously the 90A and 90R scattering geometries. For this purpose we apply the opto-acoustic dispersion function $D^{90R}(T)$ [4, 19–21] to the f^{90R} and f^{90A} Brillouin data obtained in the slow-motion regime, yielding

$$D^{90R}(T) = n(T) = \sqrt{\frac{1}{2} \left\{ \left[\frac{f_L^{90R}(T)}{f_L^{90A}(T)} \right]^2 + 1 \right\}} \quad (3)$$

where n is the refractive index. Figure 2 shows the calculated $n(T)$ curve and the related linear least-squares fits for the liquid and the glassy state. The Lorentz–Lorenz [24] relation

$$\rho(T)r = \frac{n(T)^2 - 1}{n(T)^2 + 2} \quad (4)$$

is a valuable relation between the mass density ρ and the refractive index. In figure 2 we also show the density data derived from equation (4) having calibrated our data with those in [22, 23] at 315 K. Again, we used linear least-squares fits for the high-temperature and the low-temperature branches.

Equations (3) and (4) can be used to determine the volume expansion coefficient $\alpha(T)$:

$$\alpha(T) = -\frac{1}{\rho} \frac{d\rho(T)}{dT} = -\frac{6n(T)}{n(T)^4 + n(T)^2 - 2} \frac{dn(T)}{dT} \quad (5)$$

exclusively from Brillouin data. It is interesting to note that, in contrast with the determination of $\rho(T)$, the calculation of $\alpha(T)$ does not need knowledge of the specific refractivity r .

3.3. The determination of $\gamma(T)$ of poly(vinyl acetate)

We have determined the LMGP within the liquid as well as in the glassy phase of PVAC. Table 1 gives $\gamma(T)$ -values at the ideal glass transition at $T_g = 295$ K and at 310 K. The γ -values at 295 K range between 2.5 and 3.8. At 310 K γ ranges between 4.8 and 5.9. These data clearly indicate a kind of discontinuous temperature behaviour of the LMGP in the glass transition zone. $\gamma(T)$ is generally higher in the liquid phase than in the glassy phase, indicating a stronger anharmonicity within the liquid state.

Table 1. Volume expansion coefficient α , absolute temperature derivative (df/dT) and relative temperature derivative δ of the sound frequency f^{90A} , and LMGP γ of PVAC.

	α (10^{-4} K $^{-1}$)		df/dT (MHz K $^{-1}$)		δ (10^{-4} K $^{-1}$)		γ		Comment
	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$	$T < T_g$ (295 K)	$T > T_g$ (310 K)	$T < T_g$ (295 K)	$T > T_g$ (310 K)	
2.6 (295 K) (figure 3, curve (c))	5	(310 K) (figure 3, curve (c))	-4.51 ± 0.05	-19.2 ± 0.06	6.4	29	2.4 (figure 3, curve (a))	6.0 (figure 3, curve (a))	δ and α from f^{90A} and f^{90K} in figure 1, curves (a) and (e)
2 [22, 23]	6	[22, 23]	-5.2 ± 0.02	-19.4 ± 0.08	7.6	29.5	3.8	4.9	δ from f^{90A} in figure 1, curve (c); α from [22, 23]
2 [22, 23]	6	[22, 23]	-4.96 ± 0.02	-19.2 ± 0.03	7.3	29.2	3.7	4.9	δ from f^{90A} in figure 1, curve (b); α from [22, 23]
2 ^a [22, 23]	6 ^a	[22, 23]	-4.52 ± 0.07	-18.8 ± 0.09	6.7	28.6	3.4	4.8	δ from f^{90A} in figure 1, curve (d); α from [22, 23]
2 ^a [22, 23]	6 ^a	[22, 23]	-4.51 ± 0.05	-19.2 ± 0.06	6.4	29	3.2 (figure 3, curve (b))	4.8 (figure 3, curve (b))	δ from f^{90A} in figure 1, curve (a); α from [22, 23]

^a α from [22, 23] corresponding to different cooling rates.

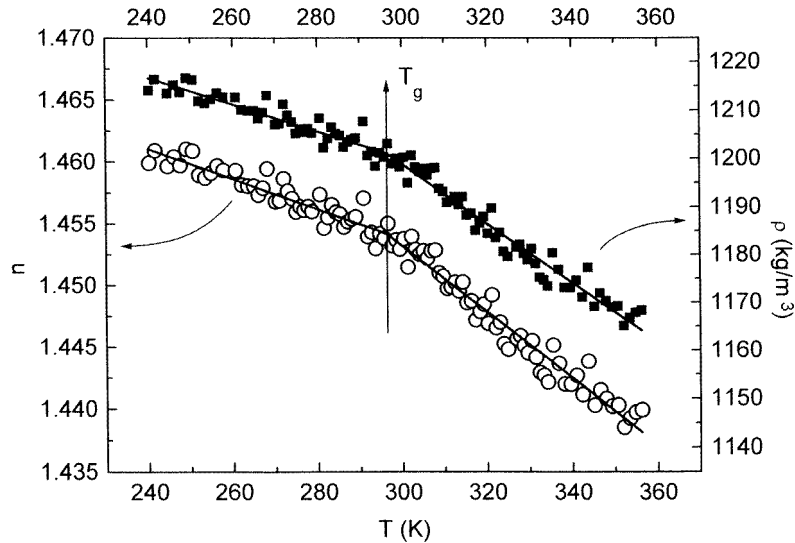


Figure 2. Refraction index $n(T)$ (\circ) and mass density $\rho(T)$ (\blacksquare) of PVAC calculated from the frequency data in figure 1, curves (a) and (e).

Moreover, although the glass transition temperature (transition interval) significantly depends on the thermal history of the sample, the amount of the discontinuity in $\gamma(T)$ is almost constant. In other words, the temperature location of the discontinuity depends on the thermal history, whereas its magnitude almost does not.

We have also studied the temperature dependence of $\gamma(T)$ in the glassy as well as in the fluid state. Figure 3, curve (a), shows the $\gamma(T)$ curve which has been purely calculated on the basis of curves (a) and (e) in figure 1. Figure 3, curve (b), shows the results having our sound frequency data but the volume expansion coefficients given in [22, 23]. Within the margin of accuracy the low-temperature data are in good agreement. $\gamma(T < T_g)$ is almost independent of temperature. Above T_g both $\gamma(T)$ curves show values of the same order of magnitude but have different slopes. This discrepancy probably arises because Aklonis and Kovacs [23] give a constant-volume expansion coefficient whereas in reality the volume expansion coefficient increases slightly with increasing temperature.

3.4. $\gamma(T)$ of $C_{17}H_{36}$

$C_{17}H_{36}$ is an interesting liquid to compare with PVAC because, on the one hand, it is considered to be a strong liquid and, on the other hand, it fulfils the condition about having no hypersonic relaxations in the temperature range under study. In order to investigate the LMGP of $C_{17}H_{36}$ we have performed 90A and 90R Brillouin measurements (figure 4) and then used equations (2), (3) and (5) to determine $n(t)$, $\alpha(T)$ and $\gamma(T)$. Figure 5 shows the temperature dependences of $n(T)$ and $\gamma(T)$. Whereas $f^{90A}(T)$, $f^{90R}(T)$ and $n(T)$ have negative slopes, $\gamma(T)$ is almost constant, having a very small positive slope.

3.5. $\gamma(T)$ of $C_{24}H_{50}$

$C_{24}H_{50}$ is homologous to $C_{17}H_{36}$ but for this material we have precision specific volume data at our disposal. The LMGP of $C_{24}H_{50}$ was determined from 90A Brillouin measurements

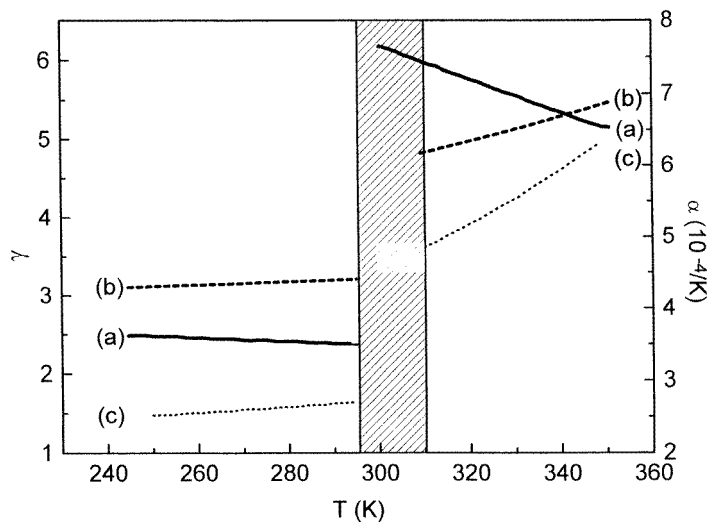


Figure 3. LMGP $\gamma(T)$ of PVAC: curve (a) γ calculated on the basis of the $f(T)$ curves in figure 1 curves (a) and (e) and α from curve (c) of this figure; curve (b), γ calculated on base of the $f(T)$ curves in figure 1, curves (a) and (e), and α from [23]; curve (c) α calculated on basis of the $f(T)$ curves in figure 1 curves (a) and (e).

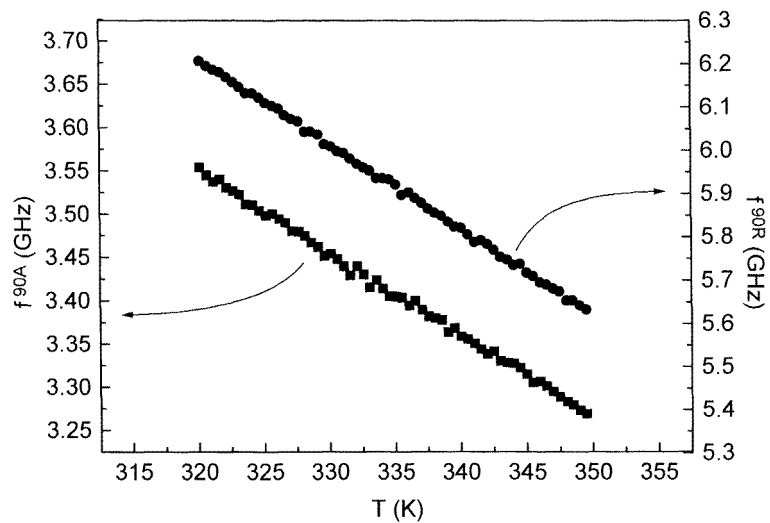


Figure 4. Hypersonic frequencies f^{90A} and f^{90R} of $C_{17}H_{36}$ simultaneously measured as a function of temperature.

given in [25] and from specific volume data taken from [26]. The resulting LMGP (figure 6) has a positive slope which is greater than that of $C_{17}H_{36}$.

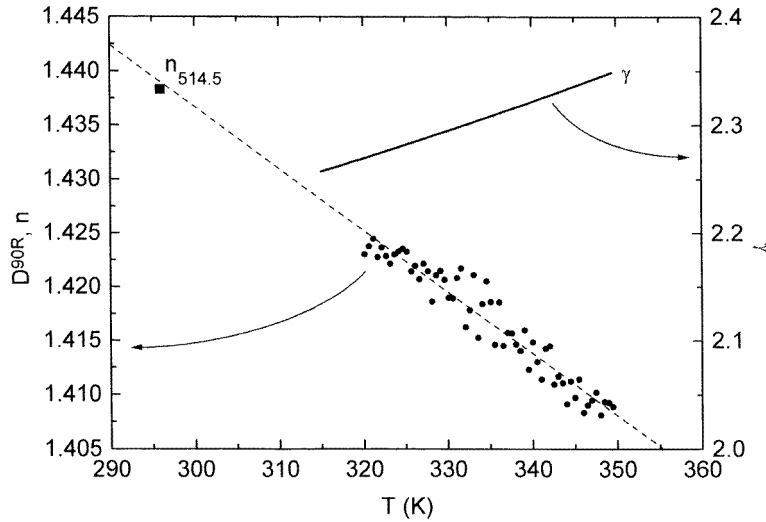


Figure 5. Refraction index $n(T)$ and LMGP $\gamma(T)$ of $C_{17}H_{36}$: ●, n calculated from f^{90A} and f^{90R} (figure 4); ■, n measured with an Abbé refractometer at $\lambda = 514.5$ nm; - - -, linear fit to $n(T)$. $\gamma(T)$ was calculated from linear fits to $f^{90A}(T)$ (figure 4) and $n(T)$.

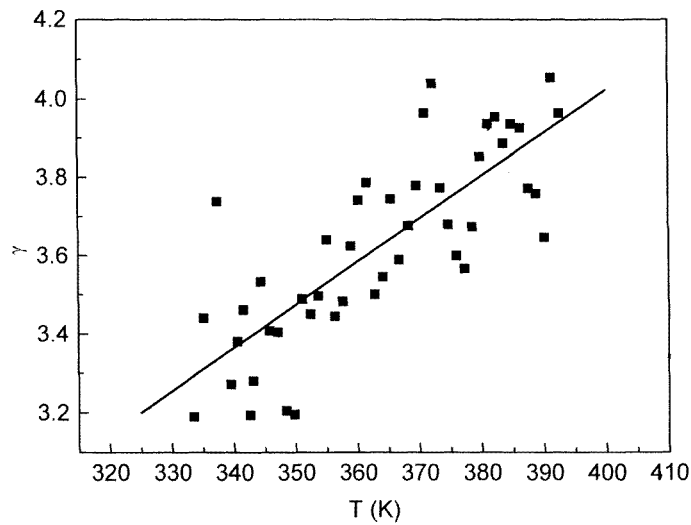


Figure 6. LMGP $\gamma(T)$ of $C_{24}H_{50}$.

3.6. $\gamma(T)$ of 4-cyano-4-6-alkylbiphenyl

6CB is a classical nematic liquid crystal which transforms at about $T_{ni} = 301$ K to the isotropic state. As has been discussed elsewhere, classical liquid crystals can hardly be frozen [27, 28] and are strong liquids. For the determination of the LMGP we have used own $f^{90A}(T)$ data on which the $c_{11}(T)$ data from [27] are based and refractive index data from Karat *et al* [29]. Figure 7 shows the corresponding $f^{90A}(T)$ and $\gamma(T)$ data. Also for this strong liquid we find a slight positive slope of $\gamma(T)$.

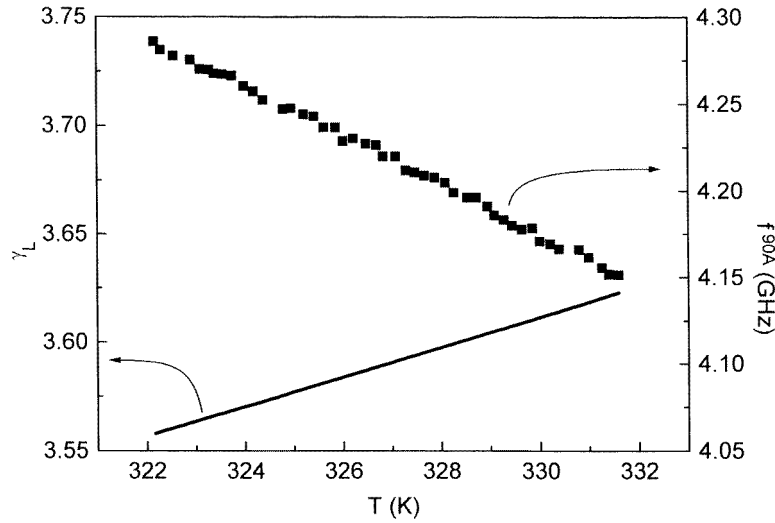


Figure 7. Hypersonic frequency $f^{90A}(T)$ and LMGP $\gamma(T)$ of 6CB.

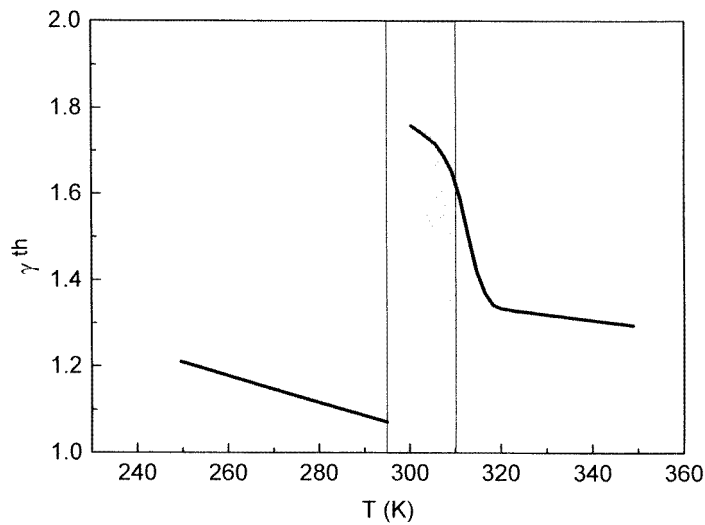


Figure 8. Thermal Grüneisen parameter γ^{th} of PVAC calculated from the frequency data of figure 1, curve (c), and c_p data from [1].

3.7. The thermal longitudinal-mode Grüneisen parameter of poly(vinyl acetate)

Using the technique of modulated DSC [30] in the quasi-adiabatic mode we have recently shown that the inflection point of the specific-heat curve is well above the Brillouin T_g although both investigations were performed at extremely low effective cooling rates [1]. As a result we found a coincidence between the Brillouin T_g and the onset temperature at which the $c_p(T)$ curve leaves the low-temperature asymptote. We have used these specific

heat data in order to determine the thermal Grüneisen parameter $\gamma^{th}(T)$ [9, 11, 12]

$$\gamma^{th} = \frac{v\alpha B_s}{c_p} \quad (6)$$

with $B_s = c_{11} - \frac{4}{3}c_{44}$.

As we have not yet measured the temperature dependence of the shear modulus we have approximated B_s by the reasonable approach, i.e. $B_s \approx 0.7c_{11}$. The resulting thermal Grüneisen parameter (figure 8) shows the same kind of discontinuity as the LMGP. Owing to the influence of the thermal history on the location of the heat capacity and the specific volume anomalies, the location of the temperature anomaly of γ^{th} also depends on the cooling or heating rate. However, as in the case of the LMGP the magnitude of the anomaly of γ^{th} remains almost constant.

4. Conclusion

Concluding our results, we find a discontinuous behaviour of $\gamma^{th}(T)$ and $\gamma(T)$ in the glass transition zone of PVAC. Although we do not know the precise temperature behaviour of the different Grüneisen parameters in the immediate transition regime this discontinuous behaviour of the Grüneisen parameters cannot disappear. However, the position of the discontinuity depends on the thermal history. A comparison between the temperature behaviour of $\gamma(T)$ within the equilibrium liquid phase of PVAC and some strong liquids indicates that the significant negative slope found for PVAC might be a fingerprint of the 'ideal glass transition'. Whether this negative slope increases further (diverges) on approaching the 'ideal glass transition temperature' has not yet been clarified. Stimulated by the anomalous behaviour of the Grüneisen parameters we believe that at the thermal glass transition the average molecular interaction force changes rather abruptly.

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