Brillouin Scattering in Salol: Determining T_c of the Mode Coupling Theory

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Brillouin scattering spectra of the molecular glass former salol were combined with ultrasonic measurements to evaluate the nonergodicity parameter of mode coupling theory $f_0(T)$. It was found to exhibit a weak cusp at a temperature $T_c^B = 275 \pm 10$ K, in reasonable agreement with the mode-coupling crossover temperature $T_c = 256 \pm 5$ K found recently by other methods. This result is in marked contrast to the recent publication of Elmroth, Borjesson, and Torell [Phys. Rev. Lett. **68**, 79 (1992)].

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Most recent experimental research on the liquid-glass transition in fragile liquids has been designed to test various predictions of the mode-coupling theory (MCT). First proposed in 1984 [1-3], MCT predicts that nonlinear interactions between density fluctuation modes induce an ergodic-to-nonergodic glass transition singularity at a crossover temperature T_c, somewhat above the calorimetric glass transition temperature T_G.

A central prediction of MCT concerns the temperature dependence of f_q, the Debye-Waller factor or nonergodicity parameter [3,4]:

$$f_q(T) = \begin{cases} f_q^c & (T > T_c), \\ f_q^c + h_q(\epsilon)^{1/2} & (T < T_c), \end{cases} \tag{1}$$

where $\epsilon = (T_c - T)/T_c$ is the dimensionless separation parameter, and f_q^c is a slowly varying function of T.

Although the magnitude of the cusp described by Eq. (1) can vary with q, the temperature T_c at which the cusp occurs should be an intrinsic property of a material and therefore independent of q.

Equation (1) has been shown to be consistent with the results of neutron scattering experiments for several materials [3,4] in which $f_q(T)$ was determined [5-9], and in particular, the independence of T_c on q was tested for a considerable range of q in [6]. Generally, T_c has been found to be about 30 to 50 K above T_G, and well below the bulk crystal melting temperature T_M. T_c has also been determined approximately for several materials by power-law fits of viscosity data [10-12] and recently by depolarized light-scattering spectroscopy [12,13]. In general, the T_c values found by different methods have been in reasonably good agreement.

Fuchs *et al.* [14] pointed out that T_c could also be determined from the relation

$$f_0 = 1 - (C_0/C_\infty)^2, \tag{2}$$

where f_0 is the $q \to 0$ limit of f_q, and C_∞ (C_0) is the high- (low-) frequency sound velocity measured above (below) the primary α-relaxation frequency. Equation (2) provides an alternative test of the prediction of Eq. (1), using the temperature-dependent sound velocities C_0 and C_∞ measured by ultrasonic or Brillouin scattering techniques.

In order to test Eq. (2) and the possible q dependence of T_c, we have undertaken a Brillouin scattering study of the molecular glass former salol (phenyl salicylate, $T_G = 218$ K, $T_M = 315$ K) for which a recent depolarized light-scattering experiment gave $T_c = 256 \pm 5$ K, in good agreement with $T_c = 265 \pm 5$ K obtained from a power-law analysis of available viscosity data [12].

Brillouin scattering measurement of the density fluctuation spectrum $S(q,\omega)$ is complicated by the fact that both the *VV* and *VH* spectra contain several different contributions. Both spectra include anisotropic scattering contributions from molecular orientational motions as well as from second-order dipole-induced-dipole (DID) scattering. These two anisotropic contributions are scattering-angle independent and have the same depolarization ratio, $I_{VH}/I_{VV} = 0.75$, so that there is no straightforward way to separate them. The *VH* spectra also include a depolarized scattering-angle-dependent contribution arising from the coupling between orientational motions and transverse current (shear) [15,16], whose intensity disappears for the backscattering geometry. The Brillouin scattering experiments described here were therefore performed close to the backscattering geometry ($\theta = 173°$) and the isotropic contribution $S(q,\omega)$ present only in the *VV* spectra was deduced from the analysis of the *VV* and *VH* spectra as described below.

The experiments were performed with an 8-pass (4+4) tandem Fabry-Pérot interferometer constructed at the Département de Recherches Physiques following the design of Sandercock [17]. The light source was a Coherent Innova 90 argon-ion laser operating at 514.5 nm. Samples were prepared as in [12].

To include the anisotropic contributions in the *VV* spectra, we have followed a procedure similar to that of Ref. [18]. At each temperature, the depolarized spectrum was fitted by a single Lorentzian of half-width $\Delta\omega_{1/2} = \Gamma_r$. The resulting values of Γ_r are given in Table I and are in good agreement with previously determined values [15]. This Lorentzian, multiplied by a constant I_{ani} treated as an adjustable fitting parameter, was then added to the theoretical expression for $S(q,\omega)$ in the analysis of the *VV* spectra.

The *VV* spectra were analyzed by a conventional nonlinear least-squares fitting to the convolution of the exper-

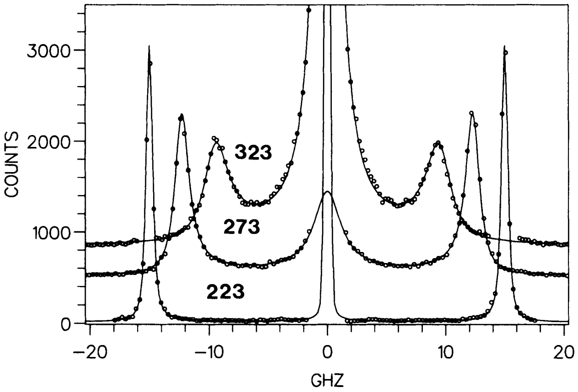

FIG. 1. Salol *VV* Brillouin spectra at $T=323$, 273, and 223 K showing the experimental data (points) and fits by Eq. (3). For clarity, only one-third of the data points are shown.

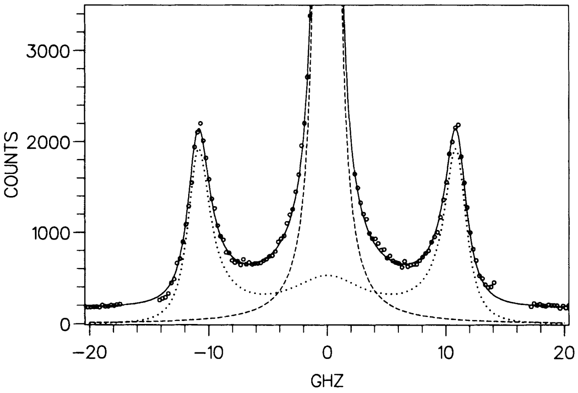

FIG. 2. Salol *VV* spectrum at $T=296$ K showing the anisotropic (---) and isotropic (· · ·) contributions and the total theoretical spectrum (——) of Eq. (3), each convoluted with the instrumental resolution function.

imentally determined instrument function with the theoretical function $I(\omega)$ given by [19]

$$I(\omega)=\frac{I_0}{\omega}\mathrm{Im}[\omega_0^2-\omega^2-i\omega\gamma-\Delta^2\{(1-i\omega\tau)^{-\beta}-1\}]^{-1}+I_{\mathrm{ani}}\frac{\Gamma_r^2}{\omega^2+\Gamma_r^2}+I_{\mathrm{bg}}\,, \qquad (3)$$

where ω_0 is the "bare" Brillouin peak frequency ($\omega_0=C_0q$) and γ is the "bare" damping constant assumed here to be temperature independent. Δ is the coupling constant between density fluctuations and the primary α structural relaxation, τ is the average structural relaxation time, and β is the stretching parameter of the corresponding Cole-Davidson distribution which can be converted to the equivalent β_K of the Kohlrausch function [20].

Equation (3) contains nine parameters. I_0, I_{ani}, and I_{bg} are the strengths of the isotropic, anisotropic, and background contributions to the *VV* spectrum which were treated as free parameters in the fitting procedure. γ was determined from a spectrum below T_G and we used the resulting value $\gamma/2\pi=0.24$ GHz in all the fits. Γ_r was found from the depolarized spectra. Of the other four parameters (β,τ,Δ, and ω_0), β and τ are strongly correlated, as are Δ and ω_0.

It is possible to obtain satisfactory fits for a large range of β values as long as τ is allowed to vary freely, as noted previously on other systems [16,21]. However, depolarized light-scattering [12] and dielectric [22] measurements in salol have determined β_K in the range of temperature of our experiment. We therefore fixed β for each spectrum using the values given in Ref. [12].

Since Δ and $\omega_0=C_0q$ in Eq. (3) were similarly too strongly correlated to be determined simultaneously we performed an ultrasonic pulse-echo experiment to determine C_0 independently [23]. Between 350 and 280 K, the 5 and 10 MHz data show that the sound velocity follows a linear temperature dependence:

$$C_0=2448-3.23T\ (\mathrm{m/s})\,. \qquad (4)$$

Below 280 K, the measured sound velocity increases towards C_∞, exhibiting dispersion and a very high attenuation so that C_0 can no longer be measured directly. We have therefore assumed, as is frequently done [21], that the linear temperature dependence of C_0 in Eq. (4) can be extrapolated to lower temperatures. With Γ_r, γ, β, and C_0 thus fixed, the remaining five adjustable parameters in the fit are I_0, I_{ani}, I_{bg}, Δ, and τ.

In Fig. 1 we show the experimental *VV* spectra and the results of the fit for three temperatures, 323, 273, and 223 K. In Fig. 2, the $T=296$ K *VV* spectrum is shown together with the isotropic and anisotropic contributions, and the total theoretical function. The parameters of the fits are listed in Table I together with the resulting reduced χ^2. We also attempted to fit the data without including the I_{ani} term in Eq. (3). For temperatures in the range 278-343 K, it was generally not possible to obtain satisfactory fits without this term.

At low temperatures, the τ values found were not well defined, since in this range, the term $(1-i\omega\tau)^{-\beta}$ in Eq. (3) is small and the fit is not sensitive to τ. At higher temperatures, there is a systematic discrepancy between τ obtained from depolarized light scattering [12] and our values [24]. Such discrepancies between τ values measured by different techniques have been discussed previously [25-27], and it has been suggested that some decoupling between the different processes probed by different techniques may be responsible. However, it has been shown [12,22] that a Kohlrausch or Cole-Davidson function chosen to fit the peak of the dielectric loss function $\varepsilon''(\omega)$ falls significantly below the data in the 3-10 GHz range where the Brillouin spectra are strongest. The different τ values found in different experiments therefore presumably reflect the consequence of optimizing the approximate Cole-Davidson function in different frequency regions [28].

TABLE I. Fitting parameters for salol *VV* Brillouin spectra. Γ_r determined from Lorentzian fits to *VH* spectra. ω_0, γ, β, fixed as described in the text. ω_B is the position of the Brillouin peak; f_0 is from Eq. (2) with $\omega_\infty = (\omega_0^2+\Delta^2)^{1/2}$. The values of Γ_r indicated by (*) were determined with poor precision since at these temperatures the *VH* signal was weak and fell primarily within the Rayleigh line. At these temperatures, f_0 is independent of the value of Γ_r. Note that all numerical values are given in GHz and not in radians^{-1}.

T	Γ_R (GHz)	ω_0 (GHz)	γ (GHz)	β	Δ (GHz)	τ (ns)	I_{ANI}/I_0	ω_∞ (GHz)	ω_B (GHz)	f_0	χ_v^2
223	-	10.86	0.24	0.50	10.45	86	-	15.07	14.91	0.48	1.9
233	-	10.63	0.24	0.50	9.67	22	-	14.37	14.19	0.45	2.0
238	-	10.52	0.24	0.50	9.38	14	-	14.09	13.94	0.44	2.6
243	-	10.40	0.24	0.50	9.19	8.9	-	13.88	13.70	0.44	2.3
248	-	10.29	0.24	0.50	9.28	8.0	-	13.86	13.60	0.45	1.3
253	-	10.17	0.24	0.50	9.02	5.3	-	13.59	13.33	0.44	1.3
258	-	10.06	0.24	0.55	8.54	1.99	-	13.20	12.87	0.42	2.4
263	-	9.95	0.24	0.57	8.45	1.27	-	13.05	12.68	0.42	1.2
268	-	9.83	0.24	0.63	8.11	0.79	-	12.74	12.35	0.40	1.5
273	-	9.72	0.24	0.68	7.70	0.58	-	12.40	12.00	0.39	1.5
278	0.69*	9.61	0.24	0.77	7.43	0.41	0.003	12.15	12.05	0.37	1.3
283	0.50*	9.49	0.24	0.77	7.24	0.34	0.010	11.94	11.50	0.37	1.4
296	0.40	9.20	0.24	0.77	7.07	0.20	0.077	11.60	10.84	0.37	1.9
313	0.76	8.82	0.24	0.77	6.71	0.13	0.055	11.08	9.85	0.37	1.5
323	0.83	8.60	0.24	0.77	6.59	0.11	0.051	10.83	9.37	0.37	1.6
333	1.25	8.38	0.24	0.77	6.27	0.09	0.034	10.47	8.95	0.36	2.0
343	1.42	8.16	0.24	0.77	6.32	0.08	0.034	10.32	8 58	0.37	1.2

In Fig. 3 we have plotted ω_0 found from the ultrasonic measurement and $\omega_\infty = (\omega_0^2+\Delta^2)^{1/2}$ found from the analysis of the Brillouin scattering data. We also include ω_B determined from the peak positions of the Brillouin components. Note that ω_0 and ω_∞ are essentially parallel down to $T \sim 280$ K where ω_∞ begins to increase more rapidly than ω_0. At $T \sim T_G$, there is a change in the slope of ω_∞ which has been noted in previous experiments [16]. Finally, from the values of ω_0 and ω_∞ determined by the analysis, we computed $f_0(T)$ via Eq. (2). The result is shown in Fig. 3. There is evidence of a small cusp at $T = 275$ K. To show that the cusp of f is not a result of the temperature dependence of β, we have also fitted the data with a T-independent $\beta = 0.77$. The cusp is still visible but slightly displaced. To take into account the possible uncertainties we propose $T_c = 275 \pm 10$ K, in reasonable agreement with the previous determination $T_c = 256 \pm 5$ K [12].

A similar Brillouin scattering study of propylene carbonate (PC) was reported recently by Elmroth, Borjesson, and Torell [29]. They found a cusp at $T_c^B = 270$ K, which is at least 60 K above the T_c found by other techniques [9,29,30] and 52 K above the melting temperature

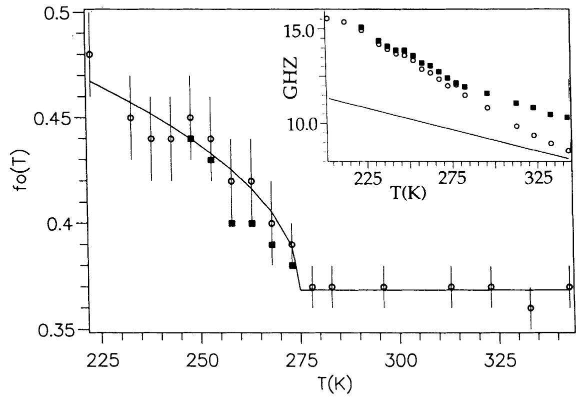

FIG. 3. $f_0(T)$ vs T from Eq. (2), using the values of $C_0/C_\infty = \omega_0/\omega_\infty$ found from the Brillouin scattering and ultrasonic data. The solid line is a fit to Eq. (1) from which $T_c = 275 \pm 1$ K, $f_q^c = 0.37 \pm 0.1$, and $h_q = 0.23 \pm 0.01$. Circles: f values computed from β from Table I; squares: f values computed with T-independent $\beta = 0.77$. Inset: Temperature dependence of $\omega_0 = C_0 q$ (solid line), ω_∞ (squares) from the fits by Eq. (3), and ω_B (circles) from the position of the Brillouin peaks (see Table I). C_0 is from the ultrasonic measurement [Eq. (4); $q = n \times 2.437 \times 10^5$ cm^{-1}, where $n = 1.60 - 4.2 \times 10^{-4}$ T(°C) is the refractive index [15]].

of PC [9]. Their result challenges the essential MCT prediction of a glass transition singularity for all modes at a common q-independent crossover temperature T_c.

In attempting to understand the different results found in these two experiments, we consider the following points to be relevant.

(i) For our salol data, it was not possible to obtain a fit by Eq. (3) for $T > 278$ K if the second (I_{ani}) term was not included. This contribution was not introduced in the analysis of Elmroth, Borjesson, and Torell [29], although they have found that $I_{VH} < 10\% I_{VV}$ which suggests that it can be ignored [31].

(ii) The validity of Eq. (2) requires that the fast decay of density fluctuations (microscopic and β-relaxation processes) occurs on a time scale much shorter than the primary α relaxation [14]. If this separation of time scales fails, then, with decreasing temperature, part of the β-relaxation process may enter into the experimental frequency "window," leading to an overestimation of f_0, as noted in [29].

(iii) Extracting the nonergodicity factor f_0 from Brillouin spectra involves a fit with numerous parameters, some of them being strongly correlated. Our experience suggests that it is not generally possible to determine reliably ω_0 and ω_∞ simultaneously from fits to Brillouin spectra.

The fact that for salol we find that the T_c determined from Brillouin scattering data via Eq. (2) is in reasonable agreement with values found by other techniques, while, for PC, Elmroth, Borjesson, and Torell find a difference of at least 60 K, indicates the need for further study of the question of the q dependence of T_c.

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