MOLECULAR DYNAMICS IN CH_2Cl_2/DECALIN GLASS

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The dielectric loss in a glassy solution of CH_2Cl_2 in decalin has been measured in the kHz and THz frequency ranges at 107–148 K. The low frequency part of the loss curve exhibits a peak which shifts upwards by about two decades with a 4 K increase in temperature, and at the glass to liquid transition temperature moves almost immediately out of the audio frequency range into the microwave. The far infrared peak in the loss is displaced by 30 cm^{-1} to 90 cm^{-1} in the glass as compared with the liquid solution at 293 K. These results are interpreted with a new version of itinerant libration whereby collective reorientations are treated as essential in explaining the complete loss profile in CH_2Cl_2/decalin glass which covers at least twelve decades of frequency. It is argued that in addition to the well documented primary and secondary losses in glasses and polymers, there exists in general a tertiary process at far infrared frequencies analogous to the Poley absorption in liquids. This is part of the dynamical evolution in a wide range of disordered solids.

1. Introduction

The influence of viscosity in the medium surrounding a particle or molecule undergoing brownian motion is of basic interest. Viscosity is a factor which can be varied conveniently through orders of magnitude by supercooling solvents such as decalin or *o*-terphenyl [1]. The purpose of this note is to demonstrate the influence of a highly viscous environment in the rotational dynamics of a small, rigid, dipolar molecule (CH_2Cl_2) in glassy decalin. These manifest themselves as a dielectric loss over a frequency range extending from audio frequencies (kHz) and below to the far infrared (or THz). This is in marked contrast to the loss in the equivalent room temperature solution [2], where it is restricted to the microwave (GHz) on the low frequency side.

In the glass the loss is a continuous twin-peaked profile, there being maxima at audio frequencies and at ca. 90 cm^{-1} in the far infrared. This form of loss curve is probably typical of those in a wide range of disordered solids, semiconductors, and polymers where at low frequencies there appears [3] a well-documented ac conductivity. At far infrared frequencies [4] the loss is expressed in terms of the power absorption coefficient, $(\alpha(\bar{\nu}) = 2\pi\bar{\nu}\epsilon''/n(\bar{\nu})$, where $\bar{\nu}$ is the wavenumber and $n(\bar{\nu})$ the refractive index), and strong librational bands are expected here as high frequency adjuncts analogous to the Poley absorption in liquids.

Here we will treat the whole of the observable loss profile in glassy CH_2Cl_2/decalin in terms of an itinerant librator theory of brownian motion [5].

2. Experimental

Capacitance and loss measurements at audio frequencies were carried out with a General Radio bridge, and far infrared optical absorption coefficients were measured with a Grubb-Parsons/N.P.L. mark III Fourier transform interferometer [2]. The sample cells were specially constructed so that a liquid sample could be cooled rapidly to temperatures approaching that of liquid N_2. Temperatures were measured with a copper–constantan thermocouple placed within the sample, and varied using two 10 W heating elements giving access to the range 107–148 K. The dielectric cell was constructed with copper electrodes separated by a teflon spacer. A reservoir cell is formed on one side, the outer wall of which being a TPX window, so that the sample could be observed for premature crystallisation.

3. Theoretical synopsis

The fundamental idea behind itinerant torsional oscillation is that the dielectric loss arises not just from the free brownian motion of individual dipoles. Instead, it is envisaged that the high frequency part of the loss profile (in the far infrared) arises from libratory movements of a dipole encaged by a group of nearest neighbours. The *collective* angular fluctuations of this group are held responsible for the low frequency loss through their influence on the encaged dipole. The mathematical formulation of this problem is presented fully elsewhere [5,6], and is tractable when:

(i) The cage is considered as a rigid entity (of moment of inertia I_1, that of the molecule being I_2).
(ii) The central molecule is bound harmonically to the cage with a frequency ω_0.
(iii) The friction between the molecule and cage is represented by coefficient β_2, and that between the cage and its surroundings by β_1 (in a glass $\beta_1 \gg \beta_2$). We have $\beta_1 = 2kT\tau_D/I_2$, where τ_D is the inverse of the audio peak frequency.
(iv) The molecules may be asymmetric tops, but their dipoles are constrained to reorient in two dimensions. Recent comparisons [5] with liquid state experimental data seem to imply that this is not a limiting constraint.

We note that the ratio I_2/I_1 may be estimated precisely enough from geometrical considerations, aided by X-ray diffraction patterns when helpful. The frequency ω_0 is identified with that of the far infrared peak. Since β_1 is also measurable from the audio-frequency peak this leaves only β_2 as an adjustable parameter. In practice, it serves to broaden the theoretical far infrared peak from a near delta function [7] ($\beta_2 = 0$, harmonic resonance). A suitable value for β_2 is that which produces approximately the observed half-width (see fig. 1).

4. Results and discussion

In figs. 1 and 2 we illustrate the low and high fre-

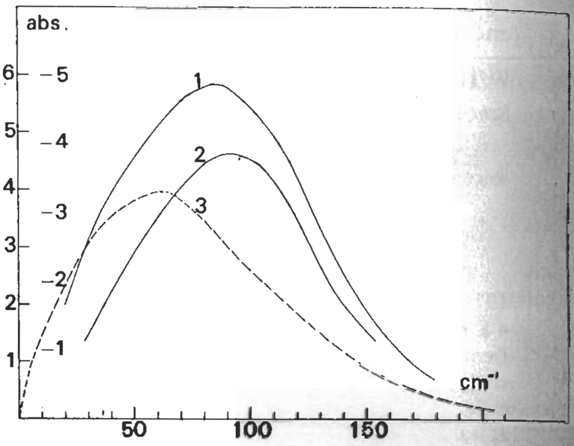

Fig. 1. Far infrared part of the total loss profile in CH_2Cl_2 solutions. (1) Glass at 118 K (inner scale). (2) Glass at 114 K (outer scale). (3) Solution (liquid) at 298 K. The ordinate is $\alpha(\bar{\nu})$/neper cm^{-1}; the abscissa is $\bar{\nu}$/cm^{-1}.

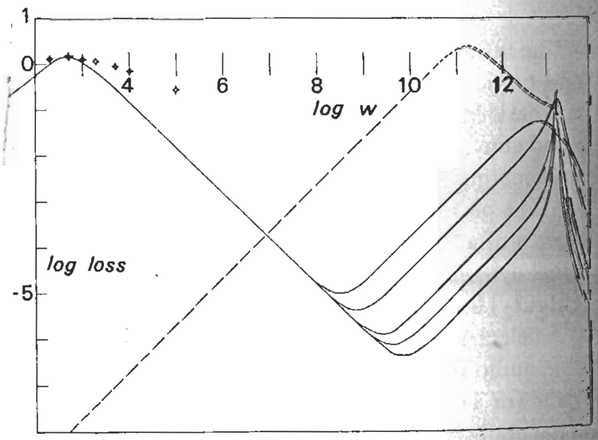

Fig. 2. —— Log(ϵ'')/log(ω) representation of the total loss profile in glassy CH_2Cl_2/decalin at 114 K (1.97×10^{21} molecules cm^{-3} of CH_2Cl_2). ⊙ Experimental points indicating that the observed low frequency loss is broader than the model loss. The various high frequency curves are for β_2 = 0.1, 2, 5, 10, and 20 THz. This illustrates the broadening effect of this friction coefficient. ––– Loss curve of a solution of CH_2Cl_2 in decalin at 296 K (room temperature).

quency parts of the experimental loss in a solution containing 1.97×10^{21} molecules cm^{-3} of CH_2Cl_2 in glassy decalin at 114 K as represented by the itinerant oscillator. A temperature difference of 4 K is enough to move the loss peak through almost two decades of frequency, so that the Arrhenius activation enthalpy for the process is high. The far infrared part of the loss is shown over the temperature range 109–113 K in fig. 1 as the absorption coefficient $\alpha(\bar{\nu})$. There is a slight shift to higher frequency as the temperature is lowered, in marked contrast to the rapid movement in the opposite direction for the low frequency part of the loss. There is also a slight drop in intensity. In comparison, the same concentration of CH_2Cl_2 in decalin liquid at 293 K produced a far infrared peak at 61 cm^{-1}, almost 30 cm^{-1} below that of the glassy solution at 109 K. The low frequency loss peak, which appears in the high microwave at 293 K (3.67 cm^{-1}), has of course shifted downwards by many decades in the glass. The data are summarised in table 1.

For $(kT/I_2\omega_0^2) < 0.1$ it is possible to calculate analytically the multi-decade loss profile. The optimum value of β_2 for best fit is $\beta_2 = 10$ THz, while $\beta_1 = 3.6 \times 10^{10}$ THz at 109 K. The total theoretical loss profile is demonstrated in fig. 2 as a continuous analytical curve, together with experimental data. In fig. 1, the $\alpha(\bar{\nu})$ part of the curve is normalised to the data so that a direct bandshape comparison can be made with a non-linear least mean square best fit. The parameter I_2/I_1 we estimate at 0.1, thus giving in our case $kT/I_2\omega_0^2 = 0.03$.

It is clear that the novel version of the itinerant oscillator (with $\beta_2 > 0$) presented here for the case where the twin loss peaks are very widely separated can be used to reproduce the gross features in the available experimental data. However, the low frequency process is broader than that predicted, i.e. a distribution of inverse frequencies is expected in reality. It follows that a corresponding distribution in ω_0 is also to be expected. Therefore β_2 should on these grounds be adjusted to produce a slightly narrower profile than that observed in the far infrared.

In this letter, we have set out merely to reproduce the major features of the complete loss profile in a glassy solution of CH_2Cl_2 in decalin. Our most urgent point is that the loss does not begin or end at the audio frequency range, but continues into the THz or far infrared range where a further peak appears whose origin is analogous to the Poley band in liquids [8]. In the supercooled viscous liquids studied by Johari [1,9], two absorption peaks (α and β processes) are often observed in cis-decalin containing rigid, asymmetric, aromatic probes such as halogen and methyl substituted benzenes and naphthalenes, and tetrahydrofuran. Below the glass transition only the secondary relaxation is still observed. The loss curve we see in glassy CH_2Cl_2/decalin rapidly shifts up to microwave frequencies over a very narrow range of temperature ($\lesssim 1$ K) at the apparent glass to liquid transition

Table 1
Multi-decade loss characteristics for CH_2Cl_2/decalin glass

Temperature (K)	Loss curve		State of matter
	peak (kHz)	frequencies (THz)	
114	0.5	17.0	glass
118	35.0	16.0	glass
296	1.1×10^8	11.5	solution [2] in decalin (ℓ)

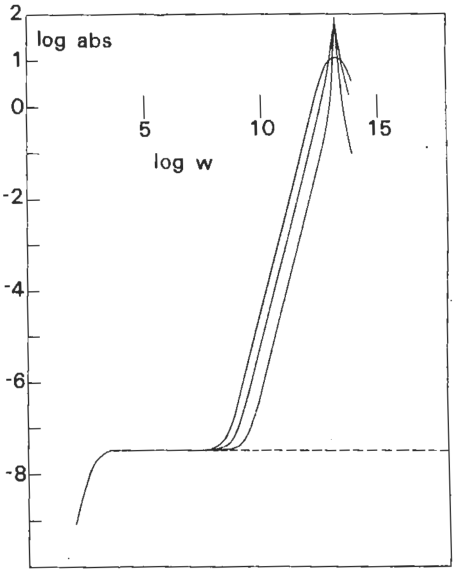

Fig. 3. Log($\alpha(\omega)$) versus log(ω) representation of the absorption in glassy CH_2Cl_2/decalin. Note the horizontal "Debye plateau" which continues as $\omega \to \infty$ for classical theories of brownian motion. The far infrared resonance rises steeply above this at 90 cm^{-1} (114 K) in itinerant oscillation.

temperature (T_c), in contrast to the systems studied by Johari. With very fine temperature control an α and β spectrum might appear in this small temperature range for CH_2Cl_2 also, so that the overall loss profile would peak three times, in the audio, MHz and THz frequency regions. It is clear on this evidence that the appearance (or otherwise) of α and β losses [10] in the viscous liquid is critically dependent on the van der Waals profile of the guest molecule. When this is fairly symmetric, as in CH_2Cl_2, rapid molecular reorientation appears directly after T_c.

It is significant, also, that β_1 is ten orders of magnitude greater than β_2, so that collective reorientation of nearest neighbours is a much slower and more energetic process than the range of harmonic librations performed by the encaged molecule. (The assumption of simple harmonicity, without considering cage reorientation or brownian movement, leads to a prediction [11] of a far infrared absorption at a single frequency

$$f_{\text{peak}} = \bar{\nu} c \propto (V/I)^{1/2} .$$

Here V is the activation energy of the harmonic oscillation, I is the moment of inertia about the dipole axis. Upon consideration of itinerant oscillation with $\beta_2 = 0$, this delta function is a little broadened and becomes naturally the THz frequency part of the audio-frequency loss curve.)

Finally, it is likely that the process described here for CH_2Cl_2 corresponds at audio frequencies to the secondary relaxation [10] which survives into the glassy state of the systems studied by Johari. The influence on the CH_2Cl_2 dipole vector of the primary process in the glass appears (if at all) probably very close to zero frequency. The libration frequencies of individual dipoles (ω_0 being the most probable) in the glass increase by 30 cm^{-1} in comparison with that in a liquid system. This is to say that the root mean square torque increases measurably [4]. It is reasonable to suggest, therefore, that there exist in a viscous liquid three loss peaks which in general may be designated to a primary, secondary and tertiary process of the overall dynamical evolution. The tertiary process is that of libration of the guest dipole showing up at THz frequencies; the secondary process in the influence of nearest neighbour cage reorientation on the libration (and vice-versa); the primary process is the influence of bulk reorientation (inclusive of next nearest neighbours etc.) on the tertiary process (and vice-versa). Certainly, all three features could be reproduced approximately by invoking itinerant oscillation with more than one cage of neighbours. These remarks should also be broadly valid for the α and β process in polymers. It is interesting, also, that by using for semiconductors a charge carrier hopping mechanism in place of rigid dipole reorientation the broad low frequency loss observable as ac conductivity is reproduced more naturally. Such a model should be extended to involve correctly the THz part of the overall loss process.

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