

Study of the nature of glass transitions in the plastic crystalline phases of cyclo-octanol, cycloheptanol, cyanoadamantane and cis-1,2-dimethylcyclohexane

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Cycloheptanol, cyclo-octanol, cyanoadamantane and cis-1,2-dimethylcyclohexane are known to form plastic crystals which can be supercooled to show a glass transition at a temperature T_g . The molecular dynamics in different plastic phases is studied in their supercooled states using dielectric spectroscopy (frequency range: 10^6 Hz– 10^{-3} Hz) and differential scanning calorimetry (DSC) over a wide temperature range. The kinetic freezing of the various dielectric processes have been critically examined in relation to the T_g found in the DSC experiments. The plastic phase I of cyclo-octanol shows two T_g 's: one at 148.5 K and the other at 164 K, the former of which is not found in well annealed phase I. The dielectric α -modes correspond to the latter. Cycloheptanol exhibits many T_g 's for the different plastic phases. Unlike the cyclic alcohols, the dielectric spectra of cyanoadamantane and cis-1,2-dimethylcyclohexane is clearly found to follow the Havriliak–Negami equation, both of which interestingly show very little molecular mobility, often referred to as the secondary relaxation in their glassy states. In addition, the temperature dependence of the relaxation rates and the dielectric strengths are critically examined for various supercooled phases to gain an insight into the nature of the molecular mobility in those phases. © 2001 American Institute of Physics. [DOI: 10.1063/1.1342811]

I. INTRODUCTION

In general, a glassy state results from an elongation of a relaxation time by cooling a material which is in a supercooled metastable state. Thus, the glassy state is looked upon as a nonequilibrium state in a thermodynamic sense.¹ In principle, every liquid, irrespective of its chemical composition, if cooled fast enough to avoid its collapse to the normal crystalline (NC) phase, can reach the glassy state, and is often referred to as structural- or liquid-glass.² Usually in a normal liquid there is a strong coupling between the rotational and translational degrees of freedom, and there is only one glassy state, the liquid-glass. However, in the case of liquids composed of molecules of high symmetry³ or molecules with different conformers,^{4,5} there exists⁶ a decoupling between the translational and rotational degrees of freedom on cooling, leading to what is known as the plastic crystalline (PC) phase, which on further cooling collapses to an NC phase. In the PC phase the molecules have translational symmetry but are rotationally disordered. Thus, this PC phase can also be supercooled to avoid its collapse to the NC phase, where the rotational disorder gets frozen kinetically. This state is generally referred to as orientational glass or glassy crystal.^{2,7,8} Since it involves only the orientational degrees of freedom and has many similarities with that of liquid-glass, it is often thought to be a simple model glass^{6,9,10} to start with.

The approach to the glassy state has been studied very well using dielectric spectroscopy.^{1,6,11–19} The temperature

dependence of the relaxation rate is found to be non-Arrhenius and the corresponding spectral response is found to be non-Debye (with alcohols as an exception.^{20–22}) This non-Debye behavior has been the subject of special interest to researchers working in dielectrics in view of the suggested universalities^{23,24} and scaling^{25,26} approaches. Although the glassy crystal is suggested to be a good model glass to understand glass formation, in general, the amount of information available on this front is not adequate. The relaxation data either do not exist throughout the temperature range because of various problems including recrystallization²⁷ to the NC phase or are available only in a few systems without much supporting information from other techniques. Also in the case of cyclic alcohols, the transition temperatures are often sensitive to the amount of impurities²⁸ (probably because of the existence of various conformers), which is further complicated by the existence of more than one PC phase (for the same reason⁵) and hence, can exhibit more than two glassy crystalline transitions.⁵

The glass transition temperature, in a general sense, can be defined as the temperature where the various physical properties exhibit a sharp change on cooling of a material. Since the approach to the glass transition is relaxational in nature, the transition (more exactly the transformation) temperature is dependent on cooling (or heating) rates. In experimental glass science, it is often customary^{1,27} to measure this at a cooling (heating) rate of $10^\circ/\text{min}$ which approximately corresponds to a relaxation time of about 100 s or to an approximate relaxation frequency of 10^{-3} Hz. The glass transition temperature is generally seen as a step-like change in specific heat measurements. It is also customary to desig-

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nate this temperature as the actual T_g as it corresponds to the onset of making/breaking of the chemical bonds (structural change) and corresponds to the enthalpy relaxation time of 100 s (at a heating rate of $10^\circ/\text{min}$). Usually in liquid glasses the T_g measured (calorimetrically) also corresponds to changes in other physical properties such as a step-like change in thermal conductivity²⁹ or a sharp change in the slope of thermal expansion (or specific volume³) or enthalpy versus temperature curves. The glass transition event at T_g can also be realized as the kinetic freezing temperature of the main dielectric relaxation event.²² This has been found to be true for most of the liquid-glasses and glassy crystals within the experimental uncertainty in the determination of these temperatures although some ambiguity exists in the case of liquid alcohols.^{21,22}

However a different situation prevails in cyclic alcohols in their plastic phases. More than one T_g has been quoted in cyclo-octanol in Differential Scanning Calorimetry (DSC)³⁰ and in thermal conductivity²⁹ measurements, but the main α -process as per the dielectric measurements of Brand *et al.*³¹ freezes at 168 K which appears to be in no way connected with the modes freezing at the T_g 's quoted above. A similar confusion exists in the case of cycloheptanol from calorimetric studies;^{6,30,32} the dielectric measurements of Shablakh *et al.*⁵ and the Nuclear Magnetic Resonance(NMR) measurements¹⁰ and also, the number of glass transition events that can be realized in this material is not clear as this material exhibits many plastic phases.⁵ In order to understand these phenomena, it is desirable to carry out both calorimetric and dielectric relaxation experiments on the same sample for a given impurity. It is with this view that the present study was taken up.

Another aspect we wish to critically examine in plastic crystals is the nature of the relaxation, especially in view of the questions raised by Brand *et al.*³¹ regarding the validity of the universal scaling law proposed by Dixon *et al.*,²⁵ where it was shown that the smaller sub- T_g processes make the contribution to the high frequency side, which has been argued to be a universal behavior of the glasses in the scaling law proposal. With these observations in mind, we have examined the dielectric spectra of two nonhydrogen bonded plastic crystals in their supercooled state, as the corresponding dielectric spectra are expected to be simpler because of the lack of hydrogen bonding between the molecules.

II. EXPERIMENT

The samples studied here are: cyclo-octanol or COOL (E. Merck, 95% purity); cycloheptanol or CHOL: sample I (E. Merck, >98%) and sample II (Aldrich Co., ~97%) and cyanoadamantane or CNADM (E. Merck, >98%) and cis-1,2-dimethylcyclohexane or DMCH (Aldrich, 99%). All are used as received without any further purification.

The DSC measurements are made by using a DuPont TA 2000 thermal analyzer using the quench cooling accessory. For the dielectric measurements, an HP 4284A precision LCR meter in the frequency range 20 Hz–1 MHz is used. For the measurements of dielectric loss at the ultra low frequency of $10^{-0.5}$ Hz – $10^{-3.0}$ Hz, a DC step response technique is used. A three terminal liquid dielectric cell similar to

TABLE I. Details of the various first order transition temperatures. L: liquid; S: crystalline solid; M: metastable.

Sample	Nature of transition	Transition temperature (K)		
COOL	SI→L	291.2	297.5	(Ref. 28)
	SII→SI	258.2	264.0	
CHOL	SI→L	276.6	280.3	(Ref. 32)
	SIV→SI	253.6	258.5	
	SV→SIV	248.2	–	
	SII→SV	237	–	
	SIII→SII	225.0	227.3	
	II'→II	167	172.2	
CNADM	III'→III	126.2	128.2	(Ref. 33)
	SI→L	468.7	458.0	
	SII→SI	285.3	280.0	
	SIII→SII (M ?)	281.2	280.0	
DMCH	SL→L	224.5	223.2	(Ref. 45)
	SII→SI	–	172.5	

the one used earlier^{21,22,27} has been used with COOL, CHOL and DMCH for this purpose. A different cell assembly has been used with CNADM which is in a powdered form. A disk 2.5 cm in diameter and about 0.2 cm in thickness is made out of the sample by pressing it in a pressure dye at a pressure of 10 K bar. The two electrodes are made from silver powder pressed at the same pressure. The sample disk is then pressed between the silver pellets at the same pressure to make the capacitor. This capacitor is held between two brass electrodes with the aid of a light weight spring. The sample temperature is measured with the help of a thermocouple kept deep inside the bottom electrode. The temperature of the assembly is then controlled in the same way as before. The experimental setup and accuracy in the measurements were as before.^{21,27}

III. RESULTS

To get information about the phase getting supercooled we have measured the first order transition temperatures corresponding to various phases using DSC which are shown in Table I. The values entered in Table I are the average values of five runs with a heating rate of $2^\circ/\text{min}$. To give some idea of the deviations of these transition temperatures from the data of others, we have also entered the corresponding values reported in the literature.^{28,32,33,45} The deviation of the transition temperatures from the reported values are probably due to impurities present in our samples. The nature of the transition has been identified on the basis of the present dielectric work and the thermal study of others. Our cycloheptanol sample (sample II) revealed two additional transitions located at 248.2 K and 237.4 K which were not observed in the earlier work³² and in sample I of our study. As we see later these corresponding phases are associated with an anomalous (large) value of the Fuoss–Kirkwood dipole correlation factor g ³⁴ and are present during heating and cooling cycles and can get supercooled. This has led to considerable difficulty in identifying the stability of the corresponding

phases. (Metastable states with high g values are also found during cooling in cyclopentanol^{27,35} and this phenomenon is not uncommon in cyclic alcohols.^{5,35}) Our sample CNADM shows two transitions around 285 K instead of one reported by Foulon *et al.*³³ We believe that this discrepancy could be due to a very high heating rate of 40°/min. adopted by these workers with which it is difficult to resolve the two closely spaced transitions. However, of the two transitions, the lower one was found to be metastable as it was found to diminish in size with annealing. The sample wise details of the measurements are described in the following subsections.

A. COOL

In view of the ambiguity in the glass transition temperatures of COOL, as pointed out in the Introduction, we have critically examined the supercooling of various phases of this material. The liquid could not form liquid-glass even at very high cooling rates. To get an idea of what the T_g of the liquid [i.e., $T_g(l)$] is, we have used propylene glycol as an additive to suppress crystallization and the $T_g(l)$ of this liquid mixture is then measured. The $T_g(l)$ of pure COOL is then determined by an extrapolation method³⁶ where the $T_g(l)$ of the mixture at various concentrations was measured as described in our recent publication.²⁷ The $T_g(l)$ of COOL is found to be 171 ± 2 K.

When the liquid of COOL is cooled it quickly crystallizes to a plastic phase which we refer to as phase I' . The subsequent melting endotherm corresponding to this phase always showed an enthalpy about 20%–40% less than what it should be. (The enthalpy associated with the $SI \rightarrow L$ transition is supposed to be about 2.04–2.10 kJ/mol²⁸.) However, we realized that phase I' after annealing for more than an hour, more or less gets transformed to phase I and the enthalpy associated with the $SI \rightarrow L$ transition is then fully established. Thus, it is clear that phase I' has some additional disorder which was not present in phase I. In view of these observations, it is expected that, if the DSC (calorimetry) experiments are done without taking care of this annealing effect, it will show a different freezing event corresponding to the additional disorder. We have taken the DSC runs for different sample histories which are given in Fig. 1. The samples are all equilibrated at 100 K for 10 min before taking the DSC scan. The heating rate is fixed at 10°/min in all of these runs.

Shown in Fig. 1(a) is the DSC scan of phase I (well annealed phase I') which shows a small but clear T_g event at 164 K. (Here the sample was actually recycled a few times in the range 150 K < T < 258 K to allow equilibrium to be established through recrystallization to a more stable phase and was then heated to a temperature of 265 K where it was annealed for about 1 h before cooling it for the DSC run. The word “well annealed” phase I' refers to this sample with this thermal background.) If phase I' is not annealed, the corresponding DSC scan would be like the one shown in Fig. 1(b), which shows a large GT event at 148.5 K. However, this step-like event starting at 148.5 K extends all the way up to 172 K. (In Fig. 1, only the DSC curves around the GT event are shown. Actually the GT event is followed by one crystallization exotherm and two endotherms corresponding

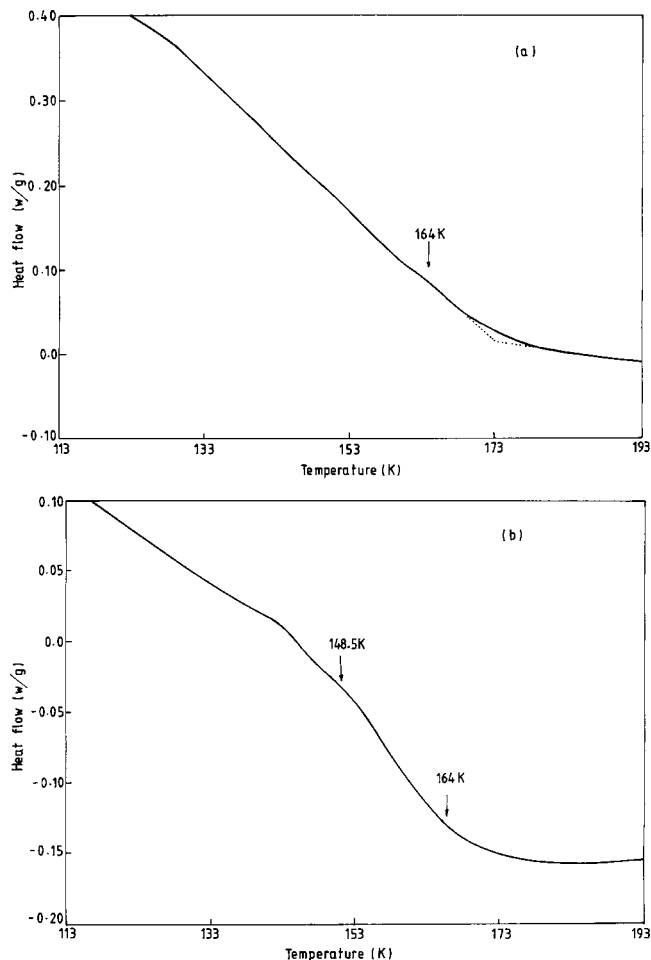


FIG. 1. DSC curves for cyclo-octanol in the glass transition region for a heating rate of 10°/min. (a) For sample cooled from well annealed phase I (sample size=8.7 mg). (b) For sample that is not deliberately annealed during cooling (sample size=14.3 mg). The dashed line in (a) corresponds to the tangents drawn using the software for the calculation of T_g .

to the transitions from $SII \rightarrow SI$ and $SI \rightarrow L$ as shown in Table I but are not shown in Fig. 1, for the sake of clarity of the glass transition event at T_g .)

The GT event shown in Fig. 1(b) for phase I' is unusually broad and looks like a superposition of two GT events, one at 148.5 K and another probably around 164 K. In order to get this clarified, we have annealed the sample at 238 K for about 20 min for the crystallization to take place in the supercooled phase I' , before it is cooled to 100 K for the DSC run. The DSC curves corresponding to these two situations are shown in Fig. 2. It can be noted that in the crystallized sample, the GT event at 148.5 K still exists and has now become sharper but the second GT event around 164 K has vanished. It is interesting to note that there is no visible crystallization exotherm during heating in curve 2. Prolonged annealing of the sample around 210 K for about 2 h, more or less removed the GT event at 148.5 K with the corresponding endotherms fully established to their expected sizes (not shown in Fig. 2). Interestingly, the corresponding DSC curves do not show any sign of a new phase which can be identified^{28,29} with phase III of the high pressure side. In addition to the above results, the DSC runs on all samples

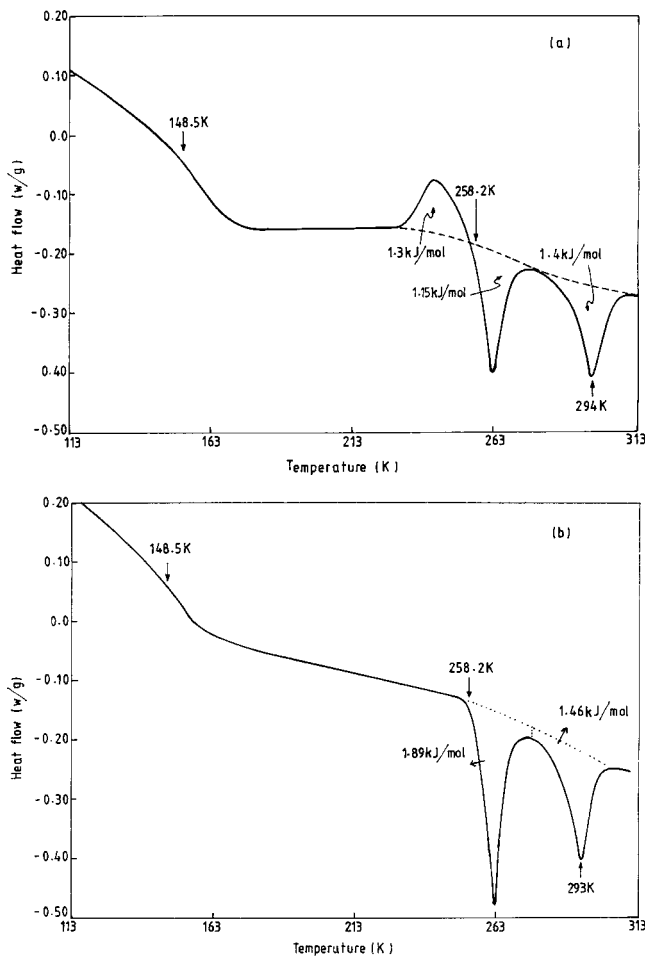


FIG. 2. DSC curves for cyclo-octanol for a heating rate of 10°/min. (a) For a sample that not deliberately annealed during cooling (sample size=14.3 mg). (b) For a sample that is annealed for 20 min in the crystallization zone of curve (a), before cooling to 100 K for the DSC run (sample size=9.7 mg). The dashed and dotted lines correspond to the (sigmoidal) base line set by the software for the calculation of the enthalpy of the transitions.

with different sample histories revealed another small step-like change around 136 K for a heating rate of 10°/min.

The dielectric measurements corresponding to this liquid in its supercooled state could not be taken as the liquid quickly solidified in the dielectric cell. The relaxation corresponding to this phase is always found to occur at much higher frequencies than the upper limit of the frequency window used here, which is 1 MHz. Solid phase I supercools and the relaxation data corresponding to this phase are shown in Fig. 3. We have used the Havriliak–Negami equation³⁷ to describe the dielectric loss curves which is given by

$$\frac{\epsilon^*(f) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \left(1 + i \left(\frac{f}{f_0} \right)^{1 - \alpha_{HN}} \right)^{-\beta_{HN}}, \quad (1)$$

where ϵ_0 , ϵ_∞ are the limiting dielectric constants at low and high frequencies, respectively, and f_0 is the mean relaxation frequency [which is related to the peak frequency f_m by the relation $f_m = f_0 \tan(\pi/2(1 + \beta_{HN}))$ for small α_{HN} values].

The temperature dependence of f_m values corresponding to the α -process ($f_{m,\alpha}$) could well be described by the power-law (PL) equation:^{5,11,13,14,20–22,27}

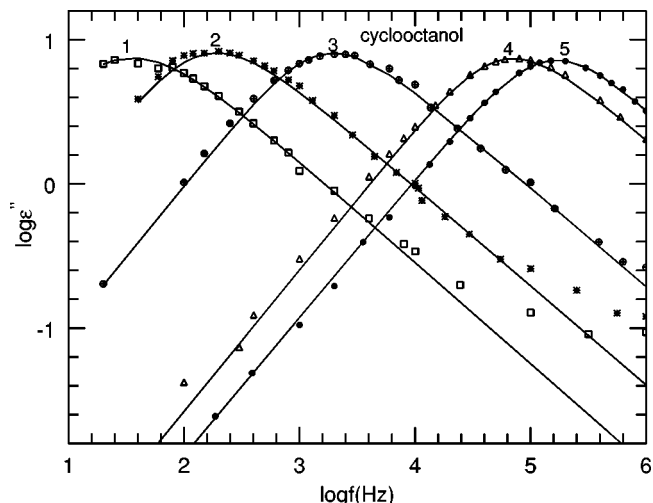


FIG. 3. Log ϵ'' vs log f for the supercooled phase I of cyclo-octanol. The thick lines correspond to Eq. (1) for the given parameters as: curve 1: $T=201.8$ K ($\alpha_{HN}=0.10$, $\beta_{HN}=0.78$); curve 2: 210.1 K (0.025, 0.703); curve 3: 222.6 K (0.015, 0.697); curve 4: 246.1 K (0.019, 0.714) and curve 5: 252.5 K (0.050, 0.825).

$$f_{m,\alpha} = A \left(\frac{T - T'_g}{T'_g} \right)^r, \quad (2)$$

where T'_g is the zero relaxation frequency temperature (i.e., the limiting glass transition) and r is the dynamic exponent. We have also used the well known Vogel–Fulcher–Tammans (VFT) equation to describe the T-dependence of $f_{m,\alpha}$, which is given by

$$f_{m,\alpha} = f_{0,\alpha} e^{(-B/T - T_0)}, \quad (3)$$

where T_0 is the limiting glass transition factor. In the above equation, the pre-exponential factor $f_{0,\alpha}$ is often identified with the lattice vibrational frequency and $B = E/R$, where E corresponds to the activation energy at high temperatures. Both Eq. (2) and Eq. (3) are found to describe the data equally well and the corresponding parameters are entered in Table II. Finally, we have plotted the f_m values corresponding to the different processes and different phases in the form of an Arrhenius diagram shown in Fig. 4. This figure also includes the resolved high temperature f_m values corresponding to the different processes observed in the liquid and solid phases by others. We have also shown the f_m values corresponding to the α -, β - and γ -processes observed by Brand *et al.*³¹ for the purpose of comparison.

It may be noted from Fig. 3, that Eq. (1) describes the data well around low and middle frequencies but not on the high frequency side. As pointed out by Brand *et al.*³¹ in their earlier investigation on this sample, these deviations probably occur due to the presence of two other relaxation processes of much smaller magnitude, which are designated as β - and γ -processes found, respectively, on lowering the temperature. We have critically examined the supercooled phase I and even the well annealed phase II of this sample for the existence of these processes. Both the β - and γ -processes were always found with the same relaxation rates for a given temperature, although the main (α) process was absent in phase II. The dispersion corresponding to these processes

TABLE II. Details of the α -relaxation process.

Sample	Phase	$T_g(pc)$ (K)	log A (Hz)	Power-law		Vogel–Fulcher equation			
				r	T'_g (K)	T_g (cal.) K	log A'	B (K)	T_0 (K)
COOL	I	164.0	6.87	14.40	142.6	172.0	14.59	3690.3	80.60
CHOL	I	144.5	4.10	10.96	122.90	150.5	10.54	2659.0	61.8
	II	...	4.35	13.96	113.69	147.5	15.60	5355.8	20.83
	III	...	3.69	11.84	117.67	149.7	10.87	2647	54.5
CNADM	I	172.3	5.81	9.13	152.9	169.5	12.35	3880.0	48.1
DMCH	I	107.8	10.68	11.12	98.5	104.3	13.83	1133.3	73.2

could well be described by a depressed Cole–Cole arc equation³⁸ which can be obtained by considering $\beta_{HN}=1$ in Eq. (1). The corresponding relaxation frequencies are fitted to the Arrhenius equation:

$$f_m = f_0 e^{-E/RT}, \quad (4)$$

the results of which are given in Table III.

We have also tried to see whether the sample history corresponding to phase I has any effect on f_m values corresponding to the α -process. We failed to notice any change in the T-dependence of the α -process within the experimental accuracy. We have also measured the static dielectric constant of the liquid up to 363 K to get an idea of the degree of correlations in this phase and to observe, if any, the deviations of $\Delta\epsilon (= \epsilon_0 - 1.05n_D^2)$, where n_D is the optical refractive index) from $\sim 1/T$ law.^{39,40} The values of $\Delta\epsilon$ thus measured are plotted in Fig. 5 against $10^3/T$, for both the liquid and plastic phase I. The values of the Fuoss–Kirkwood correlation factor g calculated³⁴ for the liquid vary from 1.09 at 356 K to 2.00 at 301.4 K. For phase I, the corresponding values

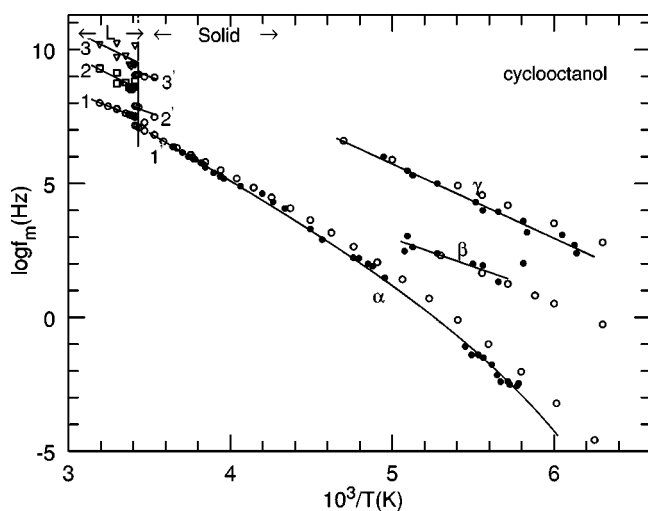


FIG. 4. Complete Arrhenius diagram of cyclo-octanol. Also shown are the liquid and solid (Refs. 26, 31, 49, 46) data of others (open circles). (Both the liquid and solid phase I have three high frequency processes designated as 1, 2, 3 and 1', 2', 3', respectively. Note that there is a discontinuity at the boundary of these phases.) The thick line on the α -process corresponds to the fit to Eq. (2) to our data. The thick lines on β - and γ -processes are fits to Eq. (4) to our data. The thick lines on the liquid-side are guides for the eye.

vary from 2.50 at 278 K, peaking to a value of 2.90 at 246.0 K, beyond which it falls to about 2.17 around 219 K.

B. CHOL

The samples we have obtained from E. Merck, Germany (sample I) and Aldrich (sample II) showed different behaviors as far as supercooling of the liquid phase is concerned. Sample I showed a large glass transition at 151 K for the liquid phase [Fig. 6 (curve 1)]. For this purpose, the sample was cooled at a rate of about a few hundred degrees per minute by dipping the sample directly into liquid nitrogen before introducing it into the DSC cell at 100 K for the DSC run. By comparing the size of the crystallization exotherms with that of the endotherms that follow the crystallization peaks, we are more or less certain that the GT event shown in Fig. 6 (curve 1) is due to the kinetic freezing of liquid. We have also measured the $T_g(l)$ of both types of samples using the binary liquid method²⁷ using propylene glycol as the second component. The $T_g(l)$ thus measured is 153.5 ± 2.5 K which more or less agrees with the above value. Shown in Fig. 6 (curve 2) is the curve corresponding to the supercooled plastic phase I of the same sample for a cooling rate of $10^\circ/\text{min}$. The T_g value for phase I is 144.6 K. The sample obtained from Aldrich Co. (sample II) did not show any tendency for the liquid to supercool. However, phase I on cooling at a rate of $10^\circ/\text{min}$ shows the GT event at ~ 143 K, which more or less agrees well with that shown in Fig. 6 (curve 2).

We have studied cycloheptanol in detail using dielectric spectroscopy by annealing the sample at appropriate temperatures for crystallization and by quenching the required phase to get the relaxation behavior at lower temperatures (Fig. 7). We have performed various heating and cooling cycles on the same sample to get a clear idea of the phase getting supercooled and which exhibits the corresponding

TABLE III. Details of sub- T_g processes [Eq. (4)].

Material	Process	log f_0 (Hz)	E (kJ/mol)
COOL	β	15.52	47.53
	γ	20.43	56.03
CHOL	γ	18.69	38.91

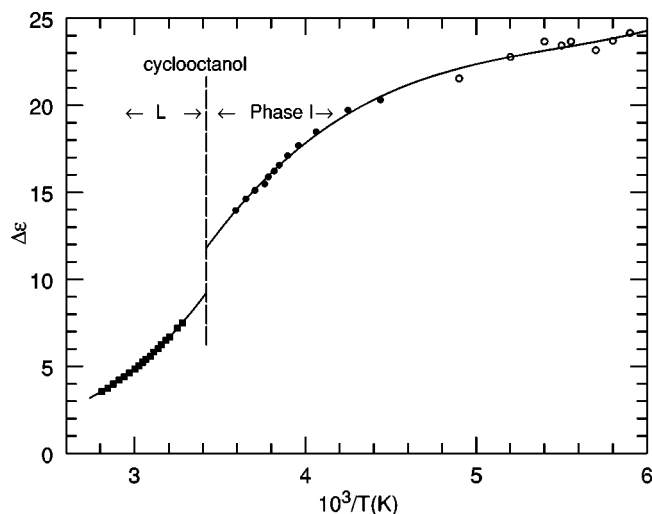


FIG. 5. Variation of dielectric strength $\Delta\epsilon$ with $10^3/T$ in cyclo-octanol for both the liquid state and plastic phase I (including the supercooled plastic phase I). Also included in the figure (open circles) are the data of others (Refs. 26, 31).

dielectric measurements. Our observations are summarized in the following subsections.

1. Liquid phase

The sample obtained from E. Merck allowed us to make measurements on the supercooled liquid state down to about 235 K before crystallization until phase I intervenes. The f_m values measured for this phase agree well with the extrapolated f_m values reported in literature for the high temperature side. This situation is shown in Fig. 8 where the f_m values are plotted again $10^3/T$ along with that of other phases. (On the other hand, the liquid phase of the sample obtained from Aldrich showed little tendency to supercool.) The relaxation spectra for the supercooled liquid yielded values of α_{HN} , β_{HN} [Eq. (1)] of 0.025, 0.8 at 245.1 K and 0.04, 0.8 at 234.1 K. We have also studied the static dielectric constant up to a temperature of 363 K from which the dielectric strength $\Delta\epsilon(\epsilon_0 - 1.05n_D^2)$ is calculated. The values of $\Delta\epsilon$ thus obtained showed slight deviation from $1/T$ law as in the case of COOL shown in Fig. 5. The values of Fuoss–Kirkwood correlation factor g calculated approximately³⁴ for this phase varies from a value of 1.26 at 357.7 K ($\Delta\epsilon = 4.57$) to 2.22 at 234.1 K ($\Delta\epsilon = 17.71$).

2. Phase I

The dielectric measurements are performed on phase I in two different ways to cover the entire temperature range down to the corresponding T_g . In the first method, the measurements are made during the cooling of the sample which enabled us to cover a few tens of degrees of temperature in its supercooled region before recrystallization intervenes. In the second method the measurements are performed near and above T_g by quenching the phase I very fast. However, in the latter method during heating the sample recrystallizes into phase III at about a temperature of 187 K and takes a time of about 2 h for completion. The relaxation behavior of this phase is found to deviate from that of Cole–Davidson⁴³ [Fig.

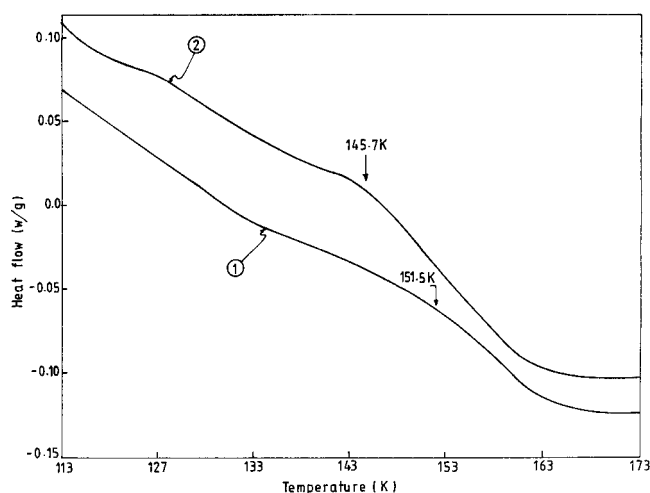


FIG. 6. DSC curves taken in the glass transition region for cycloheptanol (sample I) from 100 K at a heating rate of $10^\circ/\text{min}$. Curve 1: fast quench cooled from the liquid phase (sample size=17.1 mg); curve 2: quench cooled from phase I (sample size=18.4 mg). Curve 1 is shifted downwards by 0.025 units for the sake of clarity.

7(a)]. The corresponding values of α_{HN} and β_{HN} are found to vary from 0.05, 0.9 at 253.5 K to 0.11, 0.76 at 178.6 K. The corresponding $\Delta\epsilon$ values are found to deviate from $1/T$ law, especially on the lower temperature side similar to the case of phase I of COOL shown in Fig. 5. The corresponding g values are found to vary from 2.92 at 253.5 K to 3.1 around 220 K, below which it starts to fall to 2.25 at 178.6 K. The relaxation rates vary in a non-Arrhenius fashion as shown in Fig. 8 and the corresponding parameters are entered in Table II.

3. Phase II

Phase II could not be studied over a wide temperature range because of rapid recrystallization to other phases. The dielectric spectra [Fig. 7(b)] yielded the values of α_{HN} , β_{HN} in the range of 0.15, 0.80 at 240 K to 0.17, 0.80 at 229.4 K. The corresponding values of g vary approximately from 2.75 at 240 K to 2.58 at 229.4 K.

4. Phase III

During heating of the rapidly cooled sample, the material always recrystallizes to a phase which we believe to be phase III. This phase shows a lot of unusual features in dielectric study. The corresponding dielectric spectra [Fig. 7(c)] are found to be very symmetrical due to the unusually large α_{HN} values. The α_{HN} values vary from 0.5 to 0.2 on the decrease of temperature from 216 to 174 K. The dielectric strength showed a tendency to increase with decreasing temperature. These values approximately correspond to a g factor of 1.10 to 2.75 over the same temperature interval. It is also observed that phase III superheats to phase I (during heating) by-passing all the intermediate phases.

5. Phase IV (and V)

It is observed that during the slow cooling of phase I, the material recrystallizes to a phase which showed anomalous

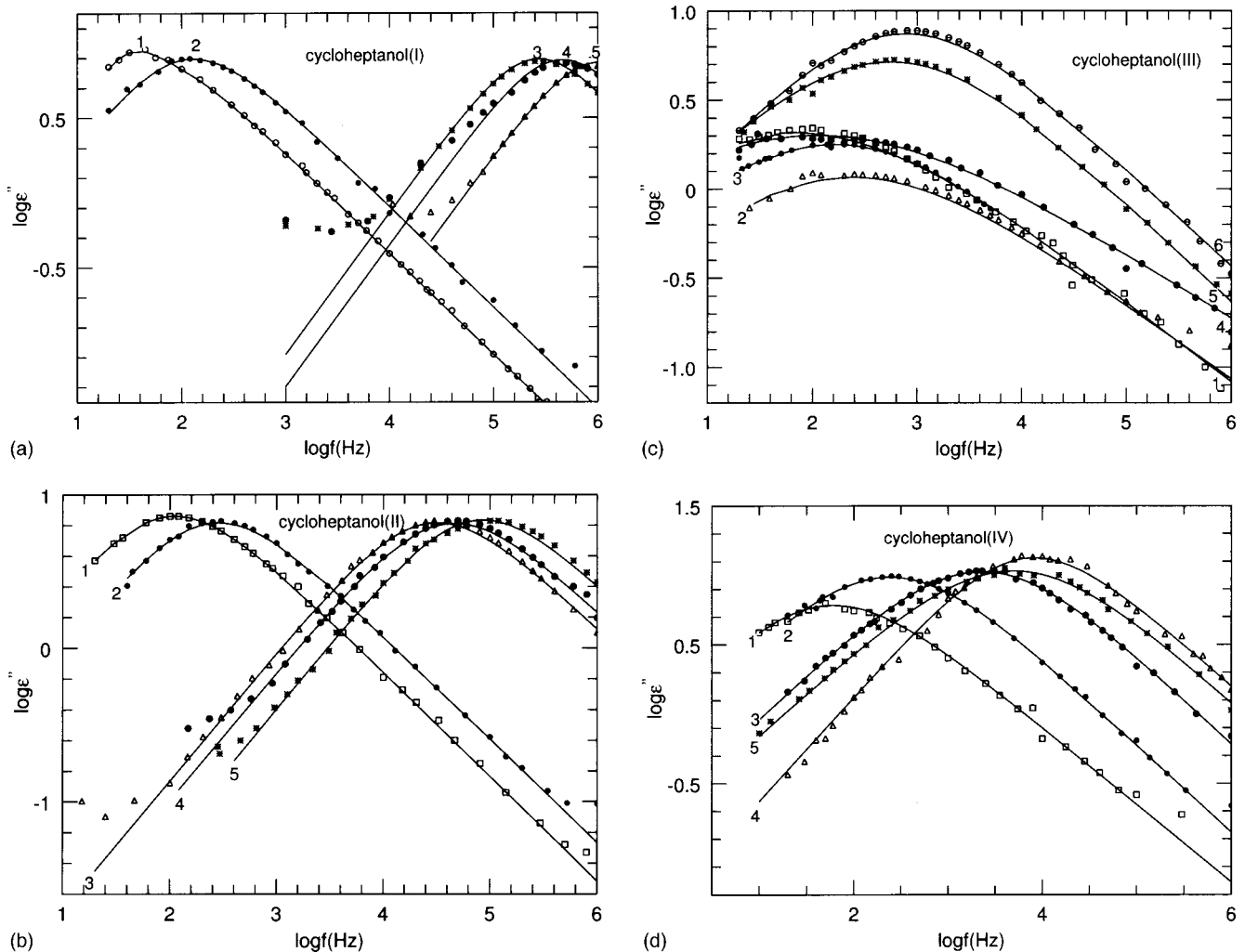


FIG. 7. Log ϵ'' vs $\log f$ in the various (supercooled) phases of cycloheptanol. The thick lines correspond to Eq. (1) corresponding to the parameters shown in the brackets, as below: (a) Phase I: curve 1: $T=178.6$ K ($\alpha_{HN}=0.11$, $\beta_{HN}=0.76$); curve 2: 183.5 K (0.11 , 0.76); curve 3: 240.0 K (0.05 , 0.90); curve 4: 245.5 K (0.05 , 0.89); and curve 5: 253.5 K (0.05 , 0.90). Deviations of the data on the lower frequency side from Eq. (1) are due to dc conduction loss [the dipolar loss obtained on subtraction, falls on the thick lines corresponding to Eq. (1)]. (b) Phase II: curve 1: $T=184.9$ K ($\alpha_{HN}=0.148$, $\beta=0.8$); curve 2: $T=187.6$ K (0.152 , 0.8); curve 3: 230.6 K (0.185 , 0.8); curve 4: 232.9 K (0.165 , 0.8); and curve 5: 239.9 K (0.150 , 0.8). (The data corresponding to curves 1 and 2 may have some contribution from supercooled phase I.) (c) Phase III: curve 1: $T=199.6$ K ($\alpha_{HN}=0.540$, $\beta_{HN}=0.99$); curve 2: 216.4 K (0.47 , 0.80); curve 3: 206.6 K (0.45 , 0.90); curve 4: 216.1 K (0.56 , 0.84); curve 5: 216.5 K (0.43 , 1.0); and curve 6: 217.7 K (0.37 , 0.88). (d) Phase IV (or V): Curve 1: $T=200.6$ K ($\alpha_{HN}=0.30$, $\beta=0.80$); curve 2: 211.7 K (0.34 , 0.96); curve 3: 228.6 K (0.35 , 0.99); curve 4: 231.8 K (0.24 , 0.80); and curve 5: 234.8 K (0.38 , 0.99).

dielectric strength; it is also found that this phase could be supercooled without the intervention of recrystallization to any other phase. (It is difficult to distinguish between phase IV and phase V in the dielectric measurements.) The $\Delta\epsilon$ values in this phase correspond to high g values of approximately 6.67 at 261 K to about a value of 2.5 at 188 K. This phase also has unusual dielectric behavior in the sense that the corresponding dielectric spectra are symmetrical with high α_{HN} values in the range of 0.3 to 0.4 [Fig. 7(d)]. Although no definite trend exists in the variation of α_{HN} with temperature, these values are found to be smaller than those of phase III. The f_m values corresponding to this phase are almost the same as those of phase III and are found to be slightly non-Arrhenius in T-dependence (Fig. 8).

During our investigation we also noticed that the polarization corresponding to cycloheptanol has never fallen to zero even after prolonged annealing in the supercooled phases. Thus, it appears that there is no normal crystalline

state for this material, or that it may require prolonged annealing³² than that is used in the present study. The details of the non-Arrhenius parameters corresponding to the various phases are given in Table II. In addition to the above, all the glassy states revealed the presence of a sub- T_g process (designated as the γ -process in Fig. 8), the details of which are given in Table III.

C. CNADM

The previous dielectric studies⁴²⁻⁴⁴ on the sample CNADM revealed an unusual behavior in the relaxation spectra and the T-dependence of the static dielectric constant ϵ_0 . However, exact information about the nature of the relaxation spectra is not clearly available prior to this investigation because of the problems associated with the cell assembly employed before (please refer to Ref. 42 for details). The DSC run on this sample shows a glass transition at 170

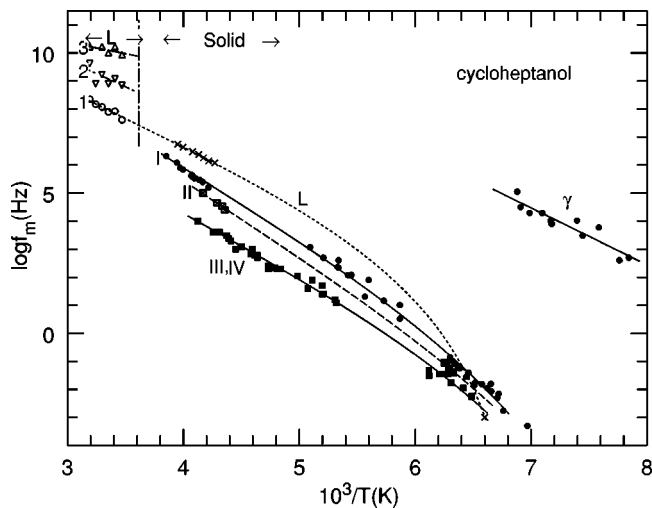


FIG. 8. Complete Arrhenius diagram of cycloheptanol. Also shown in the figure are the data points (o) corresponding to the liquid state taken from Refs. 39 and 40. The dotted line is the approximated α -process corresponding to the supercooled liquid using high T data and the $T_g(l)$ (which corresponds to an approximate f_m of 10^{-3} Hz). The solid lines are the P.L. fits [Eq. (2)]. The thick lines in the γ -process corresponds to Eq. (4).

K followed by a two step exotherm associated with recrystallization and two endotherms at 281.2 K and 285.3 K corresponding to the two recrystallization peaks (Fig. 9). However, the transition associated with the endotherm at 281.2 K appears to be metastable because it is dependent on the sample history and is also diminished in size in very well annealed samples. Foulon *et al.*³³ report only one transition (which corresponds to our lower endotherm) in their DSC scan. It is possible that the two endotherms could not be resolved in their study because of the high heating rate of 40°/min used. In Fig. 10, we have shown the variation of dielectric loss ϵ'' in relation to frequency for the supercooled plastic phase. The ϵ'' values could be well represented by Eq. (1) over the entire frequency range employed here. The

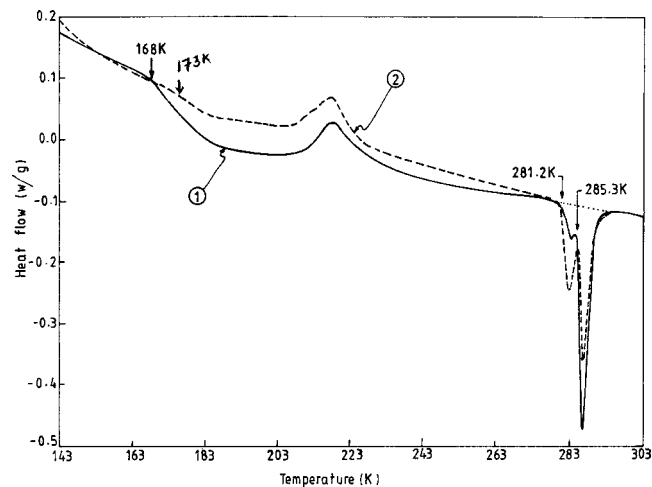


FIG. 9. DSC curves for a heating rate of 10°/min for 1 cyanoadamantane for a sample cooled from 393 K (curve 1) and cooled from room temperature (curve 2), respectively, at an average rate of 10°/min (sample size=8.4 mg). Note that there is a change in the value of $T_g(pc)$ from 173 K to 168 K. The dotted line on curve 1 corresponds to the base line set by the thermal analysis software.

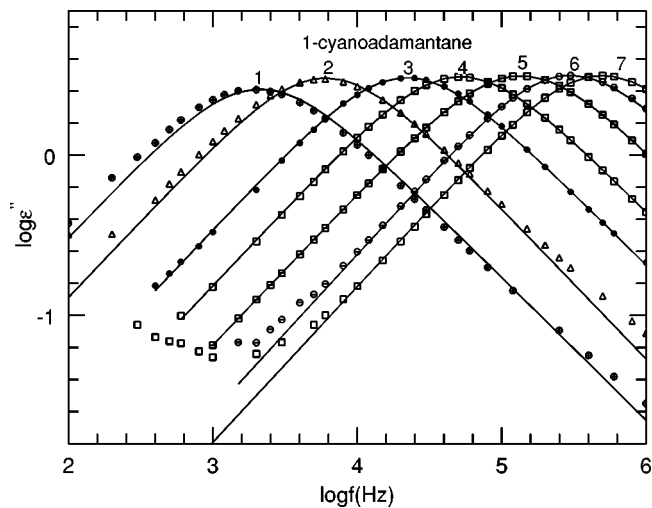


FIG. 10. Log ϵ'' vs log f in the supercooled phase I of 1 cyanoadamantane. The thick lines correspond to Eq. (1) for the given parameters as: curve 1: T=226.5 K ($\alpha_{HN}=0.09, \beta_{HN}=0.97$); curve 2: 235.3 K (0.049, 0.937); curve 3: 244.6 K (0.047, 0.939); curve 4: 257.5 K (0.045, 0.938); curve 5: 269.2 K (0.045, 0.943); curve 6: 280.0 K (0.054, 0.966); curve 7: 292.5 K (0.019, 0.87); and curve 8: 300.2 K (0.028, 0.906).

corresponding Arrhenius diagram is shown in Fig. 11. In Fig. 12 the variation of the static dielectric constant ϵ_0 and the corresponding HN parameters with temperatures are shown. We have critically examined the variation of $\epsilon_0, \alpha_{HN}, \beta_{HN}$ and $\log f_m$ values with temperature to see the possible effect of recrystallization on these values. This has been done by using heating and cooling cycles. It has been noticed that there is a probability of recrystallization below 240 K, but this process was found to be so slow during the time taken for the dielectric spectra that we did not find any change in the dielectric parameters. This indicates that the observed dielectric spectra actually correspond to the supercooled sample.

We have also examined the temperature variation of ϵ_0 and ϵ_∞ values during heating and cooling cycles, around the temperature 225–240 K. Although we have found some

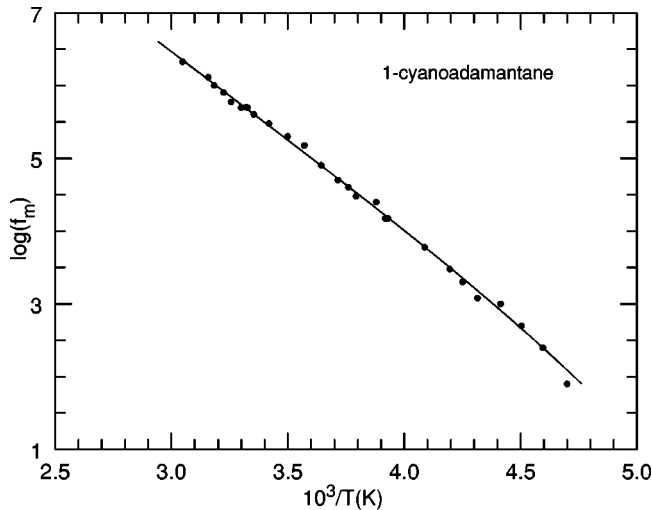


FIG. 11. Arrhenius diagram for the supercooled phase I of 1 cyanoadamantane. The thick line corresponds to the fit to Eq. (2).

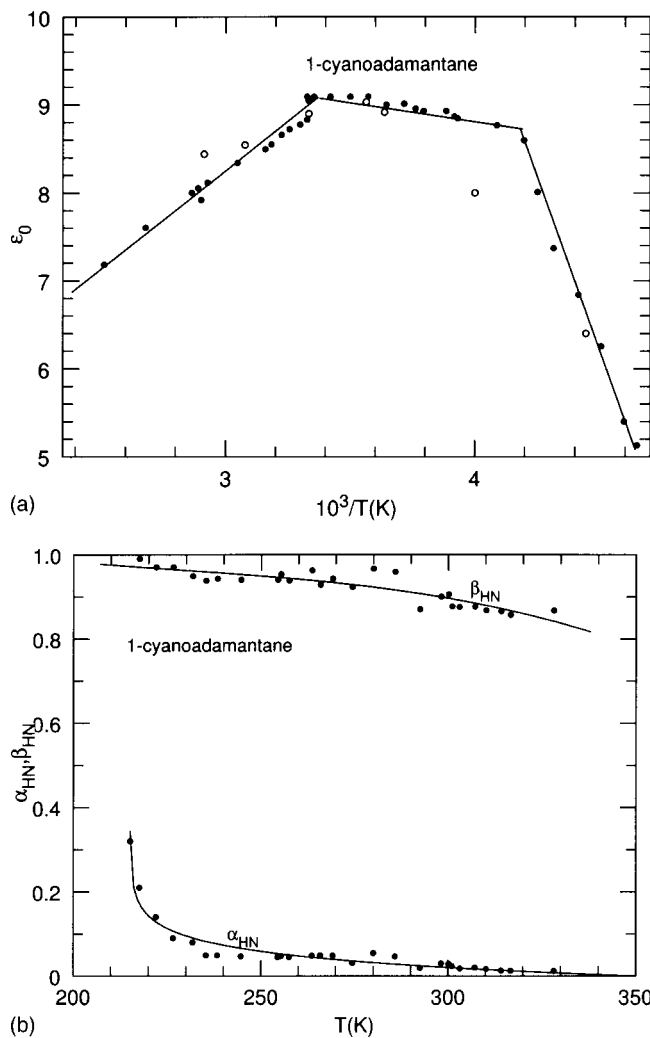


FIG. 12. (a) Variation of ϵ_0 with temperature and (b) variation of α_{HN} and β_{HN} with temperature for equilibrium phase I of 1 cyanoadamantane and its supercooled state. The thick lines are guides for the eye.

slight differences in these values during cooling and subsequent heating, there appears to be some ϵ_0 values which are characteristic of the supercooled phase at equilibrium.⁴² However, when the sample is cooled much below 218 K, a clear change is noticed in the ϵ_0 values during heating and cooling cycles, indicating recrystallization. However, in this context, it is interesting to note that even highly crystallized samples showed a residual dispersion whose f_m values and shape parameters more or less coincide with that of the α -process during cooling and subsequent heating. This indicates that this residual dispersion has originated from the unoriented matrix (in which $g > 0$) embedded in stable oriented (completely anti-ferroelectric) domains in which g is zero.

The high values of α_{HN} in the case of CNADM prompted us to examine the dielectric spectra of another non-hydrogen bonded plastic crystal. In Fig. 13, we show the α -relaxation of supercooled plastic phase of DMCH. The $T_g(pc)$ of this material is 107.8 K^{27} and the corresponding NC to PC transition is at $172.5 \text{ K}^{27,45}$ (see Ref. 27 for further details). This material, in its supercooled phase I, is known to be very stable against recrystallization to the NC phase and

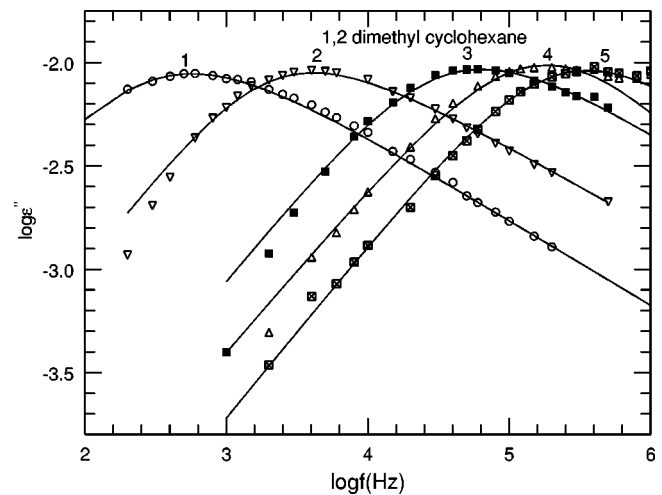


FIG. 13. $\log \epsilon''$ vs $\log f$ in cis-1,2-dimethylcyclohexane. The thick lines correspond to Eq. (1) for the parameters given as: Curve 1: $T=117.5 \text{ K}$ ($\alpha_{HN}=0.190$, $\beta_{HN}=0.508$); curve 2: 121.5 K (0.125, 0.442); curve 3: 128.9 K (0.140, 0.534); curve 4: 130.4 K (0.197, 0.588) curve 5: 133.0 K (0.162, 0.615).

the time required for this transition is of the order of days. Thus, the high α_{HN} values (Fig. 13) [or the deviation from Cole–Davidson (CD) behavior] are a true characteristic of the supercooled plastic phase and do not include the time dependence of recrystallization. The corresponding variation of $\Delta \epsilon$ shows little variation with temperature in the supercooled phase (the reader may refer to Ref. 27 for more details). The corresponding T-dependence of f_m values is found to be strongly non-Arrhenius and hence, this material can be rated as very ‘‘fragile’’ plastic material. This situation is shown in Fig. 14, where we have given the fragility plot for all the materials under study. We have plotted the $\log f_m$ values against $1/T$ where T is normalized to the corresponding $T_g(pc)$, for comparison purposes.

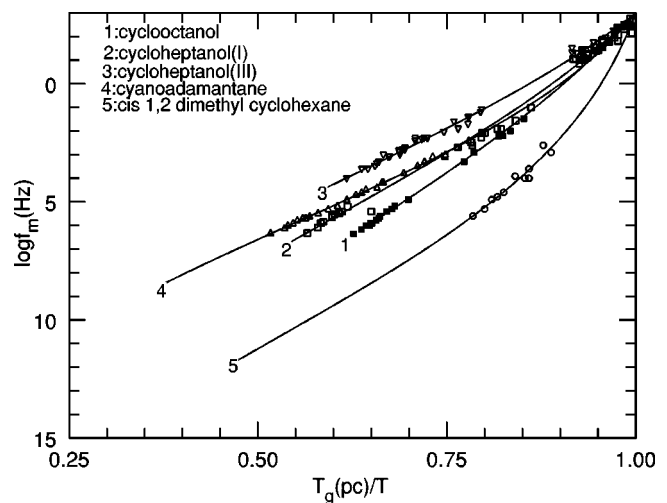


FIG. 14. Fragility plot for the plastic crystalline phases of all the samples. The $T_g(pc)$ used for normalization of the $1/T$ axis corresponds to the $T_g(cal)$ in Table II. The thick lines correspond to the fits to Eq. (2).

IV. DISCUSSION

A. Cyclo-octanol

(i) The $T_g(pc)$ of this material is 164 K [Fig. 1(a)] and the main dielectric relaxation event (α -process) found in dielectric measurement corresponds to this event (Fig. 4). The α -branch corresponds to the same process (designated as process 1 in Fig. 4) that is seen in the liquid state which is usually attributed²¹ to the $-OH$ group flipping within the H-bonded clusters or chains. The γ -process appears to be the event that is seen as a small but clear dielectric process observed in the microwave frequency range by Stockhausen and Hornhardt⁴⁶ (especially see Fig. 1 of Ref. 46). This process was referred to as the third process in their paper⁴⁶ (and in our Fig. 4 as well). The high activation energy of 56.0 kJ/mole for the γ -process (Table III) tempts us to attribute it to conversion from one conformer to the other. This view is also supported by the dielectric study of Davies and Swain⁴⁷ on cyclohexyl derivatives in a frozen polystyrene matrix. This E value is also much larger than what is expected for the rotation of a single molecule in an otherwise rigid matrix as found in binary liquids.⁴⁸

The β -relaxation does not seem to be simply related to the second process⁴⁶ obtained for the liquid and solid states (there is also some doubt regarding the existence of the second process which could be an artifact of the analysis adopted by Stockhausen and Hornhardt⁴⁶ and Shimoniya,⁴⁹ where the main process was assumed to be Debye which may not be true). However, it is interesting to note that the freezing of the β -process corresponds to the small steplike change found in DSC results around 136 K. The corresponding activation energy (Table III) is so high that it may not be due to a simple single molecular orientation. In addition both β - and γ -processes exist even in phase II implying that they are not characteristic of the glassy state and (hence) should be taken as the characteristic of some intra-molecular process.

It is also interesting to note that there is no dielectric process corresponding to the GT event at 148.5 K.

B. Cycloheptanol

The molecule of CHOL is expected to have as many as 42 kinds of distinguishable conformations³² which is also reflected in the existence of many crystalline phases and glass transitions.⁵ Apart from the $T_g(l)$ ($\approx 152.5 \pm 2.5$ K) of the liquid, there are at least four different $T_g(pc)$'s corresponding to phases I, II, III and IV which are obtained by supercooling of these phases. However, the $T_g(pc)$'s corresponding to these phases are all located in a short temperature range of 5–6 deg from 144.5 to 149 K. All the supercooled phases show non-Arrhenius dependence (Fig. 8 and Table II). It is interesting to note that a fall in the f_m values as one goes from L \rightarrow SI \rightarrow SII \rightarrow SIII are in accordance with the fall of the g values as discussed in Sec. III. In addition to that, the corresponding dielectric spectra are also found to become more and more symmetric as one moves away from liquid toward SIV [see Figs. 7(a)–7(d)].

The $T_g(pc)$ reported in all the previous investigations^{10,30,32} probably corresponded to SI. Adachi *et al.*³² have

clearly identified one $T_g(pc)$ of 140 K corresponding to SI. However, the corresponding heating rate is 2 K/min. They also report that the enthalpy relaxation time of this sample is about 24 h at 133.3 K; which corresponds to an f_m value of 1.8×10^{-6} Hz. This value more or less agrees well with the extrapolated α -process of SI (see Fig. 8 and Table II).

The γ -process found for this material is extant in all the glassy crystalline phases and has a high activation energy (Table III) similar to that of the γ -process in cyclo-octanol. And hence, it may be attributed to the conversion from one conformer to the other.

C. Cyanoadamantane

Prior to this investigation, there was some ambiguity regarding the nature of dielectric relaxation in the supercooled state for two reasons: (i) the difficulty^{43,44} in maintaining an air free sample as the material is in a powdered form (where air gaps are known⁵⁰ to affect $\Delta\epsilon$ values and to some extent the f_m values); and (ii) contraction of the sample during transformation from the supercooled phase I to the NC state as faced by Pathmanathan and Johari.⁴² We have minimized these two errors by using the kind of dielectric cell assembly described in Sec. II.

CNADM has a very large dipole moment⁴ of 3.83 D but the corresponding static dielectric constants are not that large as expected for free dipolar reorientations. As explained by the previous workers,^{42,43} the molecules are arranged in an fcc lattice in such a way that for each particular molecule some positions are impossible due to the steric hindrance between first and second next-neighbor molecules, there thus exists a local order. According to the structural description, two very different motions may exist, of which only the slow tumbling reorientation of the dipole moment between $\langle 001 \rangle$ axes of the cubic lattice is to be considered at the frequencies of interest (i.e., below 10^6 Hz). The previous dielectric studies^{42–44} show that the smaller static dielectric constant is due to a smaller correlation factor of about 0.15 at 190 K which indicates an antiferroelectric order (also supported by Raman spectral studies³³) which is also clear from the ϵ_0 values given in Fig. 12.

Our dielectric study (Figs. 10 and 12) indicates: (a) a sharp spectral change below 240 K where the spectral shape parameter α_{HN} continues increasing as the temperature lowers, which as discussed in Sec. III, is a true equilibrium property of the supercooled phase. This is also accompanied by a fall in the value of $\Delta\epsilon$. This behavior is quite similar to that found in the ordering of the molecular orientations in crystalline phases of dichloro, tetramethyl benzene and trichloro, trimethyl benzene.⁵¹ (b) On further lowering of the temperature below about 210 K, the $\Delta\epsilon$ value collapses relatively faster to a value of $1.05 n_D^2$.

Thus, the transformation to the NC phase occurs in two phases where in the first phase gradual orientational ordering, which is in equilibrium with temperature, occurs. In this phase the α_{HN} , β_{HN} values, ϵ_0 values and f_m are all reversible with temperature and the ϵ_0 value falls and α_{HN} increases as the temperature decreases. However, in the second phase, part of the material collapses to the NC phase, where

a time dependent fall of ϵ_0 at a given temperature is expected and hence, the corresponding ϵ_0 values are not reversible with temperature in the supercooled phase. Thus, it is interesting to note that the α_{HN} values reflect the orientational ordering, which can also be viewed as a measure of steric hindrance to the molecular orientations. At this point it is not clear in what way the two crystalline phases present (Fig. 9) during the cooling of the plastic phase are connected with this behavior and also why there is a sample history dependent $T_g(p_c)$ of about 5–6 deg (Fig. 9). In this context it is interesting to see that phase III and phase IV of cycloheptanol have high values of α_{HN} indicating a high steric hindrance to the orientations in these phases.

For temperatures above 235 K, the Arrhenius equation, $f_m = f_0 e^{-E/RT}$ is good enough to describe the situation with the pre-exponential factor $f_0 = 10^{13.87}$ which is more or less of the order of lattice vibrational frequency (see Fig. 11 and Table II). Deviation from this Arrhenius behavior coincides with an increase in α_{HN} and increasing occurrence of orientational ordering. Thus, the behavior of this material in the supercooled state is different from that of phase I of cyclooctanol and cycloheptanol. DMCH also exhibits high α_{HN} values in the supercooled state (Fig. 13) where corresponding $\Delta\epsilon$ values are more or less constant in the supercooled phase I.

D. Shape of the dielectric spectra

In both the non-H-bonded systems studied here, there is no sign of any secondary relaxation process in the frequency range shown in Figs. 10 and 13 and interestingly, this relaxation spectra can well be described by HN equation [Eq. (1)]. The high frequency tail advocated²⁵ to be the universal characteristic of glassy relaxation is not found. Apart from this, both these systems have high α_{HN} values which if plotted according to the “original” scaling formalism introduced by Dixon *et al.*,²⁵ show deviations on the lower frequency side from the universal scaling (not shown in any figure). This has been found to be true with some other materials as well (e.g., polyvinylacetate)^{53,57} which exhibit a nonzero α_{HN} in Eq. (1). Even in the case of cyclo-octanol, where the scaling formalism has been shown to be valid by Pelecky and Birge,^{8,26} we see here that the contributions to the high frequency side come from β - and γ -processes (see Fig. 4) which are extant in all phases, and hence the high frequency tail consisting of these processes cannot be considered a universal feature of the glassy dynamics. Brand *et al.*³¹ have shown this by using a much wider frequency range than ours, where on subtraction of these contributions the relaxation spectra follows as a Cole–Davidson (CD) equation⁴¹ which is a special case of Eq. (1) for $\alpha_{HN} = 0$.

Apart from these two cases, the scaling formalism in its original form is also not found to describe the relaxation data corresponding to the other plastic phases of cycloheptanol viz., phases II, III and IV which exhibit high α_{HN} values (Fig. 7). High α_{HN} values have also been noticed in the supercooled phases of camphor,¹³ where the molecular orientations are highly hindered.

E. Strength and fragility

The concept of strength of a glassy system as advocated by Angell^{1,52} can simply be taken as a measure of the ability of a system to retain its high temperature Arrhenius character down to its T_g . As is known in dielectrics,⁴⁰ the system whose polarization characteristic or the orientation of the dipoles can be described by a double potential well, leads to a Debye relaxation and the corresponding relaxation rates exhibit Arrhenius T-dependence. Thus increasing deviations from the Arrhenius equation may be visualized in terms of increasing deviation from Debye character, i.e., increasing non-Arrhenicity will usually be accompanied by increasing non-Debyeness. From our point of view, non-Debyeness in this particular context should be understood as the degree of cooperativity which is usually reflected in the asymmetric parameter in the CD equation [i.e., β_{HN} in Eq. (1) for a special case of $\alpha_{HN} = 1$]. A quick look at the fragility plot for all the samples in their plastic phases (Fig. 14) more or less reflects this view with DMCH being the most fragile plastic phase and CNADM being the strongest of the plastic phases. This view is also supported by the specific heat C_P change at T_g ^{52,54,55} i.e., $\Delta C_P(T_g)$, which in the case of DMCH⁴⁵ is about 63 J/mol/K and in CNADM³³ it is about 16 J/mol/K.

However, if one looks at the $\Delta C_P(T_g)$ for phase I of COOL as given in Fig. 1(a), it is about 9 J/mol/K which is much less than that of CNADM, and hence the plastic phase of COOL should be considered as stronger than that of CNADM. Similarly on the basis of $\Delta C_P(T_g)$, CHOL (phase I) should be considered more fragile than that of COOL which is not the case in Fig. 14.

Similarly if one looks at the half-width of the dielectric loss spectrum as the criteria, then CNADM at lower temperatures should be considered more fragile than COOL or CHOL (phase I), which is not the case in Fig. 14. Similarly, if one considers the half-width of phase III of CHOL, it must be as fragile as DMCH which is not the case.

The point we wish to emphasize is that the moment the value of $\alpha_{HN} \neq 0$, problems in correlating the non-Arrhenicity with half-width arise. But this problem can be eliminated if β_{HN} alone is considered and, interestingly, all the curves shown in Fig. 14 more or less are arranged according to the value of β_{HN} . Thus, β_{HN} appears to retain its meaning of the degree of cooperativity as in the CD equation and thus, the parameter $(1 - \beta_{HN})$ may be considered as a measure of fragility.

F. Power law [Eq. (2)] vs V.F.T. [Eq. (3)]

Within the experimental accuracy both P.L. [Eq. (1)] and V.F.T. [Eq. (3)] describe the T-dependence of f_m more or less with the same accuracy (Table II). In Table IV, the limiting glass transitions, i.e., T'_g in Eq. (2) and T_0 in Eq. (3), are compared with the experimentally measured zero excess configurational entropy temperature T_2 .⁵⁶ (T_2 is the temperature at which the excess configurational entropy of the supercooled phase over the corresponding ground state vanishes.) In all cases, the T_0 value falls well below T_2 , indicating the existence of configurational states even below T_2 if the plas-

TABLE IV. Details of T'_g [Eq. (2)], T_0 [Eq. (3)] and T_2 .

Material	T'_g (K)	T_0 (K)	T_2^a (K)
Cycloheptanol	127.2–126	74–76	125
Cyclohexanol	139.0	120	128
Dimethylcyclohexane	98.5	73.2	80–90 ^b

^aTaken from Ref. 56.

^bVery approximate calculation based on the data of Ref. 47 and is also based on the fact (Refs. 52, 56) that many fragile systems have T_2 's about 15–20 deg below T_g .

tic phase is allowed to come to equilibrium (at very very slow cooling rates), which is physically meaningless. This problem does not exist if one considers the P.L., where the limiting T_g for the infinitely slow cooling rate is always greater than or equal to T_2 .^{48,55} This indicates that P.L. as given by Eq. (2) is probably a better description of the T-dependence of f_m of the α -process. Although the physical meaning of the dynamic exponent r in Eq. (2) is not yet clear, it is interesting to see that if Eq. (2) is applied to the dielectric α -process, the corresponding value of r is always located in a narrow range of 9–13 for supercooled systems which includes both the liquids^{11,13,14,20–22,55} and the plastic crystals.²⁷

V. CONCLUSIONS

(1) Both the cyclic alcohols studied here reveal two or more GT events corresponding to the freezing of the disorder associated with the various plastic phases. Significantly, the corresponding $T_g(p_c)$'s are lower than the T_g values obtained for the liquid phases by about 7–8 deg, which is in accordance with our recent observation.²⁷

(2) In both the cyclic alcohols studied here, the dielectrically dominant process (i.e., the α -process) is not found to be very sensitive to the impurities although the corresponding equilibrium transition temperatures are somewhat sensitive to their presence (see Table I). Further, the sub- T_g processes referred to as the β - and γ -process are present in all phases indicating that perhaps it is related to the intramolecular process and, hence, is not a universal feature of the glassy dynamics.

(3) The study of the relaxation in the two non-H-bonded crystals revealed an α -process which more or less follows Havriliak–Negami equation with high α_{HN} values. Interestingly these systems show little or no presence of the β - or γ -relaxation process. This relaxation also does not fit into the “original” scaling formalism because of high α_{HN} values. Similar behavior is also found in the plastic phases of CHOL.

¹J. Wong and C. A. Angell, *Glass Structure: By Spectroscopy* (Marcel Dekker, New York, 1976).

²C. A. Angell, L. E. Busse, E. I. Cooper, R. K. Kadiyala, A. Dworkin, M. Ghelfenstein, H. Szwarc, and A. Vassal, *J. Chim. Phys.* **82**, 267 (1985).

³A. R. Ubbelohde, *The Molten State of Matter* (Wiley, Chichester, UK, 1978).

⁴*The Plastically Crystalline State*, edited by J. N. Sherwood (Wiley/Interscience, New York, 1979).

⁵M. Shablakh, L. A. Dissado, and R. M. Hill, *J. Chem. Soc., Faraday Trans.* **79**, 369 (1983).

⁶S. Benkhof, A. Kudlik, T. Blockwicz, and E. Rössler, *J. Phys.: Condens. Matter* **10**, 8155 (1998).

⁷H. Suga and S. Seki, *J. Non-Cryst. Solids* **16**, 171 (1974).

⁸M. Sorai and S. Seki, *Mol. Cryst. Liq. Cryst.* **23**, 299 (1973).

⁹D. L. Leslie-Pelecky and N. O. Birge, *Phys. Rev. Lett.* **72**, 1232 (1994).

¹⁰A. H. Fuchs, J. Virlet, D. Andre, and H. Szwarc, *J. Chim. Phys.* **82**, 293 (1985).

¹¹S. S. N. Murthy, J. Sobhanadri, and Gangasharan, *J. Chem. Phys.* **100**, 4601 (1994).

¹²G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).

¹³Gangasharan and S. S. N. Murthy, *J. Chem. Phys.* **99**, 9865 (1993).

¹⁴S. K. Nayak and S. S. N. Murthy, *J. Chem. Phys.* **99**, 1607 (1993).

¹⁵C. A. Angell and D. L. Smith, *J. Phys. Chem.* **86**, 3845 (1982).

¹⁶L. Wu, *Phys. Rev. B* **43**, 9906 (1992).

¹⁷G. P. Johari, *Ann. N.Y. Acad. Sci.* **279**, 117 (1976).

¹⁸G. Williams, in *Dielectric and Related Molecular Processes, Special Periodical Report* (Chemical Society, London, 1975), Vol. 2, p. 151.

¹⁹Gangasharan and S. S. N. Murthy, *J. Phys. Chem.* **99**, 12349 (1995).

²⁰S. S. N. Murthy and S. K. Nayak, *J. Chem. Phys.* **99**, 5362 (1993).

²¹S. S. N. Murthy, *J. Phys. Chem.* **100**, 8508 (1996).

²²S. S. N. Murthy, *Mol. Phys.* **87**, 691 (1996).

²³A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectric, Chelsea, London, 1983).

²⁴A. K. Jonscher, *Universal Relaxation Law* (Chelsea Dielectric, Chelsea, London, 1994).

²⁵P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Cairini, *Phys. Rev. Lett.* **65**, 1108 (1990).

²⁶D. L. Leslie-Pelecky and N. O. Birge, *Phys. Rev. B* **50**, 13250 (1994).

²⁷S. S. N. Murthy, *Therm. Chem. Acta* **359**, 143 (2000).

²⁸R. Edelmann and A. Wurfinger, *Mol. Cryst. Liq. Cryst.* **148**, 249 (1987).

²⁹O. Andersson and R. G. Ross, *Mol. Phys.* **71**, 523 (1990).

³⁰A. Dworkin, A. H. Fuchs, M. Ghelfenstein, and H. Szwarc, *J. Phys. (France) Lett.* **43**, 121 (1982).

³¹R. Brand, P. Lunkeheimer, and A. Loidl, *Phys. Rev. B* **56**, R5713 (1997).

³²K. Adachi, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.* **45**, 1960 (1972).

³³M. Foulon, J. P. Amoureux, J. L. Sauvajol, J. P. Cavrot, and M. Muller, *J. Phys. C* **17**, 4213 (1984).

³⁴The g values are calculated using the original Fuoss–Kirkwood formula as given by Eq. (5) of Ref. 21 assuming the density ρ to be independent of temperature. The ρ values for the liquid phase have been taken from the reference: R. C. Weast and M. J. Astle, *CRC Hand Book of Physics and Chemistry* (CRC Press, Boca Raton, FL, 1993). The ρ values for all the solid phases have been assumed to be 20% greater than the above ρ value of the liquid phase.

³⁵G. Corfield and M. Davies, *Trans. Faraday Soc.* **60**, 10 (1964).

³⁶C. A. Angell, J. M. Sare, and E. J. Sare, *J. Phys. Chem.* **82**, 2622 (1978).

³⁷S. Havriliak and S. Negami, *J. Polym. Sci., Part C: Polym. Symp.* **14**, 99 (1966).

³⁸K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

³⁹S. S. N. Murthy, *J. Chem. Phys.* **100**, 6102 (1994).

⁴⁰N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Behaviour* (Van Nostrand Reinhold, London, 1969).

⁴¹D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1485 (1951).

⁴²K. Pathmanathan and G. P. Johari, *J. Phys. C* **18**, 6535 (1985).

⁴³J. P. Amoureux, M. Castelain, M. D. Benadda, M. Bee, and J. L. Sauvajol, *J. Phys.* **44**, 513 (1983).

⁴⁴J. P. Amoureux, G. Noyel, M. Foulon, M. Bee, and L. Jorat, *Mol. Phys.* **52**, 161 (1984).

⁴⁵H. M. Huffman, S. S. Todd, and G. D. Oliver, *J. Am. Chem. Soc.* **71**, 584 (1949).

⁴⁶M. Stockhausen and S. V. Hornhardt, *Z. Naturforsch. A* **47**, 1135 (1992).

⁴⁷M. Davies and J. Swain, *Faraday Soc. Trans.* **67**, 1637 (1971).

⁴⁸S. S. N. Murthy, A. Paikaray, and N. Arya, *J. Chem. Phys.* **102**, 8213 (1995).

⁴⁹T. Shinomiya, *Bull. Chem. Soc. Jpn.* **63**, 1087 (1990).

⁵⁰S. R. Gough, E. Whalley, and D. W. Davidson, *Can. J. Chem.* **46**, 1673 (1968).

⁵¹C. Brot and I. Darmon, *J. Chem. Phys.* **53**, 2271 (1970).

⁵²C. A. Angell, *J. Non-Cryst. Solids* **13**, 131 (1991).

⁵³A. Schönhal, F. Kremer, and F. Stickel, *Phys. Rev. Lett.* **71**, 4096 (1993).

⁵⁴C. A. Angell and W. Sichnina, *Ann. N.Y. Acad. Sci.* **276**, 53 (1976).

⁵⁵S. S. N. Murthy, *J. Phys. Chem.* **93**, 3347 (1989).

⁵⁶V. P. Privalko, *J. Phys. Chem.* **84**, 3307 (1980).

⁵⁷A. Schönhal, F. Kremer, and E. Schlosser, *Phys. Rev. Lett.* **67**, 999 (1991).