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Molecular motion in plastic crystals

C N R RAO
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

1. Introduction

Many crystalline substances pass through an intermediate crystalline state before melting and the entropy of fusion is generally lower than that of the transition from the ordered crystalline state to the intermediate phase. The intermediate phase, commonly referred to as the plastic state, has high symmetry (generally cubic), and the molecules are orientationally disordered in this phase (Aston 1963; Sherwood 1979). Due to this disorder as well as the large amplitudes of molecular librations, X-ray diffraction studies provide limited structural information on the plastic crystalline state. Much knowledge has however been gained about the molecular motions in plastic crystals through spectroscopic studies. In particular, NMR spectroscopy, neutron scattering as well as Raman and infrared spectroscopy have been most useful.

It was originally believed that the plastic state was exhibited only by spherical (globular) molecules. Plastic states of many molecules, some of relatively low symmetry, have been established (see table 1). In this article, we shall briefly describe the

Table 1. Thermodynamic data on organic plastic crystals[a].

Compound	T_{cp} (K)	T_{pl} (K)	ΔS_{cp} J/mol/K	ΔS_{pl} J/mol/K	ΔH_{cp} kJ/mol	ΔH_{pl} kJ/mol
1. 2,3-Dimethylbutane	136	145	47·7	5·5	6·5	0·8
2. Carbon tetrachloride	216·5, 228	242	21·8, 3·2	7·0	4·7, 0·75	1·7
3. Cyclohexanone	222	240·5	34·5	4·7	7·6	1·1
4. t-Butylbromide	208·5, 231	256·0	27·3, 4·6	7·5	5·7, 1·0	2·0
5. t-Butylchloride	183, 219·5	248·0	9·3 26·4	8·0	1·7, 5·8	2·0
6. Cyclobutane	145·7	182	39·2	5·9	5·7	1·1
7. Carbon tetrabromide	320	363	20·8	10·8	6·6	4·0
8. 2,2-Dimethylbutane	126·8	174	42·5	3·3	5·4	0·6
9. Cyclopentane	122	180	39·8	3·3	4·9	0·6
10. Succinonitrile	236	326	11	4·6	2·6	1·5
11. Cyclohexane	186	278	36	9·0	6·7	2·5
12. Neopentane	140	257	18·5	12·6	2·6	3·2
13. t-Butylmercaptan	152	274	26·8	9·0	4·0	2·5

[a] Taken from Ganguly *et al* (1981); T_{pl} = plastic-liquid transition temperature; T_{cp} = crystal-plastic transition temperature.

nature of molecular motion in plastic crystals and the spectroscopic techniques available to study the motion. We shall then examine typical results obtained in recent years employing NMR, neutron scattering, infrared and Raman spectroscopy, ESR spectroscopy as well as computer simulation.

2. Models for reorientational motion

Existence of a high degree of orientational freedom is the most characteristic feature of the plastic crystalline state. We can visualize three types of rotational motions in crystals: free rotation, rotational diffusion and jump reorientation. Free rotation is possible when interactions are weak—this situation would not be applicable to plastic crystals. In classical rotational diffusion (proposed by Debye to explain dielectric relaxation in liquids), orientational motion of molecules is expected to follow a diffusion equation described by an Einstein type relation. This type of diffusion is not known to be applicable to plastic crystals. What would be more appropriate to consider in the case of plastic crystals is collision-interrupted molecular rotation.

The rotational diffusion model was generalized by Gordon (1966) to include molecular reorientation in angular steps of fairly large size. According to this model, the molecules are supposed to freely rotate during the intervals between collisions. Two limiting cases have been discussed by Gordon, both of which involve angular diffusion steps (of arbitrary size). These are commonly known as the J-diffusion and the M-diffusion models. In the former, the direction as well as the magnitude of the angular momentum vector of the molecule follow a Boltzmann distribution due to collisions. In the M-diffusion model, the orientation of the angular momentum vector is randomized, but the magnitude is unchanged. In Gordon's model applied to linear molecules, the general diffusion equation follows classical mechanics at short times. At longer times, the rotational frequency is unchanged in successive steps in the M-diffusion model while it follows the Boltzmann distribution in the J-diffusion model.

Another model (Hill 1963; Wyllie 1971) has been proposed wherein the molecules exhibit librations (perturbed angular oscillations), having been trapped in potential wells. Fluctuations in orientation of neighbouring molecules result in a change in the shape of the potential well and consequently give rise to angular motion of molecules with large amplitudes. It is possible that diffusion of the potential well on the surface of a sphere gives rise to reorientational motion of molecules. If the potential surface is related to the crystal space group, molecular reorientation will be associated with damped librations (Guthrie and McCullough 1961). Rotations of the crystal space group will give rise to allowed potential wells.

No single model can exactly describe molecular reorientation in plastic crystals. Models which include features of the different models described above have been considered. For example, diffusion motion interrupted by orientation jumps has been considered to be responsible for molecular reorientation. This model has been somewhat successful in the case of cyclohexane and neopentane (Lechner 1972; De Graaf 1969; De Graaf and Schieskinski 1970). What is not yet completely clear is whether the reorientational motion is cooperative. There appears to be some evidence for coupling between the reorientational motion and the motions of neighbouring molecules. It would appear that there is scope for comparative experimental studies employing complementary techniques which are sensitive to autocorrelation and monomolecular correlation.

3. Methods of studying molecular motion

The nature of rotational motion responsible for orientational disorder in plastic crystals is not completely understood and a variety of experimental techniques have been employed to investigate this interesting problem. There can be coupling between rotation and translation motion, the simplest form of the latter being self-diffusion. The diffusion constant D is given by the Einstein relation,

$$D = \langle r^2 \rangle / 6\tau,$$

where $\langle r^2 \rangle$ is the mean-square-jump distance and τ is the mean time between successive jumps of a molecule at a lattice site. The diffusion constant depends on the magnitude of molecular velocity as well as the persistence velocity. Both radioactive tracer and NMR methods have been employed to measure the coefficients of self-diffusion in plastic crystals. In many cases, the two methods yield similar results since they refer to a similar process on the time scales of the velocity correlation function.

NMR spectroscopy provides spin-lattice (T_1) and spin-spin (T_2) relaxation times. Making appropriate assumptions with regard to the magnetic interactions responsible for the relaxation process, these relaxation times can be related to molecular motion. Since nuclear spin relaxation results from all processes which cause a fluctuation in the magnetic field at the nucleus, the correlation function will generally correspond to more than one kind of motion involving all possible interactions. The equations for the relaxation times are generally of the form,

$$1/T = C\tau/(1 + \omega^2\tau^2),$$

where the constant of proportionality, C, as well as τ are determined by the nature of the nucleus and the different interactions. If the relaxation process is essentially due to dipolar interactions, then NMR spectroscopy gives information on rotational diffusion. If nuclear quadrupole relaxation is dominant, then we obtain information on molecular reorientation.

Thermal or low energy neutron scattering experiments have been most valuable in throwing light on molecular motion in plastic crystals. These experiments measure changes in the centre of mass of a molecule. Diffusion constants obtained from neutron experiments differ widely from those obtained from tracer experiments since neutron scattering is mainly determined by rotational diffusion. The scattering function has the form,

$$S(\mathbf{Q}, \omega) = \int\int G(\mathbf{R}, t) \exp(i\mathbf{Q}r - i\omega t)\, \mathrm{d}\mathbf{Q} \cdot \mathrm{d}\omega$$

where $G(\mathbf{R}, t)$ is the rotational correlation function for a scattering centre, $\mathbf{Q}$, the scattering vector, ω, the angular frequency and $\mathbf{R}$, the equilibrium position vector. The inelastic part of the scattering provides information on the rotational motion while the elastic part is related to the translational motion. If the reorientational motion is diffusive, we can employ a diffusion equation similar to that mentioned earlier, the width of the quasi-elastic peak being related to rotational diffusion. One often employs different functions to see if rotational motion occurs through jumps.

One of the most direct methods of examining reorientational motion of molecules is by far-infrared absorption spectroscopy or dielectric absorption. In the absence of vibrational relaxation, the relaxation times obtained by IR and dielectric methods are equivalent. In both these techniques we obtain the correlation function,

$\langle \mu(t_0) . \mu(t_0+t) \rangle$, for the motion about a specific molecular axis with respect to the principal rotation axes and the direction of vibration. Rayleigh scattering as well as Raman scattering are most useful in the study of molecular orientational processes. With the aid of isotropic and anisotropic Raman scattering measurements, orientational processes can be delineated from other mechanisms which cause line broadening. Analysis of infrared and Raman bandshapes provides information on the short and long term behaviour of the correlation function.

Correlation times and activation energy parameters obtained from different techniques may or may not agree with one another. Comparison of these data enables one to check the applicability of the model employed and examine whether any particular basic molecular process is reflected by the measurement or whether the method of analysis employed is correct. In order to properly characterize rotational motion in plastic crystals it may indeed be necessary to compare correlation times obtained by several methods. Thus, values from NMR spectroscopy and Rayleigh scattering enable us to distinguish uncorrelated and correlated rotations. Molecular disorder is not reflected in NMR measurements; to this end, diffraction studies would be essential.

4. NMR studies

NMR spectra of molecular crystals are generally broad due to dipolar interactions between the spins. It is most useful to relate the frequency domain spectrum to the properties of the spin system by employing the van Vleck method of moments. The nth moment of the frequency domain spectrum is given by,

$$M(n) = \frac{\int_0^\infty (\omega - \omega_0)^n F(\omega) \mathrm{d}\omega}{\int_0^\infty F(\omega) \mathrm{d}\omega}$$

where $F(\omega)$ is the frequency domain spectrum and ω_0 is the centre of the resonance line. The second moment, $M(2)$ has been found to be of great value since it is directly related to the geometric arrangement of spins. Experimental second moments in the presence of thermal motion is given by,

$$M(2) = \frac{3\mu^2\hbar^2}{16\pi^2 n} \gamma^4 I(I+1) \sum_{i,j} \left[\frac{1 - 3\cos^2\theta_{ij}}{\mathbf{r}_{ij}^3} \right]$$

Here, γ is the gyromagnetic ratio, I, the spin quantum number, θ_{ij}, the orientation of the vector $\mathbf{r}_{ij}$ from spin i to j with respect to the direction of the applied magnetic field and the summation is for each of n spins i over all its neighbours j. The term in square brackets is an average over the motion as well as over the various orientations in powder samples. The above equation is applicable when $M^{1/2}(2)\,\tau \ll 1$ where τ is the correlation time for the motion of the spin-spin vector. Boden (1979) has reviewed applications of NMR spectroscopy to plastic crystals in detail.

The experimental second moment of a solid containing molecules which undergo thermally activated reorientation varies with temperature as shown in figure 1. The abrupt drop in $M(2)$ is due to motional narrowing of the resonance line and under these conditions $M^{1/2}(2)\,\tau \simeq 1$. At higher temperatures, there will be motionally averaged

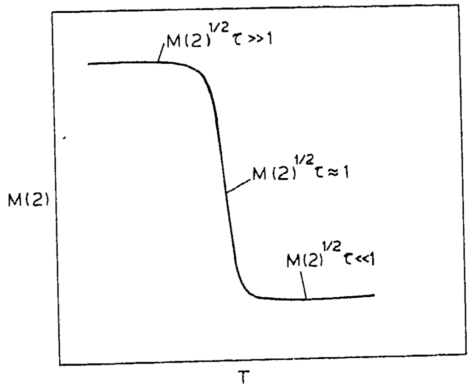

Figure 1. Temperature variation of the second moment $M(2)$ in a solid due to reorientational motion of molecules. When $M(2)^{1/2}\tau \gg 1$, we have the rigid lattice value; when $M(2)^{1/2}\tau \ll 1$, we have the motionally averaged value; motional narrowing occurs at $M(2)^{1/2}\tau \approx 1$.

$M(2)$ and under these conditions $M^{1/2}(2)\tau \approx 1$. We thus see that the mechanism of the reorientation (rotational) process giving rise to motional narrowing can be readily found from $M(2)$ measurements. In the case of protons, motional narrowing occurs when τ is of the order of 10^{-5} sec. Values of τ can be roughly estimated from experimental $M(2)$ data in the transition region from the expression,

$$M(2) = M(2)_{\text{ave}} + \frac{2}{\pi}\,(M(2)_r - M(2)_{\text{ave}}) \tan^{-1}(M^{1/2}(2)_r\tau)$$

where $M(2)_r$ and $M(2)_{\text{ave}}$ correspond to the rigid lattice and motionally averaged values (Gutowsky and Pake 1950; Andrew and Lipofsky 1972). $M(2)$ generally shows abrupt changes in structural phase transitions and the change in $M(2)$ depends on molecular shape (symmetry) and packing. Thus, in cyclohexane (Andrew and Eades 1953), we see a decrease in $M(2)$ at T_{cp} before a motionally averaged value is reached (figure 2). In adamantane, there is a large drop in $M(2)$ around 145 K but almost no change at T_{cp}. In camphor, on the other hand, there is almost no motional averaging below T_{cp}. In many instances, the nature of change in $M(2)$ reflects the occurrence of extensive disordering prior to the crystal-plastic transition and $M(2)$ changes continuously from the crystal to the plastic state, the large drop in $M(2)$ being well before T_{cp}. Boden (1979) cites several examples in his review article.

The behaviour of $M(2)$ generally appears to be independent of the shape of the molecule in the plastic state and is generally of the order of $1G^2$. The rotationally averaged value of $M(2)$ is related to the spin-spin relaxation time, T_2, and linewidth at half-maximum, $\Delta\omega_{1/2}$, as follows:

$$M(2)\tau = \frac{1}{T_2} = 1/2\,(\Delta\omega_{1/2}).$$

Linewidth measurements give useful information on molecular diffusion in plastic crystals, although the kinetic parameters thus obtained are not very reliable.

Molecular reorientational motion in the plastic phase causes frequency shifts due to

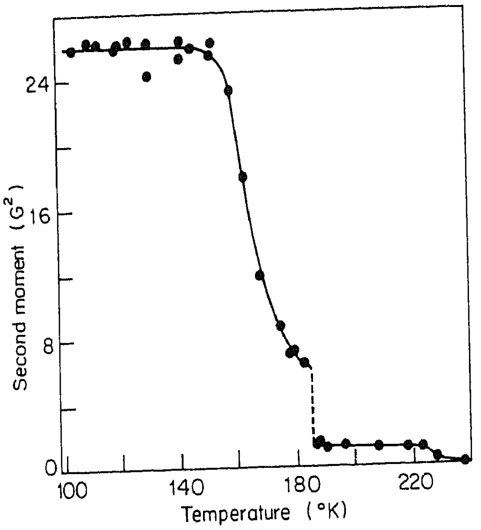

Figure 2. Temperature variation of the second moment of (the proton NMR spectra) cyclohexane (after Andrew and Eades 1953).

intramolecular dipolar interaction as well as nuclear electric quadrupole and anisotropic chemical shielding tensors to average to zero. The intermolecular dipolar interaction, is however, averaged only partially by the rotation motion and therefore affects the shape of the spectrum. Since intermolecular interactions are averaged out by the translational motion at the melting point, NMR linewidths can be used to obtain estimates of the diffusion rate. Spin relaxation measurements give much better estimates of this important property.

Both rotational and translational diffusion of molecules can be investigated effectively by spin relaxation measurements. The various quantities measured experimentally are, the spin-lattice relaxation times in laboratory and rotating frames, T_1 and T_{1r}, and the spin-spin relaxation time, T_2. Relations between these relaxation times and the reorientational correlation (autocorrelation) time, τ_2, are as follows:

$$\frac{1}{T_1}=\frac{2}{3}M(2)\frac{\tau_2}{1+\omega_0^2\tau_2}+\frac{4\tau_2}{1+4\,\omega_0^2\tau_2^2},$$

$$\frac{1}{T_{1r}}=\frac{1}{6}M(2)\frac{4\tau_2}{1+4\omega_0^2\tau_2^2}+\frac{10\tau_2}{1+\omega_0^2\tau_2^2}+\frac{6\tau_2}{1+4\omega_1^2\tau_1^2},$$

$$\frac{1}{T_2}=\frac{1}{6}M(2)6\tau_2+\frac{10\tau_2}{1+\omega_0^2\tau_2^2}+\frac{4\tau_2}{1+4\omega_0^2\tau_2^2},$$

where $\omega_0=\gamma B_0$ and $\omega_1=\gamma B_1$ where B_0 and B_1 are given by the applied static magnetic field and the field rotating perpendicularly about B_0 respectively. The correlation time τ_2 reflects the average life time of molecules in an equilibrium orientation and $M(2)$ is reduced due to molecular reorientation. Motions with frequencies 10^7–10^9 sec^{-1} (ω_0) and 10^4–10^6 sec^{-1} (ω_1) are detected by measurements of T_1 and T_{1r}. When the molecular reorientation is fast as at high temperatures ($\omega_0\tau_2 \ll 1$) or in the plastic phase,

$$1/T_1 = C_1\tau_2.$$

At low temperatures ($\omega_0\tau_2 \gg 1$),

$$1/T_1 = C_2/\omega_0^2\tau_2.$$

Measurements of T_1 as a function of temperature and frequency enable us to understand the nature of molecular motion and to determine the correlation time. In figure 3 we show the temperature variation of the proton relaxation times in hexamethylethane in the ordered crystalline and the plastic crystalline phases. In the low-temperature ordered crystalline phase, the reorientation of the molecule about the 3-fold axis is reflected in the measurements. The slopes of the plots of T_1 and T_{1r} are the same and both show minima as expected from theory; T_1 in the plastic phase clearly reflects the rapid reorientation of molecules ($\omega_0\tau_2 \ll 1$). Near the melting point, T_1 is affected by translational motion as well.

Measurements of T_{1r} can detect motion of molecules with frequencies of the order of ω_1. The dipolar relaxation time T_{1d} which measures the rate at which the dipolar energy relaxes to the lattice is given by

$$1/T_{1d} = 2/T_{1r} = 2/T_1,$$

when $\omega_0\tau \ll 1$ when the motion of spins is not correlated; if the motion is correlated, we have 3 instead of 2 in the numerators of the above equations.

In the case of plastic phases ($\omega_0\tau \ll 1$), T_1 measurements (note that $(1/T_1) = C_1\tau_2$

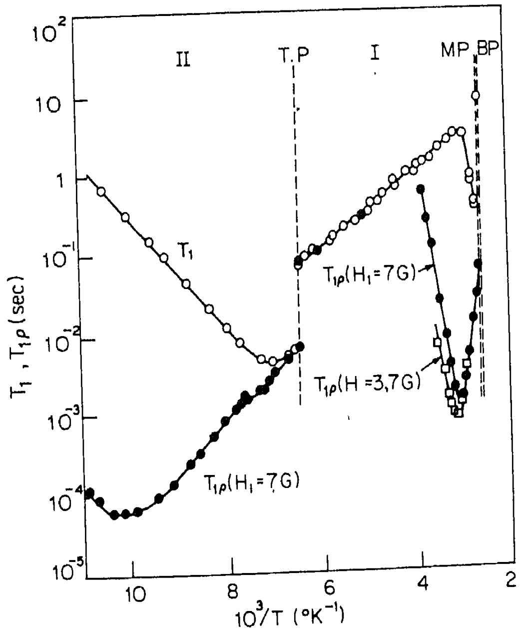

Figure 3. Temperature variation of proton relaxation times in hexamethylethane (after Chezeau *et al* 1971).

where C_1 is a constant) directly give τ_2 or the area under the rotational correlation function

$$\tau_2 = \int_0^\infty G(\tau)\mathrm{d}\tau$$

subject to lim $G_{\tau \to \infty}(\tau) = 0$. Such measurements have been carried out on several molecules in the plastic state. In table 2, we list typical values of activation energies for molecular reorientation in the plastic phases of a few compounds obtained from the slopes of the Arrhenius plots of T_1. In some cases, non-Arrhenius behaviour has been found, with the log T_1 *vs* $1/T$ plots showing more than one linear region. A continuous decrease in activation energy with temperature has also been noticed (suggesting progressive increase in orientational disorder.)

A number of systems do not show any discontinuity in T_1 across the plastic-liquid transition as illustrated by the case of C_6D_{12} in figure 4. This behaviour can be taken to

Table 2. Energies of activation for molecular motion in some organic plastic crystals obtained from NMR spectroscopy[a].

	Structure	ΔS_f[b]	E_a(kJ mol^{-1})
Adamantane	FCC	20·8	12·9
Neopentane	FCC	12·6	4.2
Cyclohexane	FCC	9·0	6·4
Pivalic acid	FCC	6·3	36
Hexamethylethane	BCC	20·0	9·2
DL-Camphene	BCC	9·5	4·9–6·5[c]

[a] Data taken from Boden (1979); [b] Entropy of fusion in J mol^{-1} k^{-1};
[c] Depending on the temperature in the range 175–323 K.

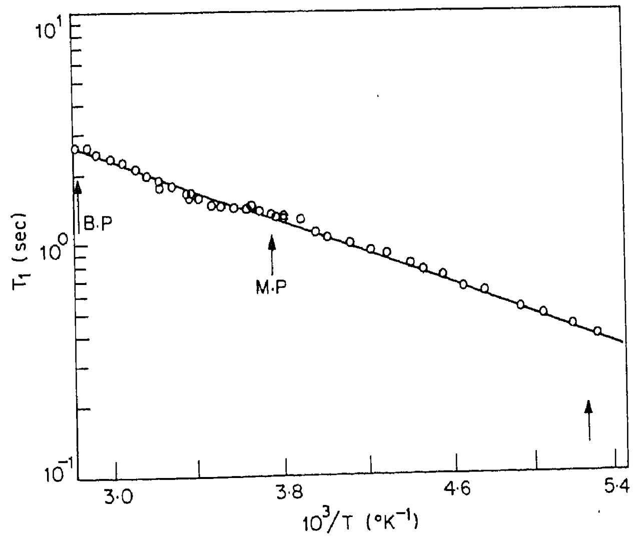

Figure 4. Spin-lattice relaxation times in C_6D_{12} (after O'Reilly *et al* 1972).

imply that the collision process controlling the molecular reorientation remains the same in both the plastic and liquid phases. Discontinuous changes have also been noticed in a few systems implying that the molecular field changes across the plastic-liquid transition. The fact that τ at the plastic-liquid transition is nearly equal to or about twice the value at the melting point shows that nearly half the nearest neighbour molecules are rotating at the same time, possibly in a correlated manner.

Translational motion of spins in the plastic crystalline state has been interpreted on the basis of a model involving random-walk of a discrete isotropic crystal lattice (Torrey 1954; Resing and Torrey 1963) or a monovacancy diffusion mechanism (Wolf 1975). Experimentally, it has been found that the measurements are consistent with Torrey's model as well as radiotracer studies in the case of solids with high entropies of fusion. No such agreement is found in the case of solids with low entropies of fusion. Typical results from NMR and radiotracer measurements are shown in table 3. Self-diffusion parameters obtained from spin relaxation measurements do not appear to be very sensitive to the microscopic model employed. The main application of NMR spectroscopy in the study of the plastic crystalline state has been in the determination of the mean time interval between translational jumps.

5. Neutron scattering studies

The equation for incoherent rotational scattering of neutrons can be written as,

$$S_r(\mathbf{Q}, \omega) = A_{\mathrm{ei}}(\mathbf{Q})\, \delta(\omega) + S_{\mathrm{qe}}(\mathbf{Q}, \omega)$$

where $S_{\mathrm{qe}}(\mathbf{Q}, \omega)$ is the quasielastic scattering and $A_{\mathrm{ei}}(\mathbf{Q})$ is the elastic incoherent structure factor which provides a measure of the time-averaged spatial distribution of the proton and therefore about the nature of the rotational motion of molecules. The rotational correlation time determines the width of $S_{\mathrm{qe}}(\mathbf{Q}, \omega)$. If we can experimentally determine $A_{\mathrm{ei}}(\mathbf{Q})$ from neutron scattering experiments, we can obtain valuable information about the time scale as well as the kind of rotational motion in plastic crystals. Correlation times shorter than $\sim 10^{-9}$ sec are generally studied with the available resolution of instruments today.

Study of the rotation of near-spherical molecules by neutron scattering enables us to determine how far the rotation is isotropic. Typical of such molecules studied are

Table 3. Data for self-diffusion in plastic crystals[a].

	Structure	ΔS_f[b]	NMR[c] $\tau(s)$	Radiotracer[c] $\tau(s)$
Adamantane	FCC	20·8	$1·6 \times 10^{-21}$ (153)	$4·6 \times 10^{-20}$ (139)
Neopentane	FCC	12·6	$1·2 \times 10^{-13}$ (33)	—
Cyclohexane	FCC	9·0	$9·1 \times 10^{-15}$ (42)	$6·3 \times 10^{-25}$ (92)
Pivalic acid	FCC	6·3	$2·7 \times 10^{-17}$ (63)	$1·3 \times 10^{-22}$ (91)
Hexamethylethane	BCC	20·0	$2·5 \times 10^{-19}$ (82)	$3·2 \times 10^{-20}$ (86)
DL-Camphene	BCC	9·5	$4·6 \times 10^{-17}$ (57)	$3·8 \times 10^{-24}$ (96)

[a] Data taken from Boden (1979); [b] Entropy of fusion in J mol^{-1} k^{-1}; [c] Activation energies are shown in parenthesis.

methane, neopentane, adamantane and cyclohexane. Leadbetter and Lechner (1979) have reviewed results on these and other systems at length. In the plastic state of adamantane, rotational jump models seem to be applicable rather than an isotropic rotation model. In the case of succinonitrile, two correlation times have been considered, one due to *gauche-trans* isomerization and another due to the rotation of the *trans* isomer. Both these correlation times have been estimated from neutron scattering experiments.

6. Raman and infrared spectroscopic studies

The experimental dipole correlation function is obtained from the observed spectral density as follows (Gordon 1965):

$$\phi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \int_{\text{band}} \hat{I}(\omega) \exp - (i\omega t) \times \mathrm{d}\omega$$

where $\hat{I}(\omega) = I(\omega) / \int_{\text{band}} I(\omega) \mathrm{d}\omega$. Normally, only the real part of $\phi(t)$ is calculated and we have,

$$\phi(t) = \int_{\text{band}} \hat{I}(\omega) \cos [(\omega - \omega_0)t] \mathrm{d}\omega$$

where ω_0 is the band centre. Dipole correlation functions obtained in this manner from bandshapes are rotation-vibration correlation functions. Vibrational relaxation contributes significantly to vibrational band shapes (Nafie and Peticolas 1972) and one has to be careful in extracting information on molecular reorientation from such data. For Raman active totally symmetric vibrations of a linear or a symmetric top molecule (Gordon 1965),

$$\phi(t) = \langle P_2[\mathbf{u}_z(0) \cdot \mathbf{u}_z(t)] \rangle.$$

For a tetrahedral molecule,

$$\phi(t) = \langle P_2[\mathbf{u}_2(0) \cdot \mathbf{u}_2(t)] \rangle,$$

where $\mathbf{u}_2$ is the unit vector along a two-fold axis. Vibration relaxation has to be included in analysing Raman bandshapes as well.

It is generally difficult to locate infrared bands of plastic crystals which are suitable for the analysis of bandshapes. This is due to the proximity of overtones, hot bands, overlapping fundamentals and combination tones. Furthermore, vibrational relaxation contributes prominently to infrared bandshapes. In Raman scattering, however, it is often possible to delineate reorientational relaxation from other band broadening mechanisms by carrying out both anisotropic and isotropic measurements. By comparing reorientational correlation times obtained from Raman studies with those from NMR studies, one can obtain valuable information on the anisotropy of molecular reorientations in plastic crystals. Applications of Raman and infrared spectroscopy to the study of plastic crystalline state of molecules have been reviewed by Bailey (1979) and we shall only briefly look at some of the results.

Raman studies of CCl_4 by Bartoli and Litovitz (1972) gave a orientational correlation time of $1 \cdot 8 \times 10^{-12}$ sec. Furthermore, τ(Raman) showed no discontinuity across the plastic-liquid transition, a behaviour also shown by other systems (Ganguly *et al* 1983). Ganguly *et al* (1983) find reorientational correlation times in the range $1{\cdot}5$–$2{\cdot}3 \times 10^{-12}$ sec in the plastic phases of *t*-butyl chloride, *t*-butyl bromide and succinonitrile. Correlation times obtained from Raman bandshapes of CCl_4 by Sundar and McClung (1973) could be fitted into the *J*-diffusion model, the τ_J from this model showing fair agreement with NMR results.

Ganguly *et al* (1981) find no discontinuity in τ (determined from infrared band shapes) across the plastic-liquid transitions of many systems (figure 5) indicating the presence of appreciable rotational motion in the plastic phase. It appears that rotational motion is not through translational jumps. In the case of neopentane, both IR and Raman spectroscopy give activation energies of 4 kJ mol^{-1} (Ganguly *et al* 1981); the values from NMR and neutron scattering measurements are also close to this value. Both *t*-butyl chloride and *t*-butyl bromide are found to have activation energies of $\sim 3{\cdot}5$ kJ mol^{-1} from infrared studies (Ganguly *et al* 1981); Raman and NMR values for *t*-butyl chloride are both around 3 kJ mol^{-1}. Raman studies of Ganguly *et al* (1983) give a value close to 3 kJ mol^{-1} for E_a in *t*-butyl bromide. IR studies give an E_a of $4{\cdot}7$ kJ mol^{-1} in the case of cyclohexane (Ganguly *et al* 1981) and the NMR value is $6{\cdot}4$ kJ mol^{-1}.

In the case of neopentane, Livingston *et al* (1973) have compared the infrared and Raman correlation functions with the functions calculated from the *J* and *M* diffusion models (figure 6). Experimental correlation functions are found to be in-between those predicted by the two diffusion models. Succinonitrile is an unusual non-globular molecule which occurs in the plastic state. The plastic state contains both *gauche* and *trans* forms, while the ordered crystalline phase contains only the former. Infrared studies of Ganguly *et al* (1981) give a very low value of E_a compared to the NMR value (25 kJ mol^{-1}); recent Raman studies (Ganguly *et al* 1983) however give a value of 12 kJ mol^{-1}. Camphor also appears to exhibit anomalous reorientational behaviour;

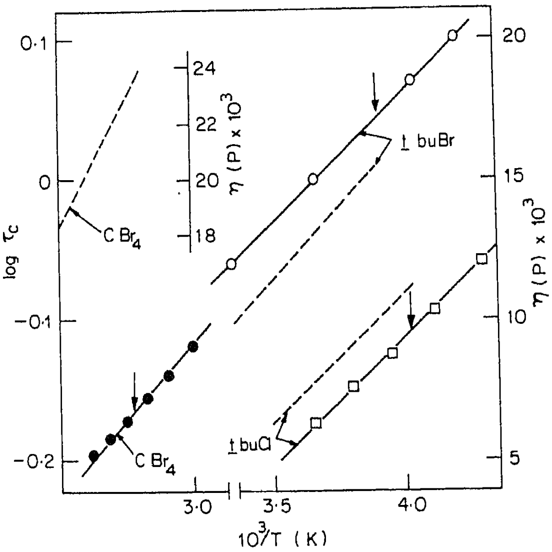

Figure 5. Plots of log τ_c (IR) against $1/T$. Arrows show liquid-plastic transition temperatures. Broken curves show plots of viscosity, η, versus $1/T$ (after Ganguly *et al* 1981).

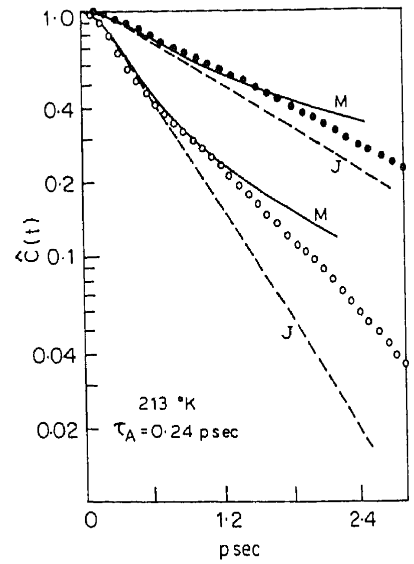

Figure 6. Raman (o) and IR (•) correlation functions for the plastic phase of neopentane (942 cm^{-1} band at 213 K) compared with the function predicted from M and J diffusion models. (after Livingston *et al* 1973).

Ganguly *et al* find an E_a of $\sim$ 7 kJ mol^{-1} from IR band shape analysis while NMR gives a value of 11 kJ mol^{-1}.

Far-infrared absorption of plastic crystals provides useful information on libration motions of molecules as influenced by collisions with neighbouring molecules. This region includes the Debye plateau (10–100 cm^{-1} region) due to the diffusion of dipoles, absorption above the plateau due to torsional oscillations of dipoles and also absorption due to dipoles induced by neighbouring molecules. Larkin (1973) and Larkin and Evans (1974) have examined this region of the infrared spectrum in plastic crystals and liquids.

Ganguly *et al* (1981) have carried out studies of solute molecules (upto a mole fraction of 0·2) dissolved in cyclohexane or carbon tetrachloride. Infrared correlation functions of *t*-butyl bromide in CCl_4 and cyclohexane solutions in the plastic state are compared with the correlation function for the pure substance (in the plastic state) in figure 7. The correlation function of pure cyclohexane is compared with the function found in CCl_4 solution in the same figure. In the case of *t*-butyl chloride (or *t*-butyl bromide) dissolved in cyclohexane, we find that the half-width of the C–Cl (or C–Br) stretching band decreases (or τ_c increases) significantly with the increase in mole fraction of the halide in the plastic phase (figure 8). This suggests that there is an increase in rotation rate, with respect to the pure material, of these solute molecules in the plastic phase when present in small concentration in the host matrix of cyclohexane. In the liquid state, however, τ_c decreases with increase in halide concentration implying that there is a decrease in the rotation rate of the halide (in the liquid state) when it is surrounded by cyclohexane solvent molecules. Camphor shows results similar to *t*-butyl halides.

The half-widths of the C–Br stretching band of *t*-butyl bromide and the CH_2

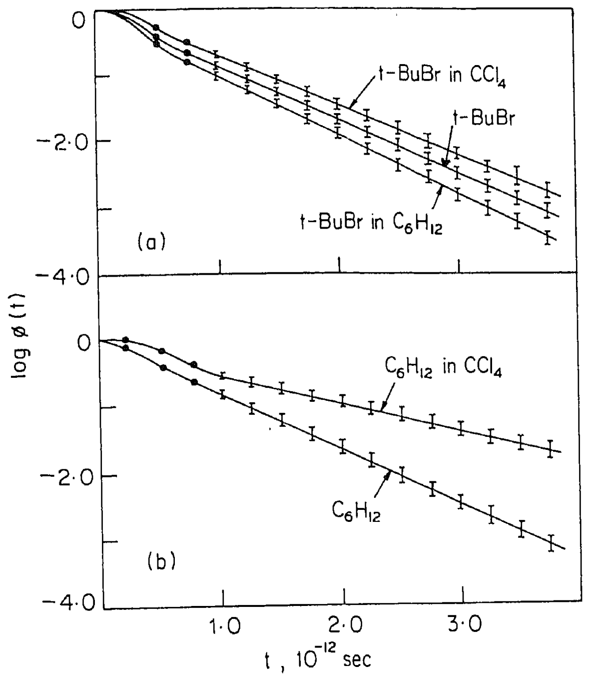

Figure 7. (a) Infrared correlation functions of pure *t*-butyl bromide and in CCl_4 and C_6H_{12} solutions, all in the plastic state at 233 K (mole fraction of *t*-butyl bromide = 0·05). (b) Correlation function of cyclohexane in the pure state and in CCl_4 solution, both in the plastic state at 233 K (mole fraction of cyclohexane = 0·05) (after Ganguly *et al* 1981).

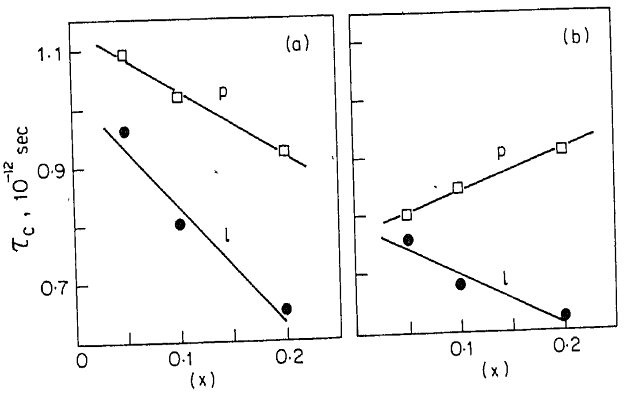

Figure 8. Plots of IR τ_c values against the mole fraction of *t*-butyl bromide in (a) CCl_4 and (b) C_6H_{12} solutions in plastic (p) (233 K) and liquid (l) (298 K) phases (after Ganguly *et al* 1981).

scissoring band of cyclohexane increase (τ_c values decrease) with increase in solute concentration in CCl_4 solvent. In figure 8 we show the case of *t*-butyl bromide; the decrease in τ_c is greater (~ 1·5 pico sec) in the case of cyclohexane over the same concentration range. This suggests that there is decrease in rotation rate of these solute molecules in the plastic phase when present in a matrix of CCl_4, a behaviour opposite to that found in cyclohexane solutions. Accordingly, the infrared correlation function of neat *t*-butyl bromide (in the plastic phase) lies in between the functions of this molecule in cyclohexane and CCl_4 solutions (figure 7). Correlation functions of cyclohexane in figure 7 show that there is a decrease in rotation when it is surrounded by CCl_4 solvent molecules. It is also interesting that unlike in cyclohexane, the concentration dependence of τ_c in CCl_4 solvent is the same both in the liquid and plastic phases. The above variations in τ_c could at least partly be due to vibrational relaxation in solutions which in turn gives rise to vibrational dephasing or inhomogenous broadening due to frequency fluctuations. Whatever be the exact origin, the trends in τ_c of solute molecules in the plastic and the liquid states are quite interesting and may provide a means of understanding the effect of solute-solvent interactions on vibrational bands. The difference in the concentration-dependence of τ_c of the solute molecule in the plastic state in cyclohexane and CCl_4 solvents may be related to the ΔS_{cp} values of the solvent relative to that of the solute molecule. In the case of cyclohexane solvent, both the *t*-butyl halides have lower ΔS_{cp} values; the ΔS_{cp} values of both *t*-butyl bromide and cyclohexane are higher than the ΔS_{cp} of CCl_4.

7. ESR studies

Ganguly *et al* (1981) have recently obtained ESR spectra of the spin-probe TEMPO in the plastic and liquid phases of cyclohexane, CCl_4 and *t*-butyl chloride; the spectra were damped out in the crystalline phase. We have evaluated the correlation times for the tumbling, τ_t, of these molecules in both the plastic and liquid states by employing McConnell's method (Stone *et al* 1965) and find them to be continuous through the plastic-liquid transition (figure 9), just as the τ values from IR and Raman spectroscopy. The activation energies calculated from the $\log \tau_t - 1/T$ plots in figure 9 are 3·5, 4·0 and 11 kJ mol^{-1} for CCl_4, *t*-butyl chloride and cyclohexane respectively. These activation energies vary in the same direction as the E_a values from IR studies and the ΔH values of the plastic-crystal transitions (4·7, 5·8 and 6·7 kJ mol^{-1} respectively for CCl_4, *t*-butyl chloride and cyclohexane). Ganguly *et al* (1981) point out that in the systems studied by them, the E_a values from IR correlation times vary in the same direction as the ΔH_{cp}.

8. Thermodynamics of organic plastic crystals

One of the important characteristics of the plastic state is that the entropy change of the crystal to plastic transition, ΔS_{cp}, is generally much larger than the entropy change of the transition from the plastic to the liquid state, ΔS_{pl}. It is instructive to examine possible systematics in the thermodynamics of the crystal-plastic and plastic-liquid phase transitions and the range of stability of the plastic phase in a few systems. In table 1, thermodynamic data on the transitions of a few chosen systems are listed. It has been found by Ganguly *et al* (1981) that the ΔH of the crystal-plastic transition, ΔH_{cp}, generally decreases as the range of stability, ΔT_{pl} ($\Delta T_{pl} = T_{pl} - T_{cp}$) increases. The ΔH of the plastic-liquid transition, ΔH_{pl}, on the other hand, increases as ΔT_{pl} increases (figure 10). Similar trends are also shown by ΔS_{cp} and ΔS_{pl} of the transitions. The ΔS_{cp} and ΔS_{pl} values show similar trends with $\Delta T_{pl}/T_{pl}$ where T_{pl} is the melting point. The

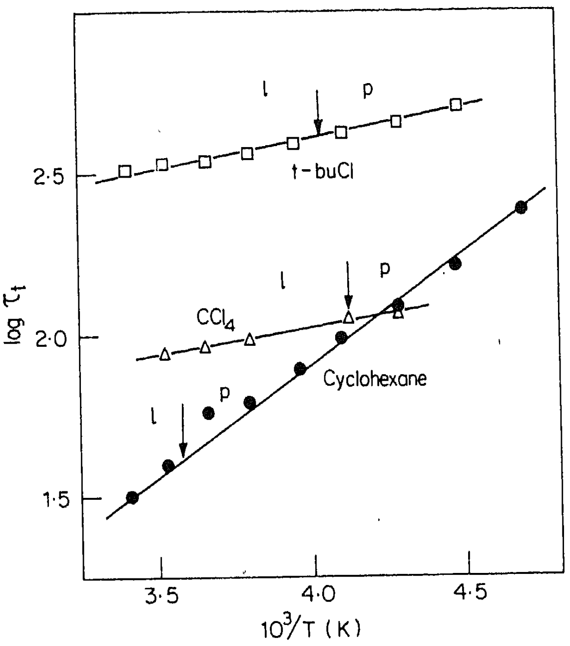

Figure 9. Plots of log τ_r (from ESR spectra of the spin probe) versus $1/T$. Arrows show plastic-liquid transitions (after Ganguly *et al* 1981).

trends in figure 10 can be understood in terms of the magnitude of randomization in the plastic state. Whenever ΔS_{cp} or ΔH_{cp} is large, there will be greater randomization in the plastic state and the plastic-liquid range, ΔT_{pl}, will be small. On the contrary, ΔT_{pl} would be large when ΔS_{cp} or ΔH_{cp} is small. It therefore appears that when ΔT_{pl} is small, ΔS_{pl} and ΔH_{pl} would normally be small.

9. Computer simulation studies

Several investigations of the orientationally disordered phases of molecular crystals by computer simulation with various intermolecular potential models have been reported in the literature in recent years. Static and dynamical structure factors obtained from these studies have been compared with those obtained experimentally from neutron scattering studies. Studies on the plastic phases of nitrogen, methane and other substances employing simple atom-atom potentials give good agreement with experiments suggesting thereby that charge-charge interactions do not play a major role (Klein *et al* 1981; Klein and McDonald 1981; Bounds *et al* 1980). Calculations on DCl show that it is necessary to consider the hydrogen bond interaction to obtain satisfactory agreement with experimental properties (McDonald *et al* 1980). Dynamical properties of the mixed crystals $(KCN)_x(KBr)_{1-x}$ and the static disorder of the CN^- ions have also been studied by molecular dynamic calculations and there is evidence for the formation of an orientational glassy state at low temperatures (Bounds *et al* 1982). Equilibrium properties of methane in the orientationally disordered phase

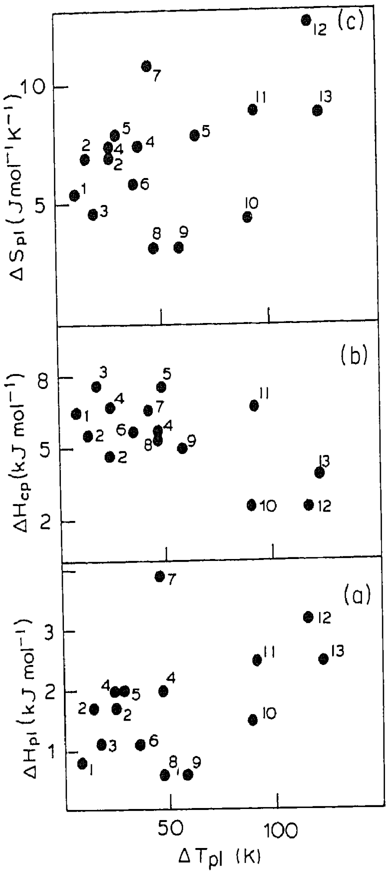

Figure 10. Variation of (a) the ΔH of the plastic-liquid transition with the plastic-liquid range, ΔT_{pl}; (b) the ΔH of the crystal-plastic transition with the plastic-liquid range, ΔT_{pl}; (c) the ΔS of the plastic-liquid transition with the plastic-liquid range, ΔT_{pl} (after Ganguly *et al* 1981). The numbers next to the points refer to the compounds in table 1.

have been calculated by molecular dynamics and the results are in satisfactory agreement with experiment. A Monte Carlo study of the quenching of the plastic phase of methane suggests the presence of an orientational glass transition, with an accompanying increase in the lifetime of reorientation of methane molecules (Yashonath and Rao 1983). Furthermore, different cooling rates are found to give rise to different final states.

Recent developments in molecular dynamics and Monte Carlo techniques have made it possible to investigate the structural phase transition from the crystal to the plastic crystal phase (Nose and Klein 1983a; Yashonath and Rao, unpublished results). A molecular dynamics study of the crystal to plastic crystal transition in CF_4 has been reported (Nose and Klein 1983b). Information regarding the molecular arrangement in the high temperature phase has been obtained employing a simple Lennard-Jones potential. A Monte Carlo study of the crystal to plastic crystal phase transition in CCl_4 obtained by isobaric heating has also been carried out (Yashonath and Rao, unpublished results). In figure 11 we show the computer simulated crystalline and

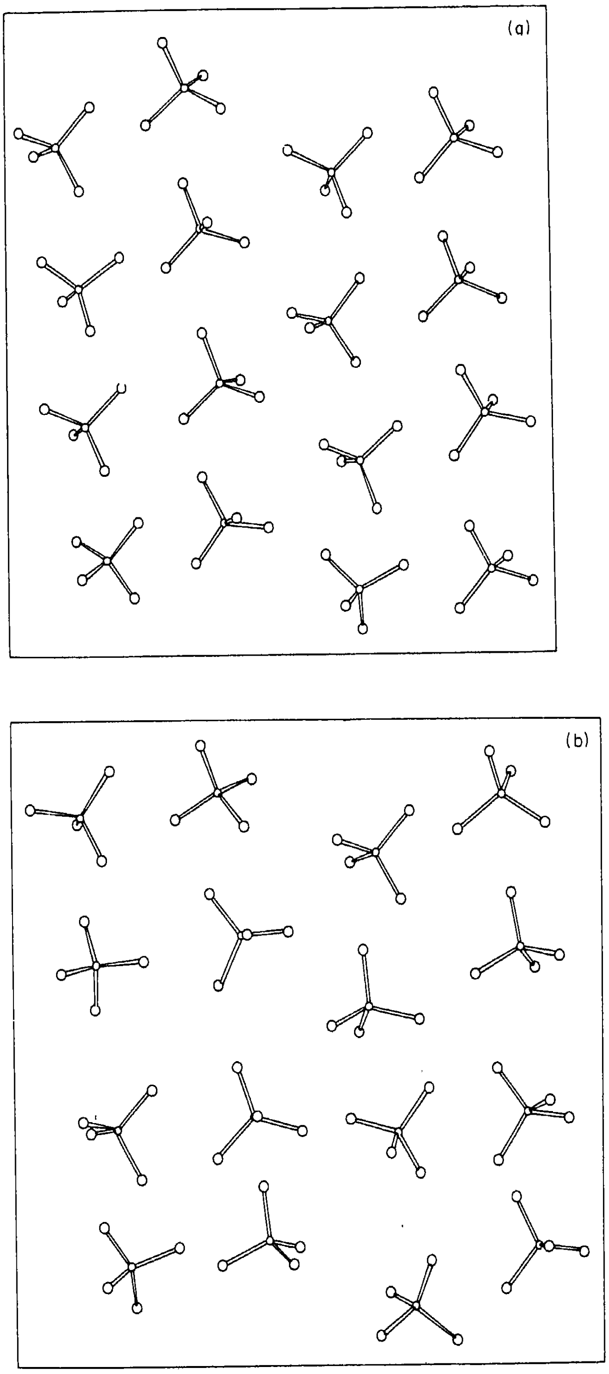

Figure 11. Monte Carlo simulation of CCl_4 (at 1 GPa): (a) crystalline phase at 380 K; (b) plastic phase at 430 K (after Yashonath and Rao, unpublished results).

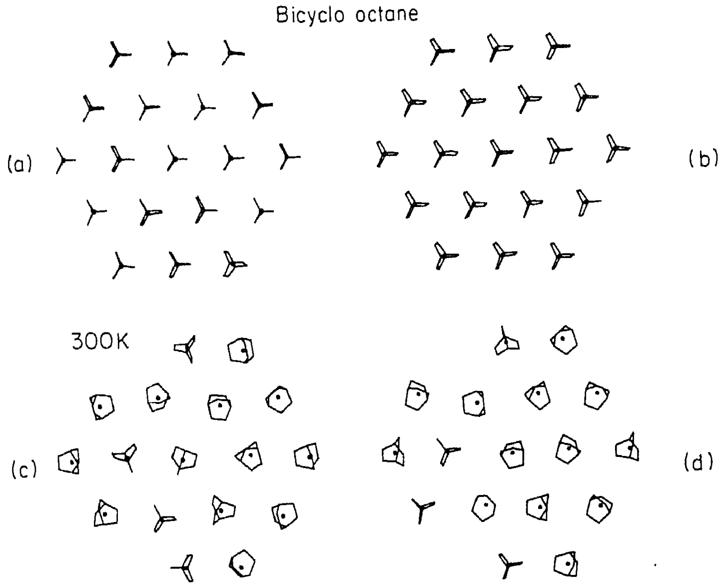

Figure 12. MD simulation of bicyclo octane (after Neusy *et al* 1984): (a) at 50 K (crystalline phase) for the 8-site model; (b) at 50 K (crystalline phase) for the 22-site model; (c) at room temperature (plastic phase) for the 8-site model; (d) at room temperature (plastic phase) for the 22-site model.

plastic phases of CCl_4. The structural transition in bicyclo-(2.2.2)octane and the computed relaxation time, reorientational dynamics and power spectra associated with translational and rotational motions have been found to be in fair agreement with experiment (Neusy *et al* 1984). In figure 12, the simulated phases of bicyclo octane are shown.

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