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Rotational Diffusion Rates in Molecular Crystals Relations to Molecular Structure and to Crystal Packing Density

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Rotational Diffusion Rates in Molecular Crystals Relations to Molecular Structure and to Crystal Packing Density

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Abstract—The rotational diffusion rates of molecules and of mobile molecule segments in crystalline solids are expressed as relaxation rates relative to the corresponding torsional oscillation rate of the molecule or molecule segment. The resulting dimensionless relaxation time $\tau_i(\Delta H_s/I_i)^{1/2}$ turns out to be a function of packing density (ρ^*) of the crystal and of the characteristic temperature $fRT/\Delta H_s$, where f is the number of external degrees of freedom per molecule. The dimensionless activation energy $\Delta E_\ddagger/\Delta H_s$ is a uniform function of the packing density for crystals composed of rigid molecules and another function of ρ^* for crystals composed of flexible molecules. The rate determining factor for molecular rotation in crystals containing hydrogen bonds appears to be the breaking energy of the hydrogen bond.

Purpose and Scope

The purpose of the present work is to find simple relations to estimate the magnitude of rotation rates of molecules in the lattice of molecular crystals from molecular structure and from crystal structure information. Such information is useful in at least two areas of current interest: Prediction of the suitability of given molecular crystalline solids as dielectrics, and assessment of the molecular basis of certain time-dependent mechanical properties of such solids. Interest in rotational diffusion has been roused by the recognition that some time-dependent mechanical properties of crystalline polymers are largely determined by molecular (segment) rotation, while those of simple substances are determined by mass diffusion of the entire molecule.

The scope of the work is restricted to the evaluation of "direct measurements" of molecule rotation, as in electric dipole rotation and n.m.r. relaxation times, and to crystalline solids composed of non-polymeric molecules. Application of the results to polymer-crystals and to their mechanical properties should be the subject of a separate investigation.

General Principles

Classical mechanics of crystals contain provisions for the torsional oscillation of polyatomic molecules in their crystal lattice. Occasionally a molecule acquires sufficient thermal energy to surmount the potential energy barrier set up by the anisotropic force fields of its nearest neighbors and rotates into a new equilibrium position. Often packing is so tight that such rotation requires cooperative motion of several neighboring molecules.

The frequency (ν_m) of molecule reorientation or rotation can be estimated by means of a theory by Bauer[1, 2] or by a somewhat cruder approximation proposed by Waugh and Fedin[3]

$$\nu_m = (2\pi\tau)^{-1} = [n^2(V^\circ/2I_i)^{1/2}]\exp(-V^\circ/RT) \qquad (1)$$

where ν_m is the frequency at which the energy absorption of the solid exhibits a maximum (at temperature T), τ is the corresponding relaxation time, V° is the height of the n-fold barrier to rotation, and I_i is the appropriate principal moment of inertia of the molecule,[1] while $n^2(V^\circ/2I_i)^{1/2}$ is the torsional oscillation frequency (ω_r) for a cosine potential. Since V° is generally not known, it is often replaced by the "apparent activation parameter(s)":

$$\Delta F_\ddagger \approx \Delta E_\ddagger - T\Delta S_\ddagger$$

(ref. (d) of Table 1). The magnitude of n depends on the symmetry number of the molecule or the group (e.g., $n=3$ for a CH_3 group and $n=6$ for a benzene molecule) and on the symmetry of molecule arrangements in the crystal.

The magnitude of V° or, more commonly, of $\Delta E_\ddagger$, should depend on the heat of sublimation ΔH_s, as a measure of the lattice energy, and on the packing density ρ^*. Hence, one should expect to find a general correlation between $\Delta E_{\ddagger}/\Delta H_s$ and ρ^*. The pre-exponential factor of equation (1) suggests a reduced relaxation time $\tau(\Delta E_{\ddagger}/I_i)^{1/2}$ or $\tau(\Delta H_s/I_i)^{1/2}$, which should—at a given reduced temperature ($fRT/\Delta H_s$)—be primarily a function of the packing density (where $f =$ number of external degrees of freedom per molecule). With liquids only one of these two variables had to be specified.[2] However, with solids ρ^* and $fRT/\Delta H_s$ are independent variables.

Phenomenologically a strong differentiation is made between "normal" hard crystals and the soft "plastic" crystal which obtains at $T_{tr} < T < T_m$. Rotational motions in the former are infrequent and are called "reorientation";† in the latter such motions occur frequently and are called "rotation". We shall see that the difference is indeed only quantitative and that both regimes are encompassed by a single correlation scheme.

While the rotation (reorientation) frequency $\nu_m(T)$ of a given substance is comparatively insensitive to the detailed history and morphology of the crystal system, the relaxation strength, i.e., the number density of moving particles, strongly reflects the crystal size, and other effects of thermal and mechanical sample history. The reason for this sensitivity is the origin of the relaxation strength, the magnitude of the energy difference ΔE_i between two equilibrium positions of each rotor. The magnitude of ΔE_i faithfully reflects the variations in potential energy among all the nearest neighbors of a given molecule (and the next nearest neighbors in turn). Hence, *a priori* statements on ΔE_i could at best be made for large single crystals, but even that has not yet been attempted.

Rigid Non-Associating Molecules

In the present context all those molecules are designated as "rigid" internal rotational motion in which is either impossible or

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† A detailed description of the types of reorientation motion associated with given molecule and lattice symmetry can be found in the recent paper by I. Darmon and C. Brot, *J. Mol. Cryst.* **2**, 301 (1967).

TABLE 1 Rotational Diffusion Parameters for Crystals Composed of Rigid Molecules; Hard or Normal Crystals (or $T < T_{tr}$)

Method: e.d.r. = electric dipole relaxation
n.m.r. = nuclear magnet relaxation
n.q.r. = nuclear quadrupole relaxation

Substance	Method	ω^g (10^{12} sec^{-1})	$\Delta E_\ddagger$ (kcal/mole)	$\frac{\Delta E_\ddagger}{\Delta H_s}$	$\frac{\Delta E_\ddagger (293)}{\Delta H_s}$	Ref.
Benzene	n.m.r.	2	3.1	0.30		a
Benzene	n.m.r.		3.7	0.35		b
Benzene	n.m.r.		3.5	0.34		c
Benzene	n.m.r.	0.02	3.95	0.35		q
Hexamethylbenzene	n.m.r.	0.9	5.3	0.33		c
Hexamethylbenzene	n.m.r.	0.16	5.2	0.32		r
Chloropentamethylbenzene	e.d.r.	200	10.0	0.50		o
Bromopentamethylbenzene	e.d.r.	30	9.2	0.43		o
Chlorodurene	e.d.r.	4000	8.1	0.43		o
1,2,4-Trimethyl-2,5,6-trichlorobenzene	e.d.r.		10.3	0.50	0.326	d
Pentachlorotoluene	e.d.r.		11.6	0.55	0.422	d
Pentachlorobenzenethiol	e.d.r.		11.8	0.49		p
Hexachlorobenzene	n.q.r.		9.9 to 12.6	0.46 to 0.59		e
1,2,3-Trichlorobenzene	n.q.r.		4.6 to 5.7	0.30 to 0.35		e
Propane	n.m.r.		3.3[i]	0.49		f
1,1,1-Trichloroethane	n.m.r.	9	4.8[i]	0.51		a
Hexachloroethane	n.q.r.		8 to 9[i]	0.56 to 0.64		h
Thiourea	n.m.r.	75	10.0	≈ 0.7[k]		j

Cyclohexane	n.m.r.		5 to 6	0.45 to 0.54		c
Cyclohexane	n.m.r.	1.0	11.0	1.0		l
Adamantane	n.m.r.	0.9	5.3	0.37		a
Hexamethylene tetramine	n.q.r.	7.6	15.6	0.87		m
Chlorobenzene	e.d.r.	4.05×10^{-5}	6.4	0.47	0.195 (T_m)	n
Bromobenzene	e.d.r.	0.82×10^{-11}	13.7	0.96	0.211 (T_m)	n
Iodobenzene	e.d.r.	3.4×10^{-10}	12.8	0.85	0.208 (T_m)	n

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[a] Waugh, J. S. and Fedin, E. I., *Sov. Phys.—Solid State* **4**, 1633 (1963).
[b] Andrew, E. R. and Eades, R. G., *Proc. Roy. Soc.* **A218**, 537 (1953).
[c] Das, T. P., *J. Chem. Phys.* **27**, 763 (1957).
[d] Meakins in *Progress in Dielectrics* **3**, 159.
[e] Tatsurzaki, I., *J. Phys. Soc. Japan* **14**, 578 (1959).
[f] Aston, J. G., *Disc. Faraday Soc.* **10**, 73 (1951).
[g] ω_r is the pre-exponential term in $\tau^{-1} = \omega_r \exp(\Delta E_{\ddagger}/RT)$.
[h] Ainbinder, N. E. *et al.*, *J. Struct. Chem.* **2**, 644 (1961).
[i] It is uncertain whether $\Delta E_{\ddagger}$ is the barrier to external or to internal rotation.
[j] Smith, D. H. and Cotts, R. M., *J. Chem. Phys.* **41**, 2403 (1964).
[k] A comparatively low value of ΔH_s (14 to 15 kcal/mole) has been estimated because the X-ray diffraction data (Goldsmith, G. J. and White, J. G., *J. Chem. Phys.* **31**, 1175 (1959)) clearly show the absence of hydrogen bonding in the crystal. Their density, however, yields $\rho^* = 0.710$.
[l] Andrew, E. R. and Eades, R. G., *Proc. Roy. Soc.* **A216**, 398 (1953).
[m] Alexander, S. and Tzalmona, A., *Phys. Rev. Letters* **13**, 546 (1964).
[n] Imanov, L. M. and Zulfugarzade, K. E., *Russ. J. Phys. Chem.* **37**, 188 (1963). (Very uncertain data.)
[o] Balcou, Y. and Meinnel, J., *J. chim. phys.* **63**, 114 (1966).
[p] Brot, C. and Darmon, I., *J. chim. phys.* **63**, 100 (1966).
[q] Anderson, J. E., *J. Chem. Phys.* **43**, 3575 (1965).
[r] Lemanceau, B. *et al.*, *J. chim. phys.* **63**, 94 (1966).

is hindered by a sufficiently high potential energy barrier to make an unobservable contribution to molecular rotation. The available data have been assembled in Tables 1 and 2 for "hard" and "plastic" crystals, respectively. Similarly, the activation energy $\Delta E_\ddagger$ has been plotted in the reduced form $\Delta E_\ddagger/\Delta H_s$ vs ρ^* in Fig. 1.

TABLE 2 Rotational Diffusion Parameters for Crystals Composed of Rigid Molecules: Plastic Phase (at $T > T_{\mathrm{tr}}$)

Substance	Method	$\frac{\Delta F_\ddagger\,(293)}{\Delta H_s}$	$\Delta E_\ddagger$ (kcal/mole)	$\frac{\Delta E_\ddagger}{\Delta H_s}$	Ref.
Furan	e.d.r.	0.35	2.0	0.21	g
Bromodurene	e.d.r.		5.1	0.26	h
Camphene	e.d.r.	0.23	1.6	0.12	a
	e.d.r.	0.21	2.2	0.16	b
d-Camphor	e.d.r.	0.18	2.7	0.16	a
	e.d.r.	0.06 (±0.05)	1.8±0.7	0.11±0.04	b
	n.m.r.		2.8	0.17	c
Bornyl chloride	e.d.r.	0.20	2.5	0.16	b
Isoborneol	e.d.r.	0.18	4.0	0.22	a
	e.d.r.	0.20	5.5	0.30	b
Neopentane	n.m.r.		1.0	0.13	d
2,2-Dichloro-propane	e.d.r.	0.19[f]	1.4	0.13	b
	n.m.r.		~3.0	0.28	d
1,1,1-Trichloro-ethane	e.d.r.	0.18[f]	(1.1)	(0.10)	b
	n.m.r.		4.5		d
t-Nitrobutane	e.d.r.	0.14[f]	0.5	0.03	b
2-Chloro-2-nitro-n-propane	e.d.r.	0.19[f]	1.3	(0.1)	b
$(CH_3)_3CCl$	n.m.r.		1.5	0.16	d

[a] Williams, D. E. and Smyth, C. P., *J. Am. Chem. Soc.* **84**, 1808 (1962)

[b] Clemett, C. and Davies, M., *Trans. Farad. Soc.* **58**, 1705, 1718 (1962).

[c] Anderson, J. E. and Slichter, W. P., *J. Chem. Phys.* **41**, 1922 (1964).

[d] Stejskal, E. O. *et al.*, *J. Chem. Phys.* **31**, 55 (1959).

[e] Reference temp. $= T_m$.

[f] $\Delta F_\ddagger$ calc. based on $\omega_r = kT/h$.

[g] Fried, F. and Lassier, B., *J. chim. phys.* **63**, 75 (1966).

[h] = Ref. (o) of Table 1.

The trends are as expected, namely, indicative of rising resistance to rotation with rising packing density.

The torsional oscillation frequency of a molecule in the crystal $\omega_r \sim (\Delta E_\ddagger / I_i)^{1/2}$. If ρ and thus ρ^* are known, $\Delta E_\ddagger$ can often be estimated from ΔH_s by means of the correlation in Fig. 1, ΔH_s almost always being available from correlations.[4] Then one should expect the existence of a correlation of the reduced relaxation time $\tau(\Delta E_\ddagger / N_A I_i)^{1/2}$ vs ρ^* and $fRT/\Delta E_\ddagger$ (where N_A = Avogadro number). With plastic crystals, often of particular interest, $\Delta E_\ddagger$ can be so small that reported values are quite unreliable, and the fit to the correlation of Fig. 1 is quite uncertain. Hence it was considered more useful to represent their data just as function of ΔH_s, namely, $\tau(\Delta H_s / N_A v_i)^{1/2}$ vs ρ^* and $fRT/\Delta H_s$ in Fig. 2. Conversion from

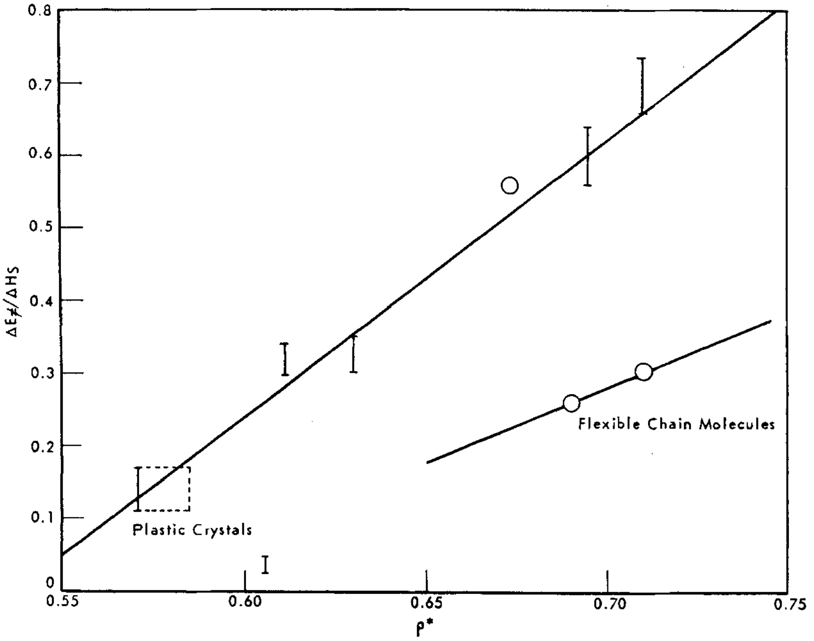


Figure 1. Dependence of the reduced activation energy for rotational diffusion of rigid molecules upon packing density.

ΔH_s to $\Delta E_\ddagger$ at a later date may well separate the points into more clearly discernible lines.

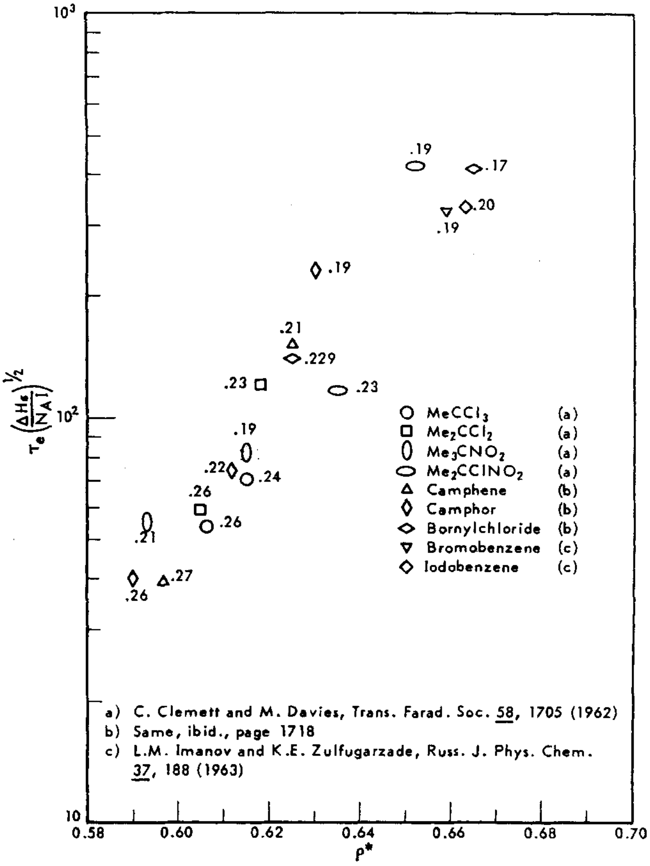


Figure 2. Plot of reduced rotational relaxation time vs packing density, parameter: reduced temperature $\frac{\mathrm{fRt}}{\Delta \mathrm{H_s}}$.

Prediction of the absolute magnitude of τ would be achieved if the correlation of Fig. 2 could be made more reliable. Another path to that goal is the correlation of the reduced free energy of activation $\Delta F_\ddagger/\Delta H_s$ with ρ^* and $fRT/\Delta H_s$ or $fRT/\Delta E_\ddagger$. Here $\Delta F_\ddagger$ can be defined as $RT\ ln\ (\tau\omega_r)$ with $\omega_r = 10^{12}\ H_z$ (as in Tables 2 to 6), or $\omega_r = kT/h$, or most correctly as in the first term of eq. (1). At present only qualitative trends can be discerned; more reliable correlations may have to await greater certainty in the experimental data.

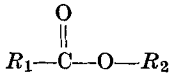
The heat of sublimation, ΔH_s, used as reducing parameter throughout this and the following sections, is taken at the lowest first order solid/solid transition temperature.[3] The use of ΔH_s appropriate to the state of the solid under consideration might have been better and may even make a significant difference with plastic crystals. In practice, that point of view is very difficult to implement, however, because ΔH_s of the plastic crystal state is *not* correlatable in terms of additive functional group increments, while ΔH_s at the lowest first order transition temperature is rather well correlated in that way.[3] The fact that one can almost always estimate the latter from molecular structure information alone is the primary justification for its use as reducing parameter for all phases of a molecular crystal.

Flexible (Monomeric) Non-Associating Molecules

The rotational motions of long flexible molecules in crystal lattices involve several additional degrees of freedom not accessible to rigid molecules. In addition to rotation or reorientation motions of the entire molecule around its longest axis, there may be (hindered) rotation of end groups, such as methyl groups, reorientation of segments either in normal (trans-trans) or in gauche trans-gauche ("crankshaft") conformation between different equilibrium conformations or locations in the crystal. Evidence for the onset of the enumerated motions is obtained by n.m.r. line width and relaxation time measurements over the temperature range from 0°K up to the melting point.

Whether electric dipole relaxation rates represent the rotational motion of parts or of the entire molecule can only be inferred from the uniformly low values of $\Delta E_{\ddagger}/\Delta H_s$ and of $\Delta F_{\ddagger}/\Delta H_s$ on Table 3 as well as on Fig. 1. The relative positions of $\tau_i(\Delta H_s/I_i)^{1/2}$ (where I_i is calculated for the rotation of the entire molecule around its longest axis) and of $\Delta E_{\ddagger}/\Delta H_s$ on the packing density correlations

Table 3 Rotational Diffusion Parameters for Crystals Composed of Flexible Molecules: Hard or Normal Crystal (at $T < T_{tr}$); All by e.d.r. Method[a]

Substance		$\frac{\Delta F_{\ddagger}(293)}{\Delta H_s}$	$\frac{\Delta E_{\ddagger}}{\text{(kcal/mole)}}$	$\frac{\Delta E_{\ddagger}}{\Delta H_s}$
Solid solutions in n-paraffin wax[b]				
$(n\text{-}C_8)_2C{=}O$		0.18	11.3	0.318
$(n\text{-}C_9)_2C{=}O$		0.17_5	11.9	0.302
$(n\text{-}C_{10})_2C{=}O$		0.18	14.7	0.338
$(n\text{-}C_{11})_2C{=}O$		0.16_7	15.5	0.327
$(n\text{-}C_{12})_2C{=}O$		0.16_8	17.7	0.345
$(n\text{-}C_{13})_2C{=}O$		0.16_8	18.7	0.337
$(n\text{-}C_{15})_2C{=}O$		0.16	20.5	0.324
$(n\text{-}C_{17})_2C{=}O$		0.15_9	20.7	0.291
$(n\text{-}C_8)_2O$		0.168	10.1	0.297
$(n\text{-}C_{12})_2O$		0.156	15.9	0.319
$(n\text{-}C_{14})_2O$		0.152	17.1	0.295
$(n\text{-}C_{16})_2O$		0.150	17.8	0.270
Ethyl stearate			17.8	0.318
Di-n-octyl nonadioate			14.4	0.260
Pure compounds  $R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R_2$				
R_1	R_2			
C_{16}	C_2	0.154	10.0	0.245
C_{18}	C_1	0.147	11	0.257
C_{18}	C_2	0.151	12.9	0.288
C_{12}	C_{10}	0.149	14.9	0.305
C_{22}	C_1	0.151	17.1	0.334
C_{22}	C_2	0.144	17	0.322
C_{14}	C_{12}	0.146	18	0.317
C_{16}	C_{16}	0.136	22	0.321
$(C_{16})_2O$		0.133	20	0.303
$(C_{18})_2O$		0.133	23	0.311

[a] From ref. (d) of Table 1 except where noted otherwise.

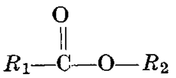
[b] Assumed $\Delta H_s = [\Delta H_{s\,(\text{solute})} \cdot \Delta H_{s\,(\text{paraffin})}]^{1/2}$.

of Figs. 1 and 2 exhibit a less than proportional increase of $\Delta F_\ddagger$ and of $\Delta E_\ddagger$ with increasing chain length. Fröhlich[6] showed that this flexibility effect can be represented by the relation

$$\Delta E_\ddagger(N_s) = \Delta E_\ddagger(1).n_0 \tanh(N_s/26)$$

where N_s = number of skeletal segments per molecule, $\Delta E_\ddagger(1)$ is the barrier to the movement of a single skeletal segment, $n_0 = f$ (energy required to twist a valence angle). The meaning of this relation is that a progressively larger portion of rotation is provided by internal rather than by external motion as the molecule length increases. The rotational diffusion rate of flexible molecules in their plastic crystalline phase is very much like that in a liquid[4] just as in the plastic crystals composed of rigid molecules. However, the temperature coefficient ($\Delta E_\ddagger$) is far larger (Table 4), so large, in fact, that one may suspect much of it to be caused by thermal expansion rather than by a genuine barrier to rotation.

TABLE 4 Rotational Diffusion Parameters for Crystals Composed of Flexible Molecules; Plastic Phase (at $T > T_{tr}$)[a]

Substance	$\frac{\Delta F_\ddagger (293)}{\Delta H_s}$	$\Delta E_\ddagger$ (kcal/mole)	$\frac{\Delta E_\ddagger}{\Delta H_s}$
$(n\text{-}C_{18})_2O$	0.170	47.4	0.64
 $R_1—C(=O)—O—R_2$			
R_1 R_2			
C_{18} C_2	0.302	43	0.96
C_{22} C_2	0.314	48	0.91
C_2 C_{18}	0.282	32	0.71
C_2 C_{20}	0.29	36	0.74
C_2 C_{22}	0.29_5	35	0.66
Succinonitrile[b]	0.26		0.15

[a] From ref. (d) of Table 1.

[b] From ref. (a) of Table 2; the value of $\Delta E_\ddagger$ applies only to the temperature range near T_m. $\Delta E_\ddagger$ increases rapidly as T_{tr} is approached, much like in very viscous liquids.

Rotational diffusion of polar flexible molecules in non-polar host lattices composed of similarly long chain n-alkanes is influenced by the host lattice as is shown by the data of Table 5. More extensive comparisons of solid solution with pure compound data are required before one can come to any valid generalizations. The slight difference in geometry between the polar molecules and the n-alkanes must cause some concentration dependent lattice distortion so that valid comparisons may require careful normalization to zero concentration or to some standard concentration of "bumps". A comparison of the rotation rate of the host lattice molecules (by n.m.r. method) with and without guest molecules would be very instructive.

TABLE 5 Effect of Chain Length of Solvent and Solute on Rotational Diffusion in Solid Solutions[a]

Solvent	Solute	$\frac{\Delta F_{\ddagger}\,(253^\circ\mathrm{K})}{\Delta H_s}$	$\Delta E_{\ddagger}$ (kcal/mole)	$\frac{\Delta E_{\ddagger}}{\Delta H_{s(\mathrm{solute})}}$
n-Hexadecane	ethyl stearate	0.116 (0.155)[b]	18.5	0.43
Paraffin wax (n-C_{26})	ethyl stearate	0.141 (0.116)[b]	17.8	0.41
n-Hexadecane	cetyl palmitate	0.122 (0.163)[b]	18.4	0.27

[a] Sillers, R. W., *Proc. Roy. Soc.* **A169**, 66 (1938).
[b] Relative to ΔH_s (solvent).

Associating Molecules

Two kinds of crystal composed of associating molecules are of general interest: (a) the hydrogen bonding compounds with their comparatively mobile associating group forming linear chains, and (b) metal oxide derivatives, such as the metal soaps, forming association sheets throughout the crystal by virtue of coordination bonds between oxygen atom on adjacent soap molecules and the metal ions.

In the case of hydrogen bonding compounds one finds that the observed rotational diffusion is generally the independent rotation of the hydrogen bonding groups rather than that of the entire molecule. With compounds such as water, hydrogen halides, etc., where the entire molecule is the "hydrogen bonding group" one finds that $\Delta E_{\ddagger}$ is virtually identical with the hydrogen bond contribution to ΔH_s as shown by the data of Table 6. Inspection of the data for alcohols given on the same table suggests that the

TABLE 6 Rotational Diffusion Parameters in Crystals Composed of Rigid Hydrogen Bonding Substances in Hard (Low Temperature) Phase[a]

Substance	Method	$\frac{\Delta F_{\ddagger}(T_m \text{ or } T_{tr})}{\Delta H_s}$	$\Delta E_{\ddagger}$ (kcal/mole)	$\frac{\Delta E_{\ddagger}}{\Delta H_s}$	$\frac{\Delta E_{\ddagger}}{\Delta H_s\text{(H-bonding)}}$[b]
Ice	e.d.r.	0.84	13.25	1.09	1.09
Ice	m.e.a.[c]	0.90	13.4	1.10	1.10
HCl	e.d.r.	0.50	2.58	0.52	1.08
HBr	e.d.r.	0.62	2.7	0.49	1.2
HI	e.d.r.	0.34	2.2	0.37	1.5
Urea[d]	n.m.r.		9.0	0.43	0.7
n-C_{18}—OH-1	e.d.r.[e]	0.249[f]	15	0.31	2.0
n-C_{22}—OH-1	e.d.r.[e]	0.022[f]	15	0.27	2.0
n-C_{26}—OH-1	e.d.r.[e]	0.204[f]	15	0.23	2.0
$(nC_9)_2CH$ | OH	e.d.r.[e]	0.37	6.5	0.21	0.9
$(nC_{13})_2CH$ | OH	e.d.r.[e]	0.19	5	0.1	0.7
$(nC_{17})_2CH$ | OH	e.d.r.[e]	0.13	4.5	0.07	0.6

[a] From ref. (d) of Table 1 except where noted otherwise.

[b] ΔH_s (H-bonding) $= \Delta H_s(\text{HX}) - H_s(\text{X}\cdot)_{\text{nonpolar}}$ in the case of the hydrogen halides.

[c] Schiller, P., *Z. Physik* **153**, 1 (1958); $\nu_0 = 530 \times 10^{12}$ sec^{-1}.

[d] Emsley, J. W. and Smith, J. A., *Trans. Farad. Soc.* **57**, 1233 (1961); this might be a barrier to motion of the —NH_2 group only.

[e] From ref. (d) of Table 1.

[f] $\Delta F_{\ddagger}$ refers to 293°K.

energies of activation are about integer multiples (1 or 2) of the hydrogen bond contribution to ΔH_s. In certain cases which can be recognized by inspection of the molecule, only intramolecular hydroxyl group rotation can be considered. Then $\Delta E_\ddagger$ is of the order of the appropriate barrier to internal rotation of the hydroxyl group. The free energies of activation of rotational diffusion in alcohols are not easily correlated by any known scheme. Hence the absolute value of the relaxation time is not readily predicted. No data are available on the rotational diffusion in metal soap or similar crystals.

Conclusion

The present analysis leads to the conclusion that the generalized rotational diffusion rate and activation energy in molecular crystals depend in crude approximation just on the packing density and a generalized temperature. Generalization requires the heat of sublimation (as measure of the lattice energy), the appropriate moment of inertia of the molecule or molecule segment, and the number of external degrees of freedom per molecule. Aside from the differentiation between rigid and flexible molecules, no large specific effects of molecular structure and of crystal structure have been noted as yet. Such specificity effects will undoubtedly become prominent as soon as far more reliable data become available than are available now.

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