Journal of Molecular Liquids, 26 (1983) 229–247
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE MOLECULAR DYNAMICS OF CAMPHOR: AN ESSAY ON THE ROLE OF CORRELATION BETWEEN ROTATION AND TRANSLATION

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(Received 23 May 1983)

ABSTRACT

The available literature on the molecular dynamics of camphor is reviewed with the purpose of explaining some observable racemic modifications in terms of the cross-correlation matrix $<\underline{v}(t)\underline{J}^T(0)>_m$. Here $\underline{v}$ is the molecular centre of mass velocity and $\underline{J}$ the molecular angular momentum in a moving frame of reference defined by the principal moments of inertia. For example, the observable pseudo-eutectic in the solid-state λ transition temperatures for various mixtures of R in S camphor may be used to provide direct information on the nature of $<\underline{v}(t)\underline{J}^T(0)>_m$ through the intermediacy of Grigolini's reduced model theory or using developments in computer simulation.

INTRODUCTION

It has become possible recently [1] to quantify the statistical correlation between molecular rotation and translation using computer simulation. This allows us to explain well known phenomena such as the melting point racemic modification in terms of cross-correlation functions exemplified by $<\underline{v}(t)\underline{J}(o)^T>_m$, where $\underline{v}$ is a molecule's centre of mass translational velocity at an instant t and $\underline{J}$ its own

0167-7322/83/$03.00

angular momentum at t = o [2,3]. $\langle\ \rangle_m$ denotes a running time average in the molecule's moving, principal moment of inertia frame. Both $\underline{v}$ and $\underline{J}$ are defined in this moving frame for the purposes of making this cross-correlation. The analytical theory of molecular diffusion is then faced with the problem of describing, self-consistently, autocorrelation functions in the usual laboratory frame, such as $\langle\underline{v}(t).\underline{v}(o)\rangle$ or $\langle\underline{J}(t).\underline{J}(o)\rangle$, together with $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$ in the moving frame [4].

Correlations such as $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$ are particularly important when dealing with the molecular dynamics of optically active molecules. Some elements of the matrix $\underline{v}(t)\underline{J}^T(o)\rangle_m$ are antisymmetric in their time dependence for the R and S enantiomers of a chiral molecule. These same elemental cross-correlation functions vanish for all t in the racemic mixture. These results were obtained [2,3] by computer simulation, and indicate for the first time that there are intrinsic, stereo-specific, differences between the molecular dynamics of two enantiomers. The differences are detectible only in a moving (molecular) frame of reference [1], but modify the physical properties of a racemic mixture with respect to those of either enantiomer in the laboratory frame. This racemic modification has been known experimentally since Pasteur's work of 1848 on the crystalline tartaric acids.

In some cases the racemic modification of the melting point is bigger than that of the boiling point, and sometimes considerably so. In other cases there seems to be no modification of the melting point at all. Some examples of melting and boiling point modifications are listed in table 1.

It is clear from table 1 that the racemic modification of the melting point varies from a hitherto undetected small fraction of a degree (e.g. in camphor or trans 1,2 cyclopropane dicarboxylic acid) to ∿40K in the canadines. Probably, examples could be found in the literature of an even bigger difference in melting point than in the representative list of table 1. In each case there is no difference between the R and S enantiomers except in the basic, stereochemical, isomeric property responsible for the dextro- or laevo-rotary effect on

TABLE 1. RACEMIC MODIFICATIONS OF THE MELTING AND BOILING POINTS FOR SOME OPTICALLY ACTIVE MOLECULAR LIQUIDS (K)

Liquid	Melting Points		Boiling Points	
	Enantiomers	Racemic Mixture	Enantiomers	Racemic Mixture
Lactic Acid	326	291	376 (2mm)	395 (16mm)
Canadine	404 ± 1	447	-	-
2 chloro butane	133	142	341	341
Camphor	453	453	477 (sub.)	477 (sub.)
trans 1,2 cyclopropane dicarboxylic acid	448	448	-	483 (30mm)
Camphoric Acid	461	481	495	496

polarised radiation. In some cases (e.g. the lactic acids) the racemic modification lowers the melting point (negative effect) and in other cases, such as that of the canadines the reverse is true. In table 1 we list three representative carboxylic acids where the modification is negative, zero and positive.

The molecular dynamics of two enantiomers are identical to lab. frame probes such as dielectric relaxation, far infra-red, infra-red, Raman, Rayleigh, Brillouin, N.M.R., ultrasound, etc. band shape analyses, inelastic neutron scattering, transient analysis of induced birefringence etc. [4] provided the probe radiation is unpolarised. Fourier transformation of data such as these produces time correlation functions which can be analysed with the phenomenological theory of molecular diffusion, which must, of necessity, describe the identical lab. frame data for the stereochemically different R and S enantiomers in exactly the same way. Our computer simulations have shown that this anomaly can only be resolved by taking into analytical consideration cross-correlations exemplified by the basically important moving frame matrix $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$.

The moving frame allows us to take into account the stereochemical difference between R and S enantiomer (the one being the other's exact mirror image). It follows from basic stereo-symmetric arguments [1] that some elements of $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$ *must* be antisymmetric in time dependence in R and S while others *must* be identical. The symmetry arguments show that the *diagonal* elements of this matrix always vanish in the absence of a symmetry breaking, physical variable applied externally.

These arguments were confirmed by our computer simulations of several systems of different molecular symmetry [5]. Among these were the bromochlorofluoromethanes and trans 1,2 dimethylcyclopropanes, chiral molecules in different symmetry groups. In both cases some elements of $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$ were distinctly and accurately antisymmetric and others identical in their time dependence. The anti-symmetric elements vanished in the racemic mixture and the others did not, within our noise uncertainty. These properties are of interest in themselves but of importance to experimentalists is the effect that moving frame cross-correlations have *in the frame of the observer* - the static laboratory frame.

The moving frame matrix $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$ must, from the basic equations of motion, have an indirect effect on the lab. frame a.c.f.'s of interest to spectroscopists, such as $\langle\underline{J}(t).\underline{J}(o)\rangle$ and $\langle\underline{v}(t).\underline{v}(o)\rangle$. This is simply because all three types of correlation function are generated from the same hamiltonian driven by the same Liouville equation. The lab. frame $\langle\underline{J}(t).\underline{J}(o)\rangle$ is therefore *not* independent of the lab. frame $\langle\underline{v}(t).\underline{v}(o)\rangle$, the link being the *moving* frame $\langle\underline{v}(t)\underline{J}^T(o)\rangle_m$, which is, of course, *non-zero* for $t > o$. *This is true for all molecular symmetries.* Unfortunately, the history of the phenomenological theory [6] has been such that equations have been written for $\langle\underline{J}(t).\underline{J}(o)\rangle$ in isolation of $\langle\underline{v}(t).\underline{v}(o)\rangle$ or vice-versa. Some authors have recognised [4] that that these two a.c.f.'s are not independent, beginning with the work of Condiff and Dahler in 1966. Several phenomenological theories of molecular "roto translation" are now available [4], but all are hampered by the fact that $\langle v(t)\underline{J}^T(o)\rangle_m$ of the *laboratory* frame *vanishes for all t* by symmetry. Indications have been obtained experimentally of the basic importance of so-called "rotation-translation coupling". Computer simulation now allows us to clarify matters considerably using the moving frame. This was first pointed out by Ryckaert et al. in 1981 for linear molecules [1].

In order to obtain *experimental* information on $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ we have available at least two general methods.

i) Obtain data on the lab. frame a.c.f.'s $\langle \underline{J}(t).\underline{J}(o)\rangle$ and $\langle \underline{v}(t).\underline{v}(o)\rangle$ using probes which isolate these a.c.f.'s separately, e.g. N.M.R. spin-lattice relaxation and tracer diffusion. Note carefully, however, that the theory behind the data reduction *must at all stages* take cognizance of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ in an entirely *self-consistent* manner from the basic equations of motion.

ii) Compare the dynamical (non-equilibrium) and thermodynamical (equilibrium) properties of an enantiomer with its racemic mixture or mixture in any proportion with its stereochemical mirror image.

In this article we are concerned exclusively with method ii).

The importance of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ is revealed through method ii) in the region between the melting points of an enantiomer and its racemic mixture. For example, if we choose from table 1 relatively simple molecules, the 2 chlorobutanes, and mix in equimolar proportion the R and S enantiomers between 133K and 142K the result will be a *solid* racemic mixture, with consequent pronounced effects on the various available spectral probes of the 2 chlorobutane molecular diffusion. The racemic mixture formed in this way is likely to be a glass [7], and therefore would support some residual molecular diffusion. One of our recent computer simulations [8] has shown that $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ exists in the glassy state of ethyl chloride, in magnitude is relatively *more* important than in the liquid state, and is distinctly different in its elemental time dependence.

We recall, now, that $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ is *different* (antisymmetric) for R and S enantiomers but $<\underline{J}(t).\underline{J}(o)>$ and $<\underline{v}(t).\underline{v}(o)>$ of the laboratory frame are identical. In other words the known stereochemical differences between the two separated enantiomers manifest themselves in a dynamical context only in $<\underline{v}(t)\underline{J}^T(o)>_m$. When the two 2 chlorobutane enantiomers are mixed, all three correlation functions change as described. The only possible explanation for this must involve $<\underline{v}(t)\underline{J}^T(o)>_m$ through some self-consistent phenomenological approach. One such approach has been developed recently by Grigolini and Marchesoni using continued fraction and adiabatic elimination procedures based on Mori theory [9] and experimental work is in progress on the 2 chlorobutanes in the recquisite temperature range between 133K and 142K [10].

When there is no measurable racemic modification, as is almost always the case for the boiling point, and sometimes the case for the melting point, then the stereo specific antisymmetry in $<\underline{v}(t)\underline{J}^T(o)>_m$ is not carried through into the laboratory frame, and the same type of self-consistent analytical approach must also explain this. Obviously this is not possible without a detailed consideration of the molecular structure itself, upon which the racemic modification is implicitly dependent. It follows, lastly, that the modification itself should be regarded as a non-equilibrium phenomenon, needing for its explanation non-linear diffusion equations of the Kramers type - as used by Grigolini et al [9] in a variety of contexts. These methods are capable, potentially, of describing phase changes using the stochastic equations of non-equilibrium statistical mechanics. The numerical technique of computer simulation should also be capable of describing the racemic modification, exemplified by the 2 chlorobutanes, given a realistic model of the pair potential [11].

Stereodynamics of Camphor - the Pseudo-Eutectic

There is available a book [12] devoted entirely to the structure and chemistry of R-(+) 1,7,7 trimethyl bicyclo [2.2.1] heptan-2-one, mentioned by Pasteur [13] in his communication of 1848 as the optically active, natural product camphor. The racemic modification is known as 2 bornanone, (±) or dl camphor. S-(-)

camphor has been synthesized and also investigated in great detail. Many hundreds of papers are available now on the enantiomers and racemic mixture of camphor, including many on its molecular dynamics. The dynamics of the solid-state phase transition in camphor have been the subject of a detailed investigation by Anderson et al [14] using N.M.R. spin-lattice relaxation times. These authors point out that R camphor is one of the most polymorphic of solids. At least eleven separate solid phases have been identified [15] in the region below 50,000 kg/cm^2. At atmospheric pressure table 1 shows that the melting points of R, S and (RS) camphor are indistinguishable. There is a phase change however below room temperature which behaves in a strikingly different way for various solid solutions of R camphor in S camphor [14]. A "Pseudo-eutectic" is observed in the curve of transition temperature vs. concentration both by measurements of the specific heat (C_p) [16] and N.M.R. spin-lattice relaxation time (T_1).

In pure R (or pure S) camphor there is a sharp but continuous (second-order) phase transition at 238K [17] above which molecular motion becomes observable by techniques such as dielectric relaxation [17-26]. In racemic camphor (50 : 50, R : S) the equivalent transition temperature is 208K [17]. Some molecular motion is observable in this case above and below the phase change to liquid nitrogen temperature. However, in a 0.75 mole fraction solution of R camphor in S camphor (or vice-versa) the transition temperature falls to well below 200K [14,16]. At these concentrations there are two singularities in the curve of transition temperature vs. isomeric composition as illustrated by Anderson et al [14]. This is the "pseudoeutectic" first reported by Schäfer et al [16 X-ray powder diffraction data of 0.5, 0.75 and 1.00 mole fraction R camphor in S camphor indicate that the three structures are apparently the same at room temperature in the so-called "rotator" phases, but are all different at 77K. This implies the existence of three distinctly different crystal habits at this temperature for the three concentrations [14].

The camphor pseudo-eutectic has never been explained clearly, and

Anderson et al [14] suppose that "some kind of specific short-range interaction that varies with isomer composition seems necessary to explain the pseudo-eutectic". In order to begin to clarify the nature of this interaction we refer to the projections of the principal cartesian coordinates of an eleven site representation of R camphor in fig. (1). The axes of these figures define the directions of the principal moments of inertia. (Despite the great amount of literature available for R camphor its bond lengths seem to be unknown, and in order to construct these figures we have idealised the structure a little by taking each C - C bond length as 1.53Å). It seems clear from a study of these projections, where the molecular centre of mass is at the origin in each case, that R camphor is an offset rotor in all its various condensed phases, i.e. is unable to rotate without causing some translational movement of its neighbours and therefore of its own centre of mass. The S enantiomer can be obtained from figs. (1) (a) to (c) by some self-consistent reflection - for example through the xy plane (table 2), and clearly, the rototranslational process in mixtures of R and S enantiomers is different from that in the R or S cases taken separately. If we now put in the CH_3- moieties at sites 7,8 and 1 of these figures, and allow these to rotate [14] with respect to the ring structure we obtain some idea of how complicated a process the overall molecular diffusion in solid or liquid camphor must be. (Recall that freely rotating R camphor, for example in the infinitely dilute gas, must obey the Euler equations of (classical) rotational motion, which constrain the principal moment of inertia frame to rotate about the centre of mass. The overall movement is therefore this superimposed on the translation of the centre of mass.)

The polymorphic nature of solid camphor [15] (R, S and solutions) must therefore be a consequence of the thermal energy available for rototranslation at a given external pressure. A single-molecule cross-correlation matrix such

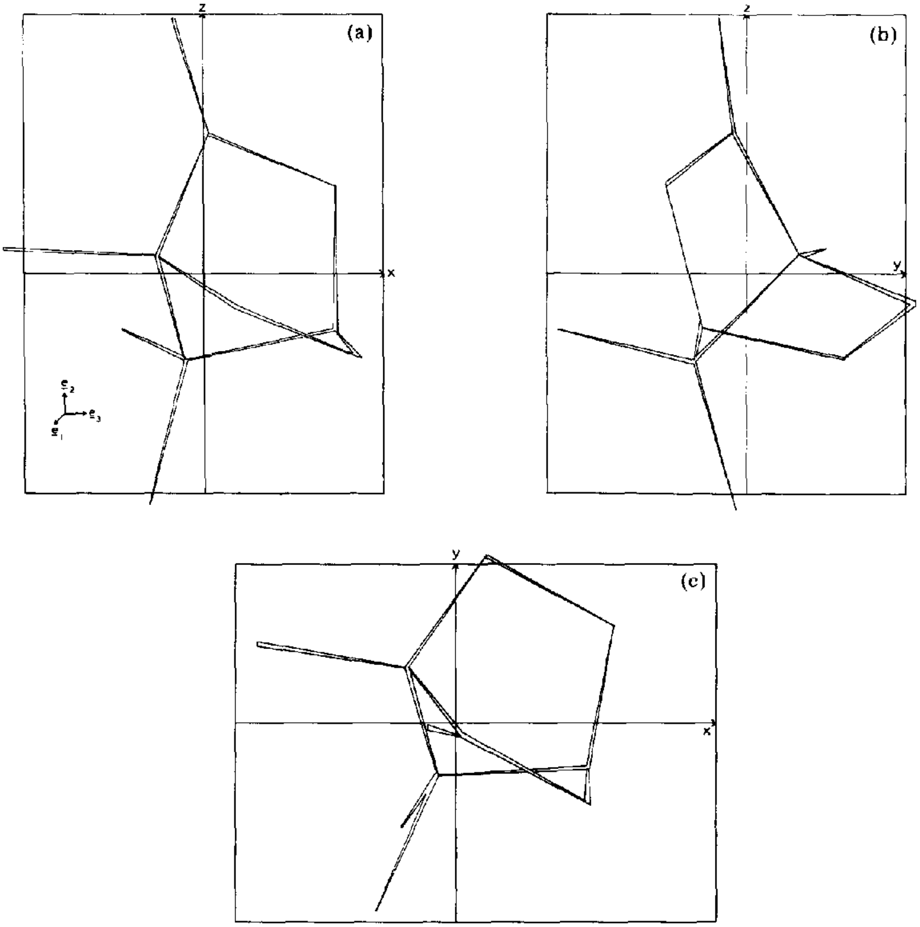

Figure. (a) Projection of an 11 site (R)-camphor skeleton onto the xz plane of the principal moment of inertia axes x and z. These axes intersect at the molecular centre of mass.

(b) yz projection.

(c) xy projection.

as $<\underline{v}(t)J^T(o)>_m$ must therefore have different characteristics for each of the eleven or so known solid phases of camphor observable by the application of external, hydrostatic pressure.

Table 2. PRINCIPAL CARTESIAN COORDINATES (Å UNITS) R-(+)- AND S-(-) CAMPHOR, ELEVEN SITE MODEL*

x($\underline{e}_3$)	y($\underline{e}_1$)	R-(+) z($\underline{e}_2$)	S-(-) z($\underline{e}_2$)	Moiety (site)
-1.98	0.79	0.25	-0.25	CH_3 (1)
-0.48	0.53	0.20	-0.20	C (2)
0.31	1.67	-0.31	0.31	CH_2 (3)
0.05	-0.12	1.41	-1.41	C (4)
-0.28	-0.03	2.57	-2.57	O (5)
-0.19	-0.53	-0.86	0.86	C (6)
-0.55	-0.11	-2.29	2.29	CH_3 (7)
-0.80	-1.90	-0.56	0.56	CH_3 (8)
1.58	0.98	-0.84	-0.84	CH_2 (9)
1.32	-0.81	0.88	-0.88	CH_2 (10)
1.31	-0.44	-0.55	0.55	CH (11)

*$\underline{e}_3$, $\underline{e}_1$ and $\underline{e}_2$ are unit vectors in the axes of the principal moment of inertia frame.

$$Izx = 684.5 \times 10^{-40} gm\ cm^2$$

$$Iyz = 642.1 \times 10^{-40} gm\ cm^2$$

$$Ixy = 493.7 \times 10^{-40} gm\ cm^2$$

The known pseudoeutectic (at 1 bar) is concerned however, with the phase change from the so-called "rotator" phase to the lower temperature phase (the λ transition) Anderson et al [14] observe that the width of the λ transition increases from the pure isomer to the racemic mixture. Above the λ transition temperature range X-ray and N.M.R. data seem to be independent of concentration of R enantiomer in S enantiomer. The broad transition regions displayed by 0.50 (racemic) and 0.625 mole fraction R camphor reflect molecular diffusion which persists far below the λ transition temperature at each concentration. The 0.75 mole fraction solution (at which the ε tectic minimises) also shows unique dynamical behaviour. The λ transitions in 0.875 and 1.000 mole fraction R camphor (the pure enantiomer) are much sharper, but the T_1 (spin-lattice relaxation time) data of Anderson et al. [15] imply that molecular motion exists at frequencies less than 10^4 Hz. Rossiter seems to have corroborated this more recently with dielectric loss measurements in the radio-frequency region, where he reports [26] distinct differences between the enantiomers and racemic mixture (e.g. his fig. (4)). Bandopadhyaya [24] has reported dielectric loss data as a function of temperature at 1, 10 and 100 kHz which indicate a λ phase transition in R camphor at 248K, and at 203K in (RS) (racemic) camphor. These temperatures compare with 238K and 208K reported by Anderson et al [14]. Again Bandopadhyaya observes dielectric relaxation below the λ transition in both enantiomer and racemic mixture. He attributes this to lattice defects in the enantiomer formed during the phase transition, and to the existence of a supercooled, "rotationally disordered" state in the racemic mixture below the λ transition. This interpretation is broadly similar to that of Anderson et al. whose X-ray powder diffraction data imply that below the λ transition both R and S enantiomers occupy definite stereospecific lattices. In mixtures of these enantiomers molecules of the other isomer can be accommodated only by the production of lattice defects, which lower the λ transition temperature. These parent lattices seem to be tetragonal in symmetry. These authors provide a tentative explanation for the pseudo eutectic in terms of secondary lattices caused by the defects.

Goc [28] has reported, using an NMR method, that R camphor shows discernible reorientational motion at all temperatures above 80K, which is "anisotropic". Above the λ transition, according to Goc, the diffusional motion becomes "isotropic"

These results are not, however, corroborated by those reported by Davies using dielectric relaxation. This author observes [21] a *temperature dependence* of the static permittivity in the range 253K to 353K in the so-called "rotator" phase of R camphor. There is also, according to Davies, a temperature variation of the apparent activation energy for reorientation of the R camphor dipole moment in this phase. This is interpreted qualitatively according to a "cooperative phenomenon". Davies [21] reports complete cessation of this dynamic process at 245K, near the λ transition temperature of R camphor. These findings can be reconciled with those of Goc [28], Bandopadhyaya [24] and Anderson et al. [14] only by assuming that the high frequency (MHz range) motion studied by Davies [21] has been shifted to much lower frequencies in R camphor below the λ transition.

Taking an overall view of the available dielectric work on the molecular dynamics of mixtures of R and S camphor there is some fragmentary evidence for the persistence of molecular motion both above and below the λ temperatures of the pseudo-eutectic. There seems to be an inherent contradiction, exemplified in the early interpretation by Davies (21], in referring to a "rotator phase" above the λ temperature of R camphor and at the same time invoking a "cooperative" interpretation of the dielectric data. If a rotator phase is to be defined by the ability of each molecule to "rotate in its own volume" without cross-correlation with the reorientational motions of its neighbours, then by this definition there can be *no* cooperativity, no energy wells and no far infra-red spectrum [4 and refs therein]. In actual fact, fig. (1) demonstrates that the centre of mass in R camphor does not coincide with the centre of the "van der Waals profile". We have already discussed the consequences of this in terms of correlated rotation about and translation of the centre of mass. *If the molecular motion in the "rotator phase" is to be in any sense "cooperative", then the single molecule moving frame matrix* $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ *must exist.* This matrix will be different in this phase (and in all the phases of camphor) for the R and S stereo-isomers and their mixtures in any proportion. Therefore the correlation matrix $<\underline{v}(t)\underline{J}^T(o)>_m$ must alos show a pseudo-eutectic for the λ transition.

We will attempt to sketch out the elements of $<\underline{v}(t)\underline{J}^T(o)>_m$ using computer simulation, but it is probably beyond the present frontiers of the art to reproduce the pseudo-eutectic with this numerical technique. The non-linear, non-equilibrium statistical mechanics [9] of Grigolini and co-workers might be able to go further than the simulation in this respect, although the remarkable (and early) work of Brot et al. [29] shows what can be done with machine simulations of disordered molecular solids when carefully controlled.

There have been numerous studies of the effect of hydrostatic pressure on solid-state camphor. Again the most detailed work is that of Anderson et al. [30] using NMR spin-lattice relaxation up to 680 bar. This work covers three of the eleven solid state phases of camphor discovered by Bridgman [15] using hydrostatic pressure. The T_1 data of Anderson et al. [30] indicate that hydrostatic pressure up to 680 bar produces no measurable change in the molecular dynamics below the λ transition (which shifts upwards in temperature from 238K to 252K with applied pressure) but does so above. The changes of T_1 with pressure in racemic camphor at the temperatures below the λ point provides additional evidence that this state of camphor is metastable. There is an irreversible change in T_1 with pressure annealing produced by a decrease in molecular mobility. The spin-lattice relaxation times tend towards those in pure R camphor upon application of pressure, and this is explained by Anderson et al [30] in terms of a decrease in the number of lattice defects produced by pressure treatment. The ratio of measured volume of activation (14.5 ml mole^{-1}) to molar volume (152 ml mole^{-1}) for the "rotator" phase of camphor is approximately the same as that typical of molecular liquids, but much lower than that typical of metallic solids. The organic solids therefore require much greater volume to begin their diffusion.

Klimowski et al [31] have confirmed the observation by Anderson et al [30] of a shift with pressure of the λ transition temperature. Ferri et al [32] and Wilkinson et al. [33] have studied solutions of R camphor in n hexane by Raman spectroscopy to pressure of up to 23 kbar in the range 77K to 350K. Gabrysh et al. [34] have discussed the pressure induced transitions in R camphor via the Eyring model. Spin-lattice relaxation times have also been produced in racemic camphor by Beierbeck et al., [35], Colebrook et al., Grandjean et al. [36] and Moskalev et al. [37].

It seems clear that the molecular dynamics of the λ pseudo eutectic in mixtures of R and S camphor depend on the specific stereosymmetry of the enantiomers themselves. From the voluminous but incoherent and fragmentary literature on the subject we can derive the following conclusions in the light of our discovery by machine simulation of the stereospecific properties of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ for C_1 (chiral) symmetry, and in general for all symmetries.

i) The so-called "rotator" phase of the camphors is not one where the molecules rotate without correlated centre of mass translation. In the phenomenological theory of molecular diffusion the λ eutectic cannot be explained without a detailed and specific consideration of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ in the correct moving frame of reference. This is simply because the traditional theory ignores centre of mass translation in the assumed "rotator" phase and is thereby obliged to describe the diffusional process of R and S camphor in precisely the same way. This is clear from the fact that techniques such as NMR spin-lattice relaxation or dielectric relaxation cannot distinguish between samples of pure R and pure S camphor, although their molecules are physically different.

ii) Many sources in the literature [17-21, 24, 28, 36, 38-40] describe the diffusional process in R (or S) camphor above the λ transition as isotropic: meaning, for example, that the Cole-Cole plot is semicircular and describable phenomenologically by the well known Debye relaxation time (τ_D). This is precisely the same for R and S camphor, and apparently similar for racemic camphor. In this context τ_D has virtually no physical meaning because it is representative of a very simple, purely rotational theory [6] that cannot distinguish between two enantiomers (or any mixture thereof) in a dynamical context. It is therefore also meaningless to expect the dielectric relaxation time to be three times that of the N.M.R. relaxation time in the so called "rotator" phase. Anderson et al. [14] find that this is not, in fact, the case.

iii) At and below the λ temperatures the dynamical properties of enantiomeric and racemic camphor become wholly different [14]. The non-equilibrium theory of molecular dynamics cannot describe this without $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$. In other words, overall molecular reorientation, or partial methyl group reorientation, is always correlated with molecular centre of mass movement even at the lowest temperatures. (The phenomenon of "phonon modes" or "lattice-vibration" in the far infra-red [4] shows that there is always some residual centre of mass motion in a molecular solid. The sharply defined frequencies of these phonon modes are "smeared out" by lattice defects or increasing temperature.)

THE FAR INFRA-RED PROPERTIES OF CAMPHOR

Pardoe [41] has reported a far infra-red spectrum of 37% w/w R camphor in liquid cyclohexane which shows clearly that the molecule has a well defined absorption band in the region below about 100 cm^{-1}. The origin of this absorption is discussed extensively throughout ref. [4] and is the high frequency adjunct of the dielectric loss reported by Crossley et al. [23] in solutions of camphor. There seems to be no published far infra-red spectrum available of R, S, or racemic camphor in the solid state. Studies in this region should provide valuable complementary evidence for the properties described by Anderson et al. [14, 30]. The far infra-red spectra provide a means of investigating the sub-picosecond scale reorientational motion of the molecular dipole moment through the correlation function of the first time derivative of this dipole moment - the so-called rotational velocity correlation function (see ref. [4] chapter 1). The theory behind the far infra-red absorption should be based self-consistently upon the three auto-correlation functions $\langle \underline{J}(t).\underline{J}(o)\rangle$, $\langle \underline{v}(t).\underline{v}(o)\rangle$ and $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ for all dipolar molecules in the appropriate condensed phases, irrespective of group symmetry or whether these molecules are chiral or not. Evans et al. [42] have reported recently the first direct experimental evidence for the existence of $\langle \underline{v}(t)\underline{J}^T(o)\rangle_m$ by simply comparing the far infra-red spectra of some pure liquid enantiomers with their racemic mixtures at the same temperature and pressure. In the liquids investigated by Evans et al. [42] these spectral differences were small but in the 133 - 142K range of 2 chloro butane, for example they would be pronounced [7], because we would be comparing a glass (the racemic mixture) with a liquid (the pure enantiomer).

Similarly, the whole of the dielectric and NMR data on R/S camphor solutions in the region of the pseudo-eutectic would be complemented by similar measurements in the far infra-red. It is clear from the work of Rossiter [26], for example, that pronounced differences between enantiomer and racemic mixture would be observable in the far infra-red below the λ transition and that these spectra would evidence the pseudo-eutectic. According to Evans et al. [42] measurable spectral differences would persist above the λ transition between enantiomers and racemic mixtures of R and S camphor. It is possible that these would continue into the liquid state, the far infra-red method being the most sensitive technique available to detect these differences.

A further interesting aspect of these investigations would be the construction, in the temperature range of the pseudo eutectic and elsewhere, of the complete zero-THz profile [7] of the molecular diffusion process. Evans et al. [7, 43, 44] have recently emphasized the importance of taking this complete multi-decade range of frequency into consideration as a basic prerequisite for the realistic interpretation of dielectric loss in terms of molecular motion. Using this line of reasoning they discovered and characterised the γ loss process in the far infra-red of supercooled liquids and glasses [7, 43, 44], thus supplementing the α and β loss features known prior to their investigation to characterise molecular motion in these materials at much lower frequencies than those of the far infra-red. The complete molecular dynamical evolution in glasses can therefore span as many as 14 decades of frequency representing molecular motion on the sub-picosecond scale to that of seconds, hours and longer. During this complete interval we are referring specifically to roto-translational molecular dynamics. The (α, β, γ) theorem of Reid and Evans was corroborated recently by Evans [8] using computer simulation of the glassy state of ethyl chloride. The matrix $\langle \underline{v}(t)\underline{J}(o)^T\rangle_m$ exists for $t > o$ in this state, as mentioned earlier in this article, and is therefore likely to be important in the description of the supercooled condition of racemic camphor below the transition temperature.

Related Work on the Molecular Dynamics of Camphor

The molecular dynamics of camphor have been investigated using the electrooptical Kerr effect [45], infra-red band-shape analysis [46], and more specialised techniques such as infra-red/radio-frequency double resonance [47, 48] and fluorscence upon excitation by circularly polarised laser radiation [49]. Mjojo [50] has discussed and developed some statistical mechanical models for thermally propagated orientational transitions in camphor crystals.

ACKNOWLEDGEMENTS

The S.E.R.C. is thanked for continuing financial support, in the form of an Advanced Fellowship.

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