Liquid State Dynamics of CH_2Cl_2

Evaluation of Models

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Absorption data in the range up to THz frequencies for pure liquid CH_2Cl_2 and in isotropic solutions in cholesteryl linoleate are used to evaluate critically some recent modelling of the liquid state N-body problem, and to detect some prescience of cholesteric behaviour in monofringent solutions. Adjustable parameters are avoided as far as is necessary to produce the fundamental theoretical absorption contour. The models used can all be expressed as various early approximants of the Mori continued fraction expansion of the Liouville equation, and therefore describe the absorption data accurately only at low frequencies, or equivalently at long times when the orientational autocorrelation function decays exponentially. In contrast to the confused and often contradictory evaluations drawn from the available literature on Raman, infrared and n.m.r. spectroscopy, together with depolarised Rayleigh wing and incoherent neutron scattering studies on liquid CH_2Cl_2 it is shown that the zero to THz absorption profile discriminates clearly between models such as rotational diffusion, extended rotational diffusion, planar itinerant libration and Brownian motion of coupled dipoles. A scheme is suggested for a self-consistent evaluation of the available data from all sources within the context of the Mori continued fraction. This aims at a satisfactory evaluation of such quantities as the mean square torque, and derivatives, so that some statistical assessment may be made of the potential part of the total N-particle hamiltonian. At present, features of observed spectra are reflected in model correlation times which are often physically meaningless and directly contradictory.

In this paper we aim to demonstrate that : (i) absorption and dispersion data over the whole range of frequencies up to and including the THz region [1] (far infrared) provide a means of discriminating easily between currently popular models of the isotropic fluid state. (ii) The related problem of anisotropic molecular motions in mesophases may be approached more readily by spectroscopic studies on suitably chosen solutes acting as probes.

There are many models from which to choose.[2] Those we consider here may be described in general terms as approximants (*i.e.*, truncations) of the Mori continued fraction expansion of the Liouville equation of motion. In what follows adjustable parameters have been eliminated as far as possible, in order that the underlying theoretical characteristics become visible in their barest form. We aim at a least mean squares minimisation by iteration on parameters only when this seems necessary to define the directions along which further development of a particular model might proceed. The models considered here are listed below in the order in which they succeed in defining satisfactorily the potential energy part of the total hamiltonian of

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the N molecules ($\sim 10^{23}$) being considered. Successive approximants of the Mori continued fraction each define the mean intermolecular potential energy more accurately by incorporating higher derivatives such as the mean square angular velocity, mean square torque, etc. (i) The Langevin equation for the angular Brownian motion of the asymmetric top, developed recently by Morita,[4] and by Lewis, McConnell and Ford.[5] The angular momentum memory is a delta function. (ii) The Chandler binary collision approximation [6,7] for rotation dipoles embedded in the inertial spherical top. This is equivalent to the J-diffusion model as demonstrated by Bliot et al.[8] (iii) An approximant of the Mori continued fraction equivalent to a gaussian orientational memory function. The adjustable variables used before in this model [9] are eliminated here using a simple technique. (iv) Finally we chose a form of the Mori equation of motion [eqn (2) below] to which may be ascribed [10] more than one useful physical meaning in terms of clearly definable dipolar motion and interaction. Due to its heuristic nature we have made use of adjustable parameters with the purpose outlined above.

The motion of CH_2Cl_2 molecules in the pure liquid and in solution is monitored by sweep frequency,[11] microwave klystron [12] and optical interferometric techniques [13] (Martin/Puplett and Michelson). This molecule is chosen for reasons of its intense absorption, especially in the THz range [14] so that induced absorption effects are minimal in comparison. Also, a recent review [15] emphasises the considerable extent to which parallel studies have been carried out by incoherent inelastic neutron scattering and other techniques. Models (i) and (ii) have been used for interpretation in this context. In this paper we use it also as a convenient probe into the environment provided by macroscopically isotropic (monorefringent) solutions in cholesteryl linoleate. In this condition some prescience of the cholesteric condition is detectable on the molecular scale, as evidenced by intensity effects, especially at the higher frequencies.

GENERAL THEORY AND RELATION TO MODELS

Consider a dynamical array of N interacting molecules ($N \approx 10^{23}$). Let $A(t)$ denote an $n \times 1$ column vector of n linearly independent variables $A_j(t)$, which each obeys the Liouville equation of motion:

$$\dot{A}_j(t) = [A_j(t), H] \equiv i\mathscr{L}A_j(t) \tag{1}$$

where H is the system hamiltonian and $\mathscr{L}$ the Liouville operator. Our basic equation (model–independent) is then the Mori relation:[3]

$$\dot{A}(t) = i\Omega_A A(t) - \int_0^t d\tau\, \phi_A(t-\tau)A(\tau) + F_A(t) \tag{2}$$

where Ω_A is a resonance frequency operator and the matrix kernel $\phi_A(t)$ is a memory function (or effective Liouvillian). The random force or torque $F_A(t)$ is Mori-propagated from $A(0)$ and is a generalised stochastic variable. $F_A(0)$ is the component of $\dot{A}(0)$ orthogonal to $A(0)$, whereas $F_A(t)$ is propagated from $F_A(0)$ by the special propagator $\exp(iQ\mathscr{L}t)$, where Q is a projection operator of an arbitrary vector G into the orthogonal complement of the subspace spanned by $A(0)$ in Liouville space.

A physical realisation [16] of eqn (2) occurs in the rotational Brownian motion of a spherical top, or equivalently of a disc about a fixed axis through its centre perpendicular to its plane.[17] Eqn (2) then becomes:

$$\frac{DJ}{Dt} + \int_0^t d\tau\, \phi_J(t-\tau)J(\tau) = F_J(t) \tag{3}$$

where J is the angular momentum of the rotator, the operator Ω_J is null, $\phi_J(t)$ is a time-dependent friction tensor, and $F_J(t)$ is a random driving torque of finite correlation time with zero mean. D/Dt denotes the rate of change of the components of each vector referred to principal body-axes. In the case of the disc [model (iv)] there is only one component, but for the asymmetric top cross-terms appear in eqn (3), rendering it analytically intractable except in the case of our model (i), which is now briefly discussed.

LANGEVIN EQUATION, ASYMMETRIC TOP

This has been solved recently [4, 5] and corresponds to a friction tensor which has delta function elements in time, with null resonance operator in eqn (2). Physically the process considered is one of rotational diffusion of the asymmetric top, *i.e.*, one of infinitesimally small reorientations taking place infinitely rapidly. (Classical Debye theory describes this for the dipole embedded in the inertia-less spherical top). The solutions, with inertial effects, for the asymmetric top are given in full by Morita [4] and by McConnell *et al.*,[5] and involve the friction coefficients β_x, β_y and β_z along the inertial principal axes x, y, z. These are estimated in this paper by the ellipsoidal shape factor analysis of Budo *et al.*[18] applied to CH_2Cl_2 ($I_x = 26.3 \times 10^{-40}$, $I_y = 278 \times 10^{-40}$, $I_z = 253 \times 10^{-40}$ g cm^2). There are no parameters adjusted for best fit to the observed spectrum other than these, which are fixed by observation of the loss frequency maximum at 110 GHz.

CHANDLER BINARY COLLISION THEORY

Consider the solution of eqn (3) for the spherical top with the assumption that the memory kernel obeys an eqn of the form:

$$\phi(t) = \phi_{FR}(0) \exp(-t/\tau_\omega) \tag{4}$$

where τ_ω is a characteristic time of the dynamical system. Here $\phi_{FR}(0)$ is the memory kernel for a gaussian ensemble of non-interacting rotors. The resulting spectrum [the Fourier transform of $\langle J(t)J(0)\rangle \equiv \langle \omega(t) \cdot \omega(0)\rangle$ where ω is the angular velocity about the dipole axis of the spherical top] is analytically identical with that from the Gordon J-diffusion model,[7] and the Chandler collision operator theory [6] where binary events only are considered. The physical meaning of these systems are clear-cut and both correspond to first-order approximants of the Mori continued fraction.

The analytical correspondence was first demonstrated by Bliot *et al.*,[8] and the first application of this approximant to the far infrared spectra of liquids was attempted by van der Elsken *et al.*[19] who developed it further with the introduction of more adjustable parameters. Cukier *et al.*[20] have completed a statistical generalisation. Here we restrict ourselves to the original concept represented by eqn (4) where τ_ω is the mean angular velocity relaxation rate. This is adjustable for best fit or estimable roughly from kinetic theory. We use this rather out-dated model to emphasize the most characteristic and discriminating feature of the zero to THz absorption in liquid CH_2Cl_2, its large shift in power absorption peak to a higher frequency with respect to the root mean square angular velocity:

$$\langle \omega^2 \rangle^{\frac{1}{2}} = \left(kT \left[\frac{1}{I_x} + \frac{1}{I_y} \right] \right)^{\frac{1}{2}} = 21.5 \text{ cm}^{-1}.$$

Eqn (4) implies that this shift cannot be followed by J-diffusion theory, essentially because of the underlying Poisson statistics. Also interactions are elastic, so that the r.m.s. torque is not defined, since the torque is infinite at collision.

ORIENTATIONAL MORI SERIES

Consider eqn (2) where A contains one element $\boldsymbol{u}$, the dipole unit vector. The resonance frequency operator $\Omega_{\boldsymbol{u}}$ is null and $\phi_{\boldsymbol{u}}(t-\tau)$ is an orientational memory function. The vector $\boldsymbol{u}$ is embedded in the asymmetric top reorienting in space. A tractable expression for $C_{\boldsymbol{u}}(t) = \langle \boldsymbol{u}(t) \cdot \boldsymbol{u}(0) \rangle$, the orientational autocorrelation function, may be obtained by methods (fully described elsewhere)[9] which involve truncating the Mori continued fraction at what we term second order, a stratagem intended to treat the effect of interactions in the molecular ensemble in terms of the mean square torque $[\phi_{\boldsymbol{u}}^{(1)}(0)]$ factor, and a characteristic frequency γ which was considered originally as an adjustable parameter. This is the inverse of the characteristic relaxation time of the second memory function:

$$\phi_{\boldsymbol{u}}^{(1)}(t) = \phi_{\boldsymbol{u}}^{(1)}(0) \, e^{-\gamma t}. \tag{5}$$

Recently Halley et al.[21] have demonstrated in another context that eqn (5) corresponds to a gaussian memory $\phi_{\boldsymbol{u}}(t)$, and that for consistency there must exist the following relation between γ and $\phi_{\boldsymbol{u}}^{(1)}(0)$:

$$\gamma = \left[\frac{\pi}{2} \phi_{\boldsymbol{u}}^{(1)}(0) \right]^{\frac{1}{2}}. \tag{6}$$

The remaining parameter $\phi_{\boldsymbol{u}}^{(1)}(0)$ may be estimated by differentiating the model absorption coefficient with respect to ω, whereupon $\phi_{\boldsymbol{u}}^{(1)}(0)$ can be obtained from the measured peak frequency of the far infrared, ω_m. A physical meaning may be given to this formalism insofar as it represents a rigorous and tractable approximation to the equation of motion of $\boldsymbol{u}$:

$$\dot{\boldsymbol{u}} = i\mathscr{L}\boldsymbol{u}(t). \tag{7}$$

This is recovered by taking the orientational continued fraction to infinity, convergence being discussed by Tokuyama and Mori.[22] Finally, we mention that it is possible to take the next approximant:

$$\phi_{\boldsymbol{u}}^{(2)}(t) = \phi_{\boldsymbol{u}}^{(2)}(0) \exp \left\{ -\left[\frac{\pi}{2} \phi_{\boldsymbol{u}}^{(2)}(0) \right]^{\frac{1}{2}} t \right\} \tag{8}$$

and estimate both $\phi_{\boldsymbol{u}}^{(2)}(0)$ and $\phi_{\boldsymbol{u}}^{(1)}(0)$ without recourse to least mean squares iteration $[\phi_{\boldsymbol{u}}^{(0)}(0)$ is known already as $\langle \omega^2 \rangle]$. We make use of the relation between power absorption $\alpha(\omega)$ and dielectric loss $[\varepsilon''(\omega)]$:

$$\alpha(\omega) = \omega\varepsilon''(\omega)/n(\omega)c. \tag{9}$$

Here $n(\omega)$ is the refractive index. Since $\varepsilon''(\omega)$ peaks at a much lower frequency than $\alpha(\omega)$, differentiation of each with respect to frequency yields two simultaneous equations for $\phi_{\boldsymbol{u}}^{(2)}(0)$ and $\phi_{\boldsymbol{u}}^{(1)}(0)$ within the analytical framework of eqn (2) and (8).

PLANAR ITINERANT OSCILLATOR AND DIPOLE–DIPOLE INTERACTION

Consider fig. 1 and 2 defining the angles θ and ψ. Fig. 1 described the geometry of the planar itinerant librator model of stochastic angular motion (described fully elsewhere)[10] in a form in which there is no friction (β_2) between the inner disc and the surrounding ring. Here the disc is drawn out by the planar angular motion of a dipole embedded in the asymmetric top and bound harmonically at a frequency ω_0 to a rigid cage of nearest neighbours undergoing collective planar reorientation against a hydrodynamic friction β_1. Defining Ω_0 as $(I_2/I_1)\,\omega_0$, where I_1 and I_2 are the moments of inertia respectively of the annulus drawn out by the reorienting rigid

cage and that of the inner ring, the dynamical system evolves according to eqn (2) with:

$$A(t) = \begin{bmatrix} \theta(t) \\ \dot{\psi}(t) \end{bmatrix}; \quad \phi_A = \begin{bmatrix} \beta_2\delta(t)+\omega_0^2 & -\omega_0^2 \\ -\Omega_0^2 & \beta_1\delta(t)+\Omega_0^2 \end{bmatrix}; \quad F_A = \begin{bmatrix} W_2 \\ W_1 \end{bmatrix} \quad (10)$$

and a null resonance operator. Here W_2 and W_1 are Wiener processes.[10] This is a special case of the system developed by Damle et al.[23] for translational itinerant oscillation in space for use with neutrons scattered incoherently from a bath of atoms.
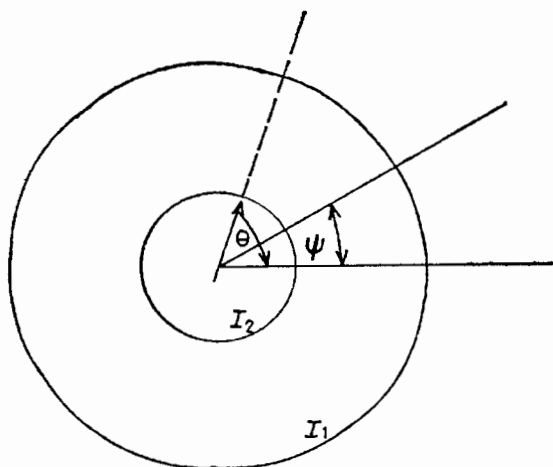

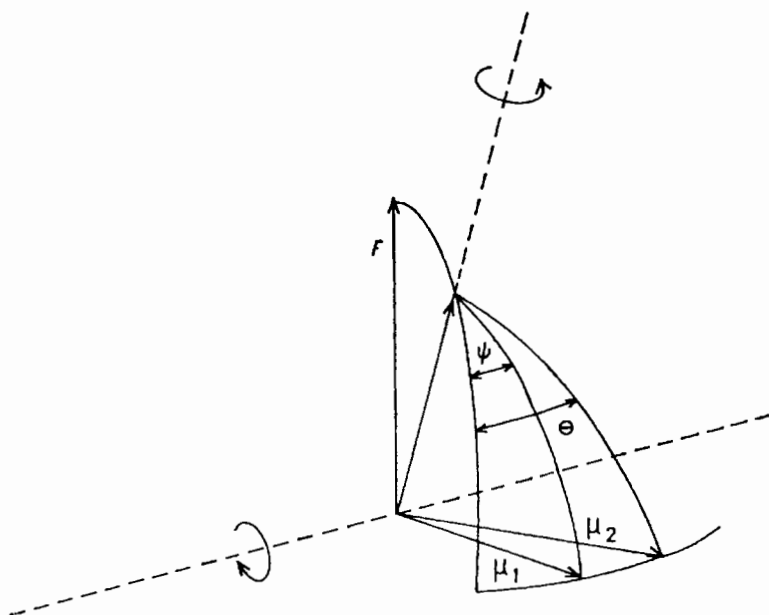FIG. 1 —Schematic diagram of the disc/annulus interpretation of eqn (10).

FIG. 2.—Schematic diagram of the dipole–dipole interpretation of eqn (10).

Fig. 2 describes another physical interpretation of eqn (10) in terms of an interaction pair of dipoles undergoing Brownian motion, under the following conditions.

(a) The potential between the dipoles has the form

$$V(\theta - \psi) = \tfrac{1}{2}I_2\omega_0^2(\theta - \psi)^2. \tag{11}$$

(b) The measuring field is applied *in the same plane* of rotation of the dipoles μ_1 and μ_2, which rotate about an axis through their common centre perpendicular to the plane containing the field.
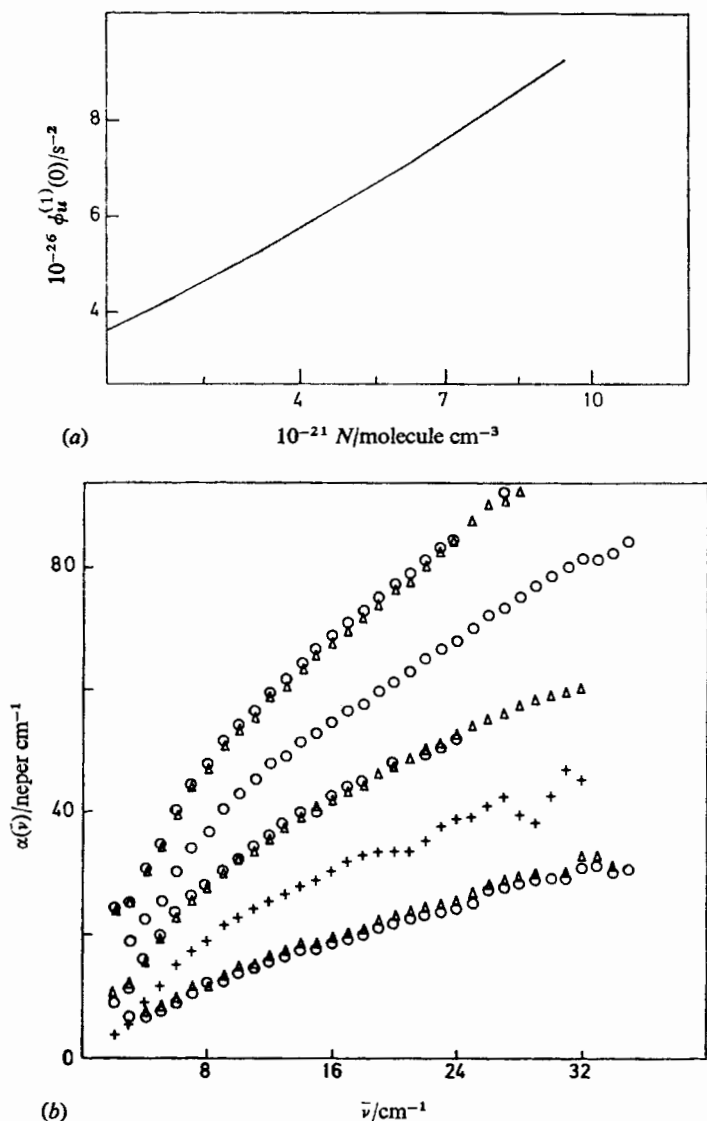

(a) $10^{-21}\,N/\text{molecule cm}^{-3}$

(b) $\bar{\nu}/\text{cm}^{-1}$

FIG. 3.—(a) Variation of $\phi_u^{(1)}(0)$ with molecular number density (N) of CH_2Cl_2 in solution [14] in CCl_4 and decalin. (b) Power absorption coefficients for CH_2Cl_2/CCl_4 solutions (this paper) in the region (2-30 cm^{-1}) bridging the gap between the microwave and far infrared.

In this interpretation I_1 and I_2 are the moments of inertia of the dipoles μ_1 and μ_2 respectively, about a central axis perpendicular to their own plane. β_1 and β_2 are the opposing friction coefficients arising from the surroundings. It is reasonable to suppose in pure CH_2Cl_2 that $\beta_1 = \beta_2$ and $I_1 = I_2$.

Both interpretations are artificially planar as opposed to spatial but the second is capable of considerable development to take account of more realistic potentials than eqn (11) and of space reorientations. Should eqn (11) be accepted for the moment, then ω_0 is a measure of the importance of dipole–dipole coupling. However, ω_0 in the ring/annulus context is a libration frequency purely dynamic in origin. Furthermore, we have, by geometrical considerations, $I_1 > I_2$ in the interpretation of fig. 1, contrary to $I_1 = I_2$ of fig. 2 for a fluid made up solely of CH_2Cl_2 dipoles. Finally, in a dilute solution of CH_2Cl_2 dipoles in an isotropic non-dipolar medium (*e.g.*, CCl_4) dipole–dipole interaction should be considerably weakened, whereas CH_2Cl_2 libration would remain within cages of CCl_4 molecules. To begin to resolve these conceptual constraints we have adopted criteria for comparing these models with the experimental data as described below.

EXPERIMENTAL

The data in the 2-40 cm^{-1} region were gathered with a Martin–Puplett interferometer built by Dr. G. J. Davies and described fully elsewhere.[13b] Reproducibility between successive interferograms was $\pm 2\%$ of the power absorption coefficient over most of the range and the overlap between klystron and Michelson interferometric data [14] at high frequencies is satisfactory (fig. 3).

Sweep frequency and klystron methodology is standard [11, 12] and solutions were made up to within the nearest 0.1 mg by weight/weight methods. Polarising microscope measurements [11, 12] were used to ascertain whether the solutions were macroscopically isotropic.

RESULTS AND DISCUSSION

The sweep frequency and microwave results are tabulated for CH_2Cl_2, and in solution in CCl_4 and cholesteryl linoleate. We emphasize that the latter solution is isotropic (not birefringent). The overlap between the sweep frequency, klystron, polarising and Michelson interferometric data is within the experimental uncertainty estimated for each technique separately (fig. 3). The information contained within the total absorption profile may be classified as follows. (i) The *complete* zero to THz bandshape describes the evolution of the molecular dynamics from an arbitrary $t = 0$. (ii) The integrated absorption intensity per molecule $\left(A_0 = \int_{\text{band}} \alpha(\bar{\nu}) \mathrm{d}\bar{\nu}/N \right)$ is a measure of Kirkwood correlation [24] and the internal field band effect together with interaction induced absorption.[25] (iii) The peaks in $\varepsilon''(\omega)$ and $\alpha(\omega)$ are measures of the extent of molecular interaction embodied in the potential part of the total hamiltonian. In principle these frequencies may be calculated given an analytical form for the intermolecular potential (*e.g.*, by the method of computer simulation using an empirical Lennard-Jones form).[26]

By using the approximation embodied in model 3 above, we can estimate to a first approximation the mean square torque contribution to the mean potential energy and this is plotted against N in fig. 3. Here N is the molecular number density of CH_2Cl_2 in CCl_4 solutions.[14] The corresponding variation of $\alpha(\bar{\nu})$ in the crucial region 2-30 cm^{-1} is shown in the same figure. (These data were obtained at the P.O. Telecommunications Centre by Dr. G. J. Davies using a Martin–Puplett polarising interferometer). There is no variation of A_0 with dilution of CH_2Cl_2 in

CCl_4 or decalin although there is apparently a considerable decrease [14] for mono-refringent solutions in cholesteryl linoleate and cholesteryl oleyl carbonates. Part of the purpose of this paper is to monitor such solutions at microwave frequencies and below.

The dielectric results for the solutions of CH_2Cl_2 in cholesteryl linoleate and carbon tetrachloride (table 1) are remarkable in that the static permittivities for the same concentration of CH_2Cl_2 (1.97×10^{21} molecule cm^{-3}) are widely different. The intensity trend here is opposite to that which is observed in terms of $\alpha(\bar{v})$, the power absorption coefficient, in the far infrared in that the integrated loss per molecule is greater in the cholesteryl linoleate environment.

TABLE 1.—DIELECTRIC PARAMETERS FOR SOLUTIONS OF CH_2Cl_2 IN CCl_4 AND CHOLESTERYL LINOLEATE AT 298 K

solution	ε_0	ε_m''	β	τ/ps	μ/D	n_D
pure CH_2Cl_2	9.08	3.36	0.96	1.45	1.50	1.4241
7.22×10^{21} molecules cm^{-3} of CH_2Cl_2 in cholesteryl linoleate	7.06	2.55	0.91	1.66	1.58	
1.97×10^{21} molecules cm^{-3} in cholesteryl linoleate	3.90	0.65	0.82	2.09	1.87	1.4966
1.97×10^{21} molecules cm^{-3} in CCl_4	3.24	0.50		1.44		

In light of these results the decrease in A_0 at sumillimetre wavelengths seems reasonable, a possible explanation would probably be based on anisotropy of reorientation, governed by inertial effects which show up more obviously with these wavelengths. This effect appears in a macroscopically monorefringent liquid which seems to imply that the loss in A_0 would be large in the cholesteric environment itself. The study of this phase unfortunately requires an impractically low concentration of CH_2Cl_2.

EVALUATION OF MODELS

CRITERIA AND METHODS

At a long enough time after $t = 0$ the molecular interactions and motions in a densely packed N molecule ensemble evolve such that the decay in the correlation functions $\langle A_j(t)A_j(0)\rangle$ is exponential. This is to say that after suffering many interruptions in its initial trajectory, the probability of finding a molecule with, for example, an orientation $\boldsymbol{u}(t)$, given an initial $\boldsymbol{u}(0)$ decays eventually as a gaussian function of time.[16] This is a long time law obeyed by all four models considered here. (It is not obviously obeyed in a dilute gas of rarely interacting quantised rotors, where the autocorrelation function of $\boldsymbol{u}$ is periodic).[27] Therefore we assume in what follows that the low frequency loss curve should be modelled accurately and $\alpha(\omega)$ of the far infrared extrapolated therefrom. Using this method it will be shown (fig. 4) that deviations from the observed high frequency behaviour are often large. (i) The frictions β_x, β_y and β_z are fixed as described already from the loss curve peak.[28] The loss is converted then to power absorption using the model-independent relations:

$$\alpha(\bar{v}) = 2\sqrt{2}\pi\varepsilon''(\bar{v})\bar{v}/\{[\varepsilon'(\bar{v})^2 + \varepsilon''(\bar{v})^2]^{\frac{1}{2}} + \varepsilon'(\bar{v})\}^{\frac{1}{2}}$$

$$\omega = 2\pi\bar{v}c$$

and the far infrared spectrum calculated. (ii) The mean angular velocity relaxation rate τ_ω is adjusted to provide a least mean squares best fit to the whole zero-THz band. Alternatively τ_ω could be fixed from the exponential law (low frequency loss curve) as in model (i). Naturally τ_ω from both methods ought to agree. This is necessarily a rough approximation since we are dealing in reality with the motion of an asymmetric, not spherical, top. (iii) We have used for the sake of comparison a two-variable l.m.s. fit on $\phi_{uu}^{(1)}(0)$ and γ; but the more useful method with no adjustable parameters has been used to fix the theoretical bandshape from a knowledge of the far infrared peak frequency only. (iv) For the planar itinerant librator the friction coefficient between the ring and disc (β_2) has the spectroscopic effect of broadening the far infrared band centred on ω_0. From geometrical considerations it is estimated that $I_1 = 10 I_2$, on average. However, for heuristic reasons we have also allowed I_1 to vary along with β_2 for best fit.

DIPOLE–DIPOLE INTERPRETATION

In this case, in pure CH_2Cl_2, $I_1 = I_2$. $\beta_1 = \beta_2$ is also a reasonable estimate. This eliminates adjustable variables. However, the ratio I_1/I_2, β_1 and β_2 have also been simultaneously iterated for best fit. This is in order to estimate which interpretation of the moment of inertia ratio does better justice to the experimental data.

DEDUCTIONS

In this section the inter-model comparison is used to define the paths along which crabwise progress may be avoided in dealing with the N body interaction problem.

MODEL (i)

The delta function memory is not capable in spectroscopic terms of producing the far infrared Poley absorption [1] of CH_2Cl_2 (fig. 4). In physical terms the mean intermolecular potential energy is inaccurately defined (e.g., its derivative with respect to orientation, the root mean square torque is left undefined). Therefore, the concept of molecular torsional oscillation within wells between such potentials is in this context meaningless. There is room for further progress by using successive approximants of the continued fraction if the problems caused by cross-terms can be overcome analytically.

MODEL (ii)

The J-diffusion model has been discussed in great breadth and depth since its inception and is in a sense the opposite pole of model (i) since the liquid state problem is approached *via* collision interrupted free rotation. The underlying physical process is one where collisions randomise onto a Poisson distribution the angular momentum magnitude and direction. Collisions are elastic, so that again the torque is singular. Van der Elsken et al.[19] have attempted to remedy the failure to shift $\langle\omega^2\rangle^{\frac{1}{2}}$ away from its gas phase value by invoking a statistical distribution of angular momentum which is basically Poisson, but with an additional " pseudo-phonon peak " adjusted arbitrarily for best fit. This seems artificial, especially since the intermolecular potential is still ill-defined (hard-sphere collisions). Curve 2 of fig. 4(a) is one where τ_ω has been optimised for best fit, which is poor. Progress in this type of model may be pursued analytically by using the concept of inelastic collisions, as has been demonstrated by computer simulation of rough spheres [29] and discs [30] using slipping interactions. Satisfactory definition of a time of collision, and thus of a
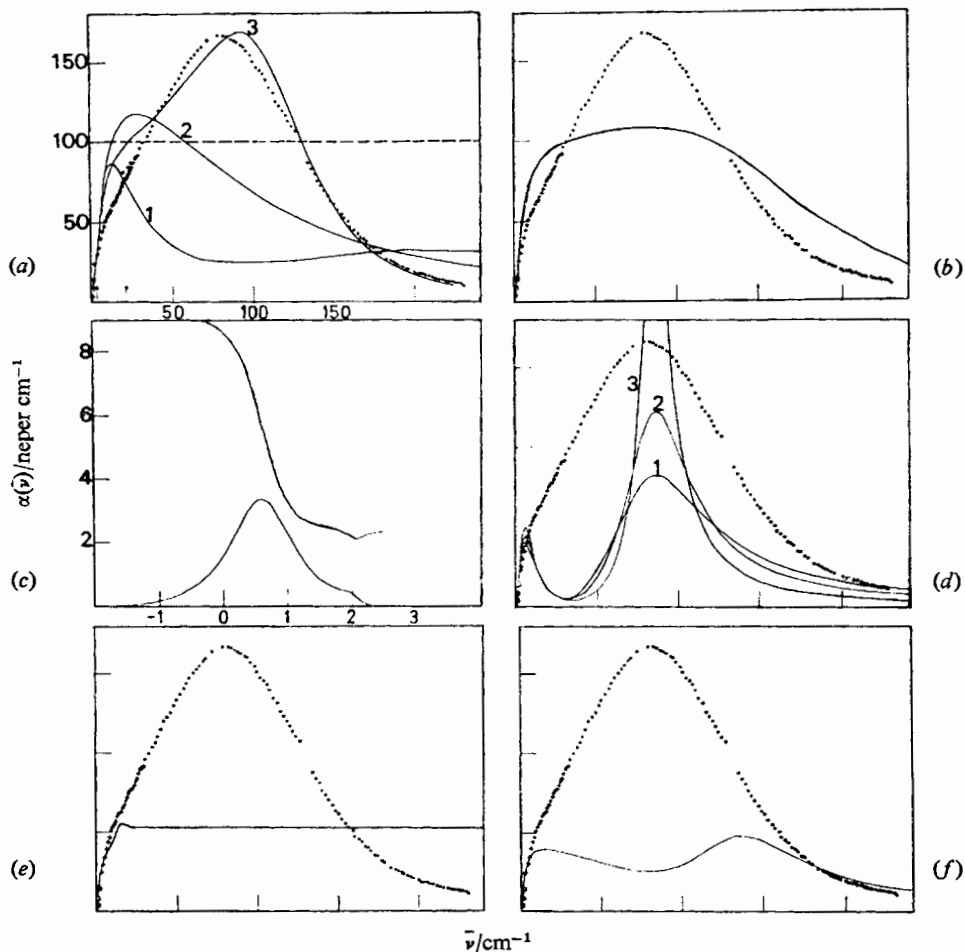
FIG. 4.—Absorption in terms of $\alpha(\bar{\nu})$ of pure CH_2Cl_2 liquid: (a) $\square$, microwave klystron results; $\diamondsuit$, Martin–Puplett interferometer (P.O. Telecommunications H.Q.); $\odot$, Michelson interferometer (Grubb/Parsons/N.P.L. at Aberystwyth); (– – –), spherical top Debye plateau.[1] (1) Langevin equation, asymmetric top, $\beta_x = 2.0$, $\beta_y = 25.7$, $\beta_z = 2.2$ THz. Inverse of loss peak frequency = 1.45 ps. (2) J-diffusion model, spherical top, best fit, with $\beta_\omega = 7.4$ in units of $[kT(1/I_x + 1/I_y)]^{\frac{1}{2}} = \langle \omega^2 \rangle^{\frac{1}{2}}$. (3) Model (iii) Mori approximant of $\hat{\boldsymbol{u}} = i\mathcal{L}\boldsymbol{u}$, iterating separately on $\gamma (= 4.9 \langle \omega^2 \rangle^{\frac{1}{2}}$ for best fit) and $\phi_{uu}^{(1)}(0) = 27.8 \langle \omega^2 \rangle$. (b) As for fig. 4(a) the solid curve is model (3) with γ related as in the text to $\phi_{uu}^{(1)}(0)$ calculated as $58 \langle \omega^2 \rangle$. The latter can be calculated also as $57.3 \langle \omega^2 \rangle$ from the loss peak frequency. Further approximants are clearly needed since the calculated curve is too broad. (c) Loss curve and dispersion corresponding to curve (3) of fig. 4(a). (d) As for fig. 4(a), showing the effect of varying β_2 in model (iv) for $I_1/I_2 = 10$, $\beta_1 = 1.23$ THz (calculable), $\omega_0 = 15.26$ THz (far infrared peak). (1) $\beta_2 = 10$; (2) $\beta_2 = 15$; (3) $\beta_2 = 5$ THz. (e) As for fig. 4(a), iterating on $I_1 (< I_2$ for best fit) and β_2, with β_1 of the disc/annulus interpretation fixed at 1.23 THz. The very poor result illustrates that iteration of this kind is often unhelpful, since the system merely tends to rotational diffusion, giving a slow return to h.f. spectral transparency. (f) The dipole–dipole interpretation of model (iv) with $I_1 = I_2 = 4.8 \times 10^{-39}$ g cm^2 (the mean of these $\perp$ to $\boldsymbol{\mu}$ of CH_2Cl_2), and with $\beta_1 = \beta_2 = 1.23$ THz, $\omega_0 = 15.26$ THz.

mean square torque would enable the desired shift in $\langle\omega^2\rangle^{\frac{1}{2}}$ to take place.   Obviously, zero to THz bandshapes are sensitive measures of analytical realism in this respect, and will also be useful in evaluating density expansions of the memory operator, which allows one to take into account multiple collisions.

MODEL (iii)

Here the mean square torque is related to $\phi_u^{(1)}(0)$, and is well-defined.   However, the bandshape calculated with no adjustable variables is rather too broad in comparison with the data (fig. 4).   Iterating on γ and $\phi_u^{(1)}(0)$ (separately) improves the fit but in doing so obscures the fact that further approximants are needed before the mean intermolecular potential energy is satisfactorily described.   Such work is in progress.   The disadvantage of this approach is that it is not possible to obtain an analytical relation between $\langle u(t) \cdot u(0)\rangle$ and other autocorrelation functions of interest, such as $\langle\omega(t) \cdot \omega(0)\rangle$, unlike the other three models considered.

MODEL (iv)

Using the geometrical relation $I_1 \approx 10\,I_2$ for various values of β_2 (with $\beta_1 = kT\tau_D/I_2$, where τ_D is the inverse of the loss peak frequency) it is obvious (fig. 4) that the resonance around ω_0 is too narrow in frequency range.   The original concept [10] with $\beta_2 = 0$ would produce therefore an even sharper peak.   However, iteration on I_1 and β_2 rectifies matters at the expense of physical realism in the disc/annulus sense, since for a poor best fit $I_1 < I_2$ (mathematically corresponding to the overdamped case).   A parallel result was found by Damle et al.[23] for the translational space itinerant oscillator, where β_2 and β_1 are memory functions.   At this point the following remarks may be made.   Firstly the planar itinerant librator with $\beta_2 = 0$ corresponds exactly with the 2nd Mori approximant to $\langle\omega(t) \cdot \omega(0)\rangle$, the dipole angular velocity autocorrelation functions.   The equilibrium averages $\phi_\omega^{(0)}(0)$ and $\phi_\omega^{(1)}(0)$ this time contain information on the mean square torque and the mean square torque derivative respectively.   We have in addition:

$$\phi_\omega^{(0)}(0) = \omega_0^2; \qquad \phi_\omega^{(1)}(0) = (I_2/I_1)\omega_0^2. \tag{12}$$

Now in general it is perfectly reasonable that $\phi_\omega^{(1)}(0)$ should exceed $\phi_\omega^{(0)}(0)$ if the rate of change of torque is large, so that from eqn (12), apparently $I_2 > I_1$ in this case, in direct contradiction with the geometrical expectation that the rigid cage moment of inertia should exceed that of the disc.   This might mean that a dipole–dipole interpretation is to be preferred.   Secondly the model described by eqn (10) is one sense a zero'th order approximant of the system devised by Damle et al. and perhaps successive approximants would improve the fit if the problem of too many adjustable parameters could be overcome.   Damle et al. used six of these, four of which were independent.   The main advantage of this formalism was discussed by Evans [31] in the case $\beta_2 = 0$, since the orientational autocorrelation function is constructed very well, (being even up to the t^6 term in its time expansion) and the mean intermolecular potential is defined in terms of both the mean square torque and the mean square torque derivative.   To regard $\phi_\omega^{(0)}(0)$ and $\phi_\omega^{(1)}(0)$ as terms in the Mori continued fraction treatment of:

$$\dot{\omega} = i\mathscr{L}\omega \tag{13}$$

is undoubtedly the most profitable view point at the moment.

Using $I_1 = I_2$, $\beta_1 = \beta_2 = kT\tau_D/I_2$ in the dipole interaction formalism of fig. 2 produces a poor fit, (fig. 4), while iteration on β_1, β_2 and I_1/I_2 is barely an improvement.   This suggests that a more realistic potential V [of eqn (11)] is necessary.

Certainly extension to space reorientation is feasible. However, $\phi_\omega^{(0)}(0)$ and $\phi_\omega^{(1)}(0)$ are not wholly electrostatic in origin and an interpretation of the far infrared absorption solely in these terms is obviously to be avoided (since the Poley absorption persists to infinite dilution).[32]

COMPARISON WITH NEUTRON SCATTERING EXPERIMENTS

Recently Brier and Perry [15] have obtained some time of flight neutron scattering data on liquid CH_2Cl_2 and have tested their results with four different models of the liquid state. They have also reviewed critically the available n.m.r., i.r./Raman, and depolarised Rayleigh wing results. The information is confused and sometimes contradictory, these reviewers concentrating their effort on evaluating the anisotropy of the molecular angular motion. In this section we compare the zero to THz results with the neutron-scattering data available and suggest a self-consistent stratagem for further progress in this field, based on the Mori equation [eqn (2)].

J- AND M-DIFFUSION MODELS

These models were used regarding CH_2Cl_2 as an inertial symmetric top, i.e., assuming that axial symmetry of angular motion about the a axis (of least moment of inertia). [This assumption is however contradicted by n.m.r. results, giving $\tau_2(H—H) \neq \tau_2(C—H)$]. An Egelstaff-Schofield form was used for the translational correlation function in the usual decoupling approximation (i.e., translation and rotation decorrelated). The conclusions drawn as to the efficacy of the model within this approximation are very similar to those of this paper : changing the values of the time between collisions alters the magnitude of the inelastic peak, its position remaining virtually constant. The maximum of the predicted inelastic intensity distribution occurs at much too low an energy transfer (frequency) for both models. Therefore, within the extended diffusion context, treating CH_2Cl_2 as a spherical top (this paper) or symmetric top (neutron scattering) makes little difference to the final result, which is poor. It is important to realize that this does not imply that the data are insensitive to asymmetry of orientational or rototranslational motions, but rather that the use of unrealistic and over-simplified assumptions leads to the same kind of result (i.e., oversimplified and unrealistic). Also, Brier and Perry are working within the further severe assumption (common to nearly all neutron-scattering studies of molecular motion) of complete decoupling of rotation from translation. Berne and Montgomery [33] have shown recently that even for rough and hard *spheres* the decoupling assumption (standard notation) :

$$\langle e^{iq \cdot \Delta r(t)} P_n[u(t) \cdot u(0)] \rangle = \langle e^{iq \cdot \Delta r(t)} \rangle \langle P_n[u(t) \cdot u(0)] \rangle \qquad (14)$$

is unjustified. In our zero to THz absorption process q is very small, so that this problem vanishes. Indeed, the main result of Brier and Perry, that neutron scattering measurements in molecular liquids are not sensitive to anisotropy of angular motion, is true only within the approximation represented by eqn (14). It should be judged in the light of the fact that the analytical *rototranslation* neutron scattering spectrum of a rough sphere fluid is completely different from that of a smooth hard sphere fluid. Not unnaturally, therefore, the use of different translation models with a given rotational model in the r.h.s. of eqn (14) will lead to confusion.

A self-consistent approach is clearly needed to the rototranslation problem in neutron scattering and this could be supplied [16] within the framework of the Mori equation [eqn (2)], and a rototranslational continued fraction developed for the correlation function on the l.h.s. of eqn (14) in the general molecular, as opposed

to spherical, context. This would aim at an appreciation of the spectrum in terms of successive equilibrium averages such as $\phi_{u,r}^{(0)}(0)$, *etc.* and, therefore, of the likely form taken by the intermolecular potential.

DEPOLARISED RAYLEIGH SCATTERING, I.R./RAMAN AND N.M.R. COMPARISONS

Studies of the depolarised Rayleigh wing [34] complement the zero to THz band except insofar as the former type of data are roughly equivalent to $\varepsilon''(\omega)/\omega$ while the latter are available as approximately $\omega\varepsilon''(\omega)$ and $\varepsilon''(\omega)$. Brier and Perry [15] have discussed fully the depolarised Rayleigh, Raman, i.r. and n.m.r. data available on the molecular dynamics in liquid CH_2Cl_2. The dielectric and Rayleigh scattering results provide information on collective effects [35] while, ideally, the other types of experiment deal with single molecule motion describable solely in terms of auto-correlation functions.[1,2]

The correlation times available from these techniques are confusingly disparate.[15] An explanation is attempted in the review [15] based on the asymmetric top Langevin equation, which in the light of fig. 4 is meaningless. It is significant that only the zero to THz absorption shows up clearly enough the discrepancy between rotational diffusion and observation. Another feature is that interpretation in terms of jump models gives directly contradictory results.

It is clear only that the available data on liquid CH_2Cl_2 have been interpreted using many different models with each of which are associated usually adjustable parameters so that an overall viewpoint is not attained. We propose below a scheme to remedy this to a modest degree.

FUTURE SCHEME OF STUDY

A computer simulation, using an empirical intermolecular potential (*e.g.*, atom–atom Lennard-Jones interactions) should be carried out on CH_2Cl_2, and desired quantities such as the mean square torque, mean square torque derivative, various autocorrelation functions and collective correlation functions extracted. These should then be compared with the values extracted from self-consistent Mori approximants [21] used with the far infrared and depolarised Rayleigh data, these being free from the uncertainties of vibrational relaxation, hot bands *etc.* The effect of cross-correlations may be easily estimated from the zero-THz band by dilution [14] and compared with those simulated.

Isotropy or otherwise of angular orientations may be simulated in detail [26] and compared with the considerable amount of n.m.r. data available. Rototranslational effects may be simulated and compared with the available neutron scattering data.

In this way we hope that the empirical intermolecular potential may be refined by evaluation against the spectroscopic data, especially if these were available over a broad enough range of number density and temperature. Alternatively, if the empirical potential were considered adequate, the efficacy of the continued fraction approximation could be measured in the context of approximating the Liouville equation.

PROBE STUDIES ON LIQUID CRYSTALS

The zero to THz results indicate that there are effects on the motion of CH_2Cl_2 dissolved in cholesteryl linoleate in the isotropic phase which mirror those found by n.m.r. in, for example, hexasubstituted benzene dissolved in mesophases.[36] By an extension of such a scheme as the above these interesting effects could be further elucidated.
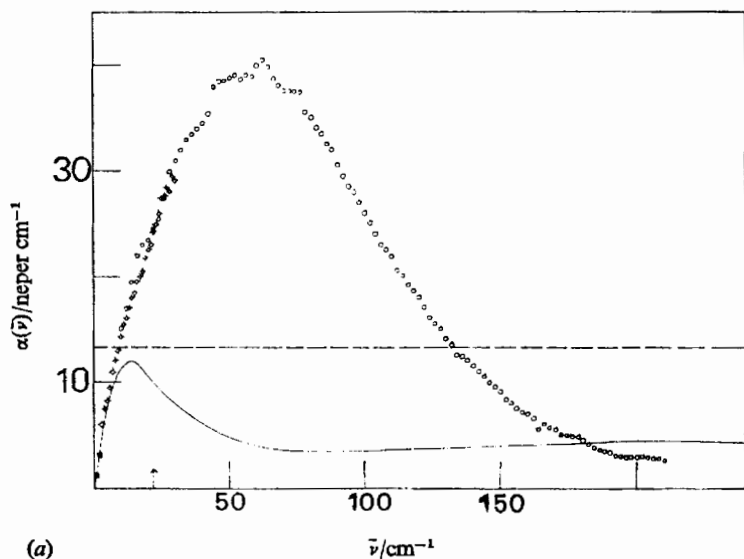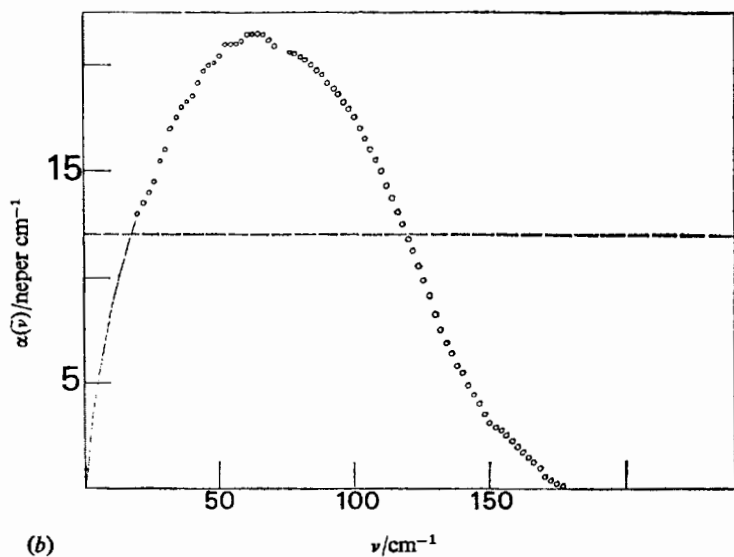
FIG. 5.—(a) Far infrared absorption and klystron data for CH_2Cl_2 in CCl_4 at a number density of 1.97×10^{21} molecules cm^{-3}. (b) The same for CH_2Cl_2 in monorefringent cholesteryl linoleate medium. There is a marked loss of intensity (after the standard correction for solvent absorption).

[1] M. W. Evans, *Dielectric and Related Molecular Processes* (Chem. Soc. Specialist Periodical Report, London, 1977), vol. 3.
[2] W. A. Steele, *Adv. Chem. Phys.*, 1976, **34**.
[3] H. Mori, *Prog. Theor. Phys.*, 1965, **34**, 299; 1965, **33**, 423.
[4] A. Morita, *J. Phys. D*, 1978, in press.
[5] Work carried out at D.I.A.S. Dublin, in press.
[6] D. Chandler, *J. Chem. Phys.*, 1974, **60**, 3508.
[7] R. Gordon, *Adv. Magnetic Resonance*, 1968, **3**, 1.
[8] F. Bliot, C. Abbar and E. Constant, *Mol. Phys.*, 1972, **24**, 241.
[9] G. J. Evans and M. W. Evans, *J.C.S. Faraday II*, 1976, **72**, 1169.
[10] J. H. Calderwood and W. T. Coffey, *Proc. Roy. Soc. A*, 1977, **356**, 269; W. T. Coffey, G. J. Evans, M. W. Evans and G. H. Wegdam, *J.C.S. Faraday II*, 1978, **74**, 310; W. T. Coffey, *Mol. Phys.*, in press, W. T. Coffey and M. W. Evans, *Mol. Phys.*, in press.
[11] M. Davies, R. Moutran, A. H. Price, M. Beevers and G. Williams, *J.C.S. Faraday II*, 1976, **72**, 1447.
[12] V. K. Agarwal and A. H. Price, *J.C.S. Faraday II*, 1974, **70**, 188.
[13] (a) Third Int. Conference on Submillimetre Waves, Guildford, 1978, *Infrared Physics*, to be published; (b) G. J. Davies and M. W. Evans, *J.C.S. Faraday II*, 1978, **74**, 57.
[14] G. J. Evans, C. J. Reid and M. W. Evans, *J.C.S. Faraday II*, 1978, **74**, 343.
[15] P. N. Brier and A. Perry, *Adv. Mol. Relaxation Int. Proc.*, in press.
[16] A. R. Davies and M. W. Evans, *Mol. Phys.*, 1978, **35**, 857.
[17] M. W. Evans, *Mol. Phys.*, 1977, **34**, 963.
[18] A. Budo, E. Fischer and S. Miyamoto, *Phys. Z.*, 1934, **40**, 337.
[19] D. Frenkel, G. H. Wegdam and J. Van der Elsken, *J. Chem. Phys.*, 1972, **57**, 2691.
[20] K. Lindenberg and R. I. Cukier, *J. Chem. Phys.*, 1975, **62**, 3271; R. I. Cukier, *J. Chem. Phys.*, 1974, **60**, 734; R. I. Cukier and K. Lakatos-Lindenberg, *J. Chem. Phys.*, 1972, **57**, 3427.
[21] M. Drawid and J. W. Halley, *J. Phys. Chem. Solids*, 1977, **38**, 1269.
[22] M. Tokuyama and H. Mori, *Prog. Theor. Phys.*, 1976, **55**, 411.
[23] P. S. Damle, A. Sjölander and K. S. Singwi, *Phys. Rev.*, 1968, **165**, 277.
[24] A. Gerschel, I. Darmon and C. Brot, *Mol. Phys.*, 1972, **23**, 317.
[25] M. W. Evans, *Adv. Mol. Relaxation Int. Proc.*, 1977, **10**, 203 (review).
[26] see, for example, W. B. Streett and D. J. Tildesley, *Proc. Roy. Soc. A*, 1977, **355**, 239.
[27] G. J. Evans, G. Wegdam and M. W. Evans, *Chem. Phys. Letters*, 1976, **42**, 331.
[28] R. E. D. McClung, *Adv. Mol. Relaxation Int. Proc.*, 1977, **10**, 83 (review).
[29] J. O'Dell and B. J. Berne, *J. Chem. Phys.*, 1975, **63**, 2376.
[30] F. Hermans, E. Kestemont, R. van Loon and R. Finsy, 3rd Int. Conf. Submillimetre Waves, *Infrared Physics*, to be published, 1978.
[31] M. W. Evans, *Chem. Phys. Letters*, 1976, **39**, 601.
[32] M. Davies, *Ann. Rep. Chem. Soc.*, 1970, **67**, 65.
[33] B. J. Berne and J. A. Montgomery, *J. Mol. Phys.*, 1976, **32**, 363.
[34] P. van Konynenburg and W. A. Steele, *J. Chem. Phys.*, 1972, **56**, 4476.
[35] J. S. Rowlinson and M. Evans, *Ann. Rep. Chem. Soc.*, 1975, 5.
[36] D. Canet, *These d'Etat* (University of Nancy, 1973).