

N° 72. — AN EVALUATION OF TWO THEORETICAL MODELS FOR THE REORIENTATION OF POLAR SYMMETRIC-TOP MOLECULES

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SUMMARY

The Langevin equation for rotational Brownian motion has recently been solved for symmetric top molecules by Morita and for the needle and sphere by McConnell. Here, using numerical techniques, the self consistency of their solutions is established. We compare and evaluate their theoretical approach with experimental observations and with a formalism based on a generalised Langevin equation in which the correlation of a vector property of the phase space is linked to its n 'th derivative or memory function. It is seen that an inertia corrected Langevin equation alone fails to explain the short time details of the reorientational process of polar, symmetric-top molecules in the fluid state.

SOMMAIRE

L'équation de Langevin pour le mouvement rotatoire Brownien a été récemment résolue pour les molécules toupies symétriques par Morita, et pour l'aiguille et la sphère par McConnell. Ici, utilisant les techniques numériques nous y établissons la cohérence interne de ces solutions. Nous comparons et évaluons l'approche théorique avec des observations expérimentales, utilisant un formalisme fondé sur l'équation de Langevin généralisée, dans laquelle la corrélation d'une propriété vectorielle de l'espace de phase est reliée à sa dérivée d'ordre n , ou la fonction de mémoire.

On y voit que l'équation de Langevin corrigée de l'inertie ne peut seule expliquer les détails de la réorientation aux temps très courts pour des molécules polaires du type toupie symétrique dans l'état liquide.

Introduction and theoretical considerations.

A molecule immersed in a fluid is subjected to a great number of random independent pulses due to collisions with neighbouring molecules. In the classic context stochastic processes ⁽¹⁾ provide

models to describe this physical phenomenon in Brownian motion. The angular velocity ω is supposed to obey a Langevin equation:

$$I\dot{\omega} + \omega \times (I\omega) + I\beta\omega = I\dot{\Gamma} \quad (1)$$

where I is the moment of inertia, $I\beta\omega$ is the frictional couple and $I\dot{\Gamma}$ is the couple due to the random driving forces caused by the thermal fluctuations of the environment.

The solution of this stochastic differential equation for the rotary dynamics is simplified by neglecting the molecular inertia. For the asymmetric top Perrin's equation then follows. Here the complex permittivity is given by:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{\mu^2} \left(\frac{M_x^2(D_y + D_z)}{i\omega + D_y + D_z} + \frac{M_y^2(D_x + D_z)}{i\omega + D_x + D_z} + \frac{M_z^2(D_x + D_y)}{i\omega + D_x + D_y} \right) \quad (2)$$

where:

$$D_i = \frac{kT}{I_i\beta_i} \quad \text{and} \quad \mu^2 = M_x^2 + M_y^2 + M_z^2$$

in which M_i is the permanent dipole moment along the principal axis denoted by i and β_i is the friction coefficient. By substituting $D = D_i$ in equation (2) the result simplifies further to the particular case of the rotational Brownian motion of a sphere as treated by Debye ⁽²⁾. Debye's theory of a dielectric relaxation for a spherical polar molecule in a non-polar medium has been used extensively to describe low frequency single relaxation time processes. This inertialess model provides an adequate description of the reorientation process only at long times when the diffusive steps are limited to infinitesimally small angles and occur infinitely fast. It corresponds ⁽²⁾ to a randomisation of molecular position at each

collisional impact and fails to predict the observed return to spectral transparency at high frequencies. This neglect of all dynamical coherence is a gross and unacceptable approximation of equation (1).

Inertial effects were first considered by Gross (4) and by Sack (5). Sack's investigations were based on a diffusion equation, which is a Liouville equation supplemented by Kramers terms. More recently McConnell (6) has solved the Langevin equation for the rotational Brownian motion of a dipole embedded in a sphere and a needle. In brief, McConnell, using a Bogoliubov-Mitropolsky method, gives the real $\left(\frac{\alpha'(\omega)}{\alpha(0)}\right)$ and imaginary $\left(\frac{\alpha''(\omega)}{\alpha(0)}\right)$ parts of the complex polarisability $\alpha^*(\omega)$ for

1) the sphere as:

$$\frac{\alpha'(\omega)}{\alpha(0)} = 1 - (F(0))^{-1} \left[\frac{\omega'^2}{G'^2 + \omega'^2} - \frac{2\gamma\omega'^2}{(1 + G')^2 + \omega'^2} + \gamma^2 \left(\frac{3/2\omega'^2}{(2 + G')^2 + \omega'^2} - \frac{4(1 + G')\omega'^2}{[(1 + G')^2 + \omega'^2]^2} - \frac{2\omega'^2}{(1 + G')^2 + \omega'^2} \right) - \gamma^3 \left(\frac{6(1 + G')^2\omega'^2 - 2\omega'^4}{[(1 + G')^2 + \omega'^2]^3} + \frac{8(1 + G')\omega'^2}{[(1 + G')^2 + \omega'^2]^2} + \frac{2\omega'^2}{(1 + G')^2 + \omega'^2} + \frac{3(2 + G')\omega'^2}{[(2 + G')^2 + \omega'^2]^2} + \frac{17/9\omega'^2}{(3 + G')^2 + \omega'^2} \right) \right] + \dots$$

$$\frac{\alpha''(\omega)}{\alpha(0)} = (F(0))^{-1} \left[\frac{G'\omega'}{G'^2 + \omega'^2} - \gamma \frac{2(1 + G')\omega'}{(1 + G')^2 + \omega'^2} - \gamma^2 \left(\frac{2[(1 + G')^2 - \omega'^2]\omega'}{[(1 + G')^2 + \omega'^2]^2} + \frac{2(1 + G')\omega'}{(1 + G')^2 + \omega'^2} - \frac{(3 + 3/2G')\omega'}{(2 + G')^2 + \omega'^2} \right) - \gamma^3 \left(\frac{2[(1 + G')^3\omega' - 3(1 + G')\omega'^2]}{[(1 + G')^2 + \omega'^2]^3} + \frac{4[(1 + G')^2 - \omega'^2]\omega'}{[(1 + G')^2 + \omega'^2]^2} + \frac{2(1 + G')\omega'}{(1 + G')^2 + \omega'^2} + \frac{3/2[(2 + G')^2 - \omega'^2]\omega'}{[(2 + G')^2 + \omega'^2]^2} + \left(\frac{17}{3} + \frac{17}{9}G' \right) \omega' \right) \right] + \dots$$

where

$$\begin{aligned} \gamma &= kT/I\beta^2; \\ \omega' &= \omega/\beta; \\ G' &= 2\gamma + \gamma^2 + 7/6\gamma^3 + 25/18\gamma^4 + \dots; \\ (F(0))^{-1} &= 1 + 2\gamma + 9/2\gamma^2 + 125/9\gamma^3 + \dots; \end{aligned}$$

And

2) the needle as:

$$\begin{aligned} \frac{\alpha'(\omega)}{\alpha(0)} &= 1 - (F(0))^{-1} \left[\frac{\omega'^2}{G'^2 + \omega'^2} - \frac{2\gamma\omega'^2}{(1 + G')^2 + \omega'^2} - \gamma^2 \left(\frac{8(1 + G')\omega'^2}{[(1 + G')^2 + \omega'^2]^2} + \frac{4\omega'^2}{(1 + G')^2 + \omega'^2} - \frac{\omega'^2}{(2 + G')^2 + \omega'^2} \right) - \gamma^3 \left(\frac{24(1 + G')^2\omega'^2 - 8\omega'^4}{[(1 + G')^2 + \omega'^2]^3} + \frac{40(1 + G')\omega'^2}{[(1 + G')^2 + \omega'^2]^2} + \frac{6\omega'^2}{(1 + G')^2 + \omega'^2} + \frac{4\omega'^2}{(2 + G')^2 + \omega'^2} + \frac{4/9\omega'^2}{(3 + G')^2 + \omega'^2} \right) \right] - \dots \\ \frac{\alpha''(\omega)}{\alpha(0)} &= (F(0))^{-1} \left[\frac{G'\omega'}{G'^2 + \omega'^2} - \frac{2\gamma(1 + G')\omega'}{(1 + G')^2 + \omega'^2} - \gamma^2 \left(\frac{4[(1 + G')^2 - \omega'^2]\omega'}{[(1 + G')^2 + \omega'^2]^2} + \frac{4(1 + G')\omega'}{(1 + G')^2 + \omega'^2} - \frac{2(1 + G')\omega'}{(2 + G')^2 + \omega'^2} \right) - \gamma^3 \left(\frac{8[(1 + G')^3\omega' - 3(1 + G')\omega'^2]}{[(1 + G')^2 + \omega'^2]^3} + \frac{20[(1 + G')^2 - \omega'^2]\omega'}{[(1 + G')^2 + \omega'^2]^2} + \frac{4(2 + G')\omega'}{(2 + G')^2 + \omega'^2} + \frac{6(1 + G')\omega'}{(1 + G')^2 + \omega'^2} + \frac{4/9(3 + G')\omega'}{(3 + G')^2 + \omega'^2} \right) \right] - \dots \end{aligned} \tag{4}$$

where

$$\begin{aligned} \gamma &= kT/I\beta^2; \\ \omega' &= \omega/\beta; \\ G' &= 2\gamma + 2\gamma^2 + 16/3\gamma^3 + \dots; \\ (F(0))^{-1} &= 1 + 2\gamma + 7\gamma^2 + 274/9\gamma^3 + \dots; \\ \beta &= 2kT\tau_0/I. \end{aligned}$$

and where τ_0 is the Debye relaxation time, I the moment of inertia and ω the angular frequency.

The above results are clearly true for $\omega = 0$. For $\omega \rightarrow \infty$ it can be shown, neglecting terms proportional to γ^3 that both the spherical top and needle reduce to:

$$\frac{\alpha^*(\omega)}{\alpha(0)} = -\frac{2\gamma}{\omega'^2} - \frac{2i\gamma}{\omega'^3}$$

in agreement with Sack (7).

In a separate study Morita (8) has solved the Eulerian equations of motion for a diffusing asymmetric top. Confining ourselves to the particular case of a symmetric top, where a dipole M_z lies along the axis of symmetry, the Fokker-Planck-Kramers equation for the probability density function $W(\omega_x, \omega_y, \omega_z, \theta, \psi, t)$ in angular velocity Eulerian space yields the Laplace transform of the dipole correlation function $\langle M'_z(0), M'_z(t) \rangle$ as:

$$\Pi(p) = \frac{M_z^2/\beta}{2kT/I_x} \left[\frac{1}{p + \beta_x + \frac{2kT/I_x}{p + 2\beta_x + \frac{4kT/I_x}{p + 3\beta_x}}} + \frac{(kT/I_x)(I_z/I_x)}{p + \beta_x + \beta_z + \frac{(2kT/I_x)(I_z/I_x)}{p + \beta_x + 2\beta_z + \frac{2kT/I_x}{p + 2\beta_z}}} \right] \tag{5}$$

where $\omega_i(t)$ ($i = x, y$ or z) is the angular velocity about the principal axis labelled i , I_i is the moment of inertia, $I_i \beta_i \omega_i(t)$ is the damping torque, (θ, φ, ψ) are the Eulerian angles specifying the orientation of the top ⁽⁹⁾, k is the Boltzmann constant, T the absolute temperature and p the Laplace variable.

It is the intention here to:

1) Show by numerical computation that eqn. (5) reduces, in appropriate limits, to the sphere and needle expressions as given by McConnell [equations (3) and (4)].

2) To compare and evaluate these theoretical approaches with experimental observation covering a wide range of frequency.

3) To compare with a more general formalism ⁽¹⁰⁾ in which a) the friction coefficient of the original Langevin equation is made time dependent; b) $\Gamma(t)$ is non-Gaussian; c) $\Gamma(t)$ may have a finite correlation time.

For completeness a brief synopsis of this non-Markovian kinetic equation is now presented.

Absorption spectra $C_A(\omega)$ have related time correlation functions denoted by ⁽¹¹⁾:

$$C_A(t) = \int_0^\infty \cos \omega t dC_A(\omega) \quad (6)$$

which assumes that the fluctuation of the molecules is a continuous, stochastic process stationary in time. Of course, spectral functions are frequency distributions of the probability of occurrence of the events from which they originate, and are themselves statistical in nature. The temporal and frequency domains are linked by Fourier's integral theorem so that correlation and spectral functions are Fourier transform pairs.

Basically, the non Markovian equation links the correlation of our chosen vector to that of its n 'th derivative or memory function. The phase function $\Lambda(t)$ evolves in time as determined by the Liouville operator, L , for the system:

$$\dot{\Lambda}(t) = \exp(iLt)\Lambda(0) \quad (7)$$

A formally exact equation of motion for $C_A(t)$ is now derived using the projection operator formalism of Zwanzig ⁽¹⁰⁾

$$\frac{\partial}{\partial t} C_A(t) = - \int_0^t K(t-\tau) C_A(\tau) d\tau$$

This is a fundamental equation of statistical physics applicable to *any* vector property of phase space. The kernel K is the memory function and is related to the memory, or dynamical coherence of the system. The correlation functions depend only on the values of the memory function for all times τ prior to t .

If a property $\Gamma(t)$ is defined such that:

$$\dot{\Gamma}(t) = ([\exp i(1-\hat{p})Lt]iL)\Lambda \quad (8)$$

where \hat{p} is a projection operator defined onto the well behaved function of phase Λ then it follows that:

$$\frac{\partial \Lambda}{\partial t} = - \int_0^t K(t-\tau)\Lambda(\tau) d\tau + \Gamma(t) \quad (9)$$

This is the *generalised* Langevin equation, first proposed by Kubo et al. and derived in a way that embodies no assumptions other than the N particle

ensemble obeys the Liouville equation of motion. We attempt to show here that this describes more realistically the motion of a molecule embedded in a fluid than the simple Langevin equation.

Choosing u as our vector property of the phase space (where u is the unit dipole vector), recalling the second fluctuation-dissipation equation of Kubo ⁽¹²⁾ and Laplace transforming yields Mori's continued fraction representation of the time correlation function as:

$$\tilde{C}_m(p) = \frac{\tilde{C}_m(0)}{p + \tilde{K}_0(p)} = \frac{\tilde{C}_m(0)}{p + \frac{\tilde{K}_0(0)}{p + \tilde{K}_1(p)}} \quad (10)$$

The associated complex spectral density $\tilde{C}_m(-i\omega)$ is obtained by truncating this infinite series with a suitable functional representation of $\tilde{K}_n(t)$. A first order termination ($n=1$) with an exponential memory function has proven to be satisfactory and is again adopted here.

In the following section we give appraisals of these theoretical approaches. In the past intensive theoretical efforts to elucidate the dynamical mechanism in fluids have been hampered by a lack of experimental data over the whole frequency range of interest. It is unacceptable to compare models with experimental low or high frequency data in isolation. This spectroscopic region only becomes sufficiently discriminating when both sets of data are treated in unison. In this respect Gerschel ⁽¹⁴⁾ has carefully studied the symmetric tops CH_3F and CHF_3 over the whole density and temperature range beneath the critical region in both the microwave and f.i.r. These are particularly favourable systems with which to assess merits or limitations of the present theoretical approaches. They are highly dipolar species ($\mu_{\text{CH}_3\text{F}} = 1.85 \text{ D}$; $\mu_{\text{CHF}_3} = 1.65 \text{ D}$) absorbing strongly in the f.i.r. region. This is significant because the absorption cross-sections in this frequency range are always enhanced ⁽³⁾ by temporary dipoles induced by the effect on a molecule of the resultant fields of its neighbours. This problem of induced dipole absorption is minimised in liquids with intense permanent absorptions predominant.

The problem of relating the many particle reorientational spectrum to the single particle spectrum has been discussed by Kivelson and Madden ⁽¹⁵⁾. The two spectra have the same functional form and sample shape effects do not qualitatively change this result. In deriving their conclusions these authors considered slowly varying torques not represented by a « white » torque, similarly to our eqs. (9) and (10). To check this point we have carried out molecular dynamics simulations of the cross-correlation function of velocity in liquid nitrogen. It was found that the auto correlation function and the cross-correlation function decayed similarly. Strong dipole-dipole interactions might affect this result, but it is well-known ⁽³⁾ that the observed far infrared bands of strongly dipolar solutes do not shift considerably when dipole-dipole interactions are removed by non-dipolar solvents.

In eqn (1) ω represents the *total* angular velocity. In general the non-linear term is difficult to deal with, but Ford et al. ⁽²⁰⁾ have shown that when $\omega(t)$ is the *stationary* solution, then $\omega^{(0)}(t)$ in the expansion:

$$\omega(t) = \omega^{(0)}(t) + \varepsilon \omega^{(1)}(t) + \varepsilon^2 \omega^{(2)}(t) + \dots$$

is the steady-state solution of the corresponding homogenous equation and because of the damping term $\beta\omega$, this is identically zero. Then the $\omega^{(n)}$ for $n \geq 1$ satisfy linear inhomogenous equations. In this paper we quote the results of Ford et al. who have solved in this way the general asymmetric top eqn. (1). These solutions reduce numerically to those of McConnell and Morita, who have also taken full account of cross-terms, where these exist.

Results and Discussion.

In the absence of an internal field the identity

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{\alpha^*(\omega)}{\alpha(0)} \tag{11}$$

relates the complex polarisability to the complex permittivity and is used in this study to give dielectric loss and dispersion relations for the spherical top and needle of McConnell's equations [(3) and (4) respectively] and for Morita's symmetric top representation [equation (5)]. These are in turn related to the absorption coefficient [$\alpha(\bar{\nu})$ in neper cm^{-1}] by the Maxwell equation:

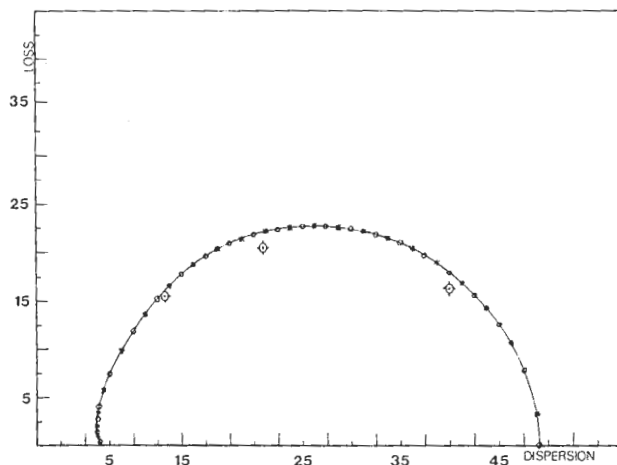
$$\alpha(\bar{\nu}) = \frac{2\sqrt{2}\pi\epsilon''\bar{\nu}}{((\epsilon'^2 + \epsilon''^2)^{1/2} + \epsilon')^{1/2}} \tag{12}$$

The only parameter of McConnell's model, β , is evaluated from the measured Debye relaxation time. Both friction coefficients are unknown in Morita's symmetric top model. However, since the model reduces in the inertialess limit to Perrin's formula, one of the β_i is determined using microwave data. Alternatively the β_i can be regarded as parameters and calculated by iterative fitting of the observed low frequency data.

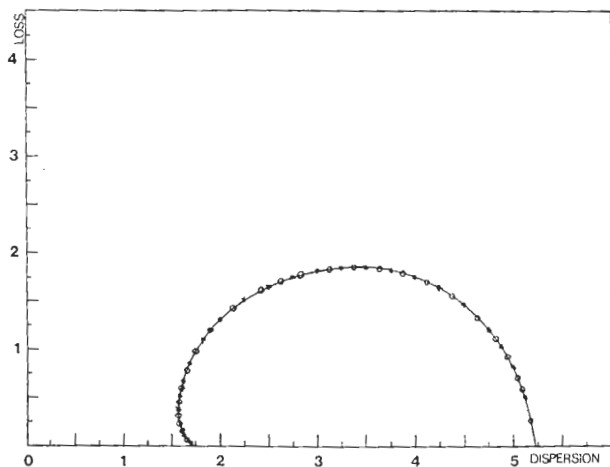
Figure 1 shows some numerical results for fluoroform (at 293 K and in the gas phase) and for MeF (at 133 K), two examples covering extremes of molecular number density. These models, which represent the motion of polar molecules in media where the electrostatic interactions between different molecules, giving rise to the so-called 'dynamic internal field' are significant, are expected to approximate reasonably well to the first system but less so the second.

The agreement with experiment observed at low frequencies is as to be anticipated for models which reduce in appropriate limits to the inertialess sphere as treated by Debye. Morita's symmetric-top model produces numerical results for the spherical top and needle in accord with those of McConnell demonstrating the self-consistency of their solutions. What is surprising, however, is that the needle, the sphere and the symmetric top representations yield absorption and dispersion profiles which are superimposable to a high degree of proximity. For realistic values of the molecular parameters, β_2 in equation (5) appears to be redundant and has no affect on the band contour once β_1 , the other friction coefficient, is fixed at its calculated value.

The evaluation is extended into the more discriminating far infrared frequency region. Figure 2 shows the absorptions, both theoretical and experimental, for fluoroform at 293 K. Again, the needle, sphere and symmetric top representations are



(a)



(b)

Fig. 1.

- a) Cole-Cole plot for CH_3F at 133 K.
 - Morita's model for a symmetric-top, needle and spherical-top molecule.
 - *** McConnell's model for a needle
 - 0 0 0 McConnell's model for a spherical top
 - Experimental [Gerschel (14)]
 - b) Cole-Cole plot for CHF_3 at 293 K
 - Morita's model for a symmetric-top, needle and spherical-top molecule
 - *** McConnell's model for a needle
 - 0 0 0 McConnell's model for a spherical top
- } Individual points shown for clarity

coincident but now some distance removed from the experimental band profile. The frequency of maximum absorption is both too low and intense, and the return to spectral transparency too slow.

To reproduce these results more satisfactorily a further extension of the fundamental Langevin equation is required. We resort to using a simplified version of the non-Markovian kinetic equation. Again making no corrections for the internal field the dielectric loss ϵ'' and permittivity ϵ' are given by (15):

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) \cdot \omega \cdot \text{Real} [\tilde{C}(-i\omega)] \tag{13}$$

$$\epsilon' = \epsilon_0 - (\epsilon_0 - \epsilon_\infty) \cdot \omega \cdot \text{Im} [\tilde{C}(-i\omega)] \tag{14}$$

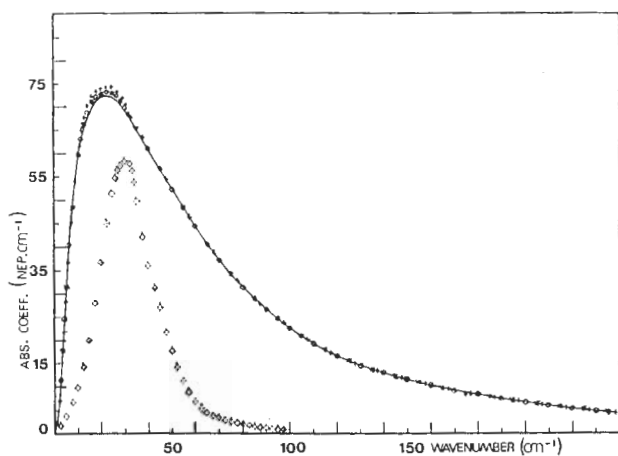


Fig. 2. — The far infra-red absorption of fluoroform at 293 K.
 — Morita's model for a symmetric-top, needle and spherical-top molecule.
 * * * * McConnell's model for a needle
 0 0 0 McConnell's model for a spherical top
 + + + Morita's model for an asymmetric top reduced to the symmetric top.
 ⊙ Experimental [Gerschel (14)]

where ϵ_0 is the static permittivity, ϵ_∞ is the permittivity at about 250 cm^{-1} , $\tilde{C}(-i\omega)$ is the spectral Fourier transform of $C(t)$ and is obtained by replacing the Laplace variable p by $-i\omega$ in equation (10). Here

$$\text{Real } [\tilde{C}(-i\omega)] = K_0(0)K_1(0) \int_0^\infty f(t) \cos \omega t dt / D \quad (15)$$

and

$$I_m [\tilde{C}(-i\omega)] = [A(\omega) \cdot (K_1(0) \int_0^\infty \sin \omega t dt - \omega) + \omega B(\omega)] / D \quad (16)$$

where:

$$A(\omega) = K_0(0) + \omega K_1(0) \int_0^\infty f(t) \sin \omega t dt - \omega^2, \quad (17)$$

$$B(\omega) = K_1(0)^2 \left(\int_0^\infty f(t) \cos \omega t dt \right)^2 \quad (18)$$

and

$$D = A^2(\omega) + \omega^2 B(\omega) \quad (19)$$

For an exponential $K_1(t)$ we have in the low frequency limit:

$$\epsilon'' = \frac{(\epsilon_p - \epsilon_\infty) K_0(0) K_1(0) \gamma \omega}{\gamma^2 K_0(0) + [K_0(0)^2 + K_1(0)^2 + 2K_0(0)(K_1(0) - \gamma^2)] \omega^2} \quad (20)$$

$$\epsilon' = \epsilon_0 \frac{(\epsilon_p - \epsilon_\infty) \omega^2 [\gamma^2 (K_0(0) - \omega^2) + (K_1(0) - \omega^2)(\omega^2 - (K_0(0) + K_1(0)))]}{\gamma^2 K_0(0) + [K_0(0)^2 + K_1(0)^2 + 2K_0(0)(K_1(0) - \gamma^2)] \omega^2} \quad (21)$$

and $\alpha(\bar{\nu})$ is given again by eqn. (12).

We fit Gerschel's precision data for MeF and fluoroform by minimisation of squared deviations from the analytical curves. Figure 3 shows the agreement for MeF at 133 K. At this temperature the low and high frequency peaks, shown in loss representation, have separated out and offer a severe test for the evaluation of any dynamical formalism.

We fit the absorption data over the whole of the frequency range of interest. An apparently good fit to part of the frequency range alone can be deceptive (16). Part of the difficulty arises from the

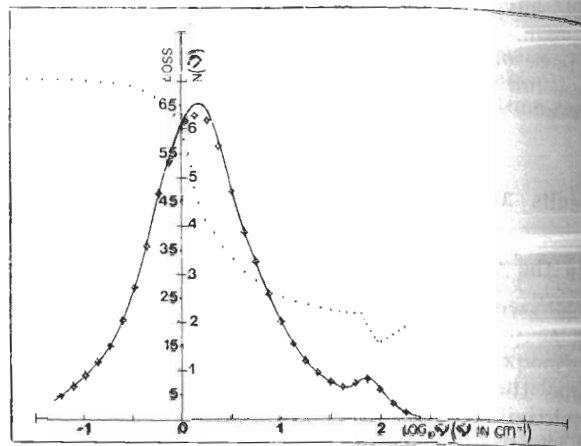


Fig. 3. — The theoretical l.m.s. fitting of the whole of the microwave and far infrared region for CH_3F at 133 K.
 — Theoretical curve using a generalised Langevin equation with $\gamma = 3.6$ and $K_1(0) = 38.3$ (ϵ in arbitrary units)
 ⊙ Experimental
 ■ ■ Predicted refractive index ($n(\bar{\nu})$) curve using the analytical theory.

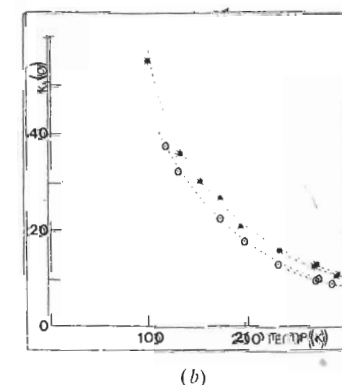
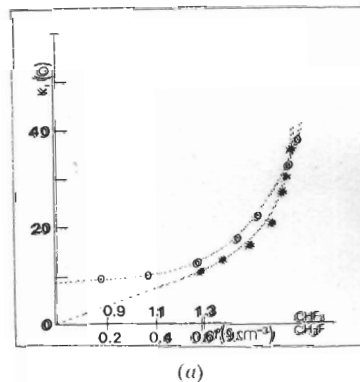


Fig. 4.

a) The dependence of the mean-square torque term $K_2(0)$ on temperature for CH_3F (*) and fluoroform (●).
 b) The dependence of the mean square torque term $K_1(0)$ on the fluid density for CH_3F (*) and fluoroform (●).

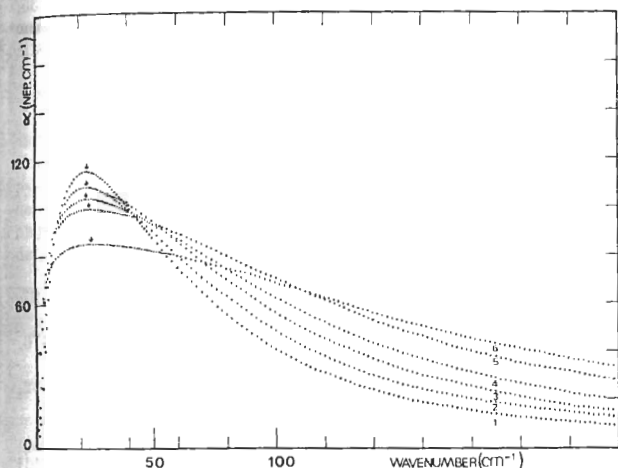
use of two measures of absorption ϵ'' and $\alpha(\bar{\nu})$ and of dispersion ϵ' and $n(\bar{\nu})$. Each weights grotesquely a part of the frequency range under investigation and used in isolation can lead to misconceptions. The loss representation for instance reduces the whole of the infrared to an insignificant shoulder on the high frequency side of the loss curve, whereas the power representation does just the opposite.

Using calculated values for the parameters in Morita's formalism we found it impossible to separate out the two loss peaks. Such a separation is only accomplished using unrealistic values for the friction coefficients and molecular moments of inertia. However, the generalised formalism reproduces the experimental contour satisfactorily, small deviations occurring only in intensity near the maximum in the loss peak. In the fitting procedure $K_0(o)$ is kept at its auto-correlated value of 1 [$K_0(o) = \frac{2kT}{I_B}$ for a symmetric top molecule]. γ , a frequency parameter, and $K_1(o)$, a parameter related to the

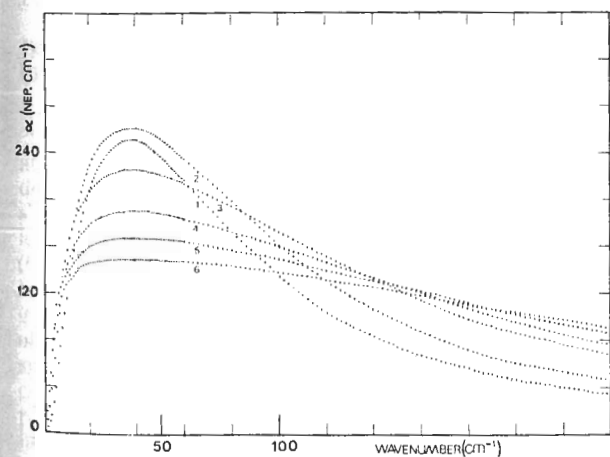
intermolecular mean square torque (in units of $(\frac{2kT}{I_B})^{-\frac{1}{2}}$ and $(\frac{2kT}{I_B})^{-1}$ respectively) only were allowed to vary. In Figure 4 the dependence of the mean square torque term ($K_1(o)$, calculated with the l.m.s. fitting procedure) on density and temperature for both fluoroform and MeF is illustrated. For a symmetric top $K_1(o)$ is simply related to the mean square torque by:

$$K_1(o) = 2(\langle \dot{u}(o)^2 \rangle)^2 \left(1 + \frac{I_A}{4I_B} \right) + \frac{\langle \dot{0}(\nu)^2 \rangle}{I_B^2} - (\dot{u} \langle \dot{0}^2 \rangle)^2 \quad (22)$$

where I_A and I_B are the moments of inertia of the top and $\langle \dot{u}(o)^2 \rangle$ is the equilibrium mean square



(a)

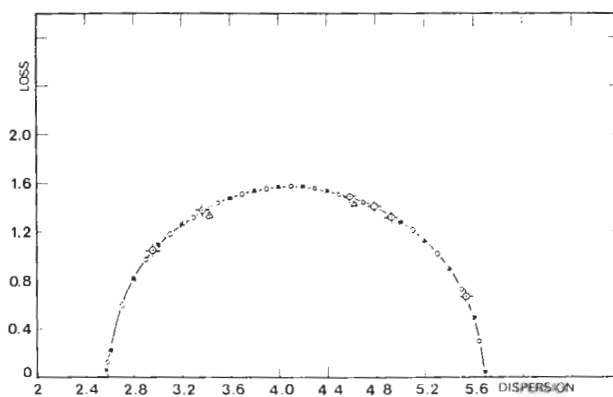


(b)

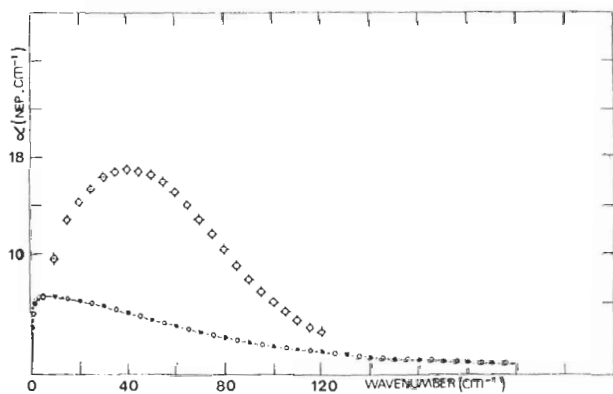
Fig. 5.

a) The theoretical far infrared absorptions for CHF_3 . Morita's model at temperatures of: 1) 253 K, 2) 233 K, 3) 213 K, 4) 193 K, 5) 153 K, 6) 133 K.

b) The theoretical far infrared absorptions for CH_3I . Morita's model at temperatures of: 1) 273 K, 2) 233 K, 3) 193 K, 4) 173 K, 5) 153 K, 6) 133 K.



(a)



(b)

Fig. 6.

a) Cole-Cole plot for chlorobenzene at 295 K.
— Morita's model for the asymmetric-top, symmetric-top, needle and sphere.

*** McConnell's model for a needle.

0 0 0 McConnell's model for a spherical top.

○ and △ Experimental (18).

b) The far infra-red absorption of chlorobenzene at 295 K.

... Morita's model for the asymmetric-top

— Morita's model reduced to the symmetric-top, needle and spherical top.

*** McConnell's model for a needle

0 0 0 McConnell's model for a spherical-top

○ Experimental M.N. Afsar (private communication).

angular velocity. It is easily shown that ⁽¹³⁾

$$\langle \omega(v)^2 \rangle = K_I(0)I_B^2 - kT(2I_B + I_A) \quad (23)$$

The observed temperature dependence of Morita's model is markedly different and not in accord with experiment. Figure 5 shows that the wavenumber of maximum absorption ($\bar{\nu}_{\max}$) shifts to higher frequency and the half width increases significantly with increasing temperature. This behaviour is the reverse of experimental observation for polar molecules in the far infrared ⁽¹⁷⁾.

To date we have considered only the symmetric top molecules CH_3F and CHF_3 . However, the observations made above appear to be consistent for all molecular geometries. Solutions have recently been reported for the full asymmetric top ⁽⁸⁾. Figure 6 shows some numerical results for chlorobenzene, a molecule extensively studied in the microwave and far infrared. Again the expressions reduce, in appropriate limits to the needle and sphere of McConnell. However, as for the symmetric-top, only one β_i and one moment of inertia appear to characterise the computed spectrum. This asymmetric top solution is to be the subject of a future publication where a fuller and more detailed appraisal is given.

In concluding, the inadequacies of the simple inertia corrected Langevin equation are clearly manifested in the small number of sample results presented in this report. The inclusion of molecular moment of inertia in the simple Langevin equation alone, does not satisfactorily explain the « excess » or Poley absorption characteristic of all polar molecules in the far infrared. Further generalisations are required. Our simple kinetic equation is a convenient starting point for such an extension.

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