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THE MORI FORMALISM, A CRITICAL DISCUSSION OF ITS USE IN REPRESENTING FAR INFRARED AND MICROWAVE ABSORPTIONS

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The three variable Mori formalism for molecular dynamics in the fluid state is evaluated using some extensive data of Gerschel's on three strongly dipolar symmetric tops in the microwave and far infrared region of the electromagnetic spectrum. It is found that the use of loss and power absorption coefficients can lead to misleading results when theory and experiment are compared and it is essential in general to get the data over the whole frequency range of interest. Using this procedure it is found that the second memory function of the Mori continued fraction is difficult to approximate satisfactorily with a simple decay (such as an exponential) and it is unlikely that successive memory functions of the total orientational correlation function are simpler functions of time than the latter.

1. Introduction

There has been a fairly intensive theoretical effort in the past few years [1–3] to elucidate the dynamical mechanism responsible for the absorption of dipolar molecules in the far infrared/microwave region of the spectrum in the dense fluid state. Unfortunately this has been hampered by a lack of definitive data for the same system over the *whole* frequency range of interest. In addition the total correlation function, $C(t)$, of the absorption band is made up of at least three identifiable components so that

$$C(t) = C_{\mathrm{p}}(t) + C_{\mathrm{ind}}(t) + C_{\mathrm{ip}}(t) . \tag{1}$$

Here $C_{\mathrm{p}}(t)$ represents auto- and cross-correlations of the permanent dipole ($\boldsymbol{\mu}$):

$$C_{\mathrm{p}}(t) = \sum_i \langle \boldsymbol{\mu}_1(0) \cdot \boldsymbol{\mu}_i(t) \rangle , \tag{2}$$

where the angular brackets denote canonical averaging in phase space. $C_{\mathrm{ind}}(t)$ does the same for the induced (temporary) dipole M present in any molecule due to the effect of the resultant electrostatic field of the others at any instant t. The component $C_{\mathrm{ip}}(t)$ represents auto- and cross-correlations between $\boldsymbol{\mu}$ and $\boldsymbol{M}$.

Very recently, Gerschel has made a careful study of the highly dipolar fluids CH_3F, CH_3Cl and CHF_3 over the whole density and temperature range beneath the critical region in the microwave and far infrared frequency domains [4]. In these fluids the second two terms of eq. (1) are now negligible compared with the first, but the intensity of the induced absorption is very small compared with that due to the large permanent dipole. Our observations are thus restricted to manifestations of $C_{\mathrm{p}}(t)$, since the Gordon sum rule [5] for the integrated absorption intensity of all rotational type absorptions is obeyed to within a few percent [6] *. Therefore in this note we wish to apply the dynamical formalism of Mori [1,6], a series expansion in successive memory functions of $C_{\mathrm{p}}(t)$, to this complete set of data with a view to testing assumptions inherent in the method used to bypass the complex

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* Examples of recent use of this are refs. [7–9].

many-body analysis which the fluid state demands.

2. Formalism

Starting from the equation for the general time evolution of the *auto*correlation function, $C_a(t)$, of a dynamical vector (say $\boldsymbol{u} = \boldsymbol{\mu}/|\boldsymbol{\mu}|$) in N particle phase space it is possible to show [10] that the equation:

$$\dot{C}_a(t) = -\int_0^t K_a(t-\tau) C_a(\tau)\,d\tau \tag{3}$$

follows without any more assumptions being made other than the fundamentals that the system obey the Liouville equation of motion and be canonical in nature. In eq. (3) K_a, the memory function, is defined in Laplace space (p) by $\widetilde{K}_a(p) = \widetilde{\phi}(p)/[1 - \widetilde{\phi}(p)/p]$, with $\phi(t) = -\langle \dot{\boldsymbol{u}}(0) \cdot \dot{\boldsymbol{u}}(t)\rangle$. In this letter we assume that $C_p(t)$ is governed by the same type of equation (being, after all, a sum of vector dot products such as $C_a(t)$), so that K_p would be a memory function embodying both auto- and cross-correlation terms in C_p. Classically, both $C_p(t)$ and $K_p(t)$ are even functions of time with no odd powers of t when expanded in series. Since the memory tensor $K_a(t-\tau)$ is also a correlation function eq. (3) may be developed into a series of coupled Volterra equations [11]:

$$\partial^{(n)}K_p/\partial t = -\int_0^t {}^{(n)}K_p(t-\tau)\,{}^{(n-1)}K_p(\tau)\,d\tau\,, \tag{4}$$

which is a continued fraction in Laplace space. Quentrec and Bezot [12] have shown that truncating this with an exponential is equivalent [12] to taking a set of fast dynamical variables and assuming that this set is complete in Hilbert space [13]. It is assumed that there is no coupling between these and collective hydrodynamic modes [6] (slow variables), and in particular, taking the set $[\boldsymbol{u}, \dot{\boldsymbol{u}}, \ddot{\boldsymbol{u}}]$ corresponds to

$${}^{(1)}K_p(t) = {}^{(1)}K_p(0)\exp(-\gamma t)\,, \tag{5}$$

where γ is a correlation time. That this is only an approximation can be seen from the point of view that ${}^{(1)}K_p(t)$ is theoretically devoid of odd t terms in its expansion, whereas the exponential has them all. Eq. (5) leads to the following forms for the dielectric loss (ϵ''), dispersion (ϵ') and optical absorption coefficient ($\alpha(\bar{\nu})$ in neper cm^{-1}):

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\gamma\,{}^{(0)}K_p(0)\,{}^{(1)}K_p(0)}{\gamma^2[{}^{(0)}K_p(0) - \omega^2]^2 + \omega^2\{\omega^2 - [{}^{(0)}K_p(0) + {}^{(1)}K_p(0)]\}^2}, \tag{6}$$

$$\epsilon' = \epsilon_0 - \frac{(\epsilon_0 - \epsilon_\infty)\omega^2\{\gamma^2[\omega^2 - {}^{(0)}K_p(0)] + [\omega^2 - {}^{(1)}K_p(0)](\omega^2 - [{}^{(0)}K_p(0) + {}^{(1)}K_p(0)])\}}{\gamma^2[{}^{(0)}K_p(0) - \omega^2]^2 + \omega^2\{\omega^2 - [{}^{(0)}K_p(0) + {}^{(1)}K_p(0)]\}^2}, \tag{7}$$

$$\alpha(\bar{\nu}) = 2^{3/2}\pi\epsilon''(\omega)\bar{\nu}/\{([\epsilon'(\omega)]^2 + [\epsilon''(\omega)]^2)^{1/2} + \epsilon'(\omega)\}^{1/2}\,, \tag{8}$$

with $\omega = 2\pi\bar{\nu}c$, and ϵ_0 the static permittivity. Here ${}^{(0)}K_p(0)$ and ${}^{(1)}K_p(0)$ are zero time averages; for an autocorrelation of $\boldsymbol{u}$ the former is independent of intermolecular forces represented by the mean square torque $\langle T^2\rangle$, and the latter dependent [14,15]. Taking autocorrelations for a symmetric top or linear molecule ${}^{(0)}K_p(0) = 2kT/I_B$ where I_B is the moment of inertia perpendicular to the dipole axis. Again in the autocorrelation limit: ${}^{(1)}K_p(0) = a_1 - a_2/a_1$, with $a_1 = {}^{(0)}K_p(0)$ and $a_2 = 4!\,[\frac{1}{3}(kT/I)^2 + \langle T^2\rangle/24I^2]$ for a linear molecule where: $C_a(t) = \Sigma_n(-1)^n a_n t^{2n}/(2n)!$. In this letter we wish to find whether ${}^{(0)}K_p(0)$ is still independent of $\langle T^2\rangle$ or whether any significant dynamical Kirkwood type correlation exists [16], represented by g in: ${}^{(0)}K_p(0) = 2kT/gI_B$.

3. Computation and results

Eqs. (6) and (8) were fitted to Gerschel's data using a least mean squares programme in three different ways designed to test the role of ${}^{(0)}K_\mathrm{p}(0)$ in determining the quality of the overall fit. These were as follows:

(1) The far infrared absorption $\alpha(\bar{\nu})$ was fitted with ${}^{(0)}K_\mathrm{p}(0)$ fixed at the autocorrelated value of $2kT/I_\mathrm{B}$. The result for methyl fluoride is typical and is represented in fig. 1 by the curves at 133 K, 173 K, and 270 K. At 270 K the agreement is good except for small deviations at the highest frequencies. However at 173 K the fit at the lower frequencies is poor and at 133 K it is poor throughout the whole frequency range. These findings are more clearly manifested in loss representation (fig. 1b) where at 173 K the theoretical curve peaks at too high a frequency. This is true also at 133 K, where in addition there is a pronounced misfit at the high frequency end.

(2) The far infrared region was fitted with ${}^{(0)}K_\mathrm{p}(0)$ allowed to vary in addition to ${}^{(1)}K_\mathrm{p}(0)$ and the correlation time. The results are shown in fig. 2a. It is seen that the procedure is totally unjustified by the results, since there appears no microwave absorption or dispersion! Besides, the fit in the far infrared is worse than that obtained by keeping ${}^{(0)}K_\mathrm{p}(0)$ constant at $2kT/I_\mathrm{B}$. Thus it seems that the equilibrium average for the cross correlation function has approximately this value.

(3) Thirdly we fit the whole of the microwave and far infrared region with ${}^{(0)}K_\mathrm{p}(0)$ fixed and varying. The results are typified in fig. 3 for methyl fluoride at 133 K. The curve given by the least mean square best fit:

$${}^{(0)}K_\mathrm{p}(0) = 0.9\,(2kT/I_\mathrm{B}),\quad {}^{(1)}K_\mathrm{p}(0) = 33.3\,(2kT/I_\mathrm{B}),\quad \gamma = 3.6\,(2kT/I_\mathrm{B})$$

is identical with that for the best fit:

$${}^{(0)}K_\mathrm{p}(0) = 2kT/I_\mathrm{B},\quad {}^{(1)}K_\mathrm{p}(0) = 38.3\,(2kT/I_\mathrm{B}),\quad \gamma = 3.6\,(2kT/I_\mathrm{B})^{1/2}$$

reproducing the experimental data satisfactorily except in intensity near the maximum in the loss peak.

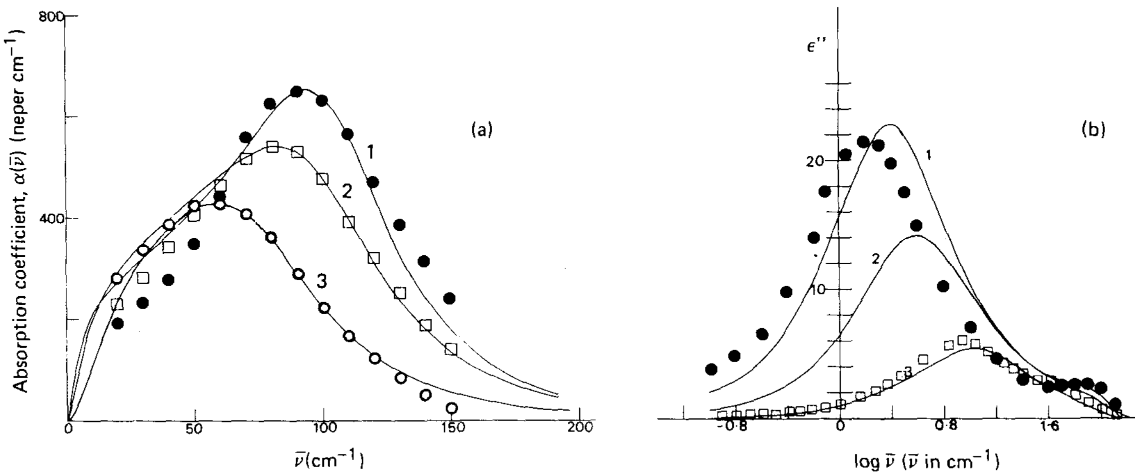

Fig. 1. (a) The experimental far infrared data for methyl fluoride least mean square (lms) fitted using a truncated Mori expansion. ● absorption at 133 K, (1) – lms best fit to the data; □ absorption at 173 K, (2) – lms best fit to the data. ○ absorption at 270 K, (3) – lms best fit to the data. (b) The loss representation of fig. 1a. – (1) theoretical curve at 133 K, ● experimental data; – (2) theoretical curve at 173 K; – (3) theoretical curve at 270 K, □ experimental data.

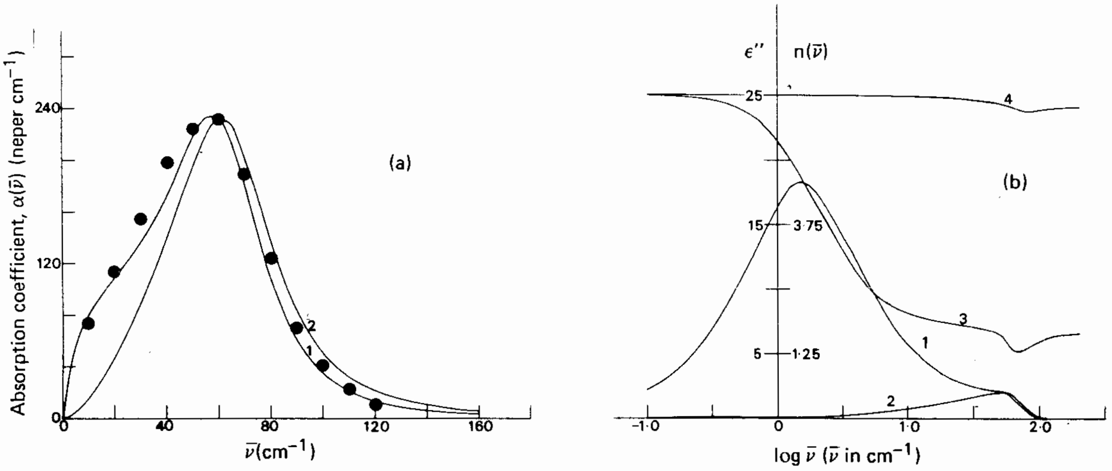

Fig. 2. (a) The experimental far infrared data for fluoroform at 130 K lms fitted using a truncated Mori expansion. ● absorption of fluoroform at 130 K, – (1) theoretical curve with $^{(0)}K_p(0)$ fixed at 1.0 ($\gamma = 4.62$, $^1K_p(0) = 32.\ 35$); – (2) theoretical curve with $^0K_p(0)$ allowed to vary in the lms fitting ($^{(0)}K_p(0) = 13.7$, $^{(1)}K_p(0) = 35.5$, $\gamma = 7.02$). (b) The loss representation of fig. 2a. – (1) $^{(0)}K_p(0)$ fixed at 1 ($\gamma = 4.62$, $^{(1)}K_p(0) = 32.35$); – (2) $^{(0)}K_p(0)$ allowed to vary in lms fitting ($^{(0)}K_p(0) = 13.7$, $^{(1)}K_p(0) = 35.5$, $\gamma = 7.02$). The theoretical dispersion: – (3) $^{(0)}K_p(0) = 1$, $\gamma = 4.62$, $^{(1)}K_p(0) = 32.35$; – (4) $^{(0)}K_p(0) = 13.7$, $\gamma = 7.02$, $^{(1)}K_p(0) = 35.50$.

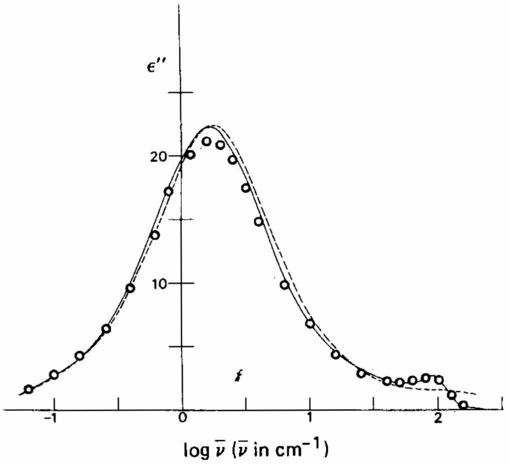

Fig. 3. Theoretical lms fitting of the whole of the microwave and far infrared region. ○ Some experimental data for MeF at 133 K. – The theoretical curve for both $^{(0)}K_p(0) = 1$, $\gamma = 3.60$, $^{(1)}K_p(0) = 38.3$ and $^{(0)}K_p(0) = 0.86$, $\gamma = 3.59$, $^1K_p(0) = 33.27$ which coincide throughout the whole of the frequency range. --- The theoretical curve predicted using the function $^{(1)}K_p(t) = {}^{(1)}K_p(0)\exp[1 - (1 + \gamma^2 t^2)^{1/2}]$.

4. Discussion

It is quite clear that the only way to test thoroughly a dynamical formalism of the fluid state in the far infrared/microwave is to use absorption and dispersion data over the whole frequency range of interest. It is no use fitting the far infrared $\alpha(\bar{\nu})$ alone where data is unavailable at the lower frequencies (especially the technically very difficult decade 1–10 cm^{-1}), since an apparent good fit can be deceptive (figs. 1a and 1b). Part of the difficulty comes from the use of two measures of absorption, and two of dispersion, the loss and power coefficient (ϵ'' and $\alpha(\bar{\nu})$), and the dispersion and refractive index (ϵ' and $n(\bar{\nu})$). These are simply related by Maxwell's equations:

$$\alpha(\bar{\nu}) = 2\pi\bar{\nu}\epsilon''/n(\bar{\nu}), \quad n(\bar{\nu}) = \{([(\epsilon'')^2 + (\epsilon')^2]^{1/2} + \epsilon')/2\}^{1/2} ,$$

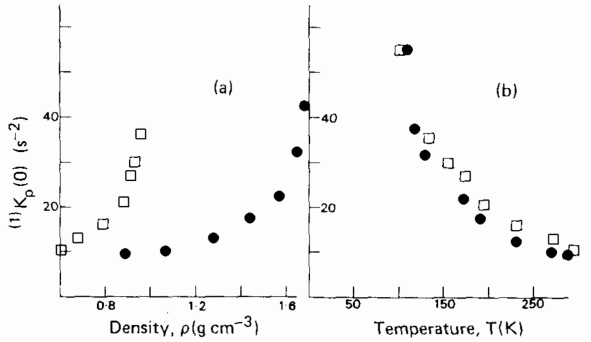

Fig. 4. (a) The dependence of the mean square torque term $^{(1)}K_p(0)$ on the fluid density for □ fluoroform, and ● methyl fluoride. (b) The dependence of the mean square torque term $^{(1)}K_p(0)$ on temperature for □ fluoroform, and ● methyl fluoride.

but each weights grotesquely a part of the frequency range under investigation and used in isolation can very easily lead to gross misconceptions. The loss representation reduces the whole of the far infrared to an insignificant shoulder on the high frequency side of the $\epsilon''(\omega)$ curve, whereas the power representation does just the opposite. In general, the best method of evaluating this type of data is to fit the pair (ϵ'', ϵ') on an Argand diagram at low frequencies and extrapolate to the far infrared $\alpha(\bar{\nu})$, since in less strongly dipolar fluids than these under consideration the integrated intensity: $A = N^{-1} \int_0^\infty \alpha(\bar{\nu})\mathrm{d}\bar{\nu}$ is known in the typical case [17] to be dominated by induced dipolar absorption.

In an attempt to inject some physical reality into the function $^{(1)}K_p(t)$ the following form was used which has an even powered series expansion in t: $^{(1)}K_p(t) = {}^{(1)}K_p(0) \exp[1 - (1 + \gamma^2 t^2)^{1/2}]$ and the absorption/dispersion calculated numerically therefrom The results of fitting the whole frequency range with $^0K_p(0)$ varying is shown in fig. 3. The fit at high frequencies is much poorer than that using an exponential $^{(1)}K_p(t)$, the $\alpha(\bar{\nu})$ curve being much too broad and flat. Thus the Mori continued fraction is unstable when confronted with truncating functions only slightly different from each other in analytical form.

It has been suggested recently [18] that the formal nature of the continued fraction does not imply mathematical rigour, and Kubo's derivation of this own fluctuation–dissipation theorem is internally inconsistent, although the final result is sound as can be demonstrated [11] using projection operators in Hilbert space. It is essential to realise that the use of an exponential for *any* memory function of the continued fraction is theoretically invalid by time reversal considerations, and that one might expect a better, not worse, result by using an even function of time as above.

However, the exponential $^{(1)}K_p(t)$ has some points in its favour as is demonstrated in figs. 4a and 4b which show that the torque term typically increases with the fluid number density and thus decreases with temperature. This is in accord with physical expectation, although at *constant number density* both models of elastic forces and harmonic torsions predict the mean square torque proportional to temperature. More, careful experimental measurements of this kind are needed and on the theoretical side, the three variable formalism ought to be extended to include such factors as coupling to hydrodynamic variables and translational fast variables.

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References

[1] H. Mori, Progr. Theoret. Phys. 33 (1965) 423.
[2] J.T. Hynes and J.M. Deutch, in: Physical chemistry, Vol. 11B, eds. H. Eyring, D. Henderson and W. Jost (Academic Press, New York, 1975) ch. 11.
[3] M. Evans, in: Dielectric and related molecular processes, Vol. 3, ed. M. Davies (The Chemical Society, London, 1977), to be published.
[4] A. Gerschel, Mol. Phys. 31 (1976) 209; 32 (1976) 679.
[5] R.G. Gordon, J. Chem. Phys. 43 (1965) 1307; 41 (1964) 1819.
[6] A.I. Baise, J. Chem. Soc. Faraday II 68 (1972) 1904.
[7] B.J. Berne and J.A. Montgomery, Mol. Phys. 32 (1976) 363.
[8] P.W. Atkins and D.S. Broomhead, Mol. Phys. 32 (1976) 487.
[9] G. Bossis and B. Quentrec, Mol. Phys. 32 (1976) 591.
[10] B.J. Berne, J.P. Boon and S.A. Rice, J. Chem. Phys. 45 (1966) 1086.
[11] B.J. Berne, in: Physical chemistry, Vol. 13B, eds. H. Eyring, D. Henderson and W. Jost (Academic Press, New York, 1975) p. 539.
[12] B. Quentrec and P. Bezot, Mol. Phys. 27 (1974) 879.
[13] D. Kivelson and T. Keyes, J. Chem. Phys. 52 (1972) 4599.
[14] G.J. Evans and M. Evans, J. Chem. Soc. Faraday II 72 (1976) 1169.
[15] G.J. Davies and M. Evans, J. Chem. Soc. Faraday II 72 (1976) 1194, 1206.
[16] I. Darmon, A. Gerschel and C. Brot, Mol. Phys. 23 (1972) 317.
[17] G.W.F. Pardoe, Thesis, University of Wales (1969).
[18] Conference on Brownian Motion, I.A.S., Dublin, Eire, August 1976.