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# Use of Generalized Langevin Theory to Describe Far Infrared Absorptions in Non-dipolar Liquids

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The Mori continued fraction representation of the Kubo response function, truncated at first order, generates a spectral function which is successful in describing absorptions of non-dipolar liquids in the high microwave and far infrared regions (1-250 $cm^{-1}$). There is some evidence that the equilibrium averages [$K_0(0)$ and $K_1(0)$] inherent in this representation are both intermolecular properties, in contrast to the case of pure dipolar absorption, where $K_0(0)$ is a single molecule property. The correlation function of the derived spectral function is compared and contrasted with that of the extended diffusion model of Gordon.

The experimental measurements are also compared with a gas phase model of bimolecular collision-induced absorption, and a " cell " model of the liquid state due to Litovitz and co-workers, both of which are less satisfactory than the generalised Langevin equation.

This paper aims to explore the advantages or otherwise of using simple models to describe the far infrared absorption bands observed [1-3] in non-dipolar liquids at ambient temperature. New and more accurate data have been obtained over a broader range of frequencies for the following liquids: benzene, cyclohexane, carbon disulphide, carbon tetrachloride, *trans*-decalin and dioxan, a series chosen because of their possible use in telecommunications technology as standard low loss dielectrics.

In addition to some frequency domain (2-250 $cm^{-1}$) comparisons of observed and model absorptions, the assessment is extended to the time domain (0-2 ps) using the direct Fourier transform [3] of the absorption coefficient per unit path length [$\alpha(\bar{\nu})$]. Fourier transforms are computed, where applicable, for:

(i) experimental results; (ii) $\alpha(\bar{\nu})$ from the gas phase model [3] of bimolecular collision induced absorption in linear, spherical top, and symmetric top molecules;[4, 5] and (iii) $\alpha(\bar{\nu})$ from the " cell " model of Litovitz and co-workers.[3, 6]

First, the time-correlation function of these bands is approximated with the repeated fraction representation of Mori,[7] and the resulting functional dependence of $\alpha$ on $\bar{\nu}$ extracted by a Fourier–Laplace transform.

## MEMORY FUNCTION FORMALISM

Any absorption band in the infrared, whatever its molecular dynamical origin, is a probability distribution of frequencies, $C(\omega)$, and is related to a correlation function $C(t)$ by the fundamental statistical theorem:[8]

$$C(t) = \int_0^\infty \cos \omega t \, dC(\omega) \qquad (1)$$

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which assumes that the orientational fluctuations of molecules in the liquid state are representable as a continuous, stochastic process, stationary in time.

Non-dipolar molecules absorb in the far infrared and high microwave frequency regions because of the latent disorder in the liquid at any given instant, *i.e.* the fields of all other molecules in the system induce a small, resultant, temporary (but not instantaneous) dipole moment on any given molecule. This can be written [4, 5] as:

$$\boldsymbol{\mu}\left(t, \sum_{i} \sum_{n=2}^{\infty} a_{i,n} R_i^{-n}\right)$$

where there are $i+1$ molecules present, and where the effect of the fields of other molecules is summarised in terms of tensor sums of point multipoles $a_{i,n}$. The intermolecular vector is $\boldsymbol{R}_i$, and the $n = 1$ term is absent when the molecules carry no permanent dipoles. We can now define a correlation function:

$$C(t) = \sum_{i,j} \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_j(t) \rangle$$

where $\boldsymbol{\mu}_i$ is the induced dipole moment on molecule $i$ at time $t$. $C(t)$ is an orientation/interaction correlation function, dependent simultaneously at time $t$ on the orientation of a molecule and on all the others in the system.

We now make the assumption that $C(t)$ can be represented by an equation of the form:

$$\dot{C}(t) = -\int_0^t K(t-\tau)C(\tau)\,\mathrm{d}\tau \tag{2}$$

in the expectation that a simple, empirical functional representation of the kernel $K$ will result in a tractable expression for $C(t)$, and for its Fourier transform $C(\omega)$. This type of equation appears in the general Langevin theory [8] of Kubo [9] and others

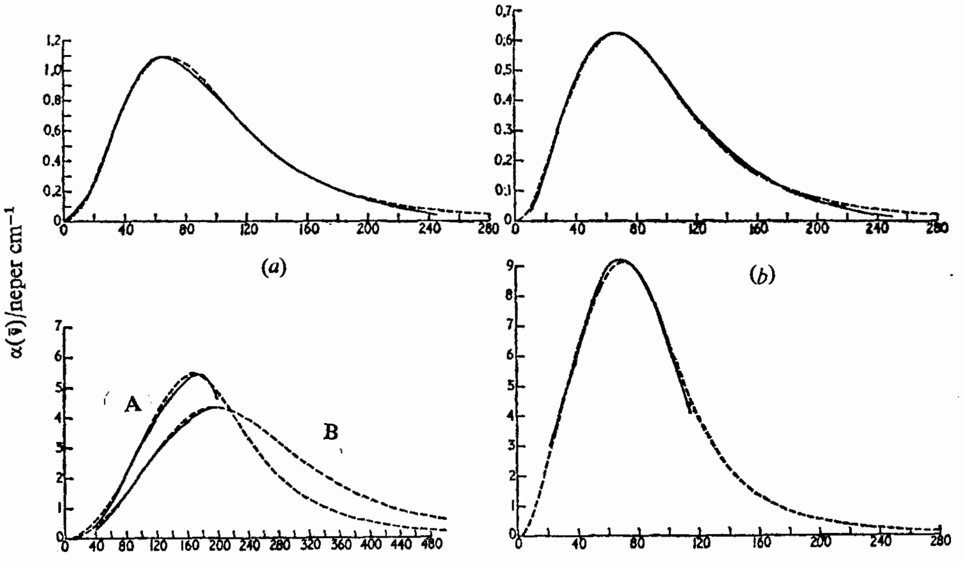


FIG. 1.—(*a*) —— exptl.[18] absorption for $N_2$(l) at 76.4 K; - - - eqn (9) with the parameters of the table; (*b*) —— exptl.[19] absorption for $CO_2$(l) at 273 K, - - - eqn (9); (*c*) —— exptl.[20] absorptions for: A, methane (rotator phase I) at 76 K, B, methane (liquid) at 98 K, - - - eqn (9) with the parameters of the table; (*d*) —— exptl.[21] absorption for $(CN)_2$(l) at 301 K, - - - eqn (9).

which is used to describe statistically the rotational and translational fluctuations of particles in condensed phases.

A particularly useful extension of eqn (2) has been developed by Mori,[7] who regarded the set of kernels $K_0(t), \ldots, K_n(t)$ as obeying the set of coupled Volterra equations such that:

$$\frac{\partial}{\partial t} K_{n-1}(t) = -\int_0^t K_n(t-\tau)K_{n-1}(\tau)\, \mathrm{d}\tau \tag{3}$$

with $n = 1, \ldots, N$. Taking Laplace transforms:

$$C(p) = \frac{C(0)}{p+K_0(p)} = \frac{C(0)}{p+\dfrac{K_0(0)}{p+K_1(p)}} = \ldots \tag{4}$$

which is a continued fraction approximation to the function $C(p)$, the Fourier–Laplace transform of a complex spectral function $C(\mathrm{i}\omega)$.

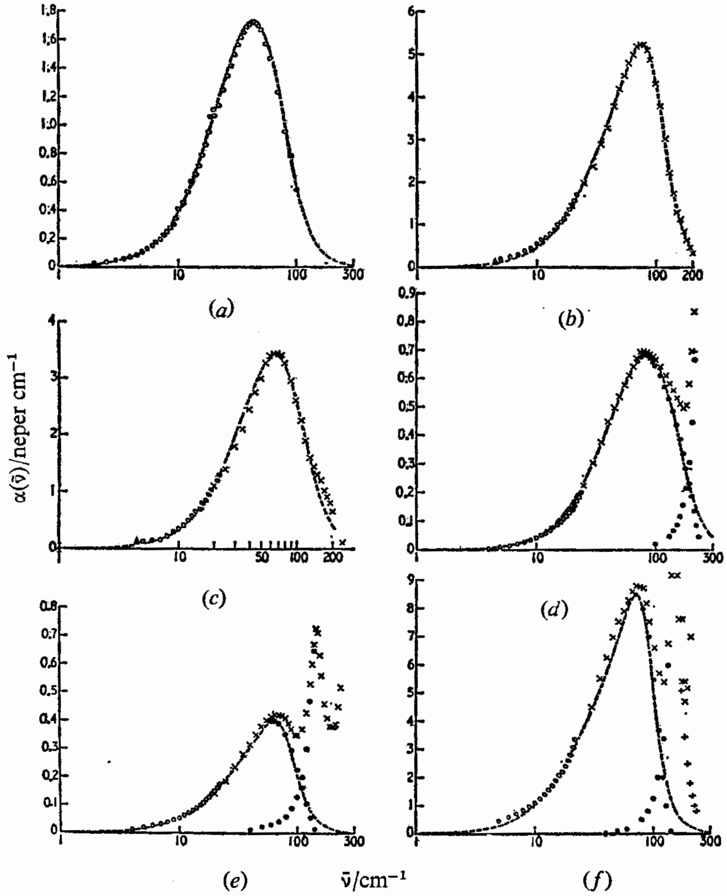


FIG. 2.—(*a*) ○ Experimental absorption (this work) for $CCl_4$(l) at 296 K, - - - eqn (9); (*b*) ○ absorption observed for benzene (l) at 296 K, - - - eqn (9); (*c*) ○ absorption of $CS_2$(l) at 296 K, - - - eqn (9); (*d*) ○ absorption of cyclohexane at 296 K. The high frequency proper mode is extrapolated using a model of collision disturbed vibrators.[13] This technique is also used in (*e*) and (*f*), - - - eqn (9); (*e*) ○ absorption of *trans*-decalin at 296 K, - - - eqn (9); (*f*) ○ absorption of 1,4-dioxan at 296 K, - - - eqn (9).

In this paper, we truncate the series (4) at a level which reproduces very well the experimental far infrared data (fig. 1 and 2) of several non-dipolar liquids. This agreement between theory and experimental observation can be taken as an *a posteriori* justification for the assumptions embodied in eqn (1)-(3). We have made no assumptions regarding the mechanism of dipolar induction on the molecular scale, be this rotational,[4, 5] rototranslational[10] or involving overlap[11] of the van der Waals fields of two or more neighbouring molecules. The intermolecular equilibrium averages $K_0(0)$, $K_1(0)$, . . . yield information only on the ensemble average effect of the field on a given molecule due to the others in the system. This is consistent with the fact that the far infrared bands themselves are statistical distributions of frequency, intermolecular in origin.

The truncation of the series (4) used in this paper is:[12]

$$K_1(t) = K_1(0)\exp(-\gamma t) \tag{5}$$

so that:

$$K_1(p) = \frac{K_1(0)}{p+\gamma} \tag{6}$$

and

$$C(p) = \frac{p^2+p\gamma+K_1(0)}{p^3+p^2\gamma+p[K_1(0)+K_0(0)]+\gamma K_0(0)}\,. \tag{7}$$

The inverse Fourier–Laplace transform of $C(p)$ gives the real part of $C(\mathrm{i}\omega)$ as:

$$\mathrm{Re}\,[C(\mathrm{i}\omega)] = \frac{K_0(0)K_1(0)\gamma}{\gamma^2[K_0(0)-\omega^2]^2+\omega^2\{\omega^2-[K_0(0)+K_1(0)]\}^2}\,. \tag{8}$$

The absorption coefficient, $\alpha(\omega)$ is then given[13] as:

$$\alpha(\omega) = \frac{(\varepsilon_0-\varepsilon_\infty)}{n(\omega)c}\omega^2\,\mathrm{Re}\,[C(\mathrm{i}\omega)] \tag{9}$$

where $(\varepsilon_0-\varepsilon_\infty)$ is the dispersion of the absorption band, and $n(\omega)$ the frequency dependent refractive index of the sample (see Appendix 2).

It is not straightforward to relate $K_0(0)$ and $K_1(0)$ to simple molecular constants such as the multipole moments of the electrostatic field and the moment of inertia; sum rules analogous to those of Gordon[14] for the behaviour of permanent dipoles need to be developed. However, in eqn (9), $C(0)$ is usually normalised to unity, and $K_0(0)$ and $K_1(0)$ have the units of $\mathrm{s}^{-2}$, and $\gamma$ of $\mathrm{s}^{-1}$.

### RELATION BETWEEN $K_0(0)$ AND $K_1(0)$

If it is assumed that the classical $C(t)$ is an even function of time,[8, 13, 14] so that its Maclaurin expansion contains no odd powers of $t$, then:

$$C(t) = \sum_{n=0}^{\infty} a_n \frac{t^{2n}}{(2n)!}\,. \tag{10}$$

Here, $a_0$ is usually unity by normalisation, and successive $a_n$ are alternatively negative and positive. From eqn (4), it follows that:

$$K_0(t) = \sum_{n=0}^{\infty} {}^0k_n \frac{t^{2n}}{(2n)!} \tag{11}$$

$$K_1(t) = \sum_{n=0}^{\infty} {}^1k_n \frac{t^{2n}}{(2n)!} \tag{12}$$

given the expansion (10). Thus:

$$^{0}k_N = -a_{N+1} - \sum_{n=1}^{N} {}^{0}k_{N-n}a_n \tag{13}$$

so that $^{0}k_N$ are known in terms of $a_N$ and their precursors. Using these relations, then:

$$K_0(0) = -a_1\,;\ K_1(0) = {}^{1}k_0 = a_1 - a_2/a_1 \tag{14}$$

$$K_2(0) = (a_2^2 - a_1a_3)/[a_1(a_2 - a_1^2)],\ etc. \tag{15}$$

If the experimental integrated absorption intensity across the band is $\int_0^\infty \alpha(\bar{\nu})\,d\bar{\nu}$, then, given the expansion (10), the coefficients $a_1$, $a_2$ and $a_3$ are defined by their spectral moments, so that:

$$a_1 = -\frac{4c^2}{(\varepsilon_0 - \varepsilon_\infty)} \int_0^\infty \alpha(\bar{\nu})\,d\bar{\nu} \tag{16a}$$

$$a_2 = \frac{16\pi^2c^4}{(\varepsilon_0 - \varepsilon_\infty)} \int_0^\infty \bar{\nu}^2\alpha(\bar{\nu})\,d\bar{\nu} \tag{16b}$$

$$a_3 = -\frac{64\pi^4c^6}{(\varepsilon_0 - \varepsilon_\infty)} \int_0^\infty \bar{\nu}^4\alpha(\bar{\nu})\,d\bar{\nu}. \tag{16c}$$

Thus one way of estimating the relative magnitude of $K_0(0)$ and $K_1(0)$ would be using eqn (12)-(16) with the proviso that experimental and theoretical integrated absorption intensities be the same. Even if $(\varepsilon_0 - \varepsilon_\infty)$ is not known accurately (as is the case for the liquids studied here), eqn (12)-(15) give:

$$|a_3| > \frac{a_2^2}{|a_1|} > |a_1^3| \text{ for positive } K_0(0) \text{ and } K_1(0)\text{, and thus:}$$

$$|K_1(0)| > |K_0(0)|.$$

In this work, we regard $K_0(0)$, $K_1(0)$ and $\gamma$ as empirical parameters, and fit eqn (9) to the experimental data by Gauss–Newton minimisation of residuals.

## EXPERIMENTAL

The absorption spectra were obtained using a Grubb–Parsons/NPL cube interferometer adapted for phase modulation.[1-3, 5] The specimen was held in a RIIC VC–01 variable path-length cell in front of a Golay SP 16 or a Rollin He(l) cooled detector. These allowed the range 2-250 $cm^{-1}$ to be examined with signal-to-noise ratios as great as $10^3$. The absorption due to water vapour was reduced by evacuation to ~ $10^{-3}$ Torr.

The power absorption coefficient per unit length $[\alpha(\bar{\nu})]$ was calculated from the ratio of the transmission of two different cell lengths. The $\alpha(\bar{\nu})$ values are significant to better than $\pm 2\,\%$, and probably to $\pm 1\,\%$ below 20 $cm^{-1}$. No quantitative data exist (to our knowledge) prior to ours in the range 2-20 $cm^{-1}$ for these liquids.

The liquids used were AnalaR or Spectrosol standard purified further by fractional distillation and dried and stored over Union Carbide type 3A zeolite. Purity was checked by g.l.c. or by comparison with the standard physical constants. Dipolar impurities, especially water,[15] must be avoided since they cause significant distortion of the induced absorption bands, which are relatively weak.

## RESULTS AND DISCUSSION

The functions generated using eqn (9) are fitted directly to the frequency domain experimental data in fig. (1) and (2). The values of $K_0(0)$, $K_1(0)$ and $\gamma$ used are listed in the table, with those for liquid methane and the simple linear molecules $N_2$, $CO_2$ and $(CN)_2$. In units of $2kT/I_B$ (see below) there is a tendency for $K_0(0)$ and $K_1(0)$ to increase as the geometrical anisotropy of each molecule. The absolute magnitude of the absorption is given in terms of an apparent $(\varepsilon_0-\varepsilon_\infty)$. This dispersion can be linked to a bulk " effective dipole moment ", or, on the other hand,[1, 2] to an " effective molecular quadrupole moment " or higher multipole, given some drastic assumption about the molecular dynamical and electrostatic origin of these very broad bands. At this stage, we prefer not to make any more assumptions other than those inherent in eqn (1)-(3).

TABLE 1.—PARAMETERS OF EQN (10) FOR VARIOUS LIQUIDS

| liquid | temp./K | $10^{40} I_B$ /g cm$^2$ | $\gamma(I_B/2kT)^{\frac{1}{2}}$ | $K_0(I_B/2kT)$ | $K_1(I_B/2kT)$ | $(\varepsilon_0-\varepsilon_\infty)$ |
|---|---|---|---|---|---|---|
| nitrogen | 76.4 | 12.2 | 10.6 | 5.9 | 37.8 | 0.005 |
| carbon dioxide* | 273 | 71.2 | 11.5 | 8.6 | 51.9 | 0.007 |
| $CCl_4$ | 296 | 484 | 14.2 | 10.9 | 80.6 | 0.019 |
| $CH_4$ (rotor phase I) | 76 | 5.34 | 10.6 | 14.7 | 47.9 | 0.009 |
| cyanogen* | 301 | 155 | 10.9 | 14.9 | 66.5 | 0.050 |
| methane | 98 | 5.34 | 14.5 | 16.8 | 75.7 | 0.007 |
| benzene | 296 | 198 | 12.8 | 20.8 | 100.6 | 0.023 |
| $CS_2$ | 296 | 259 | 20.3 | 26.2 | 170.2 | 0.026 |
| cyclohexane | 296 | 178 | 21.1 | 28.4 | 194.3 | 0.040 |
| *trans*-decalin | 296 | 1020 | 22.7 | 70.7 | 335.3 | 0.003 |
| 1,4-dioxan† | 296 | 160 | 7.8 | 10.4 | 46.5 | 0.060 |

* Liquids of low density under several atmospheres of the vapour; † anomalous behaviour.

The units of $(2kT/I_B)$ are used to enable direct comparison with the $K_0(0)$ and $K_1(0)$ of dipolar molecules,[12] where they are more easily related to molecular constants, and intermolecular parameters such as the mean square torque $\langle N^2\rangle$.[14] For dipolar linear and symmetric top molecules, Gordon has shown that:

$$K_0(0) = 2kT/I_B = -a_1.$$

Also, for linear molecules:[8]

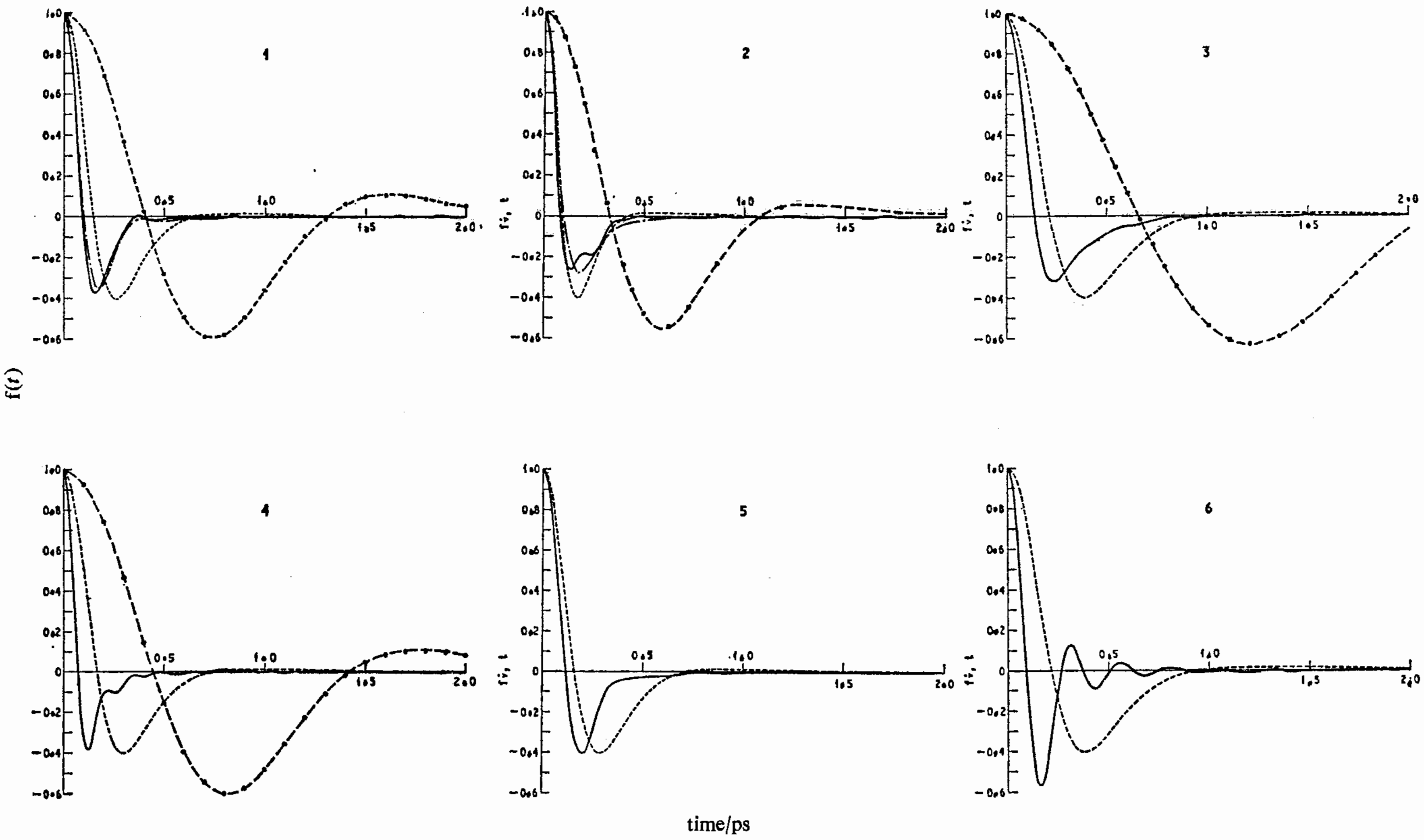
$$a_2 = \frac{1}{3}\left(\frac{kT}{I_B}\right)^2 + \frac{\langle N^2\rangle}{24I_B^2};$$

$$K_1(0) = a_1 - a_2/a_1.$$

It seems reasonable to assume that if sum rules are developed for induced dipolar absorption, they will involve the coefficients of $t^{2n}$ in units of $2kT/I_B$ or similar. It is seen from the table that, in these units, both $K_0(0)$ and, somewhat less steadily, $K_1(0)$ increase across the series of liquids:

$N_2$, $CO_2$, $CCl_4$, $CH_4$ (rotator), $(CN)_2$, $CH_4$(l),
benzene, $CS_2$, clycohexane, and *trans*-decalin;

so that intermolecular factors, and not merely inertial ones, seem to be involved in the definition of both parameters. Also $|K_1(0)|$ is always greater than $|K_0(0)|$, so that the above expansion of the correlation function in even powers of time is not counter evidenced by our observations. The very satisfactory fits to experimental data over almost three decades of frequency show that the analytical dependence of $\alpha$ upon $\bar{\nu}$ is that of eqn (9), but the physical interpretation of $K_0(0)$, $K_1(0)$ and $\gamma$ will


1
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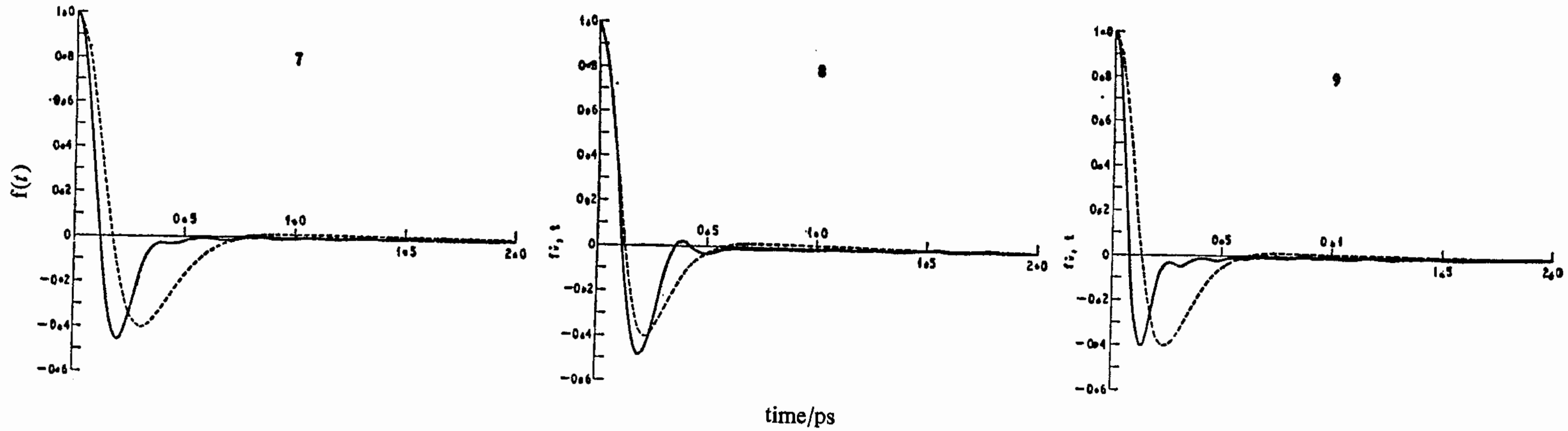

FIG. 3.—Fourier transforms of $\alpha\,(\bar{\nu})$ for some non-dipolar liquids. (1) Benzene; (2) carbon disulphide; (3) carbon tetrachloride; (4) cyclohexane; (5) *p*-difluorobenzene; (6) bicyclohexyl; (7) *trans*-decalin; (8) 1, 4-dioxan; (9) *trans*-1,2-dichloroethylene. —— experimental; –·–––·– free rotor; - - - Litovitz "cell" model; –·– function derived from eqn (9).

have to be elucidated by further work on the actual molecular mechanisms involved in the dipole induction (*i.e.*, rotational, translational and overlap modes).

It is informative to note that the memory function associated with $C(t)$ by eqn (2) is defined algebraically when the Mori series (4) is truncated according to eqn (5). We have:

$$C(p) = [p+K(p)]^{-1} = \frac{p^2+p\gamma+K_1(0)}{p^3+p^2\gamma+p[K_1(0)+K_0(0)]+\gamma K_0(0)} \tag{17}$$

so that:

$$K(p) = K_0(0)\frac{(p+\gamma)}{p^2+p\gamma+K_1(0)}.$$

Therefore, making the inverse Laplace transform:

$$K(t) = K_0(0)\left[e^{-\gamma t/2}\left(\cos at+\frac{\gamma}{2a}\sin at\right)\right]$$

if

$$K_1(0) > \gamma^2/4$$

$$= K_0(0)\left[e^{-\gamma t/2}\left(\cosh bt+\frac{\gamma}{2b}\sinh bt\right)\right] \tag{18}$$

if

$$K_1(0) < \gamma^2/4$$

$$= K_0(0)e^{-\gamma t/2}(1+\gamma t/2)$$

if

$$K_1(0) = \gamma^2/4;$$

where

$$a^2 = -b^2 = K_1(0)-\gamma^2/4.$$

Eqn (18) is useful in that memory functions can be calculated easily after $K_0(0)$, $K_1(0)$ and $\gamma$ have been found by least squares minimisation. The fit of theory to the data is usually so satisfactory (fig. 1 and 2) that these memory functions could be taken as approximating the experimental ones very well. The same is true for the correlation function $C(t)$. This has important practical implications because it is usually very difficult to calculate $C(t)$ by direct numerical transformation of $C(\omega)$ since accurate data are needed well below 1 cm$^{-1}$ [we are transforming $\alpha(\omega)/(\omega^2)$].

It is possible to evaluate $C(t)$, the inverse Laplace transform of eqn (17) to give an algebraic expression for the intermolecular correlation function. It is shown in Appendix 1 that:

$$C(t) = \left[\frac{\cos\beta t}{1+\Gamma}+\frac{1}{\beta}\left(\frac{\alpha_1+\Gamma\alpha_2}{1+\Gamma}\right)\sin\beta t\right]\exp(-\alpha_1 t)+\frac{\Gamma}{1+\Gamma}\exp(-\alpha_2 t) \tag{20}$$

where

$$\Gamma = \frac{2\alpha_1(2\beta^2-\alpha_1^2)}{\alpha_2(3\alpha_1^2-\beta^2-\alpha_2^2)} \quad \text{with:}$$

$$-\alpha_2 = s_1+s_2-\gamma/3$$

$$\alpha_1 = \tfrac{1}{2}(s_1+s_2)+\gamma/3$$

$$\beta = \frac{\sqrt{3}}{2}(s_1-s_2).$$

The parameters $s_1$ and $s_2$ are defined by:

$$s_1 = \left[-\frac{B}{2}+\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}}$$

$$s_2 = \left[-\frac{B}{2}-\left(\frac{A^3}{27}+\frac{B^2}{4}\right)^{\frac{1}{2}}\right]^{\frac{1}{3}}$$

where $A = K_0(0)+K_1(0)-\gamma^2/3$; $B = \frac{\gamma}{3}\left(\frac{2\gamma^2}{9}+2K_0(0)-K_1(0)\right).$

The time expansion of $C(t)$ begins:

$$C(t) = 1-\phi_0\frac{t^2}{2!}+\phi_1\frac{t^4}{4!}- \dots +\mathcal{O}(t^5)$$

*i.e.*, it is even up to the fourth power in time, and is well-behaved at $t = 0$. Eqn (20) can be regarded as the next step up the Mori series from the " $M$-diffusion truncation "

$$K_0(t) = K_0(0)\exp(-\gamma t)$$

which yields [13] a correlation function of the form:

$$C(t) = \frac{\tau_1}{\tau_1-\tau_2}\exp(-t/\tau_1)-\frac{\tau_2}{\tau_1-\tau_2}\exp(-t/\tau_2)$$

where $\tau_1$ and $\tau_2$ are correlation times, an equation which is even up to $t^2$ only.

The predictions of the " cell " model of Litovitz and co-workers [6] and (where applicable) of the model of multipole induced absorption in a two molecule collision[3-5] are given as direct Fourier transforms [3] of $\alpha(\bar{\nu})$ in fig. 3. Fourier transformation is a convenient way of manipulating the discrete line absorptions given by the latter model into a continuous form with time as the variable. Both models have no empirical parameters which can be adjusted for best fit, but depend on taking a Lennard-Jones form for the intermolecular potential. This is their only advantage over the Mori formalism, which at present involves fitting with three phenomenological variables. The disadvantages are that Litovitz's model can yield little information about the intermolecular mean square torque, which is probably the dominant factor in determining the position and shape of the far infrared band. It is a semi-empirical treatment in terms of calculating the molecular angular velocity from a consideration of the deformation of molecular polarisability during a collision, and has no intermolecular parameters except those of the Lennard-Jones potential. The same is true of the two-molecule (gas phase) model of multipole-induced absorption, which, from fig. 3 is inadequate in describing the more complex interactions of the condensed phase.

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## APPENDIX 1

We need the inverse Laplace transform of:

$$C(p) = (p^2+\gamma p+K_1)/[p^3+p^2\gamma+p(K_0+K_1)+\gamma K_0]. \tag{1.1}$$

Heaviside's expansion theorem states that if:

$$F(p) = G(p)/H(p)$$

where $G(p)$ has no singularities in $|p| < \infty$, and $H(p)$ has simple zeros at $p = p_1, p_2, \ldots$, then:

$$\mathscr{L}^{-1}\frac{G(p)}{H(p)} = \sum_n \frac{G(p_n)}{H(p_n)}\exp(p_n t), \tag{1.2}$$

where $H(p_n) = 0$, and $H'(p_n)$ is the derivative of $H(p)$ at $p = p_n$. In general, the roots of the denominator of eqn (1.1) are of the form:[17]

$$p_1 = -\alpha_2\,;\; p_2 = -\alpha_1 - i\beta\,;\; p_3 = -\alpha_1 + i\beta,$$

so that, using eqn (1.1) and (1.2):

$$C(t) = (x\cos\beta t - z\sin\beta t)\,e^{-\alpha_1 t} + y\,e^{-\alpha_2 t}.$$

The constants $x$, $y$ and $z$ can be found using the fact that $C(t)$ is even up to $t^4$, so that:

$$x\alpha_1 + z\beta + \alpha_2 y = 0 \tag{1.3}$$

$$x\left(\frac{\beta^2\alpha_1}{2} + \frac{\alpha_1^3}{6}\right) + z\left(\frac{\beta\alpha_1^2}{2} - \frac{\beta^3}{6}\right) + \frac{\alpha_2^3}{6}y = 0. \tag{1.4}$$

Also, if we normalise $C(0)$ to unity, then:

$$x + y = 1. \tag{1.5}$$

Solving (1.3), (1.4) and (1.5), we have:

$$x = \frac{1}{1+\Gamma}, \qquad y = \frac{\Gamma}{1+\Gamma}, \qquad z = -\frac{1}{\beta}\left(\frac{\alpha_1 + \Gamma\alpha_2}{1+\Gamma}\right)$$

where

$$\Gamma = \frac{2\alpha_1(2\beta^2 - \alpha_1^2)}{\alpha_2(3\alpha_1^2 - \beta^2 - \alpha_2^2)}.$$

The parameters $\alpha_1$, $\alpha_2$ and $\beta$ are related to $K_0$, $K_1$ and $\gamma$ by the standard formula for finding the roots of a cubic given, for example, in Abramowitz and Stegun.[17]

## APPENDIX 2

In using the relation

$$\alpha(\omega) = \frac{\omega^2(\varepsilon_0 - \varepsilon_\infty)}{n(\omega)c}\operatorname{Re}[C(i\omega)]$$

we are assuming that the molecular ensemble obeys classical equations of motion ($\hbar \to 0$). This is consistent with our basic assumption that Mori formalism is applicable to the classical correlation function $\sum_{ij}\langle \mu_i(0)\cdot\mu_j(t)\rangle$. This assumption rests on the broad and related generalisations which lie at the root of our present understanding of transport properties. These are linear response theory and the fluctuation-dissipation theorem. Classically, the latter can be derived for a canonical ensemble using the Liouville equation:

$$\frac{dB}{dt} = \left[\sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial B}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial B}{\partial p_i}\right)\right]$$

describing the motion of a property $B$ which depends on time $t$ by the intermediacy of coordinates $q_i$ and their conjugate momenta $p_i$. Using quantised mechanics the

Poisson brackets are replaced by the commutator $\hbar^{-1}[H, B]$, and the relation between a classical correlation function $\langle \mu_i(0) \cdot \mu_j(t) \rangle$ and the quantised analogue $\langle [\mu_i(0)\ \mu_j(t)] \rangle$ is:

$$\int e^{i\omega t} \langle [\mu_i(0) \cdot \mu_j(t)] \rangle \, d\omega = (1 - e^{-\hbar\omega/kT}) \int e^{i\omega t} \langle \mu_i(0)\mu_j(t) \rangle \, d\omega.$$

The quantum mechanical correlation function is real, and contains odd powers of $t$ in its Maclaurin expansion. The classical correlation function contains only even powers of $t$, in accord with the time reversibility principle of Onsager.

Mori has shown that the equation of motion of an arbitrary dynamical variable of an arbitrary system can be transformed rigorously to a linear generalised Langevin form; and Kubo shows that a subsystem of an ensemble when perturbed, will relax to thermal equilibrium via the same generalised Langevin equation. Neither the arbitrary subsystem nor the variable need be quantised. That an ensemble of molecules as small as nitrogen or methane can be treated with classical equations of motion is the basis of the technique of computer molecular dynamics, including the well known simulation of the properties of liquid water, carried out by Rahman and Stillinger.

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