

Truncated Series Expansion for the Correlation Function of Permanent and Induced Depolarised Rayleigh Bands

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Correlation functions from depolarised Rayleigh bands of molecules with permanent and induced polarisability components are simulated using an expansion in terms of successive memory functions, truncated at an early stage with an exponential decay. The results of Alder *et al.* for computer argon and Dill *et al.* for acetone, methyl iodide and benzene up to several kbar of external pressure are simulated closely in the majority of cases, but only some of the oscillations in the experimental results for benzene and methyl iodide are reproduced by the very simple truncated series expansion used here.

INTRODUCTION AND THEORY

It is shown here that depolarised Rayleigh band shapes of molecules exhibiting both anisotropy and isotropy of polarisability¹ can be simulated easily and, on the whole, closely using a series of integro-differential equations to describe statistically the motions in a fluid of the molecular polarisability tensor. If incoming light, polarised in the z axis, is incident upon a liquid or gas sample in the direction, and scattered light is observed in the y direction polarised in the x axis then what is observed is the radiation spectrum $I_{\text{VH}}(\omega)$ from a dipole induced in the x direction by an electric field along the z axis. Such a dipole is proportional to the xz element of the electric polarisability of the scattering volume. The depolarised Rayleigh spectral intensity $I_{\text{VH}}(\omega)$ is the Fourier transform of a correlation function which can be written^{2, 3} as:

$$C(t) = C_{\text{perm}}(t) + C_{\text{ind}}(t) + C_{\text{ip}}(t) \quad (1)$$

with:

$$C_{\text{perm}}(t) = \text{Tr}\langle\beta_1(0)\beta_2(t)\rangle + \sum_{i \neq 1} \text{Tr}\langle\beta_1(0)\beta_1(t)\rangle \quad (2)$$

where β_i is the anisotropy of the electric polarisability tensor for the i th molecule and the trace is over the x , y and z components of β . In eqn (1) $C_{\text{ind}}(t)$ is a contribution arising from intermolecular collisions which exists⁴ even for molecules such as CCl_4 which are optically isotropic. $C_{\text{ip}}(t)$ accounts for cross-correlation between permanent and induced anisotropies.

In the specific case of self correlation in linear molecules, $C_{\text{perm}}(t)$ is given³ by:

$$\begin{aligned} C_{\text{perm}}(t) &= \langle P_2[\cos \theta(t)] \rangle \\ &= \frac{1}{2} \langle 3[\mathbf{u}(0) \cdot \mathbf{u}(t)]^2 - 1 \rangle \\ &= 1 - 3 \frac{kT}{I} t^2 + \left[4 \left(\frac{kT}{I} \right)^2 + \frac{\langle T^2 \rangle}{8I^2} \right] t^4 \dots \end{aligned} \quad (3)$$

where \mathbf{u} is a unit vector along atomic centres, I is the moment of inertia, T the

temperature and $\langle T^2 \rangle$ the mean square torque on a molecule due to the motions of its neighbours in a fluid. Cross-correlations of permanent anisotropy components [the second term of eqn (2)], and the last two terms of eqn (1) are much more difficult to derive explicitly in terms of vectors such as u . A recent computer simulation of the characteristic exponential decay of the interaction induced Rayleigh band in argon assumed a dipole-induced dipole interaction mechanism for $C_{\text{ind}}(t)$ for which $\beta(r) = 6\alpha_0^2/r^3$ where α_0 is the atomic polarisability and r the interatomic distance.⁵ This gives $C_{\text{ind}}(t)$ as:

$$C_{\text{ind}}(t) = \sum_{k \neq l} \sum_{i \neq j} \langle \beta[r_{ij}(0)] \beta[r_{kl}(t)] P_2[\mathbf{u}_{ij}(0) \cdot \mathbf{u}_{kl}(t)] \rangle. \quad (4)$$

Here \mathbf{u}_{ij} is a unit vector along the line joining the pair ij . At long times both $C_{\text{perm}}(t)$ and $C_{\text{ind}}(t)$ decay exponentially and assuming that $C_{\text{ip}}(t)$ does so too, then $I_{\text{VH}}(\omega)$, the Fourier transform of the total correlation function $C(t)$ of eqn (1), will behave as a sum of Lorentzians at low frequencies.

The complex nature of the cross terms making up $C_{\text{ip}}(t)$ seems to be intractable analytically at the present time, but generally and fundamentally,⁶ both correlation functions $C_{\text{ip}}(t)$ and $C_{\text{ind}}(t)$ are even functions of time classically. They can be expanded in a series such as eqn (3), but with the important difference that the coefficients of time will *all* be dependent on the intermolecular potential, or its derivative with respect to orientation, the torque.

Furthermore, general fluctuation-dissipation theory^{7, 8} produces the fundamental theorem:

$$\dot{C}(t) = - \int_0^t K(t-\tau) C(\tau) d\tau \quad (5)$$

where the kernel K , often called the memory function, has itself the properties of a correlation function and thus obeys the same type of equation. This implies^{9, 10} the infinite series:

$$\frac{\partial K_{n-1}(t)}{\partial t} = - \int_0^t K_n(t-\tau) K_{n-1}(\tau) d\tau \quad (6)$$

$n \rightarrow \infty$, which expands the general correlation function classically and evenly as a quotient of polynomials in time.

Using eqn (5) and (6) alone, we can attempt to deduce an analytical form for $C(t)$, and thus for each of $C_{\text{perm}}(t)$, $C_{\text{ind}}(t)$ and $C_{\text{ip}}(t)$ by assuming a simple form for one of the memory functions $K_n(t)$, thus truncating the series (6). A particularly successful approximation¹¹ (for correlation functions pertinent to far infrared permanent and induced absorption) is:

$$K_1(t) = K_1(0) \exp(-\gamma t) \quad (7)$$

which yields $C(t)$ as a sum of three complex exponentials, so that:

$$I_{\text{VH}}(\omega) \propto \int_{-\infty}^{\infty} \exp(i\omega t) C(t) dt \quad (8)$$

$$\propto \frac{K_0(0)K_1(0)\gamma}{\gamma^2 [K_0(0) - \omega^2]^2 + \omega^2 \{ \omega^2 - [K_0(0) + K_1(0)] \}^2}$$

It is shown here that this form reproduces accurately: (i) all but one of Alder *et al.*'s⁵ computed correlation functions [$C_{\text{ind}}(t)$] for induced absorption in fluid argon [eqn (4)]; (ii) the results of Dill *et al.*¹² for $C_{\text{perm}}(t)$ in liquid acetone pressurised up to several thousand bar; but less accurately the oscillations observed¹² in $C_{\text{perm}}(t)$ for liquid benzene and methyl iodide under kilobars of external pressure.

RESULTS AND DISCUSSION

The least mean squares best fits to the experimental correlation functions of the theoretical ones defined above [eqn (7)] are shown in fig. 1 and 2, with the parameters listed in the table. $I_{\text{VH}}(\omega)/I_{\text{VH}}(0)$ from eqn (8) is shown in fig. 3 for computer argon, together with the Lorentzian to which eqn (8) reduces when $\omega^4 \ll \omega^2$, *i.e.*,

$$I_{\text{VH}}^{\text{Lor}}(\omega) \rightarrow \frac{K_0(0)K_1(0)\gamma}{\gamma^2 K_0^2(0) + [K_0^2(0) + K_1^2(0) + 2K_0(0)(K_1(0) - \gamma^2)]\omega^2} \quad (9)$$

Eqn (8) for interaction induced scattering is a Lorentzian at short times and exponential at long, reproducing well the bandshape of a recent experiment by An *et al.*⁴ on real argon at five thermodynamic states, where a roughly Lorentzian component in the bandshape accounts for about half of the total depolarised intensity.

Expanding $C_{\text{ind}}(t)$ as an even-powered Maclaurin series we have:

$$C_{\text{ind}}(t) = \sum_n a_n t^{2n}/(2n)! \quad (10)$$

with successive a_n alternatively positive and negative. The zero-time averages $K_0(0)$ and $K_1(0)$ are related¹¹ to the coefficients a_n by:

$$K_0(0) = -a_1; \quad K_1(0) = a_1 - a_2/a_1;$$

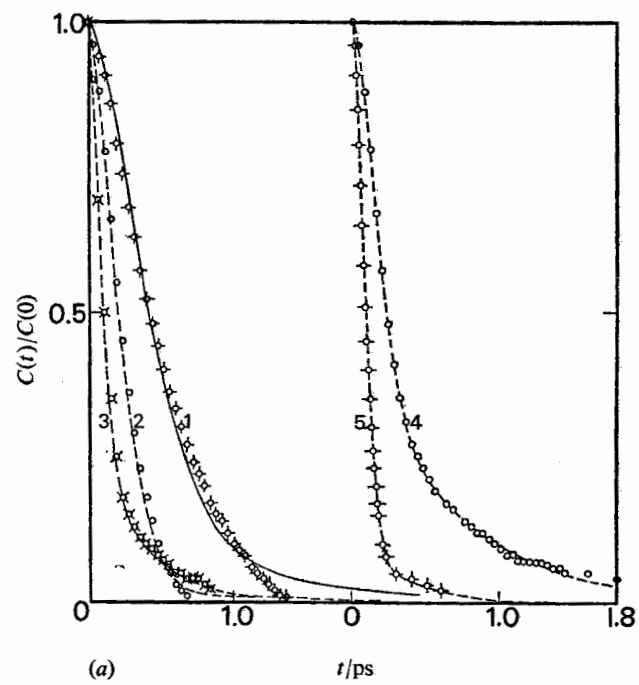
and are both intermolecular properties and related to the average mean square torque in the ensemble at any time. They should thus vary with macroscopic density and temperature as the torque, assuming that the truncation in eqn (7) is acceptable physically. The table shows up a trend where both $K_0(0)$ and $K_1(0)$ increase monotonically with density and temperature, in accord with computer dynamics results⁷ and models such as the hard sphere ensemble and of harmonic well dynamics which predict $\langle T^2 \rangle$, the mean square torque, proportional to temperature and molecular number density.

The $C_{\text{ind}}(t)$ estimated by the best fit to the computer data all have natural exponential tails which are significantly positive at fairly long times. This could be indicative of those long hydrodynamic tails (falling off as $t^{-\frac{3}{2}}$) whose origin is in the

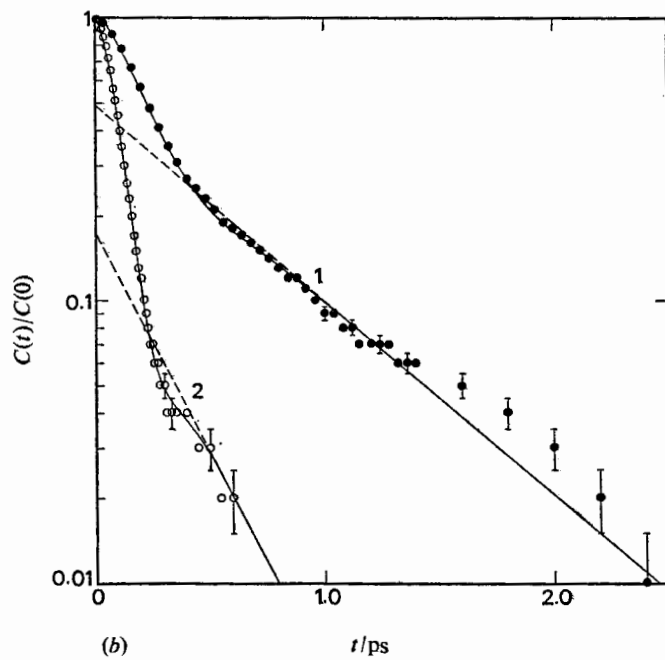
TABLE 1.—PARAMETERS FOR BEST FIT TO EXPTL. OR COMPUTED CORRELATION FUNCTIONS

system	T/K	P/amagat	$10^{-24} K_0(0)/s^{-2}$	$10^{-24} K_1(0)/s^{-2}$	$10^{-12} \gamma/s^{-1}$
computer argon ⁵	300	67	2.8	22.0	7.7
computer argon	300	473	8.9	72.0	14.1
computer argon	300	905	29.0	306.0	28.5
computer argon	90	795	8.5	101.3	16.2
computer argon	960	757	35.7	394.6	32.7
		P/kbar	$IK_0(0)/kT$	$IK_1(0)/kT$	$\gamma(I/kT)^{\frac{1}{2}}$
liquid	960	0.001	1.81	24.5	7.3
acetone ¹²	960	1.0	1.87	36.3	8.8
	960	2.0	1.50	41.1	9.7
liquid methyl	296	0.001	1.15	21.8	7.2
iodide ¹²	296	1.000	1.08	23.6	7.5
	296	2.500	1.23	42.5	9.8
liquid	296	0.001	2.08	92.9	14.4
benzene ¹²	296	0.601	1.65	156.3	19.1

I is the mean moment of inertia used, but not quoted, by the authors in ref. (12)



(a)



(b)

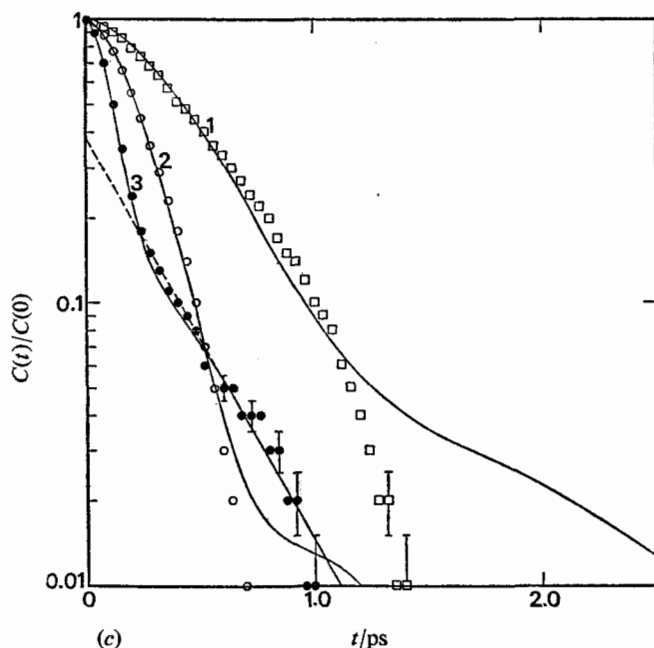
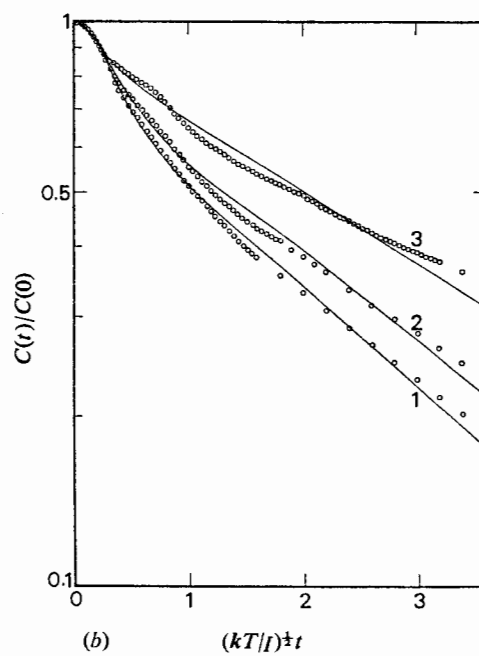
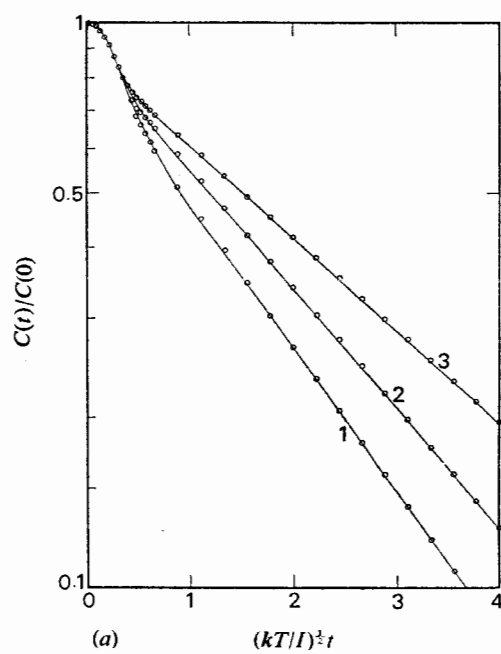


FIG. 1.—(a) (1) \diamond Computed⁴ correlation function for argon: $C_{\text{ind}}(t) = \sum_{k \neq 1} \sum_{i \neq j} \langle \beta[r_{ij}(0)] \beta [r_{kl}(0)] P_2[u_{ij}(0) u_{kl}(t)] \rangle$. (a) Least mean squares best fit using a truncated expansion in terms of memory functions, with the parameters listed in the table. (1) 300 K, 67 amagat; (2) 300 K, 473 amagat; (3) 300 K, 905 amagat; (4) 960 K, 757 amagat; (5) 90 K, 795 amagat. (b) As for fig. 1(a), on a logarithmic scale designed to emphasise the long time exponential tailing of the theoretical correlation functions. (1) 90 K, 795 amagat; (2) 960 K, 757 amagat. (c) As for fig. 1(a), (1) 67 amagat, 300 K; (2) 473 amagat, 300 K; (3) 905 amagat, 300 K.

collective, shearing mode of motion of many molecules over a significant range of molecular diameters. Long tails such as these can be seen in computer simulations⁷ of $K_0(t)$, and were the original object of Alder *et al.*'s investigation, but seem to have a much more complex dependence on time than t^{-2} or e^{-t} . Indeed, the vortex motion of which they are a manifestation^{11a} has long range implications which must mean that cross-correlations form a very important part of any correlation function observable by depolarised Rayleigh scattering. It is interesting to note from the table that γ is directly proportional to temperature and density, which means that the correlation time of the dynamical process for which $K_1(t)$ is the exponential (Markovian) correlation function is becoming much shorter.

In the case of $C_{\text{perm}}(t)$ in liquid acetone [fig. 2(a)], the fit to the experimental $C_{\text{perm}}(t)$ of Dill *et al.*¹² (corrected for induced absorption by these authors) is again good, and it is especially encouraging to see that $K_0(0)$ for best fit this time does not vary significantly over the pressure range up to a few kilobar, while $K_1(0)$ and γ increase a great deal. Why this should be so theoretically can be seen from eqn (4) where for permanent anisotropy the coefficient of t^2 is a single molecule property. For benzene and methyl iodide [fig. 2(b) and (c)], the fits are less successful, only some of the observed oscillations being followed theoretically. Possible reasons are: (i) the observed oscillations are artefacts caused by the method used¹² to estimate the induced absorption, or by uncertainties in the extrapolation of the data used in calculating the Fourier transform; (ii) accepting the experimental data as accurate, an improvement is needed in the theoretical $C(t)$ which would be made either by



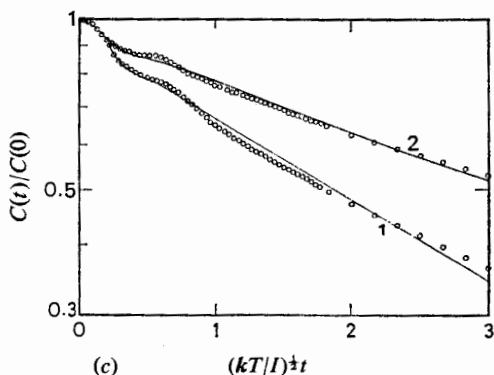


FIG. 2.—(a) $C_{perm}(t)$ from ref. (12), corrected¹² for induced absorption. — Best fit with tabulated parameters; (1) 1 bar, 296 K; (2) 1 kbar, 296 K; (3) 2 kbar, 296 K; for liquid acetone. (b) As for fig. 2(a) for liquid methyl iodide; (1) 1 bar, 296 K; (2) 1 kbar, 296 K; (3) 2.5 kbar, 296 K. (c) As for fig. 2(a) for liquid benzene; (1) 1 bar, 296 K, (2) 0.6 kbar, 296 K.

using a more realistic truncation :

$$K_1(t) = K_1(0)f(t)$$

where $f(t)$ is, for example, a damped oscillating function, or by using a multi-parameter model based upon truncating the series at higher order. Meanwhile it is encouraging to note that even the primitively simple model used here [which for $K_1(t)$ does not even accord with Onsager's reversibility principle] produces a behaviour in $K_1(0)$ which would be that expected on the basis of torque dependence. This parameter increases significantly with molecular number density, the correlation time $1/\gamma$ again becoming markedly shorter.

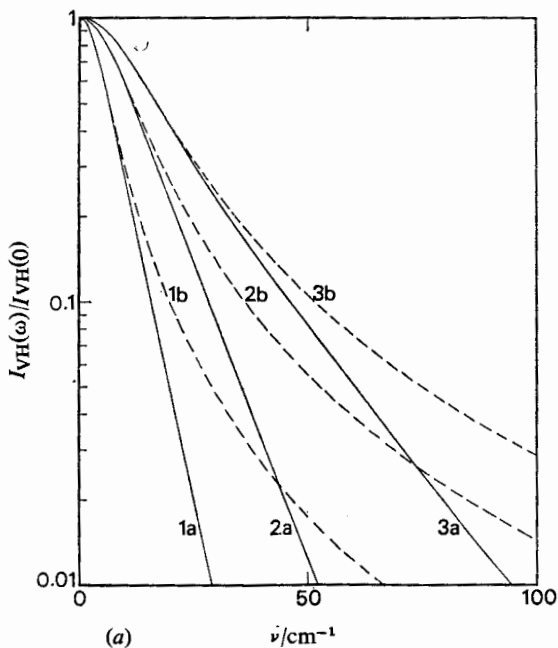


FIG. 3.—Caption overleaf.

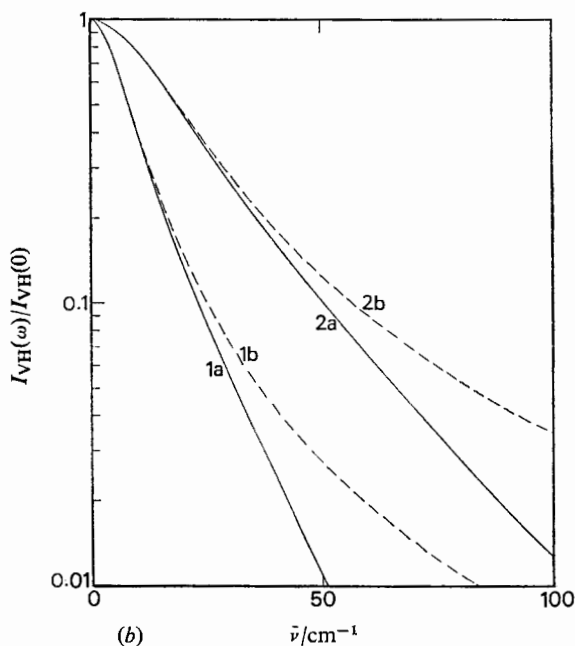


FIG. 3.—(a) $I_{VH}(\omega)/I_{VH}(0)$ calculated from eqn (8) for argon with the least mean squares best fit parameters tabulated in the text. (a) 67 amagat; 2(a) 473 amagat; 3(a) 905 amagat; 300 K. 1(b), 2(b), 3(b), the lorentzians to which eqn (8) reduces at low frequency. (b) As for fig. 3(a). 1(a), 2(a); 90 K, 795 amagat and 960 K, 757 amagat respectively.

The far infrared spectrum of benzene^{11b} is wholly collision induced, whereas the Rayleigh band discussed here is largely due to the *permanent* anisotropy of the molecular polarisability. The parameters $K_0(0)$ and $K_1(0)$ would thus take on a slightly different significance in either case, being related¹¹ to the time coefficients of the Maclaurin expansions of the relevant correlation functions. In the far infrared induced spectrum $K_0(0)$ is an intermolecular property, whereas in the depolarised Rayleigh scattering case it is a single molecule property ($3kT/I$ in the linear case). In both cases $K_1(0)$ is an equilibrium average dependent upon the intermolecular potential, but not necessarily in an identical analytical fashion.

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(PAPER 6/1710)

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