

Moment analysis of the spectrum of depolarized scattered light

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Abstract—A useful approximation to the second moment of depolarized light scattering spectra is developed. The relation of far wing Rayleigh spectroscopy to far i.r. and dielectric spectroscopy is emphasized, together with the fact that a Lorentzian model for these data cannot be justified on the grounds of fundamental theory.

INTRODUCTION

The method of moment analysis in dealing with spectra in the zero-THz region has proven useful [1-4] for the following reasons.

(i) It is possible to observe in detail the orientational auto-correlation functions $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ and $\langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle$ related respectively to $\epsilon''(\omega)/\omega$ and its second moment $\omega \epsilon''(\omega)$ by Fourier transform. Here \mathbf{u} is a unit vector fixed in the molecule.

(ii) The quantity $\omega \epsilon''(\omega)$ is related to the power absorption coefficient $\alpha(\omega)$ by Maxwell's equation: $\alpha(\omega) = \omega \epsilon''(\omega)/n(\omega)c$. Both $\alpha(\omega)$ and $\epsilon''(\omega)$ are observables, so when used in combination are much more efficacious in exposing the flaws inherent in many of the currently popular analytical models of the liquid state.

Several reviews and articles are now available describing points (i) and (ii) in relation to dielectric and far i.r. spectroscopy, but apart from isolated papers by LROVITZ *et al.* [5] and STEELE and VAN KONYNENBURG [6], very little effort has gone into extending the fundamental method of moment analysis to light scattering spectroscopy. It is the purpose of this note to explain why such an analysis of the intensity of scattered light can be a useful and sensitive test of the short time details of molecular motion which go to make up the higher frequency part of the spectrum. The moment analysis is illustrated using the method of molecular dynamics simulation of 108 triatomic molecules interacting with three centre Lennard-Jones atom-atom potentials.

THEORY

In this section we develop the 'far i.r. zoning' of, for example Rayleigh wing spectra, by using from elementary analysis the relation:

$$\omega^2 I(\omega) = - \int_{-\infty}^{\infty} \exp(-i\omega t) \frac{d^2}{dt^2} \left\langle \frac{3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1}{2} \right\rangle dt \quad (1)$$

Here $I(\omega)$ is the intensity of depolarised scattered light. For linear molecules \mathbf{u} lies along the sym-

metry axis. By the Fourier inversion theorem

$$-\frac{d^2}{dt^2} \left\langle \frac{3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1}{2} \right\rangle = \int_{-\infty}^{\infty} \omega^2 I(\omega) e^{i\omega t} d\omega \quad (2)$$

Consider in more detail the left hand side of equation (2). The average can be written, by stationarity, as

$$\frac{1}{2} \left\langle 3[\mathbf{u}(t+s) \cdot \mathbf{u}(s)]^2 - 1 \right\rangle = \frac{1}{2} \left\langle 3[\mathbf{u}(s-t) \cdot \mathbf{u}(s)]^2 - 1 \right\rangle \quad (3)$$

The first derivative of equation (3) w.r.t. t is

$$3(\mathbf{u}(s) \cdot \mathbf{u}(s+t) \mathbf{u}(s) \cdot \dot{\mathbf{u}}(s+t)) = -3(\mathbf{u}(s-t) \cdot \mathbf{u}(s) \dot{\mathbf{u}}(s) \dot{\mathbf{u}}(s-t) \cdot \mathbf{u}(s)) \quad (4)$$

The second derivative is

$$-3(\mathbf{u}(s) \cdot \mathbf{u}(s+t) \dot{\mathbf{u}}(s) \cdot \dot{\mathbf{u}}(s+t)) + 3(\dot{\mathbf{u}}(t) \cdot \mathbf{u}(0))^2 \quad (5)$$

Using equations (5) and (2) we arrive at the approximate results

$$\hat{R} \left[\int_{-\infty}^{\infty} \omega^2 I(\omega) e^{i\omega t} d\omega \right] \doteq 3(\mathbf{u}(t) \cdot \mathbf{u}(0) \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0)), \quad (6)$$

(see appendix) which directly supplements the well known far i.r. theorem

$$\hat{R} \left[\int_{-\infty}^{\infty} \alpha(\omega) e^{i\omega t} d\omega \right] = \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle, \quad (7)$$

where $\alpha(\omega)$ is the optical power absorption coefficient. There has been very little experimental work involved with comparing directly the results represented by Equations (6) and (7), i.e. measuring under the same conditions the Rayleigh wing and the far i.r. spectrum of a specimen liquid. Equation (7) is a very powerful means of analysis, especially when combined with the 'dielectric relation'

$$\hat{R} \left[\int_{-\infty}^{\infty} \frac{\epsilon''(\omega)}{\omega} e^{i\omega t} d\omega \right] = \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle, \quad (8)$$

(in its very simplest form, neglecting all complications). Naturally the correct combinatorial use of Equations (6-8) should prove much more useful than each relation used in isolation.

ILLUSTRATIONS

The product of Equations (7) and (8) gives us; as a first approximation:

$$\hat{R} \left[\frac{1}{3} \int_{-\infty}^{\infty} \omega^2 I(\omega) e^{i\omega t} d\omega \right] \\ = \hat{R} \left[\int_{-\infty}^{\infty} \alpha(\omega) e^{i\omega t} d\omega \right] \hat{R} \left[\int_{-\infty}^{\infty} \frac{\epsilon''(\omega)}{\omega} e^{i\omega t} d\omega \right] \quad (9)$$

so that the second moment of the Rayleigh wing contains information on both the far i.r. power absorption coefficient and the dielectric loss in combination. Equation (6) is the clearest way of demonstrating the fact that a Lorentzian for $I(\omega)$ is not a valid theoretical result, despite its popular usage. This is simply because the l.h.s. integral of Equation (6) diverges in this case. This is again exactly a counterpart of the fact that when $\epsilon''(\omega)/\omega$ is a Lorentzian (Debye rotational diffusion) the area beneath $\alpha(\omega)$ must diverge, producing the well-documented Debye plateau from the far infra-red out to infinite frequencies, [Fig. 1].

In contrast, when $I(\omega)$ is a Gaussian, (Rayleigh scattering from a gas of non interacting molecules) all moments (including, of course, $\omega^2 I(\omega)$) are well defined because the integral in Equation (6) always exists. An illustration of $I(\omega)$ and $\omega^2 I(\omega)$ for the Gaussian is given in Fig. 1.

Furthermore, Equation (6) has the general implication that any hydrodynamic or molecular theory for $I(\omega)$ which produces, to take an instance, a sum of terms *any one of which is a Lorentzian* will cause the integral to diverge to infinity. This holds for polarized I_{VV} as well as depolarized (I_{VH}) intensities. It follows therefore that many of the hydrodynamic mode-mode coupling theories developed primarily for the low frequency region of $I(\omega)$ (including the Rytov dip) will not work at high frequencies. *It is essential in general to work with as many spectral moments as the accuracy of the data will allow.* The second moment $\omega^2 I(\omega)$ is a means of 'enlarging' the short time details of the molecular motions responsible for the high frequency

shape of $I(\omega)$. In exactly the same way $\alpha(\omega)$ emphasizes this aspect when dealing with the dielectric loss $\epsilon''(\omega)$.

MOLECULAR DYNAMICS SIMULATION

These points may be emphasized by simulating the autocorrelation functions of interest using a convenient molecular dynamics algorithm. This is due to RENAUD and SINGER [7] (TRI 2) and uses Lagrange multipliers to solve Newton's equations for 108 triatomic molecules with atom-atom Lennard-Jones interactions. Some runs were made using running-time averages over 200 time-steps to evaluate the autocorrelation functions. The results are illustrated in Fig. 2 up to 7.3 ps (1 time-step = 0.01 ps). The molecule is C_{2v} in symmetry with bond lengths of 10^{-10} m, an included angle of 60° and masses of 2.5×10^{-25} kg for each atom. A temperature of 100 K was used, restarting in the liquid after 3000 time-steps had been rejected. Lennard-Jones parameters were $\sigma = 3 \times 10^{-10}$ m, $\epsilon/k = 173.5$ K. In Fig. 2 we show $\frac{1}{2}(3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1)$ (curve 1) its second derivative (normalized at $t = 0$ to unity) and the angular momentum autocorrelation function $\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle$ (curve 3). Note that curves (2) and (4) are undefined for rotational diffusion and for any theory for which $\omega^2 I(\omega)$ approaches a constant value (i.e. does not decay to zero) as $\omega \rightarrow \infty$.

In one of the very few experimental studies available on $\omega^2 I(\omega)$ of depolarized Rayleigh scattering [5] the data were used to construct $\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle$ by assuming (in effect) curves (2) and (3) to be identical. The simulation shows that this is a fair enough approximation. What the authors term 'angular velocity correlation function' in Fig. 6 of their paper is the multiparticle equivalent of $3\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle$ (i.e. the a.c.f. + cross-correlations).

Finally we remark that it should be possible from Equation (9) to construct the whole of the Rayleigh wing from zero-THz (dielectric/f.i.r.) data without

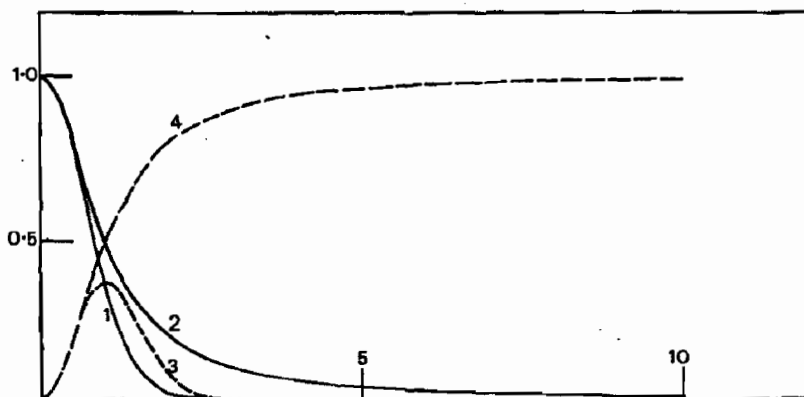


Fig. 1. Gaussian; (2) Lorentzian on the same scale; (3) second spectral moment of the Gaussian; (4) second moment, Lorentzian. Ordinate $I(\bar{\omega})$, normalized units. Abscissa $\bar{\omega}$, normalized units.

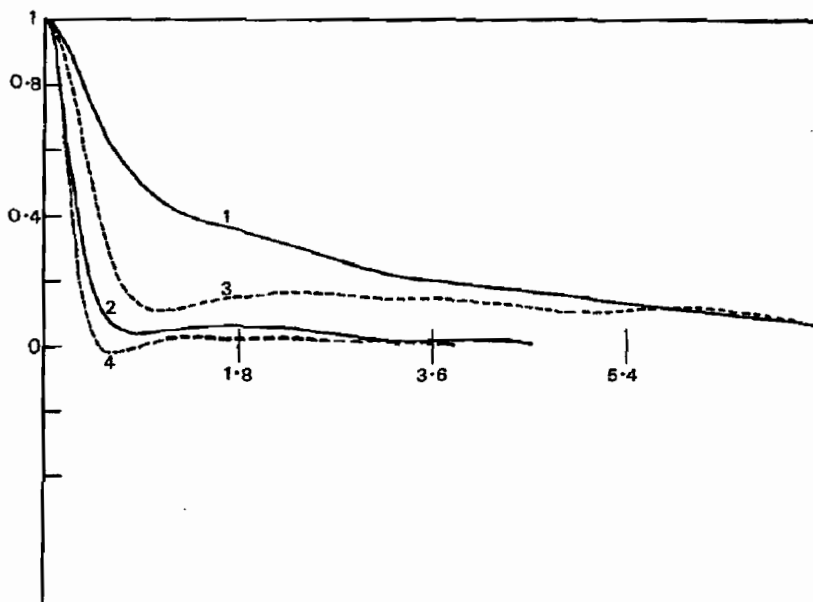


Fig. 2. Molecular dynamics simulation of a C_{2v} triatomic central forces only. (1) $\frac{1}{2}[3\langle \mathbf{e}_A(0) \cdot \mathbf{e}_A(t) \rangle^2 - 1] (= f(t))$. (2) Angular momentum autocorrelation function. (3) $\langle \mathbf{e}_A(0) \cdot \mathbf{e}_A(t) \rangle \langle \dot{\mathbf{e}}_A(0) \cdot \dot{\mathbf{e}}_A(t) \rangle$. (4) $-(d^2/dt^2)(f(t))$. Ordinate: normalized autocorrelation function. Abscissa: time/ps.

recourse to any theoretical assumption (such as (BERNE and HARP [8]) maximization of entropy). This would be a sensitive check on interexperimental consistency.

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APPENDIX

We require the second derivative of $\frac{1}{2}[3\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle^2 - 1]$. This can be written more generally as $\frac{1}{2}[3\langle \mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau) \rangle^2 - 1]$. The first derivative is

$$3 \left\langle \left[\frac{d}{dt} (\mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau)) \right] \mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau) \right\rangle$$

The second derivative is

$$3 \left\langle \left[\frac{d^2}{dt^2} (\mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau)) \right] \mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau) \right\rangle + 3 \left\langle \left[\frac{d}{dt} (\mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau)) \right] \left[\frac{d}{dt} (\mathbf{u}(t+\tau) \cdot \mathbf{u}(\tau)) \right] \right\rangle. \quad (\text{A1})$$

The first term of this may be rewritten as

$$-3\langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$$

and the second as

$$3\langle [\dot{\mathbf{u}}(t) \cdot \mathbf{u}(0)]^2 \rangle.$$

Note that when $\dot{\mathbf{u}}(t)$ and $\mathbf{u}(0)$ have different time reversal symmetry their correlation function should vanish for all t , but not necessarily its mean square. The relative importance of the terms in equation (A1) may be evaluated by computer simulation. The results are shown in Fig. 2. The second term of Equation (A1) is small compared with the first and the approximation:

$$\frac{d^2}{dt^2} \left[\frac{1}{2}(3\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle^2 - 1) \right] \doteq -3\langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle, \quad (\text{A2})$$

is adequate, at least for the triatomic simulated. Of course

$$\langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \neq \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle,$$

in general. The moment analysis is therefore useful as a means of estimating directly Equation (A2) from Rayleigh far-wing, far i.r. and dielectric data.

As a further test of equations such as (A1) and (A2) it is possible to take simple model correlation functions such as those from rotational diffusion and more complicated ones from the itinerant oscillator model developed for zero-THz spectroscopy.

In the case of rotational diffusion

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \exp(-t/\tau) = \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle / \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle,$$

so that

$$\frac{\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle}{\langle \mathbf{u}(0) \cdot \mathbf{u}(0) \rangle \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle} = \exp(-2t/\tau),$$

$$\frac{1}{2} \langle 3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1 \rangle = \exp(-3t/\tau).$$

At the short times t of interest in second moment analysis, the rotational diffusion approximation is compared with the computer simulation in Fig. 2.

Itinerant oscillator approximation

In this case

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \exp(-y(t)),$$

$$\frac{1}{2} \langle 3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1 \rangle = \exp(-2y(t)),$$

where $y(t)$ is a complicated function of t .

$$\frac{\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle}{\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle} = \frac{[\dot{y}(t)^2 - \ddot{y}(t)]}{[\dot{y}(0)^2 - \ddot{y}(0)]} \exp(-2y(t)),$$

$$\begin{aligned} \frac{d^2}{dt^2} \frac{1}{2} \langle 3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1 \rangle / \frac{d^2}{dt^2} \frac{1}{2} \langle 3[\mathbf{u}(0) \cdot \mathbf{u}(0)]^2 - 1 \rangle \\ = \frac{[2\dot{y}(t)^2 - \ddot{y}(t)]}{[2\dot{y}(0)^2 - \ddot{y}(0)]} \exp(-2y(t)). \end{aligned}$$

Note that long times (i.e. for planar rotational diffusion) the approximation is exact, i.e.

$$\begin{aligned} \frac{d^2}{dt^2} \frac{1}{2} \langle 3[\mathbf{u}(t) \cdot \mathbf{u}(0)]^2 - 1 \rangle / \frac{d^2}{dt^2} \frac{1}{2} \langle 3[\mathbf{u}(0) \cdot \mathbf{u}(0)]^2 - 1 \rangle \\ = \frac{\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \langle \dot{\mathbf{u}}(t) \cdot \dot{\mathbf{u}}(0) \rangle}{\langle \mathbf{u}(0) \cdot \mathbf{u}(0) \rangle \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(0) \rangle} \end{aligned}$$