CENTENARY LECTURE*

Light Scattering in Pure Liquids and Solutions

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1 Introduction and Development of the Theory

We start by writing some general relations between measurements of electromagnetic radiation in the time and frequency domains. The total intensity of light (electromagnetic radiation) is written as a long-time average of the instantaneous intensity, $I(t)$,

$$I = I\left(\frac{\text{energy}}{\text{area} \times \text{t}}\right) = \lim_{T\to\infty}\left\{\frac{1}{2T}\int_{-T}^{T} I(t)\,\mathrm{d}t\right\} = \langle I(t)\rangle \ , \qquad (1)$$

where the brackets indicate the long-time average. The instantaneous intensity is given in terms of the electric fields of the electromagnetic radiation according to

$$I(t) = \frac{c}{4\pi}\,E^*(t)\,E(t) \ , \qquad (2)$$

where we use the complex form for the instantaneous electric field, $E(t)$. We also define the spectral distribution function, $I(\omega)$, which has units of energy (area $\times$ t $\times$ ω)$^{-1}$. Thus, the total intensity which is equal to I in equation (1) is given by integrating $I(\omega)$ over all frequencies:

$$I = \int_{-\infty}^{+\infty} I(\omega)\,\mathrm{d}\omega = \lim_{T\to\infty}\left\{\frac{1}{2T}\int_{-T}^{T} I(t)\,\mathrm{d}t\right\} \cdot \qquad (3)$$

Substituting equation (2) into equation (3) gives

$$I = \int_{-\infty}^{+\infty} I(\omega)\,\mathrm{d}\omega = \langle I(t)\rangle = \frac{c}{4\pi}\langle E^*(t)\,E(t)\rangle \ , \qquad (4)$$

where the brackets again indicate the long-time average.

We now define the *correlation function* for the electric field,[1]

$$C(\tau) = \lim_{T\to\infty}\frac{c}{4\pi}\left\{\frac{1}{T}\int_{0}^{T} E^*(t)\,E(t+\tau)\,\mathrm{d}t\right\} = \frac{c}{4\pi}\langle E^*(t)\,E(t+\tau)\rangle \ , \qquad (5)$$

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* Based on the Centenary Lectures of the Chemical Society given in January, 1976, and on a short course on Light Scattering given at Colorado State University in June, 1976.

[1] The measurement of the correlation function from optical electromagnetic fields is discussed in B. Chu, 'Laser Light Scattering', Academic Press, New York, 1974.

where we note from equations (4) and (5) that

$$C(0) = C(\tau = 0) = \frac{c}{4\pi} \langle E^*(t)\, E(t + 0)\rangle = I \ . \tag{6}$$

It is also easy to show that $C(\tau)$ and $I(\omega)$ are Fourier transform pairs related by

$$\begin{aligned} C(\tau) &= \int_{-\infty}^{+\infty} I(\omega) \exp(-i\omega\tau)\, d\omega \\ I(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} C(\tau) \exp(i\omega\tau)\, d\tau \\ I(\omega) &= \frac{1}{\pi} \operatorname{Re} \int_{0}^{\infty} C(\tau) \exp(i\omega\tau)\, d\tau \ , \end{aligned} \tag{7}$$

where the last step indicates the real part of the $\int_0^\infty$ integral. This last important step is easily proven given that $I(\omega)$ is real.

It is now evident that if we can measure either $C(\tau)$ or $I(\omega)$, we can use the Fourier transform to obtain the other member of the pair.[2]

The above definitions and equations are general and can be used to analyse the spectrum of a given distribution of electromagnetic fields. We will now introduce the more useful ensemble average over all positions and momenta which is essential to evaluating the correlation function for a system of scattering atoms or molecules. First, we define a stationary system which requires that the time average in equation (5) leading to the correlation function is independent of the origin in time. Thus, for a stationary system we can write

$$C(\tau) = \frac{c}{4\pi} \langle E^*(t)\, E(t + \tau)\rangle = \frac{c}{4\pi} \langle E^*(0)\, E(\tau)\rangle \ . \tag{8}$$

Now for a stationary system, the ergodic hypothesis states that each scattering system in the ensemble of particles will pass through all values accessible to it, given a sufficiently long time. Thus, the time average is essentially the same for all systems of the ensemble. The result is that for a stationary ergodic system, the time average is equivalent to the ensemble average.[3] When the brackets in equation (5) indicate an ensemble average, the relation between $C(\tau)$ and $I(\omega)$ discussed above is called the Wiener–Khintchine theorem.[4]

We will find it useful to examine more carefully the properties of the correlation functions and spectra as related to a scattering experiment. Starting with zy-polarized radiation travelling along the y axis, as shown in Figure 1, we can write the complex dipole field scattered from the jth scatterer into a detector at a distance R from the origin of the scattering system according to[5]

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[2] 'Photon Correlation and Light Beating Spectroscopy', ed. H. Z. Cummins and E. R. Pike, Plenum Press, New York, 1973.

[3] F. Reif, 'Fundamentals of Statistical and Thermal Physics', McGraw-Hill, New York, 1965.

[4] C. Kittel, 'Elementary Statistical Physics', Wiley, New York, 1958.

[5] See, for instance, P. Lorraine and D. R. Corson, 'Electromagnetic Fields and Waves,' W. H. Freeman and Co., San Francisco, 2nd Edn., 1970.

$$\boldsymbol{E}_j(t) = \frac{\omega_0^2 \sin\gamma}{Rc^2} \exp(-i\omega_0 t) E^0 \boldsymbol{U}_\gamma \cdot \boldsymbol{\alpha}_j(t) \exp[-i\boldsymbol{K}\cdot\boldsymbol{r}_j(t)] , \tag{9}$$

where $\boldsymbol{U}_\gamma$ is the unit vector along the polar angle γ. ω_0 and E^0 are the frequency and amplitude of the incident radiation, respectively, $\boldsymbol{\alpha}_j(t)$ is the polarizability tensor of the jth scatterer in the laboratory-fixed axis system (which is time dependent due to the rotation of a non-spherical scatterer), $\boldsymbol{K} = \boldsymbol{k}_0 - \boldsymbol{k}_s$ is the scattering vector, which bisects the angle between the incident ($\boldsymbol{k}_0$) and scattered ($\boldsymbol{k}_s$) radiation, and $\boldsymbol{r}_j(t)$ is the centre of mass (c.m.) position of the jth scatterer from an arbitrary origin in the scattering system. $\boldsymbol{r}_j(t)$ is, of course, time dependent if the scatterer has translational freedom (liquid or gas). Figure 1 shows the basic scattering diagram where the incident light, travelling along the y axis, is plane-polarized in the vertical z direction ($E_x{}^0 = E_y{}^0 = 0$) and the scattered light is observed along a line which is at an angle of γ with respect to the z axis. The scattering angle θ_s is between the y axis and the line of observation. Of course, we could also start with x-polarized incident radiation. Of the large number of incident and scattered polarizations and values γ and θ_s, we will usually choose a set of values which corresponds to those which are most often used for experimental studies. These correspond to zy-polarized incident radiation and obser-

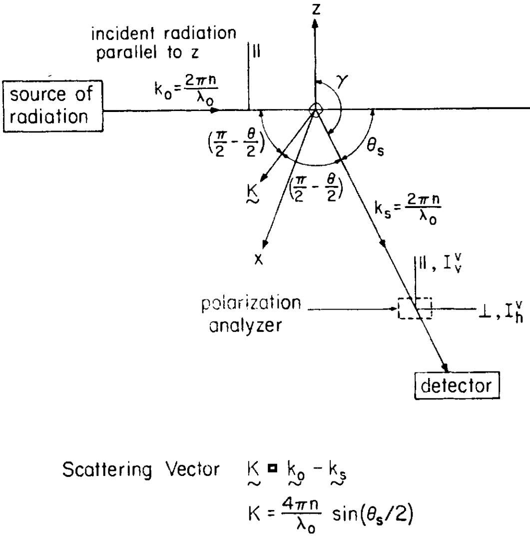

Figure 1 *Basic scattering diagram showing plane-polarized z axis (∥) incident radiation which is scattered along the line shown to the detector at angles γ and θ_s. Choosing $\gamma = \pi/2$, we note either polarized (z axis, ∥) or depolarized (xy plane, ⊥) scattered light designated by $I_v{}^v$ and $I_h{}^v$, respectively. $\boldsymbol{k}_0$ and $\boldsymbol{k}_s$ are the incident and scattered wave vectors, n is the refractive index in the scattering medium, λ_0 is the vacuum wavelength of the radiation, and $\boldsymbol{K}$ is the scattering vector.*

vation in the xy plane ($\gamma = \pi/2$) of either parallel ($\|$) or perpendicular ($\perp$) polarized scattered radiation. These choices are also shown schematically in Figure 1. A polarization analyser selects the scattered radiation which is polarized parallel to either the $z(\|)$ or $y(\perp)$ axes). These xy in-plane fields are given from equation (9).

$$\begin{aligned} \|,\ E_{zj}(t) &= \frac{\omega_0^2}{Rc^2}\, E_z^0 \alpha_{zz}{}^j(t) \exp(-\mathrm{i}\omega_0 t) \exp[\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_j(t)] \\ \perp,\ E_{yj}(t) &= \frac{\omega_0^2}{Rc^2}\, E_z^0 \alpha_{zy}{}^j(t) \exp(-\mathrm{i}\omega_0 t) \exp[\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_j(t)]\ . \end{aligned} \tag{10}$$

We can now write the total fields scattered in phase into the detector by summing over all j scatterers. Substituting this sum into equation (8) gives the correlation functions:

$$\|,\ C_z(\tau) = \frac{c}{4\pi} \langle E_z(0)^* E_z(\tau)\rangle = A \Big\langle \sum_{i,j} \alpha_{zz}{}^i(0)\, \alpha_{zz}{}^j(\tau) \exp(-\mathrm{i}\omega_0\tau) \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(\tau)]\} \Big\rangle \tag{11}$$

$$\perp,\ C_y(\tau) = \frac{c}{4\pi} \langle E_y(0)^* E_y(\tau)\rangle = A \Big\langle \sum_{i,j} \alpha_{zy}{}^i(0)\, \alpha_{zy}{}^j(\tau) \exp(-\mathrm{i}\omega_0\tau) \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(\tau)]\} \Big\rangle \tag{12}$$

$$A = \frac{\omega_0^4}{R^2c^4} (E_z^0)^2 \frac{c}{4\pi} = \frac{\omega_0^4}{R^2c^4} I_0 = \frac{k_0^4}{R^2} I_0\ ,$$

where the sums over i and j are independent with all terms in i at $t = 0$ and all terms in j at $t = \tau$ being included. I_0 is the incident intensity for the plane-polarized radiation. If the incident radiation is unpolarized, we write

$$A = \frac{\omega_0^4}{c^4R^2} (\tfrac{1}{2})(1 + \cos^2\theta_s)\ . \tag{13}$$

The correlation functions in equations (11) and (12) are written[6] in terms of the initial $t = 0$ and later $t = \tau$ positions and orientations and the brackets indicate the time average or the equivalent ensemble average according to the ergodic hypothesis.

The orientational correlation is contained in the $\alpha_{zz}{}^i(0)\, \alpha_{zz}{}^j(\tau)$ and $\alpha_{zy}{}^i(0)\, \alpha_{zy}{}^j(\tau)$ terms and the translational correlation is contained in the $\exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(\tau)]\}$

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[6] $C_y(\tau)$, which indicates the correlation function for y-polarized scattered light, is valid at any angle θ_s in the xy plane ($\gamma = \pi/2$). In this expression we use $C_y(\tau) = [c/(4\pi)] \langle E_y(t)E_y^*(t+\tau)\rangle$. However, $C_y(\tau) = [c/(4\pi)] \langle E_x(t)E_x^*(t+\tau)\rangle$ is equally valid. We can write the scattered field at angle θ_s in Figure 1 as a linear combination of $E_x(t)$ and $E_y(t)$, $E_{\theta s} = \sin\theta_s E_x + \cos\theta_s E_y$, where $\langle E_{\theta s}(t)E_{\theta s}^*(t+\tau)\rangle = \sin^2\theta_s \langle E_x(t)E_x^*(t+\tau)\rangle + \cos^2\theta_s \langle E_y(t)E_y^*(t+\tau)\rangle$, where $\langle E_x(t)E_y(t+\tau)\rangle = 0$. Now, it is easy to show that $\langle E_x(t)E_x^*(t+\tau)\rangle = \langle E_y(t)E_y^*(t+\tau)\rangle$ and, therefore, $\langle E_{\theta s}(t)E_{\theta s}^*(t+\tau)\rangle = \langle E_x(t)E_x^*(t+\tau)\rangle = \langle E_y(t)E_y^*(t+\tau)\rangle$.

phase factors. The $i = j$ terms are called the self terms and the $i \neq j$ terms are called the distinct terms. In gases, it is reasonable to assume that the dominant contributions will arise from the self terms. Of course, in liquid crystal-like systems we would expect significant $i \neq j$ contributions and in solids we expect even larger $i \neq j$ contributions.

We will now examine the nature of the polarizability tensor elements which enter the correlation functions in equations (11) and (12). We remember that in the presence of an electromagnetic field with frequency ω, the system (molecule) is described by the time-dependent function $\Psi(r, t)$ in terms of the stationary states, $\psi_i(r)$, and time-dependent coefficients, $B_i(t)$, according to $\Psi(\boldsymbol{r}, t) = \sum_i B_i(t)\,\psi_i(r)$, where $B_i(t) = \exp(-\mathrm{i}E_it/\hbar)\,C_i(t)$. Assuming that the perturbation is small and that the system is initially in the kth state, $C_i(t) \ll C_k(t) \approx 1.0$ and we write the time-dependent function as

$$\Psi(\boldsymbol{r}, t) = \psi_k(r)\exp(-\mathrm{i}E_kt/\hbar) + \sum_i{}' C_i(t)\exp(-\mathrm{i}E_it/\hbar)\,\psi_i(t)\ , \qquad (14)$$

where the prime on the summation excludes the kth term. The value of $C_i(t)$ is given from perturbation theory for the electric dipole interaction Hamiltonian perturbation, $\mathscr{H}' = -\boldsymbol{E}\cdot\boldsymbol{D}$, between the molecular dipole moment operator, $\boldsymbol{D}$, and the incident radiation electric field,

$$\boldsymbol{E} = 2E_0\cos(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)\ ,$$

by

$$C_i(t) = \frac{1}{\hbar}(\boldsymbol{E}_0\cdot\boldsymbol{D})_{ik}\left\{\frac{\exp[\mathrm{i}(\omega_{ik} - \omega)t]}{\omega_{ik} - \omega} + \frac{\exp[\mathrm{i}(\omega_{ik} + \omega)t]}{\omega_{ik} + \omega}\right\} \qquad (15)$$

$$\omega_{jk} = (E_j - E_k)/\hbar\ .$$

We can think of the kth state as a vibration–rotation state in the ground electronic state and the sum over i is over the excited electronic (vibration–rotation) states. We now calculate the average value of the D operator to first order in $C_i(t)$ for the time-dependent system described in equations (14) and (15) to give

$$\begin{aligned}(\boldsymbol{D})_{\mathrm{av}} &= \frac{\int \Psi^*(\boldsymbol{r}, t)(\boldsymbol{D})\,\Psi(\boldsymbol{r}, t)\,\mathrm{d}V}{\int \Psi^*(\boldsymbol{r}, t)\,\Psi(\boldsymbol{r}, t)\,\mathrm{d}V}\\
&= \exp(\mathrm{i}\omega_{k'k}t)\,\boldsymbol{D}_{k'k} + \frac{\boldsymbol{E}_0}{\hbar}\cdot\sum_i{}' \boldsymbol{D}_{ki}\,\boldsymbol{D}_{ik'}\\
&\qquad\times\left\{\frac{\exp[\mathrm{i}(\omega_{ik} - \omega_{ik'} - \omega)t]}{\omega_{ik} - \omega} + \frac{\exp[\mathrm{i}(\omega_{ik} - \omega_{ik'} + \omega)t]}{\omega_{ik} + \omega}\right\}\\
&\quad + \frac{\boldsymbol{E}_0}{\hbar}\cdot\sum_i{}' \boldsymbol{D}_{k'i}\,\boldsymbol{D}_{ik}\\
&\qquad\times\left\{\frac{\exp[\mathrm{i}(\omega_{ik} - \omega_{ik'} + \omega)t]}{\omega_{ik'} - \omega} + \frac{\exp[\mathrm{i}(\omega_{ik} - \omega_{ik'} - \omega)t]}{\omega_{ik'} + \omega}\right\},\end{aligned} \qquad (16)$$

where $D_{ki} = \int \psi_k^*(r)\, D\psi_i(r)\, \mathrm{d}V$ and the denominator is unity to first order in the coefficients, $C_i(t)$. We note from this expression that k and k' can represent two different vibration–rotation states in the ground electronic state and the primes on the summation omit the $i = k$ and $i = k'$ terms, respectively. Remembering that $\omega_{ik} - \omega_{ik'} = 1/\hbar\,(E_i - E_k - E_i + E_{k'}) = 1/\hbar\,(E_{k'} - E_k) = \omega_{k'k} = -\omega_{kk'}$, where ω_{ik} is an electronic transition frequency and $\omega_{kk'}$ is a vibration–rotation or rotational transition frequency in the ground electronic state, we can rewrite this equation to give

$$
\begin{aligned}
(D)_{\mathrm{av}} = \exp(\mathrm{i}\omega_{k'k}t)\,D_{k'k} + \frac{E_0}{\hbar}\,\cdot\; & \\
\sum_i{}' D_{ki}\,D_{ik'} & \left\{\frac{\exp[\mathrm{i}(\omega_{k'k} - \omega)t]}{\omega_{ik} - \omega} + \frac{\exp[\mathrm{i}(\omega_{k'k} + \omega)t]}{\omega_{ik} + \omega}\right\} \\
+ \frac{E_0}{\hbar}\cdot\sum_i{}' D_{k'i}\,D_{ik} & \left\{\frac{\exp[\mathrm{i}(\omega_{k'k} + \omega)t]}{\omega_{ik'} - \omega} + \frac{\exp[\mathrm{i}(\omega_{k'k} - \omega)t]}{\omega_{ik'} + \omega}\right\}
\end{aligned}
\tag{17}
$$

This general expression for the polarizability tensor shows that the polarizability and resultant intensity of the scattering will increase as $\omega \to \omega_{ik}$. This condition of resonant Rayleigh $(k = k')$[7] and resonant Raman $(k \neq k')$ scattering is useful in enhancing the sensitivity of the scattering if a suitable light source is available with a frequency, ω, near one of the electronic resonant frequencies, ω_{ik}. Resonant vibrational Raman scattering has been particularly useful in identifying specific local vibrations on a site in a large macromolecule.[8] Now, we note that normally $\omega_{ik} \gg \omega_{k'k}$ because ω_{ik} is the angular frequency of an electronic transition and $\omega_{k'k}$ is the angular frequency of a vibrational, vibration–rotation, or pure rotational transition. Thus, it is reasonable to assume that $\omega_{ik} = \omega_{ik'}$ for Raman and Rayleigh scattering. Now if $\omega_{ik} \simeq \omega_{ik'}$ in equation (17), we can write

$$
\lim_{\omega_{ik} \simeq \omega_{ik'}} (D)_{k'k} = \exp(i\omega_{k'k}t)\left\{D_{kk'} + \frac{2}{\hbar}E_0\cdot\sum_i{}' \frac{D_{ki}D_{ik'}\omega_{ik}\cos\omega_0 t}{\hbar(\omega_{ik}^2 - \omega_0^2)}\right\}. \tag{18}
$$

Thus, the polarizability is given from $D_{\mathrm{ind}} = \boldsymbol{\alpha}\cdot\boldsymbol{E}$ to be

$$
\boldsymbol{\alpha} = 2\exp(i\omega_{k'k}t)\sum_i{}' \frac{D_{ki}D_{ik'}\omega_{ik}}{\hbar(\omega_{ik}^2 - \omega_0^2)}. \tag{19}
$$

We can relate the space-fixed polarizability tensor in equation (19), $\boldsymbol{\alpha}(xyz)$, to the corresponding values in the molecular-fixed axes, $\boldsymbol{\alpha}(abc)$, by the direction cosine transformation, $\mathbf{C}$, which gives $\boldsymbol{\alpha}(xyz) = \mathbf{C}^{\dagger}\boldsymbol{\alpha}(abc)\mathbf{C}$. According to equations (11) and (12), we need

$$
\begin{aligned}
\alpha_{zz} &= C_{za}\alpha_{aa}C_{az} + C_{zb}\alpha_{bb}C_{bz} + C_{zc}\alpha_{cc}C_{cz} \\
\alpha_{zy} &= C_{za}\alpha_{aa}C_{ay} + C_{zb}\alpha_{bb}C_{by} + C_{zc}\alpha_{cc}\alpha_{cy}\ ,
\end{aligned}
$$

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[7] D. R. Bauer, B. Hudson, and R. Pecora, *J. Chem. Phys.*, 1975, **63**, 588.

[8] T. G. Spiro, *Accounts. Chem. Res.*, 1974, **7**, 339.

where C_{za} is the direction cosine between the a and z axes. Now if we choose a cylindrically symmetric molecule with $\alpha_{aa} \neq \alpha_{bb} = \alpha_{cc}$ (where a is the symmetry axis) and if we place the a, b, and z axes in a plane (with no loss in generality), we can relate $\boldsymbol{\alpha}(xyz)$ to $\boldsymbol{\alpha}(abc)$ through the standard spherical polar angles, θ and φ. If $x \rightarrow b$, $y \rightarrow c$, and $z \rightarrow a$ when $\theta = \varphi = 0$, we can show that

$$\begin{aligned} \alpha_{zz} &= \alpha + \tfrac{2}{3}(\alpha_{aa} - \alpha_{bb})\, P_2(\cos\theta) \\ \alpha_{zy} &= (\alpha_{aa} - \alpha_{bb}) \cos\theta \sin\theta \sin\varphi \end{aligned} \tag{20}$$

where $P_2(\cos\theta) = \frac{1}{2}(3\cos\theta - \frac{1}{2})$ is the Legendre polynomial of order $l = 2$ and $\alpha = \frac{1}{3}(\alpha_{aa} + \alpha_{bb} + \alpha_{cc})$. If the scattering (molecule) is vibrating, we must also include the vibrational dependence in the polarizability tensor elements by expanding each tensor element in the molecular-fixed axis system about the small-amplitude molecular vibrations according to

$$\alpha_{aa}(t) = \alpha_{aa}{}^0 + \sum_i \left(\frac{\partial \alpha_{aa}}{\partial Q_i}\right)_0 Q_i + \ldots, \tag{21}$$

where $\alpha_{aa}{}^0$ is the equilibrium structure polarizability. The change in polarizability with normal co-ordinate, Q_i, is evaluated at equilibrium. In summary, we now have the formal expressions to write the correlation functions in equations (11) and (12) for the general vibrating–rotating molecule.

We now return to equations (11) and (12) to examine the correlation functions at very high pressures or in the condensed phase (liquid) where the time between collisions is short relative to a molecular-rotation period. To simplify our discussion we will initially assume a rigid non-vibrating rotor and substitute equation (20) into equations (11) and (12). If the scatterers are randomly orientated in space (isotropic distribution), the averages of the $\alpha P_2(\cos\theta)_j$ and $\alpha P_2(\cos\theta)_i$ cross-terms will vanish. We also assume that all non-vibrating molecules or scatterers in the gas, liquid, or solid are equivalent and that α and $(\alpha_{aa} - \alpha_{bb})$ are time-independent. Acknowledging the above statements, we obtain

$$\begin{aligned} \|, C_z(t) = {} & A \exp(-\mathrm{i}\omega_0 t)\, \alpha^2 \left\langle \sum_{i,j} \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(t)]\} \right\rangle + \\ & \tfrac{4}{9} A \exp(-\mathrm{i}\omega_0 t)(\alpha_{aa} - \alpha_{bb})^2 \\ & \times \left\langle \sum_{i,j} P_2(\cos\theta)_{0i}\, P_2(\cos\theta)_j \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(t)]\} \right\rangle \end{aligned} \tag{22}$$

$$\begin{aligned} \perp, C_y(t) = {} & A \exp(-\mathrm{i}\omega_0 t)(\alpha_{aa} - \alpha_{bb})^2 \\ & \times \left\langle \sum_{i,j} (\cos\theta \sin\theta \sin\varphi)_{0i} (\cos\theta \sin\theta \sin\varphi)_j \right. \\ & \qquad \left. \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(t)]\} \right\rangle, \end{aligned} \tag{23}$$

where θ and φ are time-dependent due to molecular rotation. The subscript 0 are the $t = 0$ values in the correlation functions. The terms within the time-average brackets contain the independent sums over i and j. The $i = j$ are called the self terms and $i \neq j$ terms are called the distinct terms as mentioned previously. Having defined the concept of the self and distinct correlations, we now rewrite equations (22) and (23) in a form which includes both the self and distinct parts in single terms. Using the ergodic hypothesis, the correlation functions for identical scatterers are given by the following averages over position and orientation:

$$
\begin{aligned}
C_z(t) = {} & A \exp(-\mathrm{i}\omega_0 t) N\alpha^2 \int_{V_s} \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\, P(\boldsymbol{R}, t)\, \mathrm{d}V_s \, + \\
& \tfrac{4}{9} A \exp(-\mathrm{i}\omega_0 t) \frac{N(\alpha_{aa} - \alpha_{bb})^2}{4\pi} \\
& \times \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \int_{V_s} \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\, P_2(\cos\theta_0)\, P_2(\cos\theta)\, P(\boldsymbol{R}, \theta, \varphi, t) \\
& \times \mathrm{d}V_s\, \mathrm{d}\cos\theta_0\, \mathrm{d}\cos\theta\, \mathrm{d}\varphi_0\, \mathrm{d}\varphi
\end{aligned}
\tag{24}
$$

$$
\begin{aligned}
C_y(t) = {} & A \exp(-\mathrm{i}\omega_0 t) \frac{N(\alpha_{aa} - \alpha_{bb})^2}{4\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \int_{V_s} \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}) \\
& \times (\cos\theta \sin\theta \sin\varphi)_0 (\cos\theta \sin\theta \sin\varphi) \\
& \times P(R, \theta, \varphi, t)\, \mathrm{d}V_s\, \mathrm{d}\cos\theta_0\, \mathrm{d}\cos\theta\, \mathrm{d}\varphi_0\, \mathrm{d}\varphi \, .
\end{aligned}
\tag{25}
$$

N is the number of scatterers within the scattering volume V_s, and $\mathrm{d}V_s$ indicates the volume element and corresponding integral over the scattering volume (the illuminated volume which is focused onto the detector). The $P(a)$ functions in these expressions are the space–time and space–time-orientation correlation functions. $P(\boldsymbol{R}, t)$ is the probability per unit volume that if a scattering centre is at position $\boldsymbol{R} = 0$ at $t = 0$, there will also be a scattering centre at $\boldsymbol{R}$ at t. Thus, it is evident that $P(\boldsymbol{R}, t)$ contains both the self and distinct terms in both space and time as described following equation (23). $P(\boldsymbol{R}, \theta, \varphi, t)$ is the space–time-orientation correlation function which is the probability per unit volume that if a particle's centre of interaction is at $\boldsymbol{R} = 0$ with orientation θ_0 and φ_0 at $t = 0$, there will also be a particle at $\boldsymbol{R}$ with orientation θ and φ at t. The additional factor of $[1/(4\pi)]$ associated with the $P(\boldsymbol{R}, \theta, \varphi, t)$ probabilities assumes normalization of the probabilities to the $t = 0$ initial conditions of $P(\boldsymbol{R}, \theta, \phi, t) = \delta(\boldsymbol{R})\, \delta(\cos\theta - \cos\theta_0)\, \delta(\phi - \phi_0)$.

Equations (24) and (25) will be used at various points in the remaining parts of this paper to describe the scattering from rotationally quenched systems. We will use hydrodynamic theories to obtain expressions for $P(\boldsymbol{R}, t)$ and $P(\boldsymbol{R}, \theta, \varphi, t)$. For instance, $P(\boldsymbol{R}, t)$ in the first term of equation (24) is obtained for a pure liquid from a solution of three coupled equations; the continuity equation, the Navier–Stokes equation, and the energy transfer equation which leads to Rayleigh–Brillouin scattering (see next Section).

The total intensities from $C_z(t = 0)$ and $C_y(t = 0)$ are obtained by substituting the appropriate initial or static conditions into equations (24) and (25). Using

$P(\boldsymbol{R}, 0)$ and $P(\boldsymbol{R}, \theta, \varphi, 0) = P(\boldsymbol{R}, 0)\,\delta(\cos\theta - \cos\theta_0)\,\delta(\varphi - \varphi_0)$ in equations (24) and (25) gives the intensities:

$$I_v{}^v = C_z(0) = AN\bar{P}(K, 0)\,[\alpha^2 + \tfrac{4}{45}(\alpha_{aa} - \alpha_{bb})^2] = I_{\text{iso}} + \tfrac{4}{3}I_{\text{anis}} \quad (26)$$

$$I_h{}^v = C_y(0) = AN\bar{P}(K, 0)\,(\tfrac{1}{15})(\alpha_{aa} - \alpha_{bb})^2 = I_v{}^h = I_h{}^h = I_{\text{anis}}\ . \quad (27)$$

Thus, if z-polarized incident radiation is used and observations are made in the xy plane, the ratio of perpendicular to parallel polarized light intensities is

$$I_h{}^v/I_v{}^v = \frac{C_y(0)}{C_z(0)} = \frac{\frac{1}{15}(\alpha_{aa} - \alpha_{bb})^2}{\alpha^2 + \frac{4}{45}(\alpha_{aa} - \alpha_{bb})^2} = \frac{3(\alpha_{aa} - \alpha_{bb})^2}{45\alpha^2 + 4(\alpha_{aa} - \alpha_{bb})^2}\cdot \quad (28)$$

This depolarization ratio is a well-known result. Wilson *et al.*[9] have derived a number of depolarization ratios by using similar methods. Equations (26) and (27) are general for any type of molecule by replacing $(\alpha_{aa} - \alpha_{bb})^2$ with $\frac{1}{2}[(\alpha_{aa} - \alpha_{bb})^2 + (\alpha_{bb} - \alpha_{cc})^2 + (\alpha_{cc} - \alpha_{aa})^2]$. The $I_v{}^v$ and $I_h{}^v$ notation is shown in Figure 1 and the other types of $I_{\text{observed}}^{\text{incident}}$ are also evident from the geometry in Figure 1. The $I_h{}^h$ expression in equation (27) is easily derived giving a correlation function equal to the result in equation (25) with the $\cos\theta\sin\theta\sin\varphi$ dependence being replaced by $\sin^2\theta\sin\varphi\cos\varphi$. It is then easy to show that $I_h{}^h = I_h{}^v$ as indicated in equation (27).

We now return again to equations (11) and (12) and repeat the analysis described above including the effects of parallel vibrations in the linear molecule. Substituting equations (20) and (21) into equations (11) and (12) and repeating the quenched rotational state analysis described above gives

$$\begin{aligned} C_z(t) = {} & A\exp(-\mathrm{i}\omega_0 t)\,N(\alpha^0)^2\bar{P}(K, t) + \frac{4A}{9}\exp(-\mathrm{i}\omega_0 t)\,\frac{N(\alpha_{aa}{}^0 - \alpha_{bb}{}^0)^2}{4\pi} \\ & \times \bar{P}(K, \theta, \varphi, t) + A\exp(-\mathrm{i}\omega_0 t)\exp(\mathrm{i}\omega_{n'_j, n_j}t)\,\bar{G}(K, t)\,f_j\exp(-t/\tau_j) \\ & + \frac{4A}{9}\exp(-\mathrm{i}\omega_0 t)\exp(-\mathrm{i}\omega_{n'_f, n_f}t)\left(\frac{N}{4\pi}\right) \times \bar{G}(K, \theta, \varphi, t)h_j\exp(-t/\tau_j) \end{aligned}$$

$$\begin{aligned} C_y(t) = {} & A\exp(-\mathrm{i}\omega_0 t)\,\frac{N(\alpha_{aa}{}^0 - \alpha_{bb}{}^0)^2}{4\pi}\,\bar{\bar{P}}(K, \theta, \varphi, t) + A\exp(-\mathrm{i}\omega_0 t) \\ & \times \exp(\mathrm{i}\omega_{n'_j, n_j}t)\left(\frac{N}{4\pi}\right)\bar{\bar{G}}(K, \theta, \varphi, t)h_j\exp(-t/\tau_j) \end{aligned}$$

$$\bar{P}(\boldsymbol{K}, t) = \textstyle\int_{V_{\text{s}}}\exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,P(\boldsymbol{R}, t)\,\mathrm{d}V_{\text{s}}$$

$$\begin{aligned} \bar{P}(K, \theta, \varphi, t) = {} & \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_{V_{\text{s}}}\exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,P_2(\cos\theta_0)\,P_2(\cos\theta) \\ & \times P(\boldsymbol{R}, \theta, \varphi, t)\,\mathrm{d}V_{\text{s}}\,\mathrm{d}\cos\theta_0\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi_0\,\mathrm{d}\varphi \end{aligned}$$

$$\bar{G}(K, t) = \int_{V_{\text{s}}}\exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,G(\boldsymbol{R}, t)\,\mathrm{d}V_{\text{s}}$$

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[9] E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955.

$$\bar{G}(K,\theta,\varphi,t) = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_{V_S} \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\, P_2(\cos\theta_0)\, P_2(\cos\theta) \times G(\boldsymbol{R},\theta,\varphi,t)\,\mathrm{d}V_s\,\mathrm{d}\cos\theta_0\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi_0\,\mathrm{d}\varphi$$

$$\bar{\bar{P}}(K,\theta,\varphi,t) = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_{V_S} \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,(\cos\theta\sin\theta\sin\varphi)_0 \times (\cos\theta\sin\theta\sin\varphi) \times P(\boldsymbol{R},\theta,\varphi,t)\,\mathrm{d}V_{\mathrm{S}}\,\mathrm{d}\cos\theta_0\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi_0\,\mathrm{d}\varphi$$

$$\bar{\bar{G}}(K,\theta,\varphi,t) = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_{V_S} \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,(\cos\theta\sin\theta\sin\varphi)_0 \times (\cos\theta\sin\theta\sin\varphi) \times G(\boldsymbol{R},\theta,\varphi,t)\,\mathrm{d}V_{\mathrm{S}}\,\mathrm{d}\cos\theta_0\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi_0\,\mathrm{d}\varphi$$

$$f_j = \tfrac{1}{2}N_{n_j}\left\{\left(\frac{\partial\alpha}{\partial Q_j}\right)_0 \langle n_j|Q_j|0\rangle\right\}^2$$

$$h_j = \tfrac{1}{2}N_{n_j}\left\{\left(\frac{\partial(\alpha_{aa}-\alpha_{bb})}{\partial Q_j}\right)_0 \langle n_j|Q_j|0\rangle\right\}^2$$

$$\omega_{n'_j,n_j} = \frac{E_{n'_j}-E_{n_j}}{\hbar}. \tag{29}$$

N_{n_j} is the number of molecules in the n_j state.

The first two terms in $C_z(t)$ are identical to the result in equation (24) and the first term in $C_y(t)$ is identical to the result in equation (25). The remaining terms in $C_z(t)$ and $C_y(t)$ are due to parallel molecular vibrations in the cylindrically symmetric molecule ($\alpha_{aa} \neq \alpha_{bb} = \alpha_{cc}$). The probability functions and their spatial Fourier transforms (which includes the orientational averaging) use the important approximation that the integral over the scattering volume, V_{S}, can be extended to an integral over a scattering volume where $R \to \infty$ to give the spatial Fourier transform. The $P(\boldsymbol{R}, t)$ and $P(\boldsymbol{R}, \theta, \varphi, t)$ terms contain both self and distinct terms. $G(\boldsymbol{R}, t)$ and $G(\boldsymbol{R}, \theta, \varphi, t)$ differ from $P(\boldsymbol{R}, t)$ and $P(\boldsymbol{R}, \theta, \varphi, t)$, respectively, in that the G functions contain only the self terms. This is because the distinct terms in the G functions involve the molecular vibrations of pairs of different molecules which will have random phases with respect to each other. Thus, the distinct terms, involving the sums over pairs of vibrating molecules, are expected to vanish. Of course, if we are examining a system where distinct terms are in general negligible, the G and P functions will be identical. We have also added the exponential vibrational relaxation process to the correlation functions in equation (29) where τ_j is the vibrational relaxation time for the jth normal mode of vibration.

Returning to equations (26) and (27), we can generalize to include the Raman terms:

$$I_v{}^v(\omega) = I^{\mathrm{RAY}}_{\mathrm{isot}}(\omega) + \tfrac{4}{3}\, I^{\mathrm{RAY}}_{\mathrm{anis}}(\omega) + I^{\mathrm{RAM}}_{\mathrm{isot}}(\omega) + \tfrac{4}{3} I^{\mathrm{RAM}}_{\mathrm{anis}}(\omega)$$

$$I_h{}^v(\omega) = I_v{}^h(\omega) = I_h{}^h(\omega) = I^{\mathrm{RAY}}_{\mathrm{anis}}(\omega) + I^{\mathrm{RAM}}_{\mathrm{anis}}(\omega)\ , \tag{30}$$

where the superscripts RAY and RAM indicate Rayleigh and Raman scattering, respectively.

In the next Sections we will examine in detail the nature of $\bar{P}(K, t)$, $\bar{P}(K, \theta, \varphi, t)$, $\bar{G}(K, t)$, $\bar{G}(K, \theta, \varphi, t)$, $\bar{\bar{P}}(K, \theta, \varphi, t)$, and $\bar{\bar{G}}(K, \theta, \varphi, t)$ for a variety of condensed phase-scattering systems.

2 Isotropic Rayleigh and Brillouin Scattering in Dense Gases and Pure Liquids

We now examine the spectra arising from the isotropic first term in $C_z(t)$ in equation (29),

$$C_z(t) = A \exp(-\mathrm{i}\omega_0 t) N(\alpha^0)^2 \bar{P}(K, t) \ , \qquad (31)$$

where $\bar{P}(K, t)$ is also defined in equation (29) as the Fourier transform of $P(\boldsymbol{R}, t)$, the space–time correlation function. Of course, both the self and distinct correlations are contained in $P(\boldsymbol{R}, t)$. The contribution made by this $P(\boldsymbol{R}, t)$ term to the $I_v{}^v(\omega)$ spectrum in a pure liquid is most easily observed in systems where $(\alpha_{aa} - \alpha_{bb}) = 0$ and the remaining terms in $C_z(t)$ in equation (29) go to zero.

Mountain[10] and Pecora[11] have discussed the evaluation of $\bar{P}(K, t)$ in a dense gas or liquid in terms of the density–density space–time autocorrelation function. This is equivalent to evaluating $\bar{P}(K, t)$ directly from the following three coupled differential equations[12] in $P(\boldsymbol{R}, t)$ which is the reverse spatial Fourier transform of $\bar{P}(K, t)$ needed in equation (29):

the continuity equation

$$\frac{\partial P(\boldsymbol{R}, t)}{\partial t} = -\nabla \cdot \boldsymbol{I} \ , \qquad (32)$$

the Navier–Stokes equation

$$\frac{\partial \boldsymbol{I}}{\partial t} + \frac{v_s{}^2}{\gamma} \nabla P(\boldsymbol{R}, t) + \frac{v_s{}^2 \xi \rho_0}{\gamma} \nabla T(\boldsymbol{R}, t) - \left(\frac{\frac{4}{3}\eta_s + \eta_B}{\rho} \right) \nabla^2 \boldsymbol{I} = 0 \qquad (33)$$

and the energy-transport equation

$$\rho_0 C_v \frac{\partial T(\boldsymbol{R}, t)}{\partial t} - \frac{C_v(\gamma - 1)}{\xi} \frac{\partial P(\boldsymbol{R}, t)}{\partial t} - N_A \chi \nabla^2 T(\boldsymbol{R}, t) = 0 \ . \qquad (34)$$

$P(\boldsymbol{R}, t)$ is the probability per unit volume that a scatterer is at $\boldsymbol{R}$ at t and $\boldsymbol{I}$ is the probability current or flux (the number of particles passing through a unit cross-section per unit time). $T(\boldsymbol{R}, t)$ is the temperature at $\boldsymbol{R}$ at time t, v_s is the velocity of sound in the medium, $\gamma = C_p/C_v$, where C_p and C_v are the heat capacities at constant pressure and volume, respectively, ξ is the thermal expansion coefficient, η_s and η_B are the shear and bulk viscosities, χ is the thermal conductivity, and ρ is related to the number density, denoted by $\rho = (\mathrm{M}/N_A)\rho_0$, where M is the molecular weight and N_A is Avogadro's number.

The use of the above linearized equations will be valid in the hydrodynamic realm with small excursions from equilibrium. Only the longitudinal coupling

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[10] R. D. Mountain, *Rev. Mod. Phys.*, 1966, **38**, 205.

[11] R. Pecora, *J. Chem. Phys.*, 1964, **40**, 1604.

[12] K. F. Herzfeld and T. A. Litovitz, 'Absorption and Dispersion of Ultrasonic Waves', Academic Press, New York, 1959.

of the velocity to the density is included. This simplification, where angular correlations between molecules is unimportant, will limit the final results to polarized spectra, $I_v{}^v$ .We also note that density, or probability per unit volume, and temperature are used as the independent variables. Equations (32), (33), and (34) can be solved by using Laplace and Fourier transform methods to give

$$\bar{P}(K,t) \approx \bar{P}(K,0)\left\{\left(1-\frac{1}{\gamma}\right)\exp\left(-\kappa K^2 t\right)+\frac{1}{\gamma}\exp\left(-\Gamma K^2 t\right)\cos v_{\mathrm{s}}\,Kt\right\}$$

$$\varkappa = \chi N_{\mathrm{A}}/\rho_0 C_p$$

$$\Gamma = \tfrac{1}{2}\left\{\frac{\frac{4}{3}\eta_{\mathrm{S}}+\eta_{\mathrm{B}}}{\rho}+\frac{\chi N_{\mathrm{A}}}{\rho_0 C_v}\left(1-\frac{1}{\gamma}\right)\right\}. \tag{35}$$

$\bar{P}(K,0)$ is the static correlation which we will discuss later in this Section $\varkappa$ is recognized as the thermal diffusion coefficient and Γ is the *effective* mass diffusion coefficient for sound waves in the medium. Equation (35) is only valid in the limit where $v_{\mathrm{s}}K \gg \kappa K^2$. The first part of the $\bar{P}(K,t)$ in equation (35) arises from the fluctuations in entropy at constant pressure. The decay of these fluctuations have a time constant of $\tau = 1/\kappa K^2$. The second part of $\bar{P}(K,t)$ in equation (35) arises from fluctuations in pressure at constant entropy which leads to a propagating sound wave with velocity v_{s} and decay-time constant of $\tau_{\mathrm{s}} = 1/\Gamma K^2$.[13]

We now proceed to evaluate the spectra of the scattered light. Substituting equation (35) into equation (31) gives the correlation function for the isotropic scattering of

$$C_z(K,t) = AN\alpha^2\bar{P}(K,0)\left\{\left(1-\frac{1}{\gamma}\right)\exp\left(-\mathrm{i}\omega_0 t-\kappa K^2 t\right)\right.$$

$$\left.+\frac{1}{2\gamma}\left[\exp\left[-\mathrm{i}(\omega_0-v_{\mathrm{s}}K)t-\Gamma K^2 t\right]+\exp\left[-\mathrm{i}(\omega_0+v_{\mathrm{s}}K)-\Gamma K^2 t\right]\right]\right\}, \tag{36}$$

where we have expanded the $\cos v_{\mathrm{s}}Kt$ term into its complex components. The real Fourier transform of $C_z(K,t)$ [equation (7)] gives the isotropic spectrum as a sum of normalized Lorentzian functions, $\mathscr{L}_\kappa$ and $\mathscr{L}_\Gamma$:

$$I_v{}^v(K,\omega)_{\mathrm{isot}} = AN\alpha^2 P(K,0)\left\{\left(1-\frac{1}{\gamma}\right)\mathscr{L}_\kappa(\omega_0-\omega)+\frac{1}{2\gamma}\left[\mathscr{L}_\Gamma(\omega_0-v_{\mathrm{s}}K-\omega)\right.\right.$$

$$\left.\left.+\mathscr{L}_\Gamma(\omega_0+v_{\mathrm{s}}K-\omega)\right]\right\}$$

$$\mathscr{L}_\kappa(\omega_0-\omega) = \frac{1}{\pi}\left[\frac{\kappa K^2}{(\omega_0-\omega)^2+(\kappa K^2)^2}\right]$$

$$\mathscr{L}_\Gamma(\omega_0 \pm v_{\mathrm{s}}K-\omega) = \frac{1}{\pi}\left[\frac{\Gamma K^2}{(\omega_0 \pm v_{\mathrm{s}}K-\omega)^2+(\Gamma K^2)^2}\right]. \tag{37}$$

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[13] I. L. Fabilinsky, 'Molecular Scattering of Light', Plenum Press, New York, 1968. We also ignore in our discussion here any possible coupling with the internal modes of relaxation in the molecules. See R. D. Mountain, *J. Research N.B.S.*, 1968, **72A**, 95, for further details.

The isotropic spectrum predicted in equation (37) is composed of a Rayleigh line centred around the incident radiation frequency, ω_0, with half-width at half-height of $\varDelta\omega = \kappa K^2$. In addition to the central line at ω_0, there are two Brillouin lines shifted symmetrically from ω_0 by $\pm v_{\mathrm{S}}K$ on each side of the central line with half-widths given by $\varDelta\omega = \Gamma K^2$. The ratio of integrated intensities for the Rayleigh and Brillouin curves give the value of $\gamma = C_p/C_v$:

$$\frac{I_\kappa}{2I_\Gamma} = \frac{1 - 1/\gamma}{1/\gamma} = \gamma - 1$$

$$I_\kappa = AN\alpha^2\bar{P}(K, 0)\left(1 - \frac{1}{\gamma}\right)\int_{-\infty}^{+\infty}\mathscr{L}_\kappa(\omega_0 - \omega)\,\mathrm{d}\omega$$

$$I_\Gamma = AN\alpha^2\bar{P}(K, 0)\left(\frac{1}{\gamma}\right)\int_{-\infty}^{+\infty}\mathscr{L}_\Gamma(\omega_0 + v_{\mathrm{S}}K - \omega)\,\mathrm{d}\omega \tag{38}$$

This result is the well-known Landau–Placzek ratio.

Returning now to a discussion of the Rayleigh–Brillouin spectrum, we can calculate the relative half-widths at half-height of the central Rayleigh $[\varDelta v = (\Gamma K^2)/(2\pi)]$ and side-band Brillouin $[\varDelta v = (\kappa K^2)/(2\pi)]$ spectra from equation (37). We normally find that $\Gamma \gg \kappa$. Thus, the central Rayleigh spectrum is normally a sharper spectrum than the side-band Brillouin spectra.[14] Normally the Rayleigh–Brillouin triplet is observed with a Fabry–Perot interferometer.[15] The parameters obtained by light scattering according to equation (35) can also be related to the absorption coefficient, γ, for sound in the pure liquid, according to

$$\gamma = \frac{\Gamma K^2}{v_{\mathrm{S}}} = \frac{1}{\tau_{\mathrm{S}} v_{\mathrm{S}}}, \tag{39}$$

where $\tau_{\mathrm{S}} = (1)/(\Gamma K^2)$ is the sonic relaxation time. Ultrasonic techniques have been used extensively to measure molecular relaxation processes.[12] The tie-in by analysing the Brillouin half-widths has been a more recent development. In principle, according to the simple first-order theory given here, classical sound absorption experiments (γ is the absorption coefficient) which measure $\gamma/\nu_{\mathrm{S}}^2$ and v_{S} as a function of ν_{S} give exactly the same information through equation (39) as the Brillouin shifts, ν_{B}, and widths, $\varDelta\nu_{\mathrm{B}}$, which give the velocity and mass-diffusion coefficient, respectively, as a function of frequency.

In order to evaluate the static correlation, $\bar{P}(K, 0)$ in equation (37), we return to our earlier discussion of the first terms in equation (22) leading to the isotropic term in $I_v^v(\omega)$ as finally written in equation (37). Rewriting the $N\bar{P}(K, 0)$ part of $C_z(K, t = 0)$ from equations (22) and (24) gives

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[14] The width of the central line can be measured by using optical mixing techniques as shown by J. B. Lastovka and G. B. Benedek, *Phys. Rev. Letters*, 1966, **17**, 1039 who measured κ in toluene by this method.

[15] See, for instance, G. I. A. Stegeman, W. S. Gornall, V. Velfera, and B. P. Stoicheff, *J. Acoust. Soc. Amer.*, 1971, **49**, 979.

$$N\bar{P}(\boldsymbol{K},0) = N\int \exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,P(\boldsymbol{R},0)\,\mathrm{d}V_{\mathrm{s}} = \left\langle \sum_{i,j} \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(0)]\}\right\rangle$$
$$= \left\langle \sum_{i=j} \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_i(0)]\}\right\rangle + \left\langle \sum_{i\neq j} \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(0)]\}\right\rangle, \tag{40}$$

where $N = \rho_0 V_{\mathrm{s}}$ is the total number of scatterers in the scattering volume, V_{s}. We have rewritten the bracketed term as a sum of self ($i = j$) and distinct ($i \neq j$) terms. Accordingly, we can write $P(\boldsymbol{R}, 0)$ in terms of a self and distinct part. The self part of $P(\boldsymbol{R}, 0)$ is clearly a delta function in $\boldsymbol{R}$ and the second (distinct) term can be written in terms of a two-body radial distribution function, $g(\boldsymbol{R})$, giving [$g(\boldsymbol{R})$ is dimensionless]

$$P(\boldsymbol{R},0) = \delta(\boldsymbol{R}) + \rho_0 g(\boldsymbol{R}) \;. \tag{41}$$

$g(\boldsymbol{R})$ is the probability of finding a particle at $\boldsymbol{R}$ if there is another particle at the origin. $g(\boldsymbol{R})$ is normalized to unity at large distances which requires $P(\boldsymbol{R}, 0)$ to reduce to ρ_0 as $R \rightarrow \infty$. Substituting $P(\boldsymbol{R}, 0)$ in equation (41) into equation (40) and using $\int \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,\delta(\boldsymbol{R})\,\mathrm{d}V_{\mathrm{s}} = 1$, we can write

$$C_z(K,0)_{\mathrm{isot}} = A\alpha^2 N\,\bar{P}(K,0) = A\alpha^2 N[S(K) + \rho_0\delta(K)]$$
$$S(K) = \int \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,\{\delta(\boldsymbol{R}) + \rho_0[g(\boldsymbol{R}) - 1]\}\,\mathrm{d}V_{\mathrm{s}} \;. \tag{42}$$

$S(k)$ is called the structure factor for the liquid[16] and the $\delta(K)$ term leads to the forward scattered light which will be indistinguishable from the forward travelling incident light. Thus, the $S(K)$ term is the only measurable K-dependent term in the scattered light intensity. The integral in equation (42) can be simplified considerably if we are dealing with optical radiation where the distances probed by the radiation are considerably larger than the distances from $R = 0$ to the first few molecular diameters or periodic variations in $g(R)$. Under these circumstances, $\exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}) = 1 - \mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} + \ldots \approx 1$ and we can write $\rho_0 \int \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,[g(\boldsymbol{R}) - 1]\,\mathrm{d}V_{\mathrm{s}} \approx \rho_0 \int [g(\boldsymbol{R}) - 1]\,\mathrm{d}V_{\mathrm{s}}$, which can be evaluated by statistical mechanics[17] to give

$$\rho_0 \int [g(\boldsymbol{R}) - 1]\,\mathrm{d}V_{\mathrm{s}} = \rho_0 kT\left(-\frac{1}{V}\frac{\partial V}{\partial P}\right)_T - 1 = \rho_0 kT\beta_T - 1 \;. \tag{43}$$

$\beta_T = [-(1/V)\,\partial V/\partial P]_T$ is the gas or fluid isothermal compressibility at temperature T and k is Boltzmann's constant (β_T has units of inverse pressure). This final result is independent of K. Of course, if static fluctuations extend out to a distance λ_0 (radiation) or if shorter wavelength radiation were used, the $\exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})$ part of the integrand must be included leading to a K-dependence in the final result.

In summary, we note that in the low K limit where $1/K$ is large relative to the mean free path in a gas or where $1/K$ is large relative to the scatterer–scatterer

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[16] P. A. Egelstaff, 'An Introduction to the Liquid State', Academic Press, New York, 1967.
[17] T. L. Hill, 'Statistical Mechanics', McGraw-Hill, New York, 1956.

distance in a liquid, $S(K) = kT\rho_0\beta_T$, and the intensity of the isotropic scattered light (which excludes the forward scattered light) is proportional to the compressibility of the scattering medium from

$$\bar{P}(K, 0) = \rho_0\, kT\beta_T\ . \tag{44}$$

Substituting this result into equation (37) gives the complete result.

3 Anisotropic Rayleigh and Raman and Isotropic Raman Scattering in Liquids; Translational and Rotational Diffusion

Returning to equation (29) we will examine $\bar{P}(K, \theta, \varphi, t)$ leading to $I^{\rm RAY}_{\rm anis}(\omega)$, $\bar{G}(K, \theta, \varphi, t)$ leading to $I^{\rm RAM}_{\rm anis}(\omega)$, and $\bar{G}(K, t)$ leading to $I^{\rm RAM}_{\rm isot}(\omega)$. In Figure 2, the $I_v{}^v(\nu)^{\rm RAY} = I^{\rm RAY}_{\rm isot}(\nu) + \frac{4}{3}I^{\rm RAY}_{\rm anis}(\nu)$ and $I_h{}^v(\nu)^{\rm RAY} = I^{\rm RAY}_{\rm anis}(\nu)$ scattered spectra of nitrobenzene are shown. The depolarized spectrum in the lower curve is pure anisotropic and the upper curve is a combination of the isotropic and anisotropic spectra. The $I(\nu)^{\rm RAY}_{\rm isot}$ triplet arises from density fluctuations as described in the last Section. Several depolarized or anisotropic Rayleigh and Raman spectra are shown in Figure 3. We note that the half-widths at half-height for both $I(\nu)^{\rm RAY}_{\rm anis}$ and $I(\nu)^{\rm RAM}_{\rm anis}$ in CS_2 and benzene are considerably larger than in nitrobenzene. Typical spectral linewidths at $\theta_s = \pi/2$ (see Figure 1) are of the order of $\Delta\nu = 3 \times 10^9$—$3 \times 10^{11}$ Hz for these small molecules.

First, we examine $\bar{G}(K, \theta, \varphi, t)$ or $G(\boldsymbol{R}, \theta, \varphi, t)$ in equations (29) which leads to $I^{\rm RAM}_{\rm anis}(\nu)$ as shown, for instance, in Figure 3. We remember that $G(\boldsymbol{R}, \theta, \varphi, t)$ is composed entirely of self terms, the distinct terms being zero due to the random phases of vibration. Thus, $G(R, \theta, \varphi, t)$ contains only single particle contributions. We will now review the hydrodynamic Debye model for $G(\boldsymbol{R}, \theta, \varphi, t)$ which describes both the centre of mass (c.m.) position (translational diffusion) and orientation (rotational diffusion) of the particle. The Debye model assumes that many collisions are required to reorientate the molecule. Beginning with the $\bar{G}(K, \theta, \varphi, t)$ term in equation (29), we average over the initial spherical polar angles to give

$$\begin{aligned}\bar{G}(K, \theta, \varphi, t) &= \int_0^{2\pi}\int_0^{\pi} \exp\,(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\,P_2(\cos\theta)\,\mathscr{G}(\boldsymbol{R}, \theta, \varphi, t)\,\mathrm{d}V_s\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi \\ &= \int_0^{2\pi}\int_0^{\pi} P_2(\cos\theta)\,\overline{\mathscr{G}}(K, \theta, \varphi, t)\,\mathrm{d}\cos\theta\,\mathrm{d}\varphi\ ,\end{aligned} \tag{45}$$

where $\mathscr{G}(\boldsymbol{R}, \theta, \varphi, t)$ is the probability per unit volume of finding the molecular c.m. at $\boldsymbol{R}$ with orientation θ and φ at time t.

We start with a discussion of one-dimensional translational diffusion of a cylindrically symmetric molecule from a planar delta function in number density in the xy plane. The flux (number of particles per unit area per unit time), $J(z)$, away from this plane of high concentration, is proportional to the gradient of the number density, $N(z, t)$, along the z axis according to

$$J(z) = -D_{zz}\,\frac{\mathrm{d}N(z, t)}{\mathrm{d}t}\ , \tag{46}$$

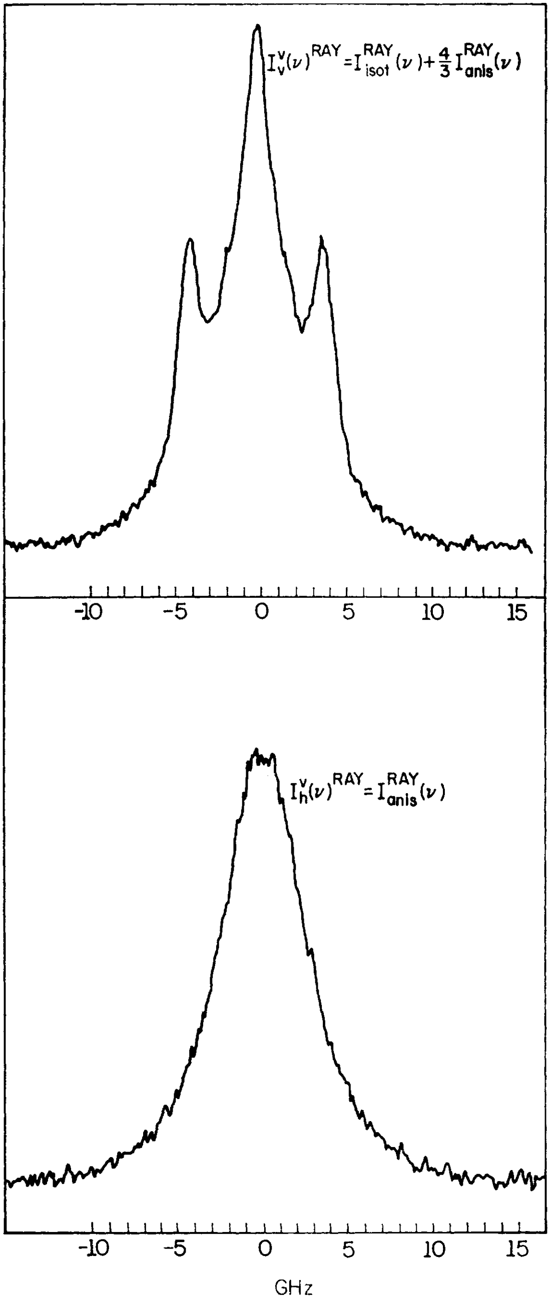

Figure 2 *The* $I_v^v(\nu)^{\mathrm{RAY}}$ *and* $I_h^v(\nu)^{\mathrm{RAY}}(\theta_S = \pi/2)$ *spectra of nitrobenzene recorded with a Fabry–Perot interferometer at* $T = 297$ K *by A. K. Burnham and S. J. Bertucci with an* Ar$^+$ *ion laser with* $\lambda_0 = 5145$ Å (*see also A. Szöke, E. Courtens, and A. Ben-Reuven,* Chem. Phys. Letters, 1967, **1**, 87). *The* $I_v^v(\nu)^{\mathrm{RAY}}$ *spectrum is a combination of the isotropic and anisotropic parts and the* $I_h^v(\nu)^{\mathrm{RAY}}$ *spectrum is due only to the anisotropic component.*

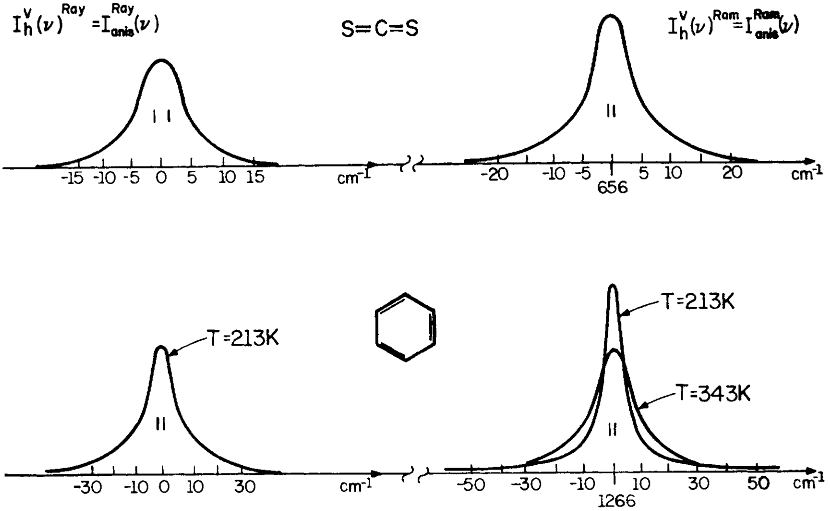

Figure 3 *Depolarized* $I_h^v(\nu) = I(\nu)_{\text{anis}}$ *Rayleigh and Raman spectra for* CS_2 *and benzene. The vertical bars indicate the approximate instrumental widths. Polarized lasers were used as radiation sources and the Rayleigh spectra on the left were taken with a Fabry–Perot interferometer and the Raman spectra on the right were taken with a grating optical spectrograph. All spectra were taken with a* $\pi/2$ *scattering angle. We also note that* 1 cm^{-1} = 30 gHz. *The data are adapted from S. L. Shapiro and H. P. Broida,* Phys. Rev., 1967, **154,** 129, *F. J. Bartoli and T. A. Litovitz,* J. Chem. Phys., 1972, **56,** 404, *and A. K. Burnham and S. J. Bertucci, unpublished work.*

where D_{zz} is the laboratory z-axis translational diffusion coefficient. In the absence of external or internal orientating fields, the fluid will be isotropic and $D_{xx} = D_{yy} = D_{zz}$. However, $D_{aa} \neq D_{bb} = D_{cc}$ for a cylindrically symmetric molecule. Using the mass-continuity equation leads to the diffusion equation,

$$\frac{\mathrm{d}N(z,t)}{\mathrm{d}t} = D_{zz}\frac{\mathrm{d}^2}{\mathrm{d}z^2}N(z,t)\cdot \tag{47}$$

The translational diffusion tensor, $\mathbf{D}(xyz)$, can be written in terms of the molecular-fixed axis (abc) according to $\mathbf{D}(xyz) = \tilde{\mathbf{C}}\mathbf{D}(abc)\mathbf{C}$, where $\mathbf{C}$ contains the direction cosines. Using arguments similar to those preceding equation (20), we find $D_{zz} = D + \frac{2}{3}(D_{aa} - D_{bb})P_2(\cos\theta)$, where $D = \frac{1}{3}(D_{aa} + D_{bb} + D_{cc})$. Substituting this result into equation (47) gives

$$\frac{\mathrm{d}N(z,t)}{\mathrm{d}t} = [D + \tfrac{2}{3}(D_{aa} - D_{bb})P_2(\cos\theta)]\frac{\mathrm{d}^2}{\mathrm{d}z^2}N(z,t)\ ,$$

where θ is the spherical polar angle as before. For an isotropic fluid, translation along the laboratory x, y, and z axes are equivalent and we generalize this expression to give

$$\frac{\mathrm{d}N(\boldsymbol{R},t)}{\mathrm{d}t} = [D + \tfrac{2}{3}(D_{aa} - D_{bb})\,P_2(\cos\theta')]\,\nabla^2 N(\boldsymbol{R},t)\;, \tag{48}$$

where θ' is now the angle between the cylindrical molecular axis and the $\boldsymbol{R}$ vector. In the absence of any rotational motion, the $P_2(\cos\theta')$ term in equation (48) vanishes over an isotropic distribution of molecules. However, if the molecule is rotating as well as translating, the $D_{aa} - D_{bb}$ term above can lead to a coupling between rotation and translation.

Using the above developments, we now write a general equation for $\mathcal{G}(\boldsymbol{R}, \theta, \varphi, \tau)$ as needed in equation (45). First, we note that the Laplacian operator, ∇^2, for a cylindrically symmetric molecule can be expressed as a sum of two terms; the first term is the c.m. Cartesian Laplacian and the second term is the internal co-ordinate part written in spherical polar co-ordinates:

$$\nabla^2 = \nabla^2_{\text{c.m.}} + \sum_i \left\{ \frac{1}{r_i}\frac{\partial}{\partial r_i}\left(r_i^2\,\frac{\partial}{\partial r_i}\right) + \frac{1}{r_i^2}\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r_i^2\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right\}$$

$$\nabla^2_{\text{c.m.}} = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\,,$$

where r_i is the distance from the c.m. to the ith atom in the molecule. We now substitute this Laplacian into equation (48) to write an equation in $\mathcal{G}(\boldsymbol{R}, \theta, \varphi, t)$. First, we note that there is no r_i dependence in $\mathcal{G}(\boldsymbol{R}, \theta, \varphi, t)$ which allows us to omit the first term in brackets in ∇^2. We are left with an equation in D_{aa}, $D_{aa} - D_{bb}$, and $\Theta = D/\sum r_i^2$, the rotational diffusion coefficient (with units of s^{-1}):

$$\begin{aligned}\frac{\partial\mathcal{G}(\boldsymbol{R}, \theta, \varphi, t)}{\partial t} &= [D + \tfrac{2}{3}(D_{aa} - D_{bb})\,P_2(\cos\theta)]\nabla^2_{\text{c.m}}\,\mathcal{G}(\boldsymbol{R}, \theta, \varphi, t)\\ &\quad + \Theta\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]\mathcal{G}(\boldsymbol{R}, \theta, \varphi, t)\;.\end{aligned} \tag{49}$$

In order to separate the rotational and translational co-ordinates in this equation the $\tfrac{2}{3}(D_{aa} - D_{bb})\,P_2(\cos\theta)$ term must vanish. We will drop this $D_{aa} - D_{bb}$ term here as $D_{aa} \approx D_{bb}$ in near spherical molecules, but we note that its effects can be obtained by using perturbation techniques. Setting $D_{aa} - D_{bb} = 0$ in equation (49) and spatial Fourier transforming the result gives

$$\frac{\partial\bar{\mathcal{G}}(K, \theta, \varphi, t)}{\partial t} = \left\{-K^2 D + \Theta\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]\right\}\bar{\mathcal{G}}(K, \theta, \varphi, t)\;. \tag{50}$$

Writing $\bar{\mathcal{G}}(K, \theta, \varphi, t)$ in terms of separated variables, $\bar{\mathcal{G}}(K, \theta, \varphi, t) = \bar{\mathcal{G}}(K, t) \times \mathcal{P}(\theta, \varphi)$, solving the corresponding differential equations, and using the $\mathcal{G}(\boldsymbol{R}, 0) = \delta(\boldsymbol{R})$ initial conditions for the self terms, leads finally to the following solutions for $\bar{G}(K, t)$ and $\bar{G}(K, \theta, \varphi, t)$:

$$\bar{G}(K, t) = \exp(-K^2Dt)$$

$$\bar{G}(K, \theta, \varphi, t) = \frac{4\pi}{5}\exp(-[6\Theta + K^2D)t]\,, \tag{51}$$

where $\tau_{\text{or}} = 1/(6\Theta)$ is the single particle reorientation relaxation time. It is also easy to show by the above methods, that $\bar{\bar{G}}(K, \theta, \varphi, t)$ in equation (29) is also equal to $\frac{1}{3}\bar{G}(K, \theta, \varphi, t)$ in equation (51) for the cylindrically symmetric scatterers considered here. Substituting these results into the appropriate parts of the correlation functions in equation (29) and Fourier transforming gives the Raman spectra in the rotationally quenched limit:

$$I^{\text{RAM}}_{\text{isot}}(\omega) = ANf_j\mathscr{L}(\omega - \omega_0 + \omega_{n'_j,n_j})_{\text{isot}}$$

$$I^{\text{RAM}}_{\text{anis}}(\omega) = \left(\frac{A}{15}\right)Nh_j\mathscr{L}(\omega - \omega_0 + \omega_{n'_j,n_j})_{\text{anis}}$$

$$\mathscr{L}(\omega - \omega_0 + \omega_{n'_j,n_j})_{\text{isot}} = \frac{1}{\pi}\left[\frac{DK^2 + 1/\tau_j}{(\omega - \omega_0 + \omega_{n'_j,n_j})^2 + [(1)/(\tau_j) + DK^2]^2}\right]$$

$$\mathscr{L}(\omega - \omega_0 + \omega_{n'_j,n_j})_{\text{anis}} =$$

$$\frac{1}{\pi}\left[\frac{DK^2 + 6\Theta + 1/\tau_j}{(\omega - \omega_0 + \omega_{n'_j,n_j})^2 + [(1)/(\tau_j) + DK^2 + 6\Theta]^2}\right]. \tag{52}$$

Normally only the Raman Stokes transitions are observed [$E_{n_j} < E_{n'_j}$ in $\omega_{n'_j,n_j} = (E_{n'_j} - E_{n_j})/(\hbar)$] due to the Boltzmann factors in f_j and h_j [equation (29)].

The $\mathscr{L}(\omega)_{\text{isot}}$ Raman spectra have a half-width at half-height of $\Delta\omega = 1/\tau_j + DK^2$ where τ_j is the vibrational relaxation time for the jth normal mode of vibration. Noting that $D \approx (10^{-4}$—$10^{-5})$ cm^2 s^{-1} for most liquids and $\tau_j \approx 10^{-12}$ s for most molecular vibrations in liquids, we can safely write $1/\tau_j \gg K^2D$ for optical radiation and any scattering angle. Thus, a measure of the Raman $\mathscr{L}(\omega)_{\text{isot}}$ gives, from the half-width at half-height, a direct measurement of the vibrational relaxation times. Several values of τ_{vib} obtained in this way are listed in Table 1.

The $\mathscr{L}(\omega)_{\text{anis}}$ Raman spectra have a half-width at half-height of $\Delta\omega = 1/\tau_j + DK^2 + 6\Theta$. Typical small molecule values of Θ range from 10^9—10^{12} s^{-1} and if we are using optical radiation we are safe in writing $6\Theta \gg DK^2$ for any scattering angle. Thus, a measure of the Raman $\mathscr{L}(\omega)_{\text{anis}}$ gives from the half-width at half-height, a direct measurement of the rotational diffusion coefficient, Θ, or the orientational relaxation time, $\tau_{\text{or}} = (1)/(6\Theta)$. Several values of τ_{or} obtained in this way are listed in Table 1. Of course, $I_v{}^v(\nu)^{\text{RAM}} = I^{\text{RAM}}_{\text{isot}}(\nu) + \frac{4}{3}I^{\text{RAM}}_{\text{anis}}(\nu)$ and $I_h{}^v(\nu)^{\text{RAM}} = I^{\text{RAM}}_{\text{anis}}(\nu)$ are measured. $I^{\text{RAM}}_{\text{isot}}(\nu)$ can be extracted from $I_v{}^v(\nu)^{\text{RAM}}$ by subtracting $\frac{4}{3}I_h{}^v(\nu)^{\text{RAM}}$.

Keeping in mind our original model of a cylindrically symmetric near-spherical shaped molecule reorientating about its symmetry axis, we note that the values

Table 1 *Vibrational relaxation times,* τ_{vib}, *and rotational orientation times* $\tau_{\text{or}} = 1/(6\Theta)$ *for several molecular liquids from the Raman spectra*

Molecule	*Vibrational transition* /cm^{-1}	$\tau_{\text{vib}}/10^{-12}$ s	$\frac{1}{6\Theta} = \tau_{\text{or}}/10^{-12}$ s
carbon disulphide CS_2	656	10.6[a]	1.5[a]
acetonitrile CH_3CN	2943	3.2[b]	0.9[b]
methyl iodide CH_3I	525	2.0[a]	1.5[a]
	1245	2.0[a]	1.4[a]
chloroform $CHCl_3$	667	2.0[a]	1.5[a]
	3019	1.1[a]	1.5[a]
bromoform $CHBr_3$	222	4.1[a]	5.3[a]
	3019	1.2[c]	4.4[c]
benzene C_6H_6	992	4.7[d]	2.8[d]
hexafluorobenzene C_6F_6	558	2.2[a]	6.6[a]

a F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, 1972, **56**, 404.
b J. E. Griffiths, *J. Chem. Phys.*, 1973, **59**, 751.
c G. D. Patterson and J. E. Griffiths, *J. Chem. Phys.*, 1975, **63**, 2406.
d K. T. Gillen and J. E. Griffiths, *Chem. Phys. Letters*, 1972, **17**, 359.

of Θ and D can be written according to $f = 6\pi\eta r$ for the frictional force constant[18] as $D = (kT)/f = (kT)/(6\pi\eta r)$ and $\Theta = (kT)/(8\pi\eta r^3) = (kT)/(6V^*\eta)$, where k is Boltzmann's constant, η is the shear viscosity of the solution, r is the effective particle radius in the fluid, and $V^* = \frac{4}{3}\pi r^3$ is the effective molecular volume.

We now examine $I^{\text{RAY}}_{\text{anis}}(\nu)$ which arises from the Fourier transform of $\bar{P}(K, \theta, \varphi, t)$ in equation (29). $\bar{P}(K, \theta, \varphi, t)$ is similar to $\bar{G}(K, \theta, \varphi, t)$ considered above where $\bar{G}(K, \theta, \varphi, t)$ contains only the self terms and $\bar{P}(K, \theta, \varphi, t)$ contains both the self terms and the distinct terms. Thus, we expect the difference between $\bar{P}(K, \theta, \varphi, t)$ and $\bar{G}(K, \theta, \varphi, t)$ or $I^{\text{RAM}}_{\text{anis}}(\nu)$ and $I^{\text{RAY}}_{\text{anis}}(\nu)$, respectively, to reveal the distinct effects or the two-particle orientational pair correlations. A direct comparison of $I^{\text{RAY}}_{\text{anis}}(\nu)$ and $I^{\text{RAM}}_{\text{anis}}(\nu)$ for CS_2 and benzene is shown in Figure 3. It is evident that the half-width at half-height of $I^{\text{RAY}}_{\text{anis}}(\nu)$ is smaller than in $I^{\text{RAM}}_{\text{anis}}(\nu)$ in CS_2, thus, reflecting the effects of the orientational pair correlations. However, in benzene it appears that the half-widths of $I^{\text{RAY}}_{\text{anis}}(\nu)$ and $I^{\text{RAM}}_{\text{anis}}(\nu)$ are the same indicating no orientational pair correlation effect. The values of $\tau^{\text{RAY}}_{\text{or}} = 1/(\Delta\omega)$ [where $\Delta\omega$ is the half-width at half-height in $I^{\text{RAY}}_{\text{anis}}(\nu)$] for several molecules are listed in Table 2. Comparing $\tau^{\text{RAY}}_{\text{or}}$ in Table 2 with τ_{or} in Table 1, for the few molecules which have entries in both tables, shows that $\tau_{\text{or}} \leq \tau^{\text{RAY}}_{\text{or}}$ or that the effects of orientational pair correlations cause an effectively longer rotational relaxation time. The orientational pair correlations also affect the integrated intensities of the anisotropic Raman and Rayleigh scattered light. According to equations (28) and (29), the above discussion, and arguments similar to those preceding equation (40), we can write

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[18] L. D. Landau and E. M. Lifshitz, 'Fluid Mechanics', Addison Wesley Publishing, Reading, Massachusetts, 1959; J. Frenkel, 'Kinetic Theory of Liquids', Dover Publishing, New York, 1955.

$$I^{\mathrm{RAY}}_{\mathrm{anis}} = \int_{-\infty}^{+\infty} I^{\mathrm{RAY}}_{\mathrm{anis}}(\omega)\,\mathrm{d}\omega = \left(\frac{AN}{3}\right)\frac{(\alpha_{aa}{}^0 - \alpha_{bb}{}^0)^2}{4\pi}\,\bar{P}(K,\theta,\varphi,0)$$

$$I^{\mathrm{RAM}}_{\mathrm{anis}} = \int_{-\infty}^{+\infty} I^{\mathrm{RAM}}_{\mathrm{anis}}(\omega)\,\mathrm{d}\omega = \left(\frac{AN}{3}\right)\left(\frac{h_j}{4\pi}\right)\bar{G}(K,\theta,\varphi,0)$$

$$N\bar{P}(K,\theta,\varphi,0) = N\bar{G}(K,\theta,\varphi,0) + \left\langle \sum_{i\neq j} P_2(\cos\theta)_{0i}\,P_2(\cos\theta)_j \exp\{-\mathrm{i}\boldsymbol{K}\cdot[\boldsymbol{r}_i(0) - \boldsymbol{r}_j(0)]\}\right\rangle \quad (53)$$

Table 2 *Rotational orientation times $\tau^{\mathrm{RAY}}_{\mathrm{or}}$, which are obtained from the half-width at half-height of the depolarized Rayleigh lines, $\Delta\omega = 1/\tau^{\mathrm{RAY}}_{\mathrm{or}}$, as shown for instance in Figure* 3. *The temperatures are near* 300 K

Molecule	$\tau_{\mathrm{RAY}}/10^{-12}$ s
carbon disulphide	1.8[a]
acetonitrile	1.7[a]
methyl iodide	2.3[a]
chloroform	2.9[b]
bromoform	10.1[c]
benzene	2.9[d]
hexafluorobenzene	14.0[e]

[a] S. J. Bertucci and A. K. Burnham, unpublished data, 1976.
[b] G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, 1973, **59**, 5310.
[c] G. D. Patterson and J. E. Griffiths, *J. Chem. Phys.*, 1975, **63**, 2407.
[d] G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, 1973, **58**, 5570.
[e] D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, 1974, **61**, 2255.

for the jth normal mode in $I^{\mathrm{RAM}}_{\mathrm{anis}}$ where $N = V_{\mathrm{S}}\rho_0$ is the number of scatterers. Substituting from equation (51) and assuming that rotational and translational motion are separable gives

$$N\bar{P}(K,\theta,\varphi,0) = \frac{4\pi}{5}N + \left\langle \sum_{i\neq j} P_2(\cos\theta)_{0i}\,P_2(\cos\theta)_j \right\rangle. \quad (54)$$

The remaining independent sum over i and j where $i \neq j$ is over all pairs of molecules within the volume element V_{S}. Thus, if each of the scattering molecules are identical, all terms in one of the sums will be the same and we can write

$$N\bar{P}(K,\theta,\varphi,0) = \frac{4\pi}{5}N + (N-1)\left\langle \sum_{j} P_2(\cos\theta)_i\,P_2(\cos\theta)_j \right\rangle, \quad (55)$$

where the last term includes the long-time average of the $N - 1$ identical i terms which are summed over j ($j \neq i$). We now use the spherical harmonic addition formula to write $P_2(\cos\theta)_i\,P_2(\cos\theta)_j$ in terms of $P_2(\cos\theta_{ij})$, where θ_{ij} is the angle between the cylindrical symmetry axes of the ij pair of molecules. Using the ergodic hypothesis, we replace the time average with a spatial average. Making these changes, we write

$$N\bar{P}(K, \theta, \varphi, 0) = \frac{4\pi}{5} N + \frac{4\pi}{5} (N - 1) \left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle = \frac{4\pi}{5} N g_2$$

$$g_2 = 1 + \frac{(N - 1)}{N} \left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle \approx 1 + \left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle, \qquad (56)$$

where the last step assumes that $(N - 1)/N = 1$ which requires a large number of particles in the scattering volume. $\left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle$ is the sum of average values of $P_2(\cos \theta_{ij}) = \frac{1}{2}(3 \cos^2 \theta_{ij} - 1)$ between the $N - 1$ ij-pairs of molecules in the fluid. Substituting the results in equations (56) and (51) into $I^{\mathrm{RAY}}_{\mathrm{anis}}$ and $I^{\mathrm{RAM}}_{\mathrm{anis}}$ respectively, in equation (53) gives the integrated intensities,[19]

$$I^{\mathrm{RAY}}_{\mathrm{anis}} = \frac{1}{15} A g_2 N(\alpha_{aa}{}^0 - \alpha_{bb}{}^0)^2$$

$$I^{\mathrm{RAM}}_{\mathrm{anis}} = \frac{A}{15} N h_j \,. \qquad (57)$$

Thus, according to these results, if a pure solution of monomeric cylindrically symmetric molecules would suddenly dimerize with symmetry axes aligned, $\left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle = 1$, and $g_2 = 2$, thereby increasing the intensity of $I^{\mathrm{RAY}}_{\mathrm{anis}}$. If the dimerization would occur with symmetry axes perpendicular, $\left\langle \sum_j P_2(\cos \theta_{ij}) \right\rangle = -\frac{1}{2}$, $g_2 = \frac{1}{2}$ and the intensity of $I^{\mathrm{RAY}}_{\mathrm{anis}}$ would decrease. Similar arguments can be made of trimers and higher order polymers. A diagram of g_2 as a function of density from $I^{\mathrm{RAY}}_{\mathrm{anis}}$ in the isotropic liquid phase in MBBA, a rod-like molecule which forms a liquid crystal phase, is shown in Figure 4. The evidence for increasing alignment with increasing density, as measured from $I^{\mathrm{RAY}}_{\mathrm{anis}}$ and the resultant g_2, is quite convincing. Of course, $g_2 \to \infty$ as the system approaches the liquid crystal phase.

In the limit of Debye diffusion, where many collisions are necessary to cause a molecular reorientation, Keyes and Kivelson[20] have shown that the time-dependent part of the correlation function also contains g_2 according to [see equation (51) where $\tau_{\mathrm{or}} = 1/(6\Theta)$]

$$\bar{P}(K, \theta, \varphi, t) = \frac{4\pi}{5} g_2 \exp \{-[1/(\tau_{\mathrm{or}} g_2) + K^2 D]t\} \,, \qquad (58)$$

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[19] We have ignored a very important problem in extracting the value of g_2 from the intensities of the scattered light. This problem involves the effects of shielding of the incident radiation field in the scattering medium; the local field problem. Fortunately, experimental methods have been devised to measure and cancel the effects of the local field (T. D. Gierke and W. H. Flygare, *J. Chem. Phys.*, 1974, **61**, 4083, and A. K. Burnham, G. R. Alms, and W. H. Flygare, *J. Chem. Phys.*, 1975, **62**, 3298.)

[20] T. Keyes and D. Kivelson, *J. Chem. Phys.*, 1972, **56**, 1057.

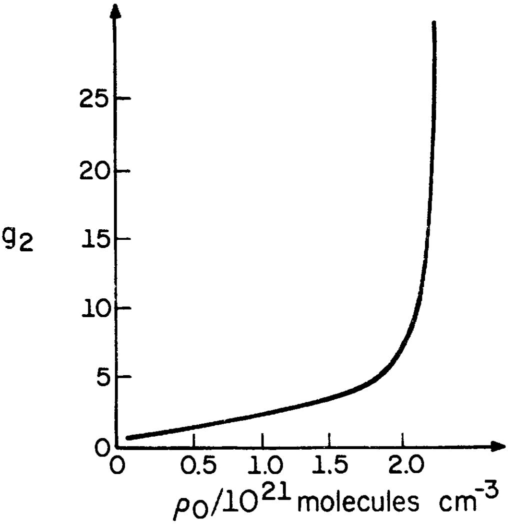

Figure 4 *Experimental determination of g_2 as a function of density from*

$$I^{\text{RAY}} = \int_{-\infty}^{+\infty} I_{\text{anis}}^{\text{RAY}}(\nu)\,\mathrm{d}\nu$$

as shown in equation (57). *The system studied is the isotropic liquid* p*-methoxybenzylidene-*n*-butylaniline* (MBBA) *at* $T = 318$ K *which is above the transition temperature for the liquid crystal phase. The data are from G. R. Alms, T. D. Gierke, and W. H. Flygare,* J. Chem. Phys., 1974, **61,** 4083.

where $\tau_{\text{or}}g_2 = \tau_{\text{or}}^{\text{RAY}}$ is defined in Table 2 as obtained from the half-width at half-height of the $I_{\text{anis}}^{\text{RAY}}(\omega)$ spectrum.

More recently, theory and experiment has been extended to a study of orientational pair correlations in a series of C_{2v} type molecules (substituted benzenes) where a definite correlation is found between the magnitude of the orientational pair correlation and the dipole moment of the molecule.[21]

Another active area of research in interpreting the depolarized light scattered from small molecules involves the interpretation of the dynamics of the diffusion process. This topic has been recently reviewed.[22]

4 Concentration Fluctuations and Electric Field Effects

In this Section a number of principles which are applied to light scattering from solute molecules in solutions are examined. Before discussing scattering from the solute molecules in a dilute solution, we remember that the *solvent* will certainly scatter light as described in Sections 2 and 3 where we considered pure liquids.

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[21] S. J. Bertucci, A. K. Burnham, G. R. Alms, and W. H. Flygare, *J. Chem. Phys.*, 1977, **66,** 605.

[22] D. Bauer, J. Brauman, and R. Pecora, *Ann. Rev. Phys. Chem.*, 1976, **27,** 443.

In this Section we will show that concentration fluctuations of solute molecules give rise to an additional *isotropic* scattering which allows the measurement of the translational diffusion coefficient of the solute molecule in the solvent. We will also show the effects of an electric field and the measurement of mobilities by light scattering.

In the case of a small dilute solute non-vibrating molecule with cylindrical symmetry ($\alpha_{aa} \neq \alpha_{bb} = \alpha_{cc}$), the distinct terms in the correlation function will be insignificant and the resulting correlation function and spectrum can be given by arguments similar to those leading to equation (52) for Raman scattering. The results for concentration fluctuations of a solute non-vibrating molecule give the following spectra:

$$I_v{}^v(\omega)^{\text{RAY}} = I_{\text{isot}}^{\text{RAY}}(\omega) + \tfrac{4}{3} I_{\text{anis}}^{\text{RAY}}(\omega)$$

$$= A\alpha^2 N\mathscr{L}(\omega - \omega_0)_{\text{isot}} + \frac{4A}{45}(\alpha_{aa} - \alpha_{bb})^2 N\mathscr{L}(\omega - \omega_0)_{\text{anis}}$$

$$I_h{}^v(\omega)^{\text{RAY}} = \frac{A}{15}(\alpha_{aa} - \alpha_{bb})^2 N\mathscr{L}(\omega - \omega_0)_{\text{anis}}$$

$$\mathscr{L}(\omega - \omega_0)_{\text{isot}} = \frac{1}{\pi}\left[\frac{DK^2}{(\omega - \omega_0)^2 + (DK^2)^2}\right] \tag{59}$$

$$\mathscr{L}(\omega - \omega_0)_{\text{anis}} = \frac{1}{\pi}\left[\frac{DK^2 + 6\Theta}{(\omega - \omega_0)^2 + (DK^2 + 6\Theta)^2}\right],$$

where A is defined in equations (12) and (13) and all other terms have been defined previously. In the case of a very dilute solute, D is the solute self-diffusion coefficient in the solvent. In a binary mixture of A and B at a higher concentration of solute, the measured diffusion coefficient will be the mutual diffusion coefficient, D_{AB}, given to first order (in an ideal A–B solution) by

$$D_{\text{AB}} = D_{\text{A}}X_{\text{B}} + D_{\text{B}}X_{\text{A}}\ , \tag{60}$$

where X_{A} is the mole fraction of A in the solution.

In order to relate the single particle intensities in equation (59) to the properties of a solute in a solution, we assume that the fluctuations in concentration which give rise to the scattered spectra in equation (59) are independent of the density fluctuations giving rise to the Rayleigh–Brillouin spectra. Under these circumstances, Tanford[23] has shown that α^2 and $(\alpha_{aa} - \alpha_{bb})$ should be replaced with

$$\alpha^2 \rightarrow \frac{M^2 n_0{}^2}{4\pi^2}\left[\left(\frac{\partial n}{\partial C}\right)_0\right]^2 \left(\frac{1}{M}\right)\left(\frac{1}{1/M + 2B_1C + 3B_2C^2 + \ldots}\right)\cdot \tag{61}$$

for the solute in the solvent where C is the concentration ($C/\rho_0 = M$), M is the mass of the scatterer, n is the refractive index of the solution, and n_0 is the refrac-

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[23] C. Tanford, 'Physical Chemistry of Macromolecules', John Wiley and Sons, New York, 1961.

tive index of the solvent. B_1 and B_2 are the virial coefficients which give rise to a decrease in the isotropic scattering intensity at higher concentrations. Substituting equation (61) into equation (59) and assuming no orientational correlations gives the complete spectral function for polarized incident radiation (Figure 1) in a dilute solution of N small solute scatterers,

$$I_v^v(\omega)^{\mathrm{RAY}} = \frac{A}{M}\left[\frac{1}{1/M + 2B_1C + 3B_2C^2 + \dots}\right]\left\{\frac{M^2Nn_0^2}{4\pi}\left[\left(\frac{\partial n}{\partial C}\right)_0\right]^2 \mathscr{L}(\omega - \omega_0)_{\mathrm{isot}}\right\} + \frac{4}{45}N(\alpha_{aa} - \alpha_{bb})^2\mathscr{L}(\omega - \omega_0)_{\mathrm{anis}}$$

$$I_h^v(\omega)^{\mathrm{RAY}} = A\left(\frac{N}{15}\right)(\alpha_{aa} - \alpha_{bb})^2\,\mathscr{L}(\omega - \omega_0)_{\mathrm{anis}}\ , \qquad (62)$$

where $\mathscr{L}(\omega - \omega_0)_{\mathrm{isot}}$ and $\mathscr{L}(\omega - \omega_0)_{\mathrm{anis}}$ are given in equation (59). The relative intensities of the isotropic concentration dependent effect in equation (62) can be compared directly with the total Rayleigh–Brillouin intensity for the isotropic density fluctuation effects considered in Section 2. Substituting equation (44) into $C(K, 0)$ in equation (36) and comparing with the frequency-integrated form of the isotropic term in equation (62) shows that the relative intensities are given by

Pure liquid	*Solute in dilute solution*
$\alpha^2N\rho_0kT\beta_T$	$\dfrac{M^2N'n_0^2}{4\pi^2}\left[\left(\dfrac{\partial n}{\partial C}\right)_0\right]^2$,

where $N = \rho_0 V_s$ is the number of pure liquid scatterers and $N' = \rho_b V_s$ is the number of solute scatterers where V_s is the scattering volume. The value of $(\partial n/\partial C)_0$ needed above can be measured for the particular system in question. We can estimate $(\partial n/\partial C)_0$ by assuming an ideal solution where the refractive index of the solution can be evaluated by the mole fraction weighted sum of the individual pure-fluid refractive indices,

$$n = n_a X_a + n_b X_b = n_a + X_b(n_b - n_a)\ . \qquad (63)$$

n is the refractive index of the solution, n_a and n_b are the refractive indices of liquids A and B, and X_a and X_b are their respective mole fractions. The mole fraction of a dilute solution of solute B in the solvent A is given by

$$X_b = \frac{\mathrm{moles}_b}{\mathrm{moles}_a + \mathrm{moles}_b} \approx \frac{\mathrm{moles}_b}{\mathrm{moles}_a} = \frac{C}{M_b\rho_a}\ , \qquad (64)$$

where C is the concentration of the solute B, M_b is the mass of a solute molecule, and ρ_a is the number density of the solvent. Substituting equation (63), differentiating with respect to the concentration of B giving $\partial n/\partial C$, and substituting this result into the above expression under 'solute in a dilute solution', gives

$$\frac{M_{\mathrm{b}}^2 \rho_b V_{\mathrm{s}} n_0^2}{4\pi^2}\left[\left(\frac{\partial n}{\partial C}\right)_0\right]^2 \approx \frac{C V_{\mathrm{s}} (n_{\mathrm{b}} - n_{\mathrm{a}})^2}{4\pi^2 M_{\mathrm{b}} \rho_{\mathrm{a}}^2}\,. \tag{65}$$

It is evident from this equation that the solute (B) scattering is proportional to the square of the difference in solvent–solute refractive index difference.

Consider now the benzene solute concentration fluctuation scattering intensity in a CCl_4 solvent at $T \approx 300$ K. The $\alpha^2 N \rho_0 k T \beta_T = \alpha^2 V_s \rho_0^2 k T \beta_T$ scattering factor for the CCl_4 solvent at 239 K can be obtained by using $\alpha = 10.5 \times 10^{-30}$ m^3, $\rho_0 = 1.04 \times 10^{27}$ molecules m^{-3}, and $\beta_T = 10.7 \times 10^{-10}$ m^2 N^{-1} to give $\alpha^2 \rho_0^2 k T \beta_T = 3 \times 10^{-27}$. The benzene solute concentration fluctuation scattering factor in a CCl_4 solvent is obtained from equation (65), where $\rho_{\mathrm{a}}(CCl_4)$ is given above, $M_{\mathrm{b}} = 1.297 \times 10^{-25}$ kg, $n_{\mathrm{a}} = 1.4590$ and $n_{\mathrm{b}} = 1.5011$, which gives $C(n_{\mathrm{b}} - n_{\mathrm{a}})^2/(4\pi M_{\mathrm{b}} \rho_{\mathrm{a}}^2) = 6.8 \times 10^{-25}\ C$. According to these numbers, the total benzene scattering intensity in the CCl_4 solvent will exceed the solvent scattering at concentrations above $C = 10$ kg m^{-3} (for equal scattering volumes), which is a relatively low concentration. We have also chosen a solute solvent $(n_{\mathrm{a}} - n_{\mathrm{b}})$ which is quite small. In conclusion, it is evident that concentration fluctuations scattering can be much more intense than the background solvent Rayleigh scattering even at relatively low concentrations.[24]

We now note that the intensity of the anisotropic Lorentzian [equation (62)] will normally be less than the isotropic term. Of course, in CCl_4, $\alpha_{aa} - \alpha_{bb} = 0$ and the anisotropic term is zero. However, assuming that $\alpha_{aa} - \alpha_{bb} = 10^{-30}$ m^3 and remembering that $\rho_0 = C/M$, we can write the multiplier of the second Lorentzian in brackets in $I_v{}^v(\nu)^{\mathrm{RAY}}$ in equation (62) as $\frac{4}{45}\rho_0(\alpha_{aa} - \alpha_{bb})^2 = \frac{4}{45}(C/M)(\alpha_{aa} - \alpha_{bb})^2 = 6.8 \times 10^{-28}\ C$, which is considerably less than the multiplier of the first Lorentzian in $I_v{}^v(\nu)^{\mathrm{RAY}}$ as shown above. Thus, the Lorentzian with $\Delta\omega = K^2 D$ normally dominates the $I_v{}^v(\omega)^{\mathrm{RAY}}$ spectrum in equation (62). It is also evident that the DK^2 half-widths considered here will be smaller than the κK^2 half-widths considered in Section 2, because $D < \kappa$.[25] Of course, we have also assumed that there is no coupling between the concentration fluctuations described here and the density fluctuations described in Section 2. As the solute particles became larger relative to the solvent molecules, the above separation between the concentration fluctuations (and the measurement of the translational diffusion) and the other effects described above become more pronounced. Several diffusion coefficients for macromolecules are listed in Table 3.

In some of the large molecules listed in Table 3, the size of the scatterer approaches the wavelength of the radiation. Under these conditions, scattering from different parts of the same molecule leads to both static and dynamic (if the molecule is rotating) correlations. The static correlations lead to a K-depen-

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[24] A thorough study of mutual diffusion in binary systems of small molecules has been given by S. J. Bertucci and W. H. Flygare, *J. Chem. Phys.*, 1975, **63**, 1 and K. J. Czworniak, H. C. Andersen, and R. Pecora, *Chem. Phys.*, 1975, **11**, 451. These efforts show that the translational diffusion in ideal binary systems can be expressed in terms of transferable molecular diameters for the molecules.

[25] P. Berge, P. Calmettes, M. Dubois, and C. Laj, *Phys. Rev. Letters*, 1970, **24**, 89.

dence in the total scattered isotropic intensity leading to a measurement of the radius of gyration. The dynamic correlations lead to spectral characteristics which allow the measurement of the rotational diffusion constant, Θ, by examining the spectrum of the isotropically scattered light.[26]

Table 3 *Diffusion constants measured at $T = 293$ K in water solutions and molecular weights in atomic mass units of several molecules of various sizes*

Molecule	$D/10^{-11}$ m^2 s^{-1}	M/u*
Glycine	93.4	75
Sucrose	45.9	342
Ribonuclease	10.7	13 683
Bovine serum albumin	6.1	67 000
Ovalbunim	7.1	45 000
Lyzozyme	11.5	14 100
Tropomyosin	2.20	93 000
Fibrinogen	2.00	330 000
Myosin	1.10	490 000
Tobacco mosaic virus	0.29	40×10^6
Latex spheres (d = 910 Å)	0.52	
Calf thymus DNA	0.2	*ca.* 5×10^6

* Data from ref. 23, and S. B. Dubin, J. H. Lunacek, and G. B. Benedek, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **57**, 1164.

We will now examine the principles involved in electrophoretic light scattering[27] which involves the observation of laser light scattered from a solution of charged macromolecules which are moving with a drift velocity $\mathbf{v}_d$ in the presence of an electric field. We will consider only relatively small molecule scattering here where equation (62) gives an appropriate description of the spectrum of the light scattered in the absence of any perturbing electric fields.

Most protein macromolecules are charged at a given pH and in the presence of an electric field the ions in solution will experience a force in the field causing them to translate with a drift velocity, $\mathbf{v}_d$, given by $\mathbf{v}_d = \mu \mathbf{E}$, where $\mathbf{E}$ is the electric field vector and μ is the scalar mobility. In the case of spheres, the mobilities and diffusion coefficients of the ionic molecules are related by $\mu/D = eZ/kT$, where e is the electronic charge, Z is the effective number of charges on the translating ion (including the effects of the electrophoretic counterions), k is Boltzmann's constant, and T is the temperature. Return now to equation (46) and consider the flux of molecules along the z axis following the concentration fluctuation in the xy plane as shown. In the presence of an electric field component along the z axis, the electrostatic force on the charged (ionic) molecules in solution will give rise to an additional flux along the y axis. The total flux is given by modifying equation (46) according to ($D_{aa} = D_{bb} = D_{cc} = D$) $J(z) = -D\, \mathrm{d}P(z,t)/\mathrm{d}y +$

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[26] For details see B. Berne and R. Pecora, 'Dynamic Light Scattering', John Wiley and Sons, New York, 1976.

[27] B. R. Ware and W. H. Flygare, *Chem. Phys. Letters*, 1971, **12**, 81.

$v_d P(z, t)$. Combining this expression with the z axis mass-continuity expression gives the modified one-dimensional Fick's law in $P(z, t)$ in the presence of the electric field according to

$$\frac{\mathrm{d}P(z,t)}{\mathrm{d}t} = D\,\frac{\mathrm{d}^2 P(z,t)}{\mathrm{d}y^2} + v_{\mathrm{d}}\,\frac{\mathrm{d}P(z,t)}{\mathrm{d}y}\,. \tag{66}$$

The solution to this equation is easily obtained by Fourier transform methods as described before to give

$$\bar{P}(K_y, t) = \bar{P}(K_y, 0)\exp\left(-K_y{}^2 Dt - \mathrm{i}K_y v_d t\right)\,,$$

where $\bar{P}(K_y, 0) = 1.0$ for uncorrelated scatterers. In three dimensions this equation takes the form

$$\bar{P}(K, t) = \exp\left(-K^2 Dt - \mathrm{i}\boldsymbol{K}\cdot\boldsymbol{v}_{\mathrm{d}} t\right) = \exp\left(-K^2 Dt - \mathrm{i}\mu\boldsymbol{K}\cdot\boldsymbol{E}t\right)\,. \tag{67}$$

$\boldsymbol{K}\cdot\boldsymbol{v}_{\mathrm{d}} = \mu\boldsymbol{K}\cdot\boldsymbol{E} = \mu KE\cos\alpha$, where α is the angle between the static electric field and the K vector. Remember that the K vector always bisects the angle between the direction of the incident and scattered light (see Figure 1). Substituting equation (67) into the first term of $C_z(t)$ in equation (29) for self terms only gives the correlation function in the presence of the electric field. Substituting α^2 from equation (61) and Fourier transforming gives, finally,

$$I_v{}^v(\omega)_{\mathrm{isot}} = \frac{A}{M}\left(\frac{1}{1/M + 2\mathrm{B}_1 C + 3\mathrm{B}_2 C^2 + \ldots}\right)\left\{\frac{M^2 N n_0{}^2}{4\pi}\left[\left(\frac{\partial n}{\partial C}\right)_0\right]^2\right\}$$
$$\times\,\mathscr{L}(\omega_0 - \omega - \mu\boldsymbol{K}\cdot\boldsymbol{E})_{\mathrm{isot}}$$
$$\mathscr{L}(\omega_0 - \omega - \mu\boldsymbol{K}\cdot\boldsymbol{E})_{\mathrm{isot}} = \frac{1}{\pi}\left\{\frac{K^2 D}{(\omega_0 - \omega - \mu\boldsymbol{K}\cdot\boldsymbol{E})^2 + (K^2 D)^2}\right\}. \tag{68}$$

It is quite apparent that the only difference between this expression and the isotropic result in equation (62) is the translation in ω of $\mu\boldsymbol{K}\cdot\boldsymbol{E}$. By using optical mixing techniques the real part of the correlation function for concentration fluctuations has been observed in solutions of bovine serum albumin (BSA) in the presence of an electric field and the data are shown in Figure 5 for several electric fields. A spectrum showing the field-dependent Doppler shift is shown in Figure 6. The experiments illustrated are all at low angles of scattering and the electric field orientation is perpendicular to the direction of the incident light. This configuration leads to the highest resolution in the electric field effect where the shift in frequency divided by the half-width of the line defines the resolution, R_θ,

$$R_\theta = \frac{\boldsymbol{v}_{\mathrm{d}}\cdot\boldsymbol{K}}{K^2 D} = \frac{v_{\mathrm{d}} K\cos(\theta/2)}{K^2 D} = \frac{\lambda_0 \mu E\cos(\theta/2)}{4\pi n D\sin(\theta/2)}\,. \tag{69}$$

For very small angles,

$$\lim_{\theta\to 0} R_\theta = \frac{\lambda_0 \mu E}{2\pi n D\theta} = \frac{Ze\lambda_0 E}{2\pi n kT\theta}\,, \tag{70}$$

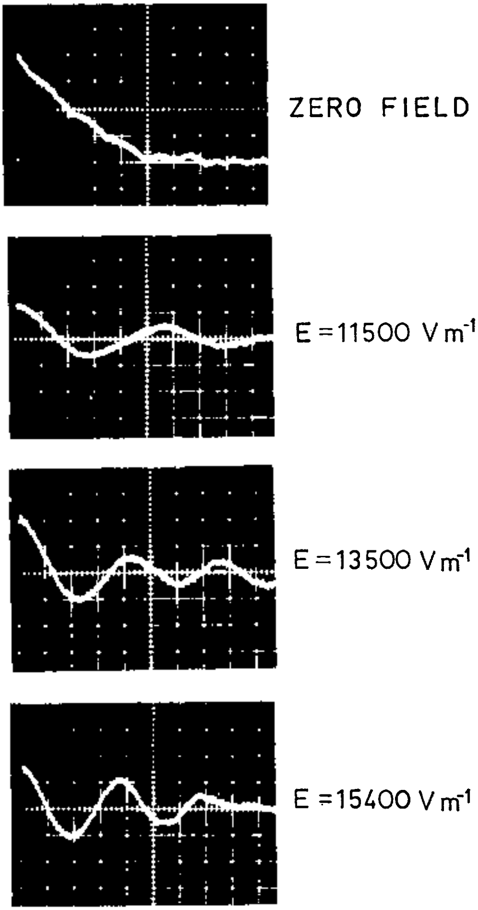

Figure 5 *The observed real part of the correlation function in equation* (67) *for several electric fields from reference* 27.

where n is the solution refractive index and $\mu/D = (eZ)/(kT)$ is also used in the last step of equation (70). Additional details and a summary of the literature in the field of electrophoretic light scattering have been given recently.[28]

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[28] W. H. Flygare, S. L. Hartford, and B. R. Ware, in 'Molecular Electro-Optics', ed. C. T. O'Konski, Marcel Dekker, New York, 1977.

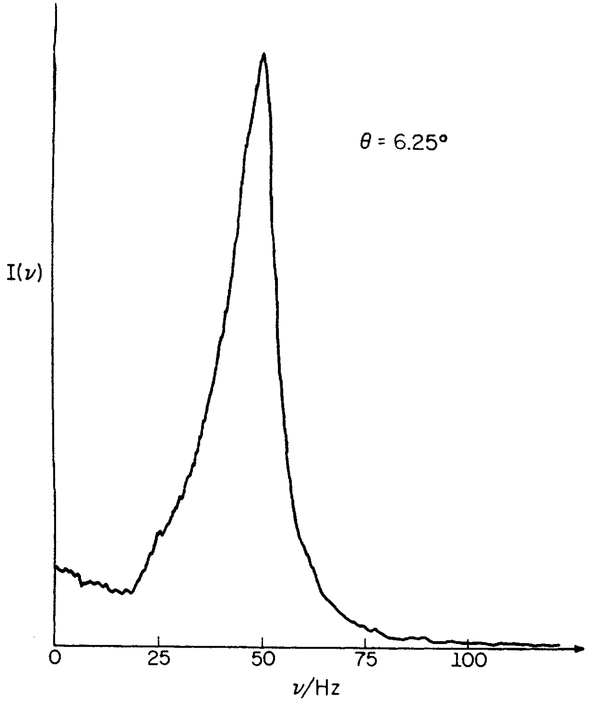

Figure 6 *The spectrum of light scattered from concentration fluctuations in calf-thymus* DNA *where optical mixing techniques reduce the laser frequency reference to zero.* 0.1 mg DNA *was dissolved per* ml *water with an ionic strength of* 0.01 *at* $T = 273$ K. *The analysis of the shift in frequency of* 50 Hz *at* 5000 Vm^{-1} *leads to a mobility of* $\mu = 3.5 \times 10^{-9}$ $\text{m}^2\text{V}^{-1}\text{s}^{-1}$. *The half-width at half-height leads to a translational diffusion coefficient of* $D = 1.2 \times 10^{-11}$ m^2s^{-1}. *The data are from S. L. Hartford* (*see also S. L. Hartford and W. H. Flygare*, Macromolecules, 1975, **8**, 80).