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Multiple scattering in light scattering spectroscopy

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Abstract. When light with a well defined frequency is scattered from a large number of small, independently fluctuating scattering centres, the resulting spectrum is 'doppler broadened'. This paper will examine the influence of multiple scattering processes on this broadening by using a classical expansion. The results indicate that, to second order in an expansion parameter (which is a function of the density of scatters and their polarizability), the spectrum of the scattered light is the same as that computed by using the single-scattering approximation. The effect of multiple scattering on the polarization, angular dependence, and statistics of the scattered light will also be discussed.

1. Light scattering spectroscopy

Light scattering has been used for a number of years as an elegant tool for probing the time dependent properties of fluctuating systems (Pecora 1964, Fabelinski 1957, Benedek 1968). Figure 1 illustrates the geometry of a typical experiment. Incident light, characterized by a well defined frequency ω_0, enters the sample volume V_1 in the direction of the wavevector $\boldsymbol{k}_0$. The primary beam illuminates the volume V_2 and the scattered light is observed through two pinholes which define the scattered light direction $\boldsymbol{k}'$. The spectrum of the scattered light will contain information about the fluctuations in the scattering region.

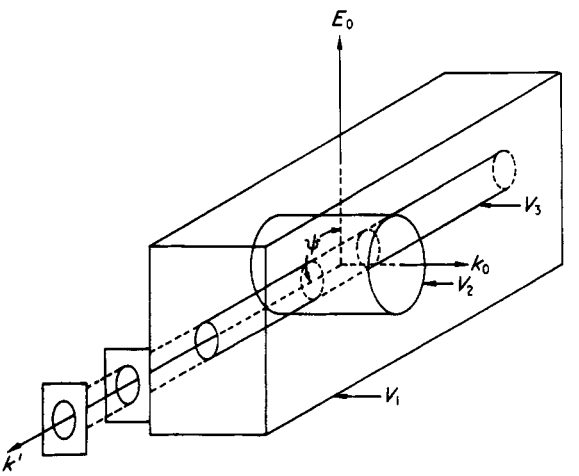

Figure 1.

In most calculations of the scattered spectrum it is assumed that the density of the scattering centres is so low that the light interacts with only a single scattering centre before it is observed. This assumption breaks down, however, in many applications of experimental interest such as scattering from materials which are near a critical point and biological samples whose concentrations approach those *in vivo*. In such samples the light may be scattered from a number of scattering centres before reaching the observer. These multiple scattering processes can often be seen in experiments involving visible light. The higher order scattering terms appear as a light glow surrounding the volume of primary illumination, V_2.

The remainder of this discussion will be devoted to a classical calculation which will indicate how multiple scattering influences the spectrum, angular properties, polarization, and statistics of the scattered light.

2. The scattering formalism

The fluctuations of the scattering medium are coupled to the spectrum of the scattered light when they produce changes in the polarizability tensor of the medium $\boldsymbol{\alpha}(\boldsymbol{r}, t)$. The equations governing an electric field passing through a region characterized by a medium of varying polarizability are as follows (Born and Wolf 1964, Komarov and Fisher 1963):

$$\begin{aligned} \boldsymbol{E}(\boldsymbol{r}, t) &= \nabla \times \nabla \times \boldsymbol{Z}(\boldsymbol{r}, t) + \boldsymbol{E}_0(\boldsymbol{r}, t) \\ (\nabla^2 + k^2)\boldsymbol{Z}(\boldsymbol{r}, t) &= -4\pi\boldsymbol{\alpha}(\boldsymbol{r}, t) \cdot \boldsymbol{E}(\boldsymbol{r}, t). \end{aligned} \tag{1}$$

Here $\boldsymbol{E}_0(\boldsymbol{r}, t)$ represents the incident electric field in the absence of the scattering medium and $k \equiv |\boldsymbol{k}|$. Equation (1) assumes that the fluctuation frequencies in $\boldsymbol{\alpha}$ are small compared with the frequency of the incident light. The function $\boldsymbol{Z}(\boldsymbol{r}, t)$ is often called the 'Hertz vector'.

Exact solutions to (1) are difficult to achieve in complex materials (Chandrasekhar 1960, Plass and Kattawar 1968). We will, however, be able to compute an iterative solution in which $\boldsymbol{E}(\boldsymbol{r}, t)$ will be written as the sum of a series of terms. The nth term in this series will represent the contribution of light scattered n times in the medium before it reaches the detector.

We will solve (1) by making use of the Green function $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ which satisfies the following equation:

$$(\nabla^2 + k^2)g(\boldsymbol{r}_1, \boldsymbol{r}_2) = -4\pi\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{2}$$

with the solution

$$g(\boldsymbol{r}_1, \boldsymbol{r}_2) = \exp(ik|\boldsymbol{r}_1 - \boldsymbol{r}_2|)/|\boldsymbol{r}_1 - \boldsymbol{r}_2|. \tag{3}$$

It can then be shown that (1) is solved by

$$\boldsymbol{E}(\boldsymbol{r}_1, t) = \boldsymbol{E}_0(\boldsymbol{r}_1, t) + \int_{\sigma(\boldsymbol{r}_1)}^{V_1} \nabla \times \nabla \times \{g(\boldsymbol{r}_1, \boldsymbol{r}_2)\boldsymbol{\alpha}(\boldsymbol{r}_2, t) \cdot \boldsymbol{E}_0(\boldsymbol{r}_2, t)\}\, \mathrm{d}^3 r_2. \tag{4}$$

The integral in (4) is taken over the entire scattering volume V_1 except for the small volume element $\sigma(\boldsymbol{r}_1)$ centred on the point $\boldsymbol{r}_1$. It is assumed that the dimensions of σ are small compared with the wavelength of the incident light.

We will now assume that the incident electric field can be written as

$$\boldsymbol{E}_0(\boldsymbol{r}, t) = \hat{\boldsymbol{e}}\mathscr{E}_0\{\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega_0 t)\} \tag{5}$$

and that the polarizability tensor $\boldsymbol{\alpha}(\boldsymbol{r}, t)$ is isotropic and has diagonal elements all equal to $\alpha(\boldsymbol{r}, t)$. The form $\nabla \times (\nabla \times g\hat{\boldsymbol{e}})$ will appear frequently in subsequent calculations and the following identity will be useful:

$$\nabla \times (\nabla \times g(\boldsymbol{r}_1, \boldsymbol{r}_2)\hat{\boldsymbol{e}}) = k^2 f_a(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\hat{\boldsymbol{e}} - (\hat{\boldsymbol{e}} \cdot \hat{\boldsymbol{n}}_{12}) f_b(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\hat{\boldsymbol{n}}_{12} \tag{6}$$

$$f_a(r) \equiv 1 + \mathrm{i}/kr - (1/kr)^2 \tag{7}$$

$$f_b(r) \equiv 1 + 3\mathrm{i}/kr - 3(1/kr)^2 \tag{8}$$

where we have used the quantity $\hat{\boldsymbol{n}}_{12} \equiv (\boldsymbol{r}_1 - \boldsymbol{r}_2)/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$.

Using equations (5)–(8) in (4) we find (for a point R outside the scattering volume)

$$\boldsymbol{E}(\boldsymbol{R}, t) = \boldsymbol{E}_0(\boldsymbol{R}, t) + k^2 \int_{V_1} \mathbf{T}(\boldsymbol{R}, \boldsymbol{r}_1) \cdot \boldsymbol{E}(\boldsymbol{r}_1, t)\, \mathrm{d}^3 r_1 \tag{9}$$

where the tensor $\mathbf{T}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is defined as follows:

$$T_{ij}(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv -g(\boldsymbol{r}_1, \boldsymbol{r}_2)\alpha(\boldsymbol{r}_2, t)\{f_a(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) - f_b(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\hat{n}_{12}(i)\hat{n}_{12}(j)\} \tag{10}$$

where $\hat{n}_{12}(i)$ represents the ith cartesian component of the unit vector $\hat{\boldsymbol{n}}_{12}$.

The iterative solution can now easily be written in powers of $\mathbf{T}$

$$E(\boldsymbol{R}, t) = E_0(\boldsymbol{R}, t) + \sum_{n=1}^{\infty} \boldsymbol{E}_n(\boldsymbol{R}, t) \tag{11}$$

$$\boldsymbol{E}_n(\boldsymbol{R}, t) = \mathscr{E}_0 k^{2n} \mathrm{e}^{-\mathrm{i}\omega_0 t} \int_{V_3} \mathrm{d}^3 r_1 \mathbf{T}(\boldsymbol{R}, \boldsymbol{r}_1) \cdot \prod_{m=1}^{n-1} \left(\int_{\sigma(\boldsymbol{r}_m)}^{V_1} \mathrm{d}^3 r_{m+1} \mathbf{T}(\boldsymbol{r}_m, \boldsymbol{r}_{m+1}) \right) \cdot \hat{\boldsymbol{e}}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_n}. \tag{12}$$

Here V_3 is the part of V_1 visible to the detector.

There is a simple physical interpretation to the terms in (11). $\boldsymbol{E}_n$ represents the contributions from light which has been successively scattered at n points.

3. Evaluation of the iterative terms

The first term in equation (11) is the conventional Born approximation:

$$\boldsymbol{E}_1(\boldsymbol{R}, t) = \mathscr{E}_0 k^2 \frac{\hat{\boldsymbol{n}} \times (\hat{\boldsymbol{e}} \times \hat{\boldsymbol{n}})}{|\boldsymbol{R}|} \int_{V_4} \mathrm{d}^3 r_1 \alpha(\boldsymbol{r}_1, t) \exp\{\mathrm{i}(\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r}_1\}. \tag{13}$$

The Born approximation is good when the intensity of the scattered light is only a small fraction of the intensity of the incident light, that is, when

$$\varphi^2 \equiv 4\pi R^2 |\boldsymbol{E}(\boldsymbol{R}, t) - \boldsymbol{E}_0(\boldsymbol{R}, t)|^2 / A\mathscr{E}_0^2 \ll 1 \tag{14}$$

where A represents the area of the incident beam.

We can obtain an estimate of the magnitude of φ by using the Born approximation

$$\varphi^2 \simeq (4\pi k^4 \sin^2\psi / A) \left| \int_{V_4} \mathrm{d}^3 r \alpha(r) \exp\{\mathrm{i}(\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r}\} \right|^2 \tag{15}$$

$$\varphi^2 \simeq (4\pi \rho V_4 k^4 \sin^2\psi / A)\alpha_0 V_0 \tag{16}$$

where α_0 is the polarizability of an individual scattering centre and V_0 is the average volume of a scattering centre.

When φ is not small, the higher order terms in (11) must be calculated. These terms are smaller than E_1 roughly as powers of the expansion parameter ϵ where ϵ is defined by

$$\epsilon^2 \equiv \frac{|E_n(R)|^2}{|E_{n-1}(R)|^2} = \frac{k^4 |\int_{V_3} \mathbf{T}(R, r) \cdot \boldsymbol{E}_n(r)\, \mathrm{d}^3 r|^2}{|E_{n-1}(R)|^2}. \tag{17}$$

It can be seen that

$$\epsilon \lesssim k^2 \alpha_0 v_0 \rho V_4 / R_0 \equiv \epsilon_0 / R_0 \tag{18}$$

where we have defined

$$R_0 \equiv (1/V_4) \int_{V_4} (1/r)\, \mathrm{d}^3 r$$

$$\epsilon_0 \equiv k^2 \alpha_0 v_0 \rho V_4.$$

We will now examine the behaviour of the first correction to $\boldsymbol{E}_1$ in some detail. Returning to equation (12) we find

$$E_2(R, t) = \mathscr{E}_0 k^4 \, \mathrm{e}^{-\mathrm{i}\omega_0 t} \int_{V_3} \mathrm{d}^3 r_1 \int_{\sigma(r_1)}^{V_4} \mathbf{T}(R, r_1) \cdot \mathbf{T}(r_1, r_2)\, \mathrm{e}^{\mathrm{i}k r_2}\, \mathrm{d}^3 r_2 \tag{19}$$

$$= (\mathscr{E}_0 / R) \exp(\mathrm{i}kR - \mathrm{i}\omega_0 t) \int_{V_3} \mathrm{d}^3 r_1 \int_{\sigma(r_1)}^{V_4} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_2 - \mathrm{i}\boldsymbol{k}' \cdot \boldsymbol{r}_1) g(\boldsymbol{r}_1 \cdot \boldsymbol{r}_2)$$

$$\times \boldsymbol{F}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \alpha(\boldsymbol{r}_1) \alpha(\boldsymbol{r}_2)\, \mathrm{d}^3 r_2 \tag{20}$$

where we have defined

$$\boldsymbol{F}(\boldsymbol{r}) \equiv f_a(|\boldsymbol{r}|) \hat{\boldsymbol{n}} \times (\hat{\boldsymbol{e}} \times \hat{\boldsymbol{n}}) - (\hat{\boldsymbol{e}} \cdot \boldsymbol{r}) f_b(|\boldsymbol{r}|) \hat{\boldsymbol{n}} \times (\boldsymbol{r} \times \hat{\boldsymbol{n}}) / |\boldsymbol{r}|^2. \tag{21}$$

The component of $\boldsymbol{E}_2(R)$ which is polarized in a direction parallel to $\boldsymbol{E}_1(R)$ can be calculated by replacing $\boldsymbol{F}$ in equation (20) with $\boldsymbol{F}_{\|}$ where

$$\boldsymbol{F}_{\|}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) = f_a(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \sin\psi - f_b(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \cos\theta_{12} \{\cos\theta_{12} \sin\psi - \cos\psi \sin\theta_{12}$$

$$\times \cos(\phi - \phi_{12})\} \tag{22}$$

where we have used $\psi \equiv \cos^{-1}(\hat{\boldsymbol{e}} \cdot \hat{\boldsymbol{n}})$, and $\theta_{12} \equiv \cos^{-1}(\hat{\boldsymbol{e}} \cdot \hat{\boldsymbol{n}}_{12})$. The term ϕ_{12} represents the angle between $\boldsymbol{k}$ and the projection of $\hat{\boldsymbol{n}}_{12}$ on the plane perpendicular to $\hat{\boldsymbol{e}}$ (see figure 2). ϕ is the angle between $\boldsymbol{k}_0$ and the projection of $\hat{\boldsymbol{n}}$ on this plane.

The component of $\boldsymbol{E}_2(R)$ which is polarized in a direction normal to $\boldsymbol{E}_1(R)$ can be computed by replacing $\boldsymbol{F}$ in equation (20) with $F_{\perp}$ where

$$F_{\perp} = f_b(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \cos\theta_{12} \sin\theta_{12} \sin(\phi - \phi_{12}). \tag{23}$$

4. The correlation functions

We are finally in a position where we can compute the spectral characteristics of the scattered light. To simplify the following calculations, we will assume that $V_1 = V_3 = V_4$ (the generalization to non-equal volumes will be obvious) and we will assume that the polarizability tensor is characterized by N discrete scattering centres all of volume v_0

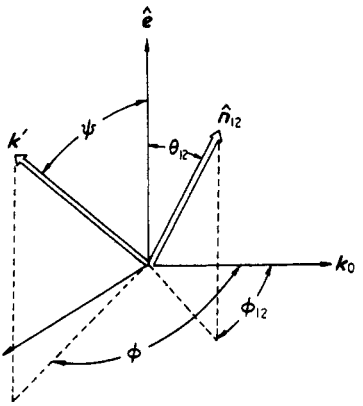

Figure 2.

where the dimensions of v_0 are small compared with the wavelength of the incident light. We can then write

$$\alpha(\boldsymbol{r}, t) = \sum_{i=1}^{N} \alpha_0 v_0 \, \delta(\boldsymbol{r} - \boldsymbol{r}_i(t)). \tag{24}$$

We will assume that each scattering centre is independent of all the others. If the point of observation $\boldsymbol{R}$ is not in the path of the incident light, we will be able to write $\boldsymbol{E}_0(\boldsymbol{R}, t) = 0$.

We will begin our calculation by computing the correlation function of the scattered light. The spectra can be determined by Fourier transforming these correlations but in several recent experiments (Jakeman *et al* 1968, Foord *et al* 1970), it has proved easiest to measure the correlation function directly.

Two correlation functions will be computed: the field correlation (Mandel and Wolf 1965)

$$\Gamma_1(R, \tau) \equiv \langle \boldsymbol{E}^*(R, t) \cdot \boldsymbol{E}(R, t+\tau) \rangle, \tag{25}$$

and the intensity correlation

$$\Gamma_2(R, \tau) \equiv \langle \boldsymbol{E}^*(R, t) \cdot \boldsymbol{E}^*(R, t+\tau) \boldsymbol{E}(R, t) \cdot \boldsymbol{E}(R, t+\tau) \rangle. \tag{26}$$

Using equations (11) and (12) we find

$$\Gamma_1(R, \tau) = \langle E_1^*(R, t) E_1(R, t+\tau) \rangle + \langle E_1^*(R, t) E_2(R, t+\tau) \rangle + \langle E_2^*(R, t) E_1(R, t+\tau) \rangle + (\text{terms of higher order in } \epsilon). \tag{27}$$

The first term in (27) is the conventional single scatter correlation function:

$$\Gamma_{11}(R, \tau) \equiv \langle E_1^*(R, t) E_1(R, t+\tau) \rangle = (\mathscr{E}_0 k^2 \sin \psi / R)^2 C(\tau) \tag{28}$$

where

$$C(\tau) = N \langle \exp\{\mathrm{i}(\boldsymbol{k} - \boldsymbol{k}') \cdot (\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t+\tau))\} \rangle. \tag{29}$$

C/N is assumed to be the same for all the scattering centres and it is assumed that the fluctuations are stationary.

The next term in (28) is given by

$$\langle E_1^*(R,t)E_2(R,t+\tau)\rangle = (N\mathscr{E}_0k^3/R)^2(\alpha_0v_0)^3\beta(\boldsymbol{k},\boldsymbol{k}')C(\tau) \tag{30}$$

where

$$\beta(\boldsymbol{k},\boldsymbol{k}') = (1/N)\sum_{n\neq m}^{N} g(\boldsymbol{r}_m-\boldsymbol{r}_n)F(|\boldsymbol{r}_m-\boldsymbol{r}_n|)[\exp\{i\boldsymbol{k}'\cdot(\boldsymbol{r}_m-\boldsymbol{r}_n)\}+\exp\{i\boldsymbol{k}\cdot(\boldsymbol{r}_m-\boldsymbol{r}_n)\}]. \tag{31}$$

If we assume that the spectrum of the scattered light is symmetric about the central frequency ω_0, we can write $C(\tau) = C^*(-\tau)$. We then find that to first order in ϵ the time dependence of Γ_1 and Γ_{11} is identical:

$$\Gamma_1(R,\tau) = (\mathscr{E}_0\epsilon_0/R)^2\{\sin^2\psi+\epsilon_0\sin\psi\ \mathrm{Re}(\beta(\boldsymbol{k},\boldsymbol{k}'))\}C(\tau). \tag{32}$$

The first term in the correlation function of the light polarized in a direction perpendicular to the polarization of $\boldsymbol{E}_1$ will be given by

$$\begin{aligned}\Gamma_1^{\perp} = (\mathscr{E}_0k^2\alpha_0v_0/R)^2(\epsilon_0^2/N)&\sum_{m\neq n}^{N}\sum_{p\neq q}^{N} g(|\boldsymbol{r}_p(t)-\boldsymbol{r}_q(t)|)g(|\boldsymbol{r}_m(t+\tau)-\boldsymbol{r}_n(t+\tau)|)\\ &\times F_{\perp}(|\boldsymbol{r}_p(t)-\boldsymbol{r}_q(t)|)F_{\perp}(|\boldsymbol{r}_m(t+\tau)-\boldsymbol{r}_n(t+\tau)|)\\ &\times\exp\{i\boldsymbol{k}\cdot(\boldsymbol{r}_p(t)-\boldsymbol{r}_q(t)\}\exp\{i\boldsymbol{k}'\cdot(\boldsymbol{r}_m(t+\tau)-\boldsymbol{r}_n(t+\tau))\}.\end{aligned} \tag{33}$$

It is clear from (33) that the correlation function of light scattered with a polarization perpendicular to that of E_1 has a spectrum which is substantially different from that of E_1. All of these terms are, however, second order in the expansion parameter.

It can also be shown that if the scattering centres are so large that (24) is no longer a valid approximation, the spectrum of Γ_1 is distorted even to first order in the expansion parameter.

We can now turn to a calculation of the intensity correlation function Γ_2. Proceeding as before, we can show that

$$\begin{aligned}\Gamma_2(R,\tau) = (N\mathscr{E}_0k^2\alpha_0v_0/R)^4\sin^3\psi(\sin\psi+4\epsilon_0\ \mathrm{Re}(\beta(\boldsymbol{k},\boldsymbol{k}'))(1+|C(\tau)|^2)\\ +(\text{terms of order }\epsilon_0^2).\end{aligned} \tag{34}$$

Thus to first order in the expansion parameter, the time dependence of Γ_2 is the same as that of the intensity correlation function calculated to zeroth order in ϵ

$$\Gamma_{21} = (N\mathscr{E}_0k^2\alpha_0v_0/R)^4(1+|C(\tau)|^2). \tag{35}$$

5. Angular dependence

The angular dependence of the double scattering process is contained in the function $\beta(\boldsymbol{k},\boldsymbol{k}')$. In calculating the properties of β it will be convenient to use a function $P(\boldsymbol{r})$ which is defined to be the probability that any two points, selected at random in the volume V, will be separated by the distance $\boldsymbol{r}$. We find that

$$P(\boldsymbol{r}) = (1/V)^2\int_V\int_V \delta(r-r_1+r_2)\exp(i\boldsymbol{k}\cdot\boldsymbol{r})\,d^3\boldsymbol{r}_1\,d^3\boldsymbol{r}_2 = (1/2\pi)^3\int d^3k|f(\boldsymbol{k})|^2 \tag{36}$$

where

$$f(\boldsymbol{k}) \equiv (1/V)\int_V e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,d^3r. \tag{37}$$

Using (33) in equation (31), we find

$$\beta(\boldsymbol{k}, \boldsymbol{k}') = (1/N) \int_V (P(\boldsymbol{r}) - 1/V) g(\boldsymbol{r}) F(|\boldsymbol{r}|) (e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + e^{i\boldsymbol{k}'\cdot\boldsymbol{r}})\, d^3r. \tag{38}$$

Equivalently, we can write

$$\beta(\boldsymbol{k}, \boldsymbol{k}') = (A(\boldsymbol{k}) + A(\boldsymbol{k}')) \sin\psi + (B(\boldsymbol{k}) + B(\boldsymbol{k}')) \sin\psi \cos\phi + (C(k) + C(k')) \cos\psi \sin\phi \tag{39}$$

where

$$A(\boldsymbol{q}) \equiv \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}} g(\boldsymbol{r}) (P(\boldsymbol{r}) - 1/V) \{ f_a(r) - (\boldsymbol{k} \cdot \boldsymbol{r}/kr)^2 f_b(r) \}\, d^3r \tag{40}$$

$$\begin{pmatrix} B(q) \\ C(q) \end{pmatrix} = \int e^{i\boldsymbol{q}\cdot\boldsymbol{r}} g(r)(P(\boldsymbol{r}) - 1/V) f_b(r) (\hat{\boldsymbol{e}} \cdot \boldsymbol{r})(\hat{\boldsymbol{e}} \times \boldsymbol{r})(1/r)^2 \begin{pmatrix} (\boldsymbol{k} \cdot \boldsymbol{r})/kr \\ (\boldsymbol{k} \times \boldsymbol{r})/kr \end{pmatrix} d^3r. \tag{41}$$

If V is a sphere, $P(\boldsymbol{r})$ will be independent of angle and we find that the only real part of β will be given by

$$\mathrm{Re}(\beta) \simeq 8\pi \sin\psi \int_0^a (P(r) - 1/V) g(r) (\sin(kr)/kr + J_0(kr)/3) r^2\, dr \tag{42}$$

where a is the radius of the sphere, and J_0 is the Bessel function of zeroth order. Thus in this case β is proportional only to $\sin\psi$ and is independent of ϕ. The angular dependence of the field and intensity correlation functions will thus be the same to first and second order.

It can also be seen from (23) that the correlation function of the fields polarized perpendicular to $\boldsymbol{E}_1$ are, to lowest order in ϵ, independent of ϕ.

6. The statistics of the higher order terms

The higher order scattering terms are not strictly gaussian random processes. We shall be able to show, however, that the departures from gaussian statistics are small except for terms involving a very large number of scattering processes.

The central limit theorem can be used to show that the term E_1 is gaussian because it can be decomposed into a sum of terms which depend only on individual scattering centres and which are therefore statistically independent (Rice 1944, 1945):

$$E_1 = \sum_{j=1}^{N} E_1(j) \tag{43}$$

$$\langle E_1^*(i) E_1(j) \rangle = (1/N) \langle |E_1|^2 \rangle \delta_{ij}. \tag{44}$$

The higher order terms can be expanded in a form similar to (43)

$$E_n(R) = \sum_{j=1}^{N} E_n(j) \tag{45}$$

$$E_n(j) = T(R, r[j]) \prod_{m=2}^{n-1} \left\{ \sum_{i(m)=1}^{N}{}' T(r[i(m-1)], r[i(m)]) \right\} T(r[i(n-1)], r[i(n)]) E(r[i(n)]). \tag{46}$$

The prime on the sums indicates that no two indices $i(m)$ and $i(n)$ may be equal.

Using (45) and (46) it can be shown that if $i \neq j$

$$\frac{\langle E_n^*(i)E_n(j)\rangle}{\langle |E_n(i)|^2\rangle} \simeq \frac{(n-1)!}{N}. \tag{47}$$

This result does not depend on the particular choice of decomposition shown in (46). We have thus shown that the fields which are obtained by n fold scattering processes depart from gaussian statistics by terms of order $(n-1)!/N$. It is clear, however, that n must be quite large before this effect has any experimental significance.

7. Conclusions

In the calculations of this paper we have assumed that primary light, having a well defined initial frequency $\omega_0 = kc$, is incident on a sample of volume V which contains N independent scattering centres each of which has a volume v_0 (whose dimensions are small compared with $2\pi/k$) and an isotropic polarizability α_0.

We have seen that the amplitudes of the scattered fields which are the result of n scattering processes, differ from that of the single scattered field by roughly $(k\alpha_0 v_0 N/VR_0)^n$, where R_0 is the average distance between points in V. (R_0 is roughly proportional to the average linear dimension of V.) The multiple scattering processes do not strictly obey gaussian statistics, their angular dependence can be different from that of simple Rayleigh scattering, and they can contain polarizations different from that of the single scattered fields. The higher order terms can have spectra different from that of the single scattering case.

Most significantly, however, we have seen that the spectra of the fields and the power spectra of the intensities of the fields containing double scattered light are the same as those of the single scattered fields and intensities. Changes in the spectrum of the scattered light will thus be smaller than the single scatter approximation by at least $(k\alpha_0 v_0 N/R_0 V)^2$.

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