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Linewidth Modifications Due to Reflections in the Scattering Cell

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Abstract Correlation data of light scattered by a solution of polystyrene calibrated spheres in glycerol-water are fitted with a bimodal exponential decay at the scattering angles 30°, 90° and 150°. It is shown that this behavior is caused by the reflection of the original laser beam in the scattering cell.

1. INTRODUCTION

In light scattering experiments one oftens measures light scattered from a secondary beam. This light source results from reflections of the original beam in optical windows or interfaces of thecontainer. Such reflections can be enhanced by metal coatings or mirror and lens assemblies if doubling the scattering intensities is advantageous. In some cases however the second antiparallel beam can be a source of error and requires some care in the spectral analysis. The reflected beam can be taken care of by one of many ingenious methods ranging from anti-reflection coatinqs to index matching and use of nonperpendicular windows. To understand quantitatively the effect, we calculated and measured the spectra obtained from a solution of spherical scatterers by photon correlation technique. The first part of this paperdescribes the calculations, which are cornpared to measurements in the second part.

2. COMPLEMIENTARY ANGLE SCATTERING

A solution of N particles illuminated with a plane electromagnetic wave of the form $\vec{E}\ \exp(i\vec{K}_L.\vec{r}-\omega_0 t)$ (where K_L is the wave vector of the incident light of angular frequency ω_0, $\vec{E}_0$ the electric amplitude vector, $\vec{r}$ and t position and time coordinates respectively) scatters light by dipole radiation. The radiation field at a position $\vec{R}$ from

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the origin at the scattering region is the sum of the fields radiated by each particle and is given by

$$\vec{E}(t) = \sum_{j=1}^{N} \vec{E}_j(t) = \sum_{j=1}^{N} \vec{E}_0' \exp\left[i\phi_j(t) - i\,\omega_0 t\right] \qquad (1)$$

where $\vec{E}_0'$ is the scattered field amplitude from an individual particle and depends on the scattering geometry (including incident and observed polarization), the size, form and relative polarizability of the scatterers, and on the original field strength. The choice of the origin inside the scattering volume is arbitrary in principle and each particle position manifests itself through the phase factor $\phi_j(t)$.

Let us iluminate this solution by two antiparallel coherent beams of the same polarization, which can be easily made using a mirror. For scattering angle θ (defined by the original beam) we have a complementary scattering from the reflected beam at the angle $\bar{\theta}$ = = (180'-O), as shown in figure 1. We then define the scattering wave vectors

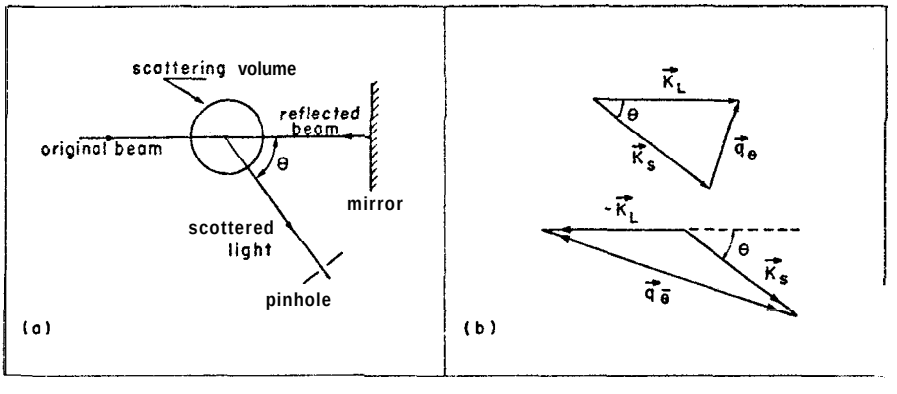

Fig.1 - a) Scattering geometry - The scattering angle θ is defined by the original beam. b) Wave vector displayed.

$$\vec{q}_\theta = \vec{K}_L - \vec{K}_S \qquad (2)$$

and

$$\vec{q}_{\bar{\theta}} = -\vec{K}_L - \vec{K}_S \qquad (3)$$

which describe the two cases of momentum conservation ($\vec{K}_S$ is the scattered wave vector). For quasi-elastic scattering we have respectively

$$q_\theta = 2K_L \text{ sen } (\theta/2) \tag{4}$$

and

$$q_{\bar{\theta}} = 2K_L \cos (\theta/2) \tag{5}$$

We now write the scattered field as

$$\vec{E}(t) = \sum_{j=1}^{N} \vec{E}'_0 \exp[i\ \phi_j(t) - i\ \omega_0 t] + \sum_{j=1}^{N} b\vec{E}'_0 [\exp[i\ \phi'_j(t) - i\omega_0 t] \tag{6}$$

where the additional term is due to the reflected beam. Here b is a factor linked to the reflectivity R and the geometrical factor $M_{\bar{\theta}}$ which represents the intensity ratio between the scattered intensities at angles $\bar{\theta}$ and θ, i.e., $M_{\bar{\theta}} = I_{\bar{\theta}}/I_\theta$. As we are dealing with the electric fields, b can be writen

$$b = (R\ M_\theta)^{1/2} \tag{7}$$

Given a choice of origin in the scattering region, we determine the phases $\phi_j(t)$ and $\phi'_j(t)$ of the fields scattered by a particle centered at $\vec{r}_j$. From figure 2 we see that the phase delay relative to the origin of the light scattered coming from

i) the original beam is

$$\phi(t) = \frac{2\pi}{\lambda} (\overline{AP} + \overline{PE} - \overline{CO} - \overline{OF}) = \frac{2\pi}{\lambda} (\overline{GP} - \overline{OH})$$

$$= [\vec{K}_L \cdot \vec{r}_j(t) - \vec{K}_S \cdot \vec{r}_j(t)] = \vec{q}_\theta \cdot \vec{r}_j(t) \tag{8}$$

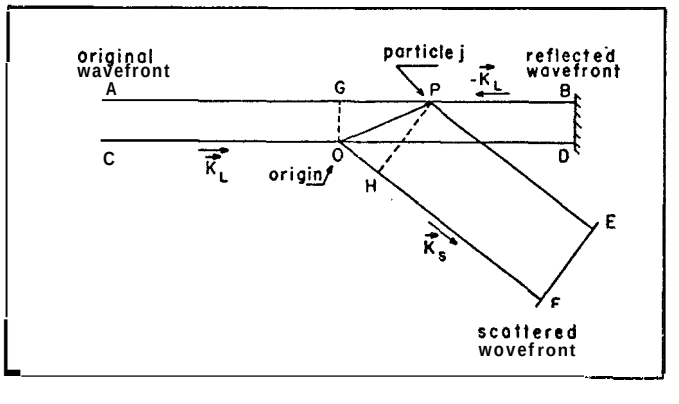

Fig.2 - Scattering geometry for phase delay determination.

ii) the reflected beam is

$$\frac{2\pi}{\lambda}\ (\overline{AP} + \overline{PB} + \overline{PB} + \overline{PE} - \overline{CO} - \overline{OD} - \overline{OD} - \overline{OF})$$

$$= \frac{2\pi}{\lambda}\ (\overline{PB} - \overline{OD} + \overline{PE} - \overline{OF}) = -\vec{K}_L \cdot \vec{r}_j(t) - \vec{K}_S \cdot \vec{r}_j(t)$$

$$= \vec{q}_{\bar{\theta}} \cdot \vec{r}_j(t) \qquad (9)$$

The reflected beam reaches the origin with a delay relative to the original beam

$$\frac{2\pi}{\lambda}\ (\overline{OD} + \overline{OD}) = 2\vec{K}_L.\vec{d} \qquad (10)$$

where $\vec{d}$ is the vector from the origin to the mirror. Thus

$$\phi'_j(t) = \vec{q}_{\bar{\theta}} \cdot \vec{r}_j(t) + 2\ \vec{K}_L.\vec{d} \qquad (11)$$

Taking eq.(8) and eq.(11) into eq.(6), the polarized component results

$$E(t) = \sum_{j=1}^{N} E'_0 \exp\left[i\ \vec{q}_\theta.\vec{r}_j(t) - i\omega_0 t\right] + b \sum_{j=1}^{N} E'_0 \exp\left[i\,2\vec{K}_L \cdot \vec{d} + i\vec{q}_{\bar{\theta}} \cdot \vec{r}_j(t) - i\,\omega_0\, t\right] \qquad (12)$$

Information about the particle diffusive movement is given by field and intensity correlation functions of the light scattered by these particles. Let us calculated these functions. From eq. (12) the first order correlation function is

$$C_E(\tau) = \langle E^*(t) \cdot E(t+\tau)\rangle =$$

$$= |E'_0|^2 \exp(-i\omega_0\tau) \Big\langle \sum_{j=1}^{N}\sum_{\ell=1}^{N} \{\exp\left[-i\vec{q}_\theta.\vec{r}_j(t)\right] + b\exp\left[-i\vec{q}_{\bar{\theta}}.\vec{r}_j(t) - 2i\vec{K}_L.\vec{d}\right]\}$$

$$\times \exp\left[i\vec{q}_\theta.\vec{r}_\ell(t+\tau)\right] + b\exp\left[i\vec{q}_{\bar{\theta}}.\vec{r}_\ell(t+\tau) + 2i\ \vec{K}_L.\vec{d}\ \right]\} \qquad (13)$$

If the solution is so dilute that the particles don't interact with each other, then terms with $\ell \neq j$ become independent and can be be factorized like $\langle e^{i\phi_j}\rangle \langle e^{i\phi_\ell}\rangle$. If the observation volume has a

typical size greater than $2\pi/q$, then each of these factors becomeszero as phases cinn assume any value, which often happens in experimental conditions. So only terms with $\ell=j$ would survive. As particles are equivalent so are the ensemble averages, and we have

$$C_E(\tau) = N|E'_0|^2 \exp(-i\omega_0\tau)\{<\theta\theta> + <\theta\bar{\theta}> + <\bar{\theta}\theta> + <\bar{\theta}\bar{\theta}>\} \tag{14}$$

Here we have used the notation

$$<\theta\theta> = <\exp[-i\vec{q}_\theta.\vec{r}(t) + i\vec{q}_\theta.\vec{r}(t+\tau)]> \tag{15}$$

$$<\theta\bar{\theta}> = b<\exp[-i\vec{q}_\theta.\vec{r}(t) + i\vec{q}_{\bar{\theta}}.\vec{r}(t+\tau) + 2\,i\vec{K}_L.\vec{d}]> \tag{16}$$

$$<\bar{\theta}\theta> = <\exp[-i\vec{q}_{\bar{\theta}}.\vec{r}(t) - 2i\vec{K}_L.\vec{d} + i\vec{q}_\theta.\vec{r}(t+\tau)]> \tag{17}$$

$$<\bar{\theta}\bar{\theta}> = b^2 <\exp[-i\vec{q}_{\bar{\theta}}.\vec{r}(t) + i\vec{q}_{\bar{\theta}}.\vec{r}(t+\tau)]> \tag{18}$$

We compute these averages using a conditional probability for a particle located at $\vec{r} = 0$ at $t = 0$ to be found at time in a volume $d^3\vec{r}$. For a "random walk" brownian movement, this is[2]

$$P(\vec{r},t/\vec{0},0) = (4\pi Dt)^{3/2} \exp(-r^2/4Dt) \tag{19}$$

Here D is the diffusion coefficient of the particle in the solvent, given by the Stockes-Einstein relation[3] for spherical particles of radius a in a solution of viscosity η at temperature T

$$D = \frac{}{6\pi\eta a} \tag{20}$$

where K_B is the Boltzmann constant.

The quantities in eqs. (15) and (18) are readily computed to give

$$<\theta\theta> = e^{-Dq_\theta^2|\tau|} \tag{21}$$

and

$$<\bar{\theta}\bar{\theta}> = b^2\, e^{-Dq_{\bar{\theta}}^2|\tau|} \tag{22}$$

but we notice the presence of origin-dependent phase factors in the other quantities, which are given by

$$<\theta\bar{\theta}> = b\, e^{2i\vec{K}_L.\vec{d}}\, e^{-Dq_{\bar{\theta}}^2|\tau|} \tag{23}$$

$$<\bar{\theta}\theta> = b\, e^{-2i\vec{K}_L.\vec{d}}\, e^{-Dq_{\theta}^2|\tau|} \tag{24}$$

These phase factors reflect the use of a conditional probability for a particle inltialy located at the origin, As we observe a volume where the typical size is at least of a wavelength, these phases must be averaged, i.e., at "time zero" a particle can be anywhere in this volume, thus defining the origin and $\vec{d}$. If we do so, we find that

$$<\theta\bar{\theta}> = <\bar{\theta}\theta> = 0 \tag{25}$$

Substituting eqs. (25), (21) and (22) into eq. (14), we get

$$C_E(\tau) = N(E_0')^2 \exp(-i\omega_0\tau)\left[e^{-Dq_{\theta}^2|\tau|} + b^2 e^{-Dq_{\bar{\theta}}^2|\tau|}\right] \tag{26}$$

Through normalization we obtain the first order correlation function

$$g_1^E(\tau) = \frac{C_E(\tau)}{C_E(0)} = \frac{\exp(-i\omega_0\tau)}{1+b^2}\left[e^{-Dq_{\theta}^2|\tau|} + b^2\, e^{-Dq_{\bar{\theta}}^2|\tau|}\right] \tag{27}$$

If the number of scatters is high enough (above 10^2) to ensure a gaussian statistics[4] the normalized first order intensity correlation function (or second order electric field correlation function) isgiven by

$$g_1^I(\tau) = g_2^E(\tau) = 1 + |g_1^E(\tau)|^2 = 1 + \frac{1}{(1+b^2)^2}\left[e^{-Dq_{\theta}^2|\tau|} + b^2\, e^{-Dq_{\bar{\theta}}^2|\tau|}\right]^2 \tag{28}$$

This result is compared to experimental measurements in the next section.

3. EXPERIMENTAL RESULTS

As scattering media we used calibrated polystyrene spheres (Dow Corning) of radius 990 Å, refractive index 1.598 and used as solvent a

mixture of 86.5% in volume of distilled glycerol in water. This solvent has index of refraction 1.452 and vfscosities[5] of 130 cP at 20.5^{o} and 160 cP at $18.1^{o}C$. The concentration of the solution was of about 10^{6} scatterers per cm . The solution was sealed in a 10 mm of diameterpyrex cylindrical tube to prevent water absorption from the atmosphere and measurements where taken at room ternperature. As pyrex has index of refraction (measured) of 1.47 the main reflectivity comes from the pyrex-air interface and is of the order of 4% in the intensity.

Correlation curves were taken at 30^{o}, 90^{o} anf 150^{o} scattering angles. The 90^{o} mounting could be single exponental fitted with the expected decay time ($1/Dq^{2}$) of 145ms (at $20.5^{o}C$). The 150^{o} mounting is shown in fig.3 together with two reference curves. The first represents the expected single exponential decay in the absence of reflectedbeam.

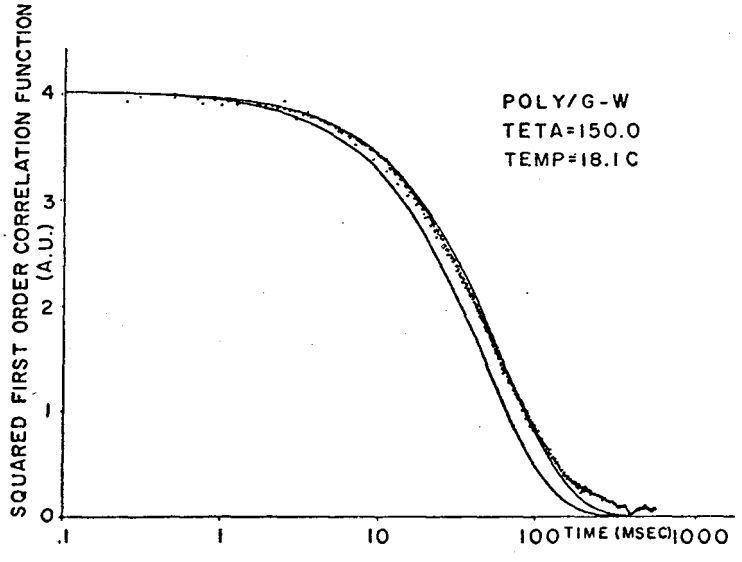

Fig.3- Correlation data for $\theta=150^{o}$ (dots) and two theoretical curves: (a) represents the expected single exponential in the absence of reflected beain ($g_2(t)=4.02\ e^{-2t/95}$); (b) represents the best single exponential fit which has a linewidth 32% greater than the expected value ($g_2(t)=4.02\ e^{-2t/125}$). Subtracted background, arbitrary units, t in msec).

The decay time would be 95 msec. The second curve represents the best single exponential fit with a decay time of 125 ms, i.e., 32% larger than the expected value. In fig. 4 we show the best fit to the 150^{o}

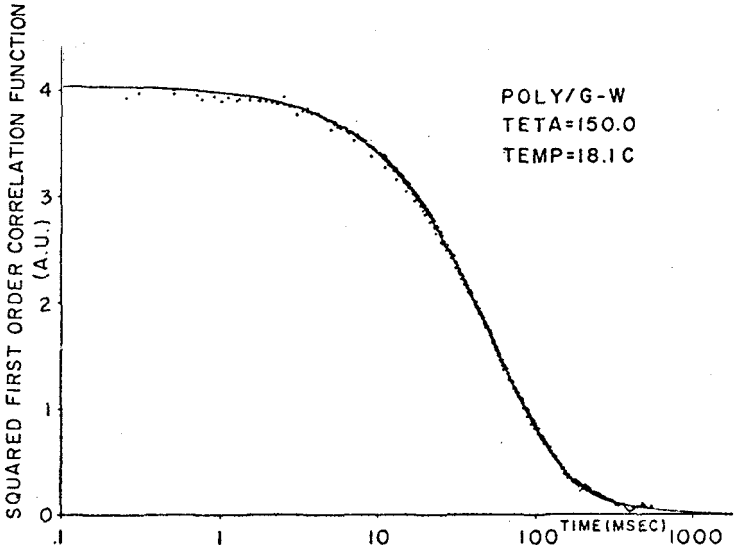

Fig.4 - Correlation data for $\theta=150^{o}$ (dots) and the best bimodal fit $g_2(t)=4.04\,[\exp(-t/95) + 0.22\,\exp(-t/1330)]^2$, where the decay times of 95 msec and 1330 ms are the expected value for scattering angles of 150^{o} and 30^{o} respectively at t = 18.1 ^{o}C.

mounting, which is given by the formula $g_2(t) = 4.04[\exp(-t/95) +$ + 0.22 $\exp(-t/1330)]^2$ (subtracted background, arbitrary units) where decay times are given in msec. Both agree with the expected decay times for scattering angles 150^{o} and 30^{o} at the temperature of 18.1°C. The second exponential weight can be best expressed as $b^2(\overline{150^{o}})$ = 0.22 $\pm$ .03. For the 30^{o} mounting the fit is much closer to a single exponential as the asymmetry in this case tends to reduce even further the intensity of the complementary scattering at the larger angle 150^{o}. We obtain in this case, where the temperature was 20.3 °C, the fit $g_2(t) = 4.03[\exp(-t/1093) + .012\,\exp(-t/78.5)]^2$. Once again decay times are as expected, and expressed in msec units. However, the percentual

precision in the weight factor $b^2(\overline{30^o}) = .012 \pm .003$ is much lower. Now, as we've done complementary measurements we can calculate R and $M_{\overline{150^o}}$ from $b^2(\overline{30^o})$ and $b^2(\overline{150^o})$ using eq. (7). We obtain $R = (5.1 \pm 1.0) \times 10^{-2}$ and $M = 4.3 \pm 0.8$, which give acceptable values if compared with values independently obtained for R and M, i.e. $R = (4.0 \pm .3) \times 10^{-2}$ and $M = 4.2 \pm .3$. The reflectivity value was obtained by the Fresnel formula after measurement of the pyrex index of refraction, and the asymmetry value was obtained by direct intensity measurements.

4. CONCLUSIONS

The considerations made are valid for any light scattering technique, whenever one has wave vector dependence. At 90^o the symmetry in the reflected beam introduces no special features in the spectra. For scatterers with sizes larger than 1/20, the asymmetry factor given by Mie theory[6] can be very different from unity and in this case one should proceed to reduce the reflectivity or else restrict measurements to low angle scattering, so as to avoid complication in the analyses of the data.

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Resumo

Dados de correlação de luz espalhada por uma solução de esferas calibradas de poliestireno em água-glicerol são ajustados com uma desintegração exponencial bimodal nos ângulos de espalhamento de 30^o, 90^o e 150^o. Mostramos que este comportamento é explicado pela reflexão do feixe de laser original na celula espalhadora.