Electronic Supplementary Information

Theoretical consideration

Theory of scattering

It is well known that scattering has a close relationship with not only density fluctuation but also the shape and size of scatters. How does the density fluctuation develop? And what is the relationship between the scattering intensity and the volume of scatters? We hope to solve-these problems the following section.[1]

Assuming that light travels through the media along *x*-axis, γ is the cross-angle between k_f and n_i (n_i is the electric field direction of incident light, along *y*-axis), α is the cross-angle between k_f and *z*-axis, and θ is the scattering angle, the scattering vector $q = k_i - k_f$, and its modulus $|q| = \sqrt{|k_i|^2 + |k_f|^2 - 2|k_i||k_i|\cos\theta}$, where k_f and k_i are the wave vectors of the scattering light and incident light, respectively, and their moduli $|k| = 2\pi n/\lambda$. Since $|k_i| = |k_f|$, we have

$$|q| = \sqrt{2|k_i|^2 - 2|k_i|^2 \cos\theta} = \sqrt{2k_i^2 \sin^2 \frac{\theta}{2}} = 2k_i \sin\frac{\theta}{2} = \frac{4\pi n}{\lambda_i}\sin\frac{\theta}{2}.$$

When the tested system and light source are determined, the scattering vector is only related to the scattering angle θ.

The scattering intensity (I_u) is equal to the average of the total light intensity of two mutually perpendicular polarized incident light beam in the scattering direction, which can be expressed as:

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$$I_u = \frac{1}{2}[I_{if} + I_{if}^{'}] = \frac{1}{2}A(\sin^2\gamma + \sin^2\alpha)\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle = \frac{1}{2}A\frac{1+\cos^2\theta}{2}\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle \qquad \text{(A-1)}$$

where $A = \dfrac{k_f^4 I_0}{16\pi^2 R^2 \varepsilon_0^2}$, and $\left|\delta\varepsilon_{if}(q)\right|$ is the fluctuation of permittivity tensor at a q scattering vector, ε_0 is the mean permittivity. Then, the Rayleigh ratio $R(q)$ can be obtained as following,

$$R_u(q) \equiv \frac{I}{I_0}R^2 = \frac{k_f^4}{16\pi^2\varepsilon_0^2}\frac{1+\cos^2\theta}{2}\left\langle\left|\delta\varepsilon_{if}(q)\right|^2\right\rangle \qquad \text{(A-2)}$$

In the region of visible light, the relationship between permittivity (ε_0) and refractive index (n) in an isotropic system can be expressed as:

$\varepsilon = n^2$, that is, $\delta\varepsilon^2 = 4n^2\delta^2 n$

So, the Rayleigh ratio is given by:

$$R_u = \frac{4\pi^2 n^2}{\lambda_i^4}\frac{1+\cos^2\theta}{2}V\cdot\left\langle\delta^2 n\right\rangle \qquad \text{(A-3)}$$

To a single-component system, the mean square fluctuation of refractive index $\left\langle\delta n^2\right\rangle_d$ is only related to the mean square fluctuation of density as shown below.

$$\left\langle\delta n^2\right\rangle_d = \left(\frac{\partial n}{\partial\rho}\right)^2\left\langle\delta\rho^2\right\rangle \qquad \text{(A-4)}$$

Besides, in a single-component system, density is a function of temperature and pressure. The density fluctuation can be expressed as:

$$\partial\rho = \left(\frac{\partial\rho}{\partial T}\right)_P\delta T + \left(\frac{\partial\rho}{\partial P}\right)_T\delta P$$

and the mean square fluctuation of density can be shown as:

$$\left\langle \delta\rho^2 \right\rangle_d = \left(\frac{\partial\rho}{\partial T}\right)_P^2 \left\langle \delta T^2 \right\rangle + 2\left(\frac{\partial\rho}{\partial T}\right)_P \left(\frac{\partial\rho}{\partial P}\right)_T \left\langle \delta P \delta T \right\rangle + \left(\frac{\partial\rho}{\partial P}\right)_T^2 \left\langle \delta P^2 \right\rangle \tag{A-5}$$

where $\left\langle \delta T^2 \right\rangle$ and $\left\langle \delta P^2 \right\rangle$ are the mean square fluctuations of temperature and pressure, respectively. $\left\langle \delta P \delta T \right\rangle$ is the cross-average fluctuation of temperature and pressure.

According to the statistical thermodynamic theory, the following relationships can be obtained:

$$\left.\begin{aligned} \left\langle \delta T^2 \right\rangle &= rkT^2/(rC_P - \alpha^2 TV) \\ \left\langle \delta P^2 \right\rangle &= C_P kT/V(rC_P - \alpha^2 TV) \\ \left\langle \delta T \delta P \right\rangle &= \alpha kT^2/rC_P - \alpha^2 TV \end{aligned}\right\} \tag{A-6}$$

where k is Boltzmann constant, C_P is molar heat capacity at constant pressure, V is micro-volume element, $r \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is constant temperature compression coefficient, and $\alpha \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is expansion coefficient at constant pressure.

$$\rho = \frac{NM}{V} \tag{A-7}$$

Based on the derivative calculation on both sides of Eq. (A-7), a relationship can be obtained: $\delta V/V = -\delta\rho/\rho$, so that $r = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T$ and $\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P$.

Combining Eq. (A-5) and Eq. (A-6), we have:

$$\left\langle \delta\rho^2 \right\rangle_d = \rho^2 rkT/V \tag{A-8}$$

and $\left\langle \delta n^2 \right\rangle_d = \left(\frac{\partial n}{\partial\rho}\right)^2 \rho^2 rkT/V$ (A-9)

Then, the Rayleigh ratio induced by density fluctuation can be written as:

$$(R_u)_d = \frac{4\pi^2 n^2}{\lambda_i^4}\frac{1+\cos^2\theta}{2}\left(\rho\frac{\partial n}{\partial\rho}\right)^2 rkT \quad \text{(A-10)}$$

If a second component is added into the pure media, the contribution of the local concentration fluctuation to the refractive index fluctuation in the blending system can be expressed as: [2]

$$\langle \delta n\rangle_c = \left(\frac{\partial n}{\partial c}\right)\langle \delta c\rangle \text{ and } \langle \delta n^2\rangle_c = \left(\frac{\partial n}{\partial c}\right)^2\langle \delta c^2\rangle$$

The Rayleigh ratio induced by concentration fluctuation is written as:

$$(R_u)_c = \frac{4\pi^2 n^2}{\lambda_i^4}\frac{1+\cos^2\theta}{2}\left(\frac{\partial n}{\partial c}\right)^2 \frac{C}{\left(\frac{1}{M_2}+2A_2C+3A_3C^2+\cdots\cdots\right)} \quad \text{(A-11)}$$

Considering the effect of both density fluctuation and concentration fluctuation on scattering intensity, the Rayleigh ratio can be given as follows:

$$R_u = (R_u)_d + (R_u)_c$$

When an electric charge particle undergoes accelerated motion, it radiates electromagnetic energy. Based on the electromagnetism theory, the corresponding Rayleigh scattering intensity can be expressed as:

$$I_s = \frac{c}{4\pi}E_s E_s^* = \frac{c}{4\pi}E_0^2\frac{\alpha^2\omega^4}{c^4 r^2}\sin^2\psi \quad \text{(A-12)}$$

Considering the effect of phase factor on scattering, the electric field strength of a multi-scatters system can be written as:

$$E_s = \sum_j (E_s)_j = -\frac{\omega^2 E_0}{c^2 r}\sin\psi\cdot e^{i(\omega t - kD)}\sum_j \alpha_j e^{-ik(rj\cdot s)} \quad \text{(A-13)}$$

where r is the distance between the scatter and the detector, which can be considered to be the same for each scatter, α is polarizability, and rj is the spatial position in the coordinate system. It can be seen from Eq. (A-13) that scattering is related to the polarizability and spatial distribution of the scatters.

References

1 R. S. Stein. Scattering and Double Refraction Method Application in Polymer Texture Research [M]. Mao Xu trans. Beijing, Science Press, 1993, pp. 2-14. (in Chinese).

2 C. S. Johnson and D. A. Gabriel. Laser light scattering. In: Ellis Bell J. Editor. Spectroscopy in Biochemistry, Vol. II. CRC Press, 1994, pp.9-11.