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Manual of Symbols and Terminology for Physicochemical Quantities and Units

APPENDIX II — DEFINITIONS, TERMINOLOGY AND SYMBOLS IN COLLOID AND SURFACE CHEMISTRY

PART 1.14: LIGHT SCATTERING

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

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DEFINITIONS, TERMINOLOGY AND SYMBOLS IN COLLOID AND SURFACE CHEMISTRY

Section 1.14 LIGHT SCATTERING

After defining key physical quantities such as elastic, inelastic, quasielastic, single, multiple, coherent and incoherent light scattering, the document deals with various elastic light scattering signals including measures of radiant intensity and polarization. This is followed by a survey of relations which deal with scattering by particles including the scattering, absorption and extinction cross sections, radiation pressure and the Rayleigh ratio. Specific expressions applicable to Rayleigh scatterers and also to small ellipsoidal particles are surveyed next. This is followed by a statement of the integral formulation of the scattering problem leading to the definition of the particle scattering function. The final sections deal with scattering by continuous media. In solids this leads to utilization of the correlation volume. In liquids scattering is attributed to thermal density and concentration fluctuations.

1.14.1 INTRODUCTION

Light scattering is the deflection of a light beam by discrete variation in refractive index due to the presence of particles or by spatial refractive index fluctuations. This section will be restricted to *elastic scattering* for which there is no wavelength shift. For *inelastic scattering* there are wavelength shifts due to molecular transitions (Raman effect, fluorescence) and for *quasielastic scattering* there are wavelength shifts and line broadening due to time dependent processes. This section considers only *single scattering* in which there is only one scattering encounter as opposed to *multiple scattering* in which there is successive rescattering of the radiation within the scattering medium.

The scattering is *coherent* whenever the phases of the signals arising from different scattering centers are correlated and *incoherent* whenever these phases are uncorrelated.

The following radiometric concepts will be utilized. *Irradiance* is the flux of radiant energy, or power divided by surface area (W m^{-2}). *Radiant intensity* is power divided by solid angle (W sr^{-1}).

1.14.2 LIGHT SCATTERING SIGNALS

The *scattering plane* contains the incident light beam and the line from the center of the scattering system to the observer. The *scattering angle*, θ , lies in the scattering plane and is measured clockwise viewing into the incident direction. *Forward scattering* is at $\theta = 0$, *back scattering* is at $\theta = 180^\circ$.

E_1 and E_2 represent the irradiances of the light scattered into a particular direction when the incident beam is linearly polarized with its electric vector vibrating perpendicular and parallel, respectively, to the scattering plane. E_u is the corresponding quantity for unpolarized incident radiation.* The symbol θ can be added to the symbol for a particular quantity when it is desired to emphasize the angular dependence [e.g., $E_u(\theta)$, $E_1(\theta)$, $E_2(\theta)$].

When the scattering in the half plane from $\theta = 0^\circ$ to 180° is symmetrical with that from $\theta = 180^\circ$ to 360° , the *dissymmetry* is defined as the ratio of the scattered irradiance at two scattering angles symmetrical about $\theta = 90^\circ$:

*The same symbol is universally used for the electric field in the theory of light scattering, and the symbol I is frequently used in the light scattering literature to denote irradiance.

$$Z_1(\theta) = \frac{E_1(\theta)}{E_1(180^\circ-\theta)}; \quad Z_2(\theta) = \frac{E_2(\theta)}{E_2(180^\circ-\theta)}. \quad (1)$$

The *Rayleigh ratio*, R , is the scattered radiant intensity in one particular direction divided by the incident irradiance and the volume under view. The Rayleigh ratio is in units of $(\text{m sr})^{-1}$.

The polarized components of the Rayleigh ratios are defined by

$$R_v = V_v + H_v, \quad (2)$$

$$R_h = V_h + H_h. \quad (3)$$

The subscripts v and h designate the states of polarization of the incident beam as defined by E_1 and E_2 , respectively. The upper case letters V and H designate the state of linear polarization of the scattered beam. Thus H_v is the component of the Rayleigh ratio polarized parallel to the scattering plane when the incident radiation is perpendicularly polarized. When H_v or V_h assume nonzero values the scattered light is said to be *depolarized*.

The total Rayleigh ratio R_u and its components are related through

$$R_u = V_u + H_u, \quad (4)$$

$$V_u = (V_v + V_h)/2, \quad (5)$$

$$H_u = (H_v + H_h)/2, \quad (6)$$

where the subscript u designates unpolarized incident radiation. The factor of one half arises because the unpolarized incident radiation consists of two polarized beams of equal irradiance with uncorrelated phases.

The polarization ratios are defined by

$$\rho_v = H_v/V_v, \quad (7)$$

$$\rho_h = V_h/H_h, \quad (8)$$

$$\rho_u = (H_v + H_h)/(V_v + V_h) = H_u/V_u. \quad (9)$$

These follow *Krishnan's relation*

$$\rho_u = \frac{1 + \rho_h^{-1}}{1 + \rho_v^{-1}}. \quad (10)$$

The *polarization or degree of polarization* is

$$P = \frac{V_v + V_h - H_v - H_h}{V_v + V_h + H_v + H_h}. \quad (11)$$

The *Stokes parameters* of elliptically polarized incident radiation are given by

$$s_0^0 = E_1^0 + E_2^0, \quad (12)$$

$$s_1^0 = E_1^0 - E_2^0, \quad (13)$$

$$s_2^0 = 2(E_1^0 E_2^0)^{\frac{1}{2}} \cos \delta^0, \quad (14)$$

$$s_3^0 = 2(E_1^0 E_2^0)^{\frac{1}{2}} \sin \delta^0, \quad (15)$$

where E_1^0 and E_2^0 specify the irradiances of the incident light polarized with their electric vectors vibrating perpendicular and parallel to the scattering plane, respectively and δ^0 is the phase difference between these electric vectors. The Stokes parameters of the scattered light are given by the matrix

equation

$$(s_0, s_1, s_2, s_3) = \mathbb{F}(s_0^0, s_1^0, s_2^0, s_3^0) \quad (16)$$

where the 4×4 scattering matrix \mathbb{F} is comprised of 16 scattering matrix elements. These matrix elements, which may originate in theory or experiment, provide a complete description of the scattered radiation in terms of the incident radiation.

The turbidity τ is the total power of scattered light divided by the incident irradiance and the observed volume. The turbidity is in units of reciprocal length.

1.14.3 SCATTERING OF PARTICLES

A. General

The refractive index or complex refractive index of a particle is

$$\hat{n} = n + ik, \quad (17)$$

where n is the real part of n , sometimes called the real refractive index, and k is the absorption index.* The absorption coefficient, as defined in the Beer-Lambert Law for a homogeneous bulk (nonscattering) sample, equals $4\pi k/\lambda_0$, where λ_0 is the vacuum wavelength. A perfectly reflecting particle is one for which n or k is infinite.

The extinction cross section of a particle C_{ext} (units of area) represent the power removed by a particle divided by the irradiance of the incident beam. It is comprised of two parts, the scattering cross section C_{sca} which represents the power of the scattered light and the absorption cross section C_{abs} which represents a power loss, usually due to degradation of radiant energy to thermal energy, i.e.

$$C_{ext} = C_{sca} + C_{abs} \quad (18)$$

The scattering efficiency, absorption efficiency and extinction efficiency are obtained by dividing the respective cross sections by the cross sectional areas A_s of the particle.

$$Q_{sca} = C_{sca}/A_s, \quad (19)$$

$$Q_{abs} = C_{abs}/A_s, \quad (20)$$

$$Q_{ext} = C_{ext}/A_s. \quad (21)$$

The albedo is the fraction of extinction which is scattered

$$A = Q_{sca}/Q_{ext} \quad (22)$$

The efficiency for radiation pressure is

$$Q_{pr} = Q_{ext} - \langle \cos\theta \rangle_{sca} Q_{sca} - \langle \cos\theta \rangle_{abs} Q_{abs}, \quad (23)$$

where, for cylindrically symmetric scattering, the asymmetry factor for scattering is

$$\langle \cos\theta \rangle_{sca} = \frac{\int_{-1}^{+1} E_u \cos\theta d(\cos\theta)}{\int_{-1}^{+1} E_u d(\cos\theta)}, \quad (24)$$

*When defining $\hat{n} = n(1 - i\kappa)$, an alternate absorption index, κ , is sometimes utilized.

and $\langle \cos \theta \rangle_{abs}$ is the asymmetry factor for reradiation of the absorbed power.

For a system in which the particle number concentration is N the turbidity is given by

$$\tau = N C_{sca} , \quad (25)$$

and the transmittance is

$$T = \exp(-N C_{ext} d) \quad (26)$$

where d is the path length. The above two relations apply only if the scattering particles are randomly positioned so that the single particle radiances can be added because of the incoherence of the separate signals.

Although E_u , E_1 and E_2 are defined phenomenologically as above, these quantities are also frequently used as the scattered signals generated by single particles. They are then related to the Rayleigh ratio by

$$R_u = \kappa^2 N (E_u / E_u^0) , \quad (27)$$

$$R_v = \kappa^2 N (E_1 / E_1^0); \quad R_h = \kappa^2 N (E_2 / E_2^0) . \quad (28)$$

where E_u^0 designates the incident irradiance for unpolarized light and κ is the distance from the scattering site to the observer. This distance is assumed to be large compared to the dimensions of the scattering volume. For incident unpolarized light the following relation applies:

$$R_u = (R_v + R_h) / 2 . \quad (29)$$

B. Lorenz-Mie Theory

The theory of scattering by particles may be formulated as a boundary value problem or as an integral. Among the analytical solutions already available are those for circular cylinders, spheres and ellipsoids of revolution. For spheres and cylinders, these may include inhomogeneous particles consisting of any number of concentric layers of different refractive index or such particles having a radially symmetric but otherwise variable refractive index. Also an extended boundary condition method has been developed which treats a particle consisting of an inner ellipsoid of revolution which may be arbitrarily placed within a larger ellipsoid of revolution.

Scattering by isotropic, homogeneous spheres is referred to as *Lorenz-Mie theory* (Mie theory). In addition to the relative refractive index,

$$m = \hat{n} / n_m , \quad (30)$$

where n_m is the refractive index of the nonabsorbing medium in which the particle is immersed, the Lorenz-Mie solution of the scattering problem involves the *size parameter*

$$x = 2\pi a / \lambda ,$$

where a is the radius and λ , the wavelength in the medium, is

$$\lambda = \lambda_0 / n_m . \quad (32)$$

C. Rayleigh Theory

When the particle radius is small compared to the wavelength, $x \sim 0.3$, and the relative refractive index is not too large ($m < 2$),* the Lorenz-Mie theory reduces to *Rayleigh theory* for which the scattered irradiance per particle for unpolarized incident radiation is

$$E_u = E_1 + E_2 = \frac{8\pi^4 a^6}{\kappa^2 \lambda^4} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 (1 + \cos^2 \theta) E_u^0 . \quad (33)$$

*For smaller x , correspondingly larger m are permitted.

where $||$ denotes the absolute value of. In the factor $(1+\cos^2\theta)$ the first term corresponds to E_1 and the second term to E_2 . This will be the case whenever this factor appears below. The following expressions also apply:

$$Q_{sca} = \frac{8}{3}x^4 \left| \frac{m^2-1}{m^2+2} \right|^2, \quad (34)$$

$$Q_{abs} = \text{Im}\left\{-4x \left(\frac{m^2-1}{m^2+2} \right)\right\}, \quad (35)$$

where Im denotes the *imaginary part of*. The Rayleigh theory leads to a Rayleigh ratio which can be written as

$$R_u = \frac{8\pi^4 N a^6}{\lambda^4} \left| \frac{m^2-1}{m^2+2} \right|^2 (1+\cos^2\theta). \quad (36)$$

Only when the scattering particles can be treated by Rayleigh theory can this Rayleigh ratio be related to the turbidity by

$$R_u = (3/16\pi)\tau(1+\cos^2\theta). \quad (37)$$

The results of the Rayleigh theory can also be obtained by assuming that the small sphere radiates as if it were an oscillating dipole whose *polarizability* is given by

$$\alpha = 4\pi\epsilon_0 \left(\frac{m^2-1}{m^2+2} \right) a^3, \quad (38)$$

where ϵ_0 is the permittivity of vacuum.

When m is very large corresponding to nearly perfectly reflecting small particles ($m > 10^2$),

$$E_u = E_1 + E_2 = \frac{8\pi^4 a^6}{\lambda^4} \left[\left(1 - \frac{1}{2}\cos\theta\right)^2 + \left(\cos\theta - \frac{1}{2}\right)^2 \right] E_u^0 \quad (39)$$

where the first term in the square bracket corresponds to E_1 and the second term to E_2 .

D. Ellipsoidal Particles

The Rayleigh ratios for an ellipsoid whose longest dimension is small compared to the wavelength can be derived by assuming three polarizabilities along the axes of the ellipsoid A, B, C , e.g.,

$$\alpha_A = 4\pi\epsilon_0 \frac{V(m^2-1)}{4\pi + (m^2-1)P_A}, \quad (40)$$

where V is the volume, and the *depolarization factor* is

$$P_A = \int_0^\infty \frac{2\pi ABC \, dy}{(y+A^2)^{3/2} (y+B^2)^{1/2} (y+C^2)^{1/2}}, \quad (41)$$

where y is an integration variable. Similar equations may be written for P_B and P_C . For a randomly oriented dispersion of ellipsoids the Rayleigh ratio at $\theta = 90^\circ$ is

$$R_u = R_{u,is} + R_{u,an} = \frac{\pi^2 N}{2\lambda^4 \epsilon_0} (\bar{\alpha}^2 + \frac{13}{45}\gamma^2), \quad (42)$$

where $\bar{\alpha}$ is the *mean polarizability* and γ is the *anisotropy factor*. Here

$$\bar{\alpha} = \frac{1}{3}(\alpha_A + \alpha_B + \alpha_C), \quad (43)$$

and

$$\gamma^2 = \frac{1}{2}[(\alpha_A - \alpha_B)^2 + (\alpha_A - \alpha_C)^2 + (\alpha_B - \alpha_C)^2] \quad (44)$$

$R_{u,is}$, the *isotropic part of the Rayleigh ratio*, is the Rayleigh ratio for

an equivolume sphere and $R_{u,an}$ is the *anisotropic part of the Rayleigh ratio*, each at 90° . These relations lead to

$$\rho_V(90) = \frac{(3/45)\gamma^2}{(\bar{\alpha})^2 + (1/45)\gamma^2} = \frac{3\delta^2}{5+\delta^2}, \quad (45)$$

where δ , the *generalized anisotropy* is

$$\delta^2 = \gamma^2/9(\bar{\alpha})^2. \quad (46)$$

The effect of the anisotropy is to increase the Rayleigh factor for 90° over that for an equivolume sphere by the *Cabannes factor for 90°*

$$C_u(90) = \frac{6+6\rho_u(90)}{6-7\rho_u(90)}, \quad (47)$$

so that

$$R_u(90) = R_{u,is}(90) C_u(90), \quad (48)$$

and to increase the scattering cross section by the following *Cabannes factor for turbidity*

$$C_T = \frac{6+3\rho_u(90)}{6-7\rho_u(90)}. \quad (49)$$

E. Integral Formation

As an alternative to the boundary value formulation, the scattering can be represented as an integral. In physical terms this corresponds to viewing the particle as an array of coherent dipoles (Rayleigh scatterers) in which each dipole is driven by a local field. This local field can be approximated by the incident field whenever the *phase shift of the longest ray* through the particle (distance d)

$$\rho_p = (\pi d/\lambda)(m-1) \quad (50)$$

is not too large (e.g., $\rho_p < 2$). This approximation known as the Rayleigh-Debye theory (sometimes also known as the Rayleigh-Gans theory) leads to

$$E_u = \frac{8N\pi^4 a^6}{9\lambda^4 \kappa^2 \epsilon_0} (1+\cos^2\theta) \left| \int \alpha(\vec{\kappa}) \exp(i\phi) dV \right|^2 E_u^0, \quad (51)$$

where ϕ is the phase at the position of the observer, relative to a common reference of the dipole emission from a volume element at location $\vec{\kappa}$ within the particle and $\alpha(\vec{\kappa})$ is the polarizability at $\vec{\kappa}$. For anisotropic media the polarizability is a tensor so that the above integral may be evaluated numerically for particles of any shape, heterogeneity or anisotropy.

The polarizability is related to the refractive index at $\vec{\kappa}$ by the Lorentz-Lorenz equation

$$\alpha(\vec{\kappa}) = 3\epsilon_0 \frac{V[m^2(\vec{\kappa})-1]}{[m^2(\vec{\kappa})+2]}. \quad (52)$$

When the particle is homogeneous and isotropic, viz., the refractive index is a scalar and is uniform throughout the particle

$$E_u = \frac{8\pi^4 a^6}{\lambda^4 \kappa^2} (1+\cos^2\theta) \left| \frac{m^2-1}{m^2+2} \right|^2 P(\theta) E_u^0, \quad (53)$$

where the *form factor* or *particle scattering function* is

$$P(\theta) = \frac{1}{V^2} \left| \int \exp(i\delta) dV \right|^2. \quad (54)$$

This can be evaluated numerically for particles of any shape or in closed form for certain regular shapes. For values of m approaching unity, the following approximation is frequently utilized

$$\frac{m^2-1}{m^2+2} \sim \frac{2}{3}(m-1) \quad (55)$$

1.14.4 SCATTERING IN CONTINUOUS MEDIA

A. Solids

Scattering in solids may arise because of local variations in the specific electric inductive capacity or *relative permittivity*, ϵ_n , where, for nonabsorbing media of unit magnetic specific inductive capacity, $\epsilon_n = m^2$. This quantity may be represented as the sum of the average value $\bar{\epsilon}_n$ and a local variation at positive \vec{k} so that

$$\epsilon(\vec{k}) = \bar{\epsilon}_n + \Delta\epsilon(\vec{k}) \quad (56)$$

The mean square value of the local deviation of the dielectric constant from $\bar{\epsilon}_n$ is designated $\overline{\Delta\epsilon^2}$ and the *correlation distance** $\overline{\Delta\epsilon(\vec{k}_1)\Delta\epsilon(\vec{k}_2)}$ is the average of the indicated product for a *separation distance* $s = |\vec{k}_1 - \vec{k}_2|$. The correlation function $\gamma(s)$ is defined by

$$\overline{\Delta\epsilon(\vec{k}_1)\Delta\epsilon(\vec{k}_2)} = \gamma(s)\overline{\Delta\epsilon^2} \quad (57)$$

Then

$$E_u = E_1 + E_2 = \frac{\pi^2}{2\kappa^2\lambda_0^4} \overline{\Delta\epsilon^2} V (1 + \cos^2\theta) \int_V \gamma(s) \exp(i\phi) dV E_u^0,$$

where ϕ is the same phase factor defined above. When $\gamma(s)$ is spherically symmetric, depending only upon the distance s , and not on the direction in space

$$E_u = E_1 + E_2 = \frac{\pi^2}{2\kappa^2\lambda_0^4} \overline{\Delta\epsilon^2} V (1 + \cos^2\theta) \int_0^\infty 4\pi s^2 \gamma(s) [\sin(hs)/hs] ds E_u^0, \quad (59)$$

where

$$h = (4\pi/\lambda) \sin(\theta/2) \quad (60)$$

The integral in the above equations is called the *correlation volume*. When the correlation function is described by an exponential

$$\gamma(s) = \exp(-s/\ell) \quad (61)$$

the parameter ℓ is called the *persistence length* or *correlation length*.

B. Liquids

Isotropic scattering from pure liquids can be attributed to *thermal density fluctuations* leading to

$$R_{u, is} = (2\pi^2 k_B T / \lambda_0^4 \beta_T) n^2 (\partial n / \partial p)_T^2 (1 + \cos^2\theta) \quad (62)$$

where k_B is Boltzmann's constant, T is the absolute temperature, n is the refractive index, p is the pressure and β_T is the isothermal compressibility, $-(1/V)(\partial V / \partial p)_T$.

Near the critical point the Rayleigh factor is given by the *Ornstein-Zernike expression*

$$R_{u, is} = \frac{(\pi^2 / 2\lambda_0^4) (1 + \cos^2\theta) [\rho (\partial n^2 / \partial p)_T]^2 k_B T}{1/\beta_T + 8\pi^2 k_B T (\ell^2 / \lambda^2) [\sin^2(\theta/2) / (T' - 1)]} \quad (63)$$

where ℓ is the correlation length based upon an exponentially decaying correlation function as defined in the previous section and T' , the reduced temperature is

$$T' = T/T_c \quad (64)$$

*This quantity is dimensionless.

where T_c is the critical temperature. This expression applies only for conditions of single scattering, i.e., sufficiently small illuminated volume and sufficiently low turbidity.

C. Binary Solutions

For dilute binary liquid solutions in which the solute can be treated as Rayleigh scatterers, the Rayleigh ratio in excess of that due to the solvent, ΔR_u , can be attributed to concentration fluctuations leading to

$$\Delta R_u = \frac{K'RT(1+\cos^2\theta)}{\rho_0(\partial\mu/\partial m)_{T,p}} \quad (65)$$

where

$$K' = \frac{2\pi^2 n^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial m}\right)_{T,p}^2 \quad (66)$$

and R is the molar gas constant, N_A is the Avogadro constant, ρ is the density of the solvent, m is the molality* and μ is the chemical potential for the solute.

When the system is anisotropic an appropriate Cabannes factor must be employed, i.e., for scattering at $\theta = 90^\circ$

$$\Delta R_u(90) = \frac{K'RT C_u(90)}{\rho_0(\partial\mu/\partial m)_{T,p}} \quad (67)$$

For nonionic solutions, application of the virial equation leads to the following

$$(K'c/\Delta R_u)(1+\cos^2\theta) = (1/M) + 2Bc + \dots, \quad (68)$$

where c is the mass concentration of solute,** M is the solute molar mass, B is a second virial coefficient and

$$K = \frac{2\pi^2 n^2}{\lambda_0^4 N_A} \left(\frac{\partial n}{\partial c}\right)_{T,p}^2 \quad (69)$$

The quantity $(\partial n/\partial c)_{T,p}$ is the refractive index increment at constant pressure and temperature. The value of M can be determined from the intercept at $c = 0$ of a plot of $(Kc/\Delta R_u)(1+\cos^2\theta)$ versus c . The second virial coefficient B is obtained from the slope of this curve.

For a multicomponent solution the appropriate relation is

$$(K'c/\Delta R'_u)(1+\cos^2\theta) = (1/M) + 2Bc + \dots, \quad (70)$$

In this case a plot of $(K'c/\Delta R'_u)(1+\cos^2\theta)$ versus c leads to values of M and B as obtained above provided K' and $\Delta R'_u$ are measured at constant values of the chemical potentials of all species other than the solute component, as well as at constant pressure and temperature, as c is varied (condition of membrane equilibrium).

Whenever the scattering particles or molecules are so large that the Rayleigh-Debye theory must be used, the appropriate relation for a binary solution is

$$(Kc/\Delta R_u)(1+\cos^2\theta) = [1/M P(\theta)] + 2Bc Q(\theta), \quad (71)$$

where $Q(\theta)$ is a combined function of the form factor $P(\theta)$ and of an intermolecular interference factor. Expansion of the form factor for small values of θ leads to

$$[1/P(\theta)]_{\theta \rightarrow 0} = 1 + h^2 R_g^2/3 + \dots, \quad (72)$$

*Note that m is used both as molality and relative refractive index (see eq. 30).

**We use c instead of ρ_i because of common usage in colloid and polymer science.

where R_g is the radius of gyration of the molecule or particle, i.e., the root mean square distance of its elements from its center of mass. It follows that

$$[(Kc/\Delta R_u)(1+\cos^2\theta)]_{\theta \rightarrow 0} = (1/M)(1+h^2R_g^2/3) + 2BcQ(\theta) . \quad (73)$$

In each case above R_u and ΔR_u should be corrected by the appropriate Cabannes factor whenever the depolarization is nonzero.

In the *Zimm plot*, the left hand side of the above equation is plotted versus $\sin^2\theta/2 + (PI)c$ where PI is a convenient plotting increment. A double extrapolation leads to two limiting curves: (1) for $c \rightarrow 0$, the slope permits estimation of R_g , (2) for $\theta \rightarrow 0$ (in which case $Q(\theta) \rightarrow 1$), the slope permits estimation of B . Each of these limiting curves intersects with the ordinate at $1/M$. Whenever there is a distribution of molar masses, the Zimm plot leads to the *mass average molar mass*

$$M_w = \sum N_i M_i^2 / \sum N_i M_i \quad (74)$$

and the *z-average radius of gyration*

$$\overline{R_g^2} = \sum N_i M_i^2 R_{g_i}^2 / \sum N_i M_i^2 . \quad (75)$$

1.14.6 BIBLIOGRAPHY

H.B. Huglin, Light Scattering by Polymer Solutions, Academic Press, New York, 1972.

M. Kerker, The Scattering of Light and Other Electromagnetic Radiation, Academic Press, New York, 1969.

H.C. van de Hulst, Light Scattering by Small Particles, John Wiley, New York, 1957.

1.14.7 ALPHABETICAL INDEX OF TERMS

<u>Symbol</u>	<u>Term</u>	<u>Section or Equation</u>
C_{abs}	absorption cross section	1.14.3 A
Q_{abs}	absorption efficiency	
k	absorption index	1.14.3 A
A	albedo	1.14.3 A
γ	anisotropy factor	1.14.3 B
$\langle \cos\theta \rangle_{abs}$	asymmetry factor for absorption	1.14.3 A
$\langle \cos\theta \rangle_{sca}$	asymmetry factor for scattering	1.14.3 A
N_A	Avogadro constant	1.14.4 C
	back scattering	1.14.3 A
k_B	Boltzmann's constant	1.14.4 B
C_u, C_τ	Cabannes factor	1.14.3 D
	coherent	1.14
	correlation distance	1.14.4 A
ℓ	correlation length	1.14.4 A
	correlation volume	1.14.4 A
P_A, P_B, P_C	depolarization factor	1.14.3 D
	depolarized	1.14.1
$Z_1(\theta)$	dissymmetry	1.14.2
Q_{pr}	efficiency for radiation pressure	1.14.3 A
	elastic scattering	1.14.1

<u>Symbol</u>	<u>Term</u>	<u>Section or Equation</u>
C_{ext}	extinction cross section	1.14.3 A
Q_{ext}	extinction efficiency	1.14.3 A
$P(\theta)$	form factor or particle scattering function	1.14.3 A
	forward scattering	1.14.2
δ	generalized anisotropy	1.14.3 D
	incoherent	1.14.1
	inelastic scattering	1.14.1
E_u, E_1, E_2	irradiance	1.14.1
	Krishnan's relation	1.14.2
	light scattering	1.14.1
M_w	mass average molar mass	1.14.4 C
$\bar{\alpha}$	mean polarizability	1.14.3 D
M	molar mass	1.14.4 C
	multiple scattering	1.14.1
	Ornstein-Zernike expression	1.14.4 B
N	particle number concentration	1.14.3 A
ϕ	phase	1.14.3 E
ρ_p	phase shift of the longest ray	1.14.3 E
α	polarizability	1.14.3 C
P	polarization (or degree of polarization)	1.14.2
ρ_u, ρ_v, ρ_h	polarization ratio	1.14.2
	quasielastic scattering	1.14.1
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\hat{n}	refractive index	1.14.3 A
$(\partial n / \partial c)_{T, P}$	refractive index increment	1.14.4 C
ϵ_r	relative permittivity	1.14.4
m	relative refractive index	1.14.3 B
θ	scattering angle	1.14.2
C_{sca}	scattering cross section	1.14.3 A
Q_{sca}	scattering efficiency	1.14.3 A
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T	transmittance	1.14.3 A
τ	turbidity	1.14.2
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R_g	z-average radius of gyration	1.14.4 C
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