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**LIGHT SCATTERING, CLASSICAL:
SIZE AND SIZE DISTRIBUTION CHARACTERIZATION**

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ABSTRACT

The use of classical, or time-averaged, light scattering methods to characterize the size and size distribution of macromolecules in dilute solutions or particles in dilute dispersions is discussed. The necessary scattering relations are presented systematically, starting with three cases at infinite dilution: the scattering extrapolated to zero angle, the scattering at small angle, and the scattering for arbitrary angle, including the inversion of the scattering data to estimate the size distribution. The relations needed to effect an extrapolation to infinite dilution from data on dilute solutions are also discussed. These sections are followed by remarks on light scattering methods, and concluding sections giving examples for several applications. The Rayleigh-Gans-Debye approximation is usually appropriate in the scattering from dilute polymer solutions, and is also adequate for the scattering from dilute dispersions of small particles. It is assumed when appropriate, but more complete theories are introduced where necessary, as in the use of the Mie-Lorentz theory for large spherical particles.

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1. INTRODUCTION

Classical, or time-averaged, light scattering methods are well suited to characterize certain properties of macromolecules in dilute solutions or particles in dilute dispersions. This technique goes under a variety of names, including static, elastic, integrated and absolute scattering. Information on the size and size distribution may be obtained, and in some cases, it may be possible to elucidate the shape of the macromolecule or particle. The theory and practice of such measurements is well represented in reviews and monographs,⁽¹⁻²⁴⁾ providing the basis for the following. In addition to these, very useful compilations of original papers are available on the scattering from macromolecules⁽²⁵⁾ and particles.⁽²⁶⁾ In the following, the scattering relations are presented systematically, starting with three cases at infinite dilution: the scattering extrapolated to zero angle, the scattering at small angle, and the scattering for arbitrary angle. The relations needed to effect an extrapolation to infinite dilution from data on dilute solutions are then discussed. These sections are followed by remarks on light scattering methods, and concluding sections giving examples for several applications. As discussed below, the Rayleigh-Gans-Debye (RGD) approximation is usually appropriate in the scattering from dilute polymer solutions, and is also adequate for the scattering from dilute dispersions of small particles. It will be assumed for much of the following, but more complete theories will be introduced where necessary, as in the use of the Mie-Lorentz theory for large spherical particles.

2. SCATTERING RELATIONS

2.1 General Remarks

Classical, or static, light scattering refers to an experiment in which an intensity $I(\vartheta)$ is determined at a scattering angle ϑ by averaging the fluctuating intensity of the light scattered from a material over a time long compared with the time scale of the fluctuations. The temporal character of the fluctuations is studied in dynamic light scattering^(1, 6, 7a, 10, 17, 27) a subject outside the purview here. For dilute solutions of macromolecules, or dispersions of particles, the averaged intensity carries information on the intramolecular properties of the molecular weight M , mean-square radius of gyration R_G^2 , and mean-square molecular optical anisotropy δ^2 , as well as the intermolecular property of the second virial coefficient A_2 , and possibly higher order virial coefficients and intermolecular interference phenomena. Furthermore, for polydisperse systems, the data may also permit assessment of any structural distribution (e.g., the molecular weight, size, or possibly shape, of a dissolved molecule or dispersed particle. The

reader should be forewarned that owing to its history and variety of applications, the nomenclature in light scattering varies among authors (e.g., see reference 21a). In the interests of consistency, the nomenclature used herein will follow that used previously by the author,^(1, 4, 10, 18) and where appropriate, these sources will be cited for further detail, in addition to, or in lieu of citations to the original literature referenced therein.

In general, it is not necessary to distinguish between solutions of macromolecules or dispersions of particles in discussing the fundamental relations for scattering, and the following applies to either case. For convenience, both macromolecules and particles will be referred to as the "solute". In most experimental arrangements of interest here, the scattered intensity in the scattering plane, the plane containing the incident and scattered beams, is determined as a function of ϑ , or modulus $q = (4\pi/\lambda)\sin(\vartheta/2)$ of the scattering vector, with $\lambda = \lambda_0/n_{\text{medium}}$, where n_{medium} is the refractive index of the solution and λ_0 the wave length of the incident light *in vacuo*, and ϑ is the angle between the incident and scattered beams. Often, the electric vector of the incident light is plane polarized perpendicular to the scattering plane, and that arrangement will be presumed in the following, unless otherwise specified. The scattered light intensity is monitored through a photomultiplier or other photon-sensitive device, either as an analog signal or a digital photon count rate. In either case, an instrument response $G(\vartheta)$ at angle ϑ is determined, with $G(\vartheta)$ proportional to the time-averaged intensity $I(\vartheta)$ of the scattered light. The latter is used to compute the Rayleigh ratio $\mathbf{R}(\vartheta)$, given by $r^2 I(\vartheta)/V I_{\text{INC}}$, with r the distance between the scattering centers and the detector, V the scattering volume, and I_{INC} the intensity of the incident light; $\mathbf{R}(\vartheta)$ is often called the differential scattering cross section in the physics literature.^(13a) The ratio $\mathbf{R}(\vartheta)/G(\vartheta)$ may be determined by an appropriate experiment for a given arrangement.^(1, 7a, 10, 18) The following section will discuss the information that may be obtained to characterize the solute in a solution (or dispersion) by analysis of $\mathbf{R}(\vartheta)$ under various conditions.

The excess Rayleigh ratio for the solution with concentration c of solute, less that due to the solvent, is usually the property of interest. This is normally calculated as $\mathbf{R}_{\text{xs}}(\vartheta, c) = \mathbf{R}_{\text{SOLN}}(\vartheta, c) - \mathbf{R}_{\text{SOLVENT}}(\vartheta)$, but alternative estimates of $\mathbf{R}_{\text{xs}}(\vartheta, c)$ may be required for very low molecular weight solute.⁽²⁸⁾ The subscripts 'xs', etc., will be suppressed throughout, and $\mathbf{R}(\vartheta, c)$ will imply the excess quantity. Here, c is the weight of the solute per unit volume of the solution. Alternatively, the number of molecules v per unit volume of the solution is sometimes used, especially in theoretical work; $v = cN_A/M_n$, with M_n the number average molecular weight determined, for example, from colligative properties.^(29a) It may be noted that the scattered intensity in discussions of the scattering from particles is sometimes expressed in intensity units per particle/volume, with an implied factor v omitted, e.g., these units are used in two well

known monographs focussed on the scattering from particles.^(21, 22)

The notation $\mathbf{R}_{Si}(\vartheta, c)$ will be used in the following to designate the polarization states of the scattered and incident light rays, where subscripts S and i will designate the polarization of the electric vectors of the scattered and incident light, respectively, relative to the scattering plane. Thus, for vertically polarized incident light, and horizontally or vertically polarized scattered light, respectively, the observed scattering may be expressed as,^(4, 10)

$$\mathbf{R}_{Hv}(\vartheta, c) = \mathbf{R}_{\text{aniso}}(\vartheta, c) \quad (1)$$

$$\mathbf{R}_{Vv}(\vartheta, c) = \mathbf{R}_{\text{iso}}(\vartheta, c) + (4/3)\mathbf{R}_{\text{aniso}}(\vartheta, c) + \mathbf{R}_{\text{cross}}(\vartheta, c) \quad (2)$$

where $\mathbf{R}_{Vv}(\vartheta, c) = \mathbf{R}_{\text{iso}}(\vartheta, c)$ for an optically isotropic scatterer, and $\mathbf{R}_{\text{cross}}(\vartheta, c)$ is a cross-term that vanishes for an optically isotropic solute or for $\vartheta = 0$. The functions $\mathbf{R}_{\text{iso}}(\vartheta, c)$ and $\mathbf{R}_{\text{aniso}}(\vartheta, c)$ are discussed in the following sections. The Rayleigh ratio $\mathbf{R}_{Hh}(\vartheta, c)$ is discussed below, but in the RGD regime, $\mathbf{R}_{Hh}(\vartheta, c) = \mathbf{R}_{Vv}(\vartheta, c)\cos^2(\vartheta)$. In much of the older work, written prior to the advent of lasers as a commonly used source of the incident light, an unpolarized (or natural) incident beam is assumed, e.g., comprising equal components of plane-polarized light with electric vectors in the vertical and horizontal directions. Consequently, the Rayleigh ratio for light with electric vector in the vertical direction might be denoted $\mathbf{R}_{Vu}(\vartheta, c)$ in such a case, with $\mathbf{R}_{Vu}(\vartheta, c) = \mathbf{R}_{Vv}(\vartheta, c)/2$ for an isotropic solute (with $\mathbf{R}_{Vh}(\vartheta, c) = \mathbf{R}_{Hv}(\vartheta, c) = 0$) if the total intensity of the incident beam is used in the calculation of each.

In most of the discussion the Rayleigh-Gans-Debye (RGD) approximation will be assumed, but this constraint will be relaxed where necessary, e.g., in the use of the complete Mie-Lorentz scattering theory for large spheres.^(13b, 21b, 22a) In the RGD approximation, the scatterer is treated as an assembly of scattering elements which scatter radiation independently of all other elements. The elements are taken to represent the smallest unit that both gives a unique refractive index tensor, and for which interference effects are negligible for rays scattered from a single element, e.g., the elements are independent Rayleigh scatterers.^(13c, 16, 18, 21b, 22b) An important property in the RGD approximation used in much of the following is that the optical contrast factor can usually be considered to be independent of the size or shape of the scatterer, but depends only on its composition relative to that of the medium. This allows a factorization assumed in much of the following for which the RGD approximation is utilized, but which must be abandoned if that approximation cannot be used. Use of the RGD approximation greatly facilitates the discussion of the effects of heterogeneity of the scatterers, permitting analytical

representations of certain averages for properties determined by analysis of $\mathbf{R}_{Vv}(\vartheta, c)/c$ and $\mathbf{R}_{Hv}(\vartheta, c)/c$, as discussed in the following. The RGD approximation fails as the phase shift of the light within an individual scatterer domain becomes too large, see below.

In most cases, the discussion will be couched in terms of the weight fraction $w_\mu = c_\mu/c$ of scattering components distinguished by some characteristic, e.g., molecular weight, shape, optical contrast relative to the supporting medium, etc., with overall concentration $c = \sum c_\mu$. As discussed below, $[\mathbf{R}_{Vv}(\vartheta, c)/Mc]_\mu$ reduces to a constant under certain conditions, but in general, this ratio depends on M , c and ϑ , reflecting interference effects from the scattered rays from different scatterers, as well as the particular characteristics of the individual scatterer. Of course, similar expressions may be written for $\mathbf{R}_{Hv}(\vartheta, c)$.

It is convenient to express $\mathbf{R}_{iso}(\vartheta, c)$ in the form^(4, 10)

$$\mathbf{R}_{iso}(\vartheta, c) = K' \psi_{solute}^2 M_{LS} S_{iso}(\vartheta, c) c \quad (3)$$

$$S_{iso}(\vartheta, c) = P_{iso}(\vartheta, c) F_{iso}(\vartheta, c) \quad (4)$$

where M_{LS} is the light scattering averaged molecular weight, $S_{iso}(\vartheta, c)$ is the structure factor (see further below), $P_{iso}(\vartheta, c)$ and $F_{iso}(\vartheta, c)$ are intramolecular and intermolecular structure factors, respectively, with $P_{iso}(0, c) = F_{iso}(0, 0) = 1$, $K' = 4\pi^2 n_{medium}^2 / N_A \lambda_o^4$, and ψ_{solute} a contrast factor; it should be noted that some authors use a notation in which $F_{iso}(\vartheta, c)$ would be denoted $S_{iso}(\vartheta, c)$.⁽³⁰⁾ For many cases discussed below, ψ_{solute} is equal to the refractive index increment $(\partial n / \partial c)_\Pi$ at osmotic equilibrium of solvent components.^(10, 16, 18) For a solute in a single component solvent, $(\partial n / \partial c)_\Pi \approx n_{medium}(\tilde{n} - 1) / \rho_{solute}$, with ρ_{solute} the density of the solute, and $\tilde{n} = n_{solute} / n_{medium}$, where n_{solute} and n_{medium} are the refractive indices of the solute and medium, respectively.⁽³¹⁾ This form is also used for a suspension of particles in a gas or vacuum for small $\tilde{n} - 1$; a revised expression for large $\tilde{n} - 1$ is discussed below.^(13b, 21b, 22a) Here, and in the following, the subscript 'LS' designates the average obtained in light scattering for solute polydisperse in its properties. The nature of that average for particular types of heterogeneity is delineated in the following sections.

In general, for a nonabsorbing isotropic solution, expansion of $P_{iso}(\vartheta, c)$ at infinite dilution gives^(10, 18, 21c, 22c, 24a)

$$P_{iso}(\vartheta, 0)^{-1} = 1 + (R_G^2)_{LS} q^2 / 3 + \dots \quad (5)$$

where $(R_G^2)_{LS}$ is the light scattering average mean-square radius of gyration of the scatterers and the notation $P_{iso}(\vartheta, 0)$ denotes the function at infinite dilution. In most cases, for optically isotropic scatterers, it is useful to express $F_{iso}(\vartheta, c)$ in the form^(4, 10, 20a, 31)

$$F_{iso}(\vartheta, c)^{-1} = 1 + c\Gamma_{iso}(c)P_{iso}(\vartheta, c)H_{iso}(\vartheta, c) \quad (6)$$

since in many cases, $H_{iso}(\vartheta, c) \approx 1$. With this representation,

$$KcM/R_{iso}(\vartheta, c) = S_{iso}(\vartheta, c)^{-1} = P_{iso}(\vartheta, c)^{-1} + c\Gamma_{iso}(c)H_{iso}(\vartheta, c) \quad (7)$$

where $K = K'\psi_{solute}^2$.

As elaborated below, in most cases, a virial expansion of $\Gamma_{iso}(c)$ suffices for the scattering from dilute solutions (i.e., solutions with $cN_A(R_G^2)_{LS}^3/M_{LS} \ll 1$)^(4, 10, 20a, 31)

$$\Gamma_{iso}(c) = 2(A_2)_{LS}M_{LS} + 3(A_3)_{LS}M_{LS}c + \dots \quad (8)$$

with $(A_2)_{LS}$ the light scattering averaged second virial coefficient, etc. The virial expansion may fail for charged scatterers in a solvent with very low ionic strength, so that electrostatic interactions are not shielded (see Examples),^(10, 16, 18, 32) and other forms for $\Gamma_{iso}(c)$ may be required for moderately concentrated (or semidilute) solutions.^(3, 4, 33) The general interpretation of the functions $P_{iso}(\vartheta, c)$, $H_{iso}(\vartheta, c)$ and the parameters M_{LS} , $(A_2)_{LS}$, and $(R_G^2)_{LS}$ may be complex for scatterers that are optically anisotropic or exhibit intramolecular and/or intermolecular heterogeneity.^(10, 18) These cases will be the subject of much of the following discussion. It should be noted that these relations, and those to follow, apply to either polymeric or colloidal solute, and that similar relations also obtain for the scattering of x-rays and neutrons (with revision of the definition for K ^(34, 35)), with the principal experimental difference being the range of wavelength normally encompassed.

Similarly, $R_{aniso}(\vartheta, c)$ may be expressed as^(4, 10)

$$R_{aniso}(\vartheta, c) = (3/5)K'\gamma_{solute}^2(\delta/\delta_0)_{LS}^2M_{LS}S_{aniso}(\vartheta, c)c \quad (9)$$

where $(\delta/\delta_0)_{LS}^2$ is the light scattering averaged mean-square molecular optical anisotropy form factor, $S_{aniso}(\vartheta, c)$ is a structure factor, and γ_{solute} is an anisotropic contrast factor, conveniently expressed as

$\psi_{\text{solute}}\delta_o$ if $\psi_{\text{solute}} \neq 0$, with δ_o the optical anisotropy of a scattering element, see the Examples below.⁽¹⁰⁾ As above, the factor $K'\gamma_{\text{solute}}^2$ must be modified if the RGD approximation is not valid. A similar set of expressions to those for $S_{\text{iso}}(\vartheta, c)$ may be written for $S_{\text{aniso}}(\vartheta, c)$, with $P_{\text{aniso}}(\vartheta, c)$ replaced by $P_{\text{aniso}}(\vartheta, c)$, etc. In most cases of interest here, $\Gamma_{\text{aniso}}(c)$ is considerably smaller than $\Gamma_{\text{iso}}(c)$, $H_{\text{aniso}}(\vartheta, c) \approx 1$, and $P_{\text{aniso}}(\vartheta, c) \neq P_{\text{iso}}(\vartheta, c)$, except for $\vartheta = 0$,⁽¹⁰⁾ see below.

2.2 Scattering at zero angle and infinite dilution

2.2.1 Isotropic solute in the RGD regime. In this limit, attention is focussed on $[\mathbf{R}_{\text{Vv}}(0, c)/c]^o$ (or $[\mathbf{R}_{\text{Hv}}(0, c)/c]^o$ below), with the implicit assumption that the extrapolations to zero angle and infinite dilution can be accomplished--these extrapolations are discussed in section 2.6. The superscript "o" indicates the extrapolation to infinite dilution throughout, and unless stated otherwise, it is assumed that $\psi_{\text{solute}} \neq 0$, as would usually be the case in applications of interest in light scattering. In this regime, $S_{\text{iso}}(\vartheta, c) = S_{\text{aniso}}(\vartheta, c) = 1$, simplifying the analysis. For example, $[\mathbf{R}_{\text{Vv}}(0, c)/K'\psi_{\text{solute}}^2 c]^o$ is equal to the parameter M_{LS} , which as seen below, may be equal to the weight average molecular weight M_w under certain conditions, but will often be a more complex function of the properties of the scatterers. Beginning within the RGD approximation, for an optically isotropic solute comprising a number of components, possibly differing in chemical composition^(10, 18)

$$M_{\text{LS}} = [\mathbf{R}_{\text{Vv}}(0, c)/K'\psi_{\text{solute}}^2 c]^o \quad (10a)$$

$$M_{\text{LS}} = \sum_{\mu} w_{\mu} M_{\mu}^{-1} (\sum_i \psi_i m_i)_{\mu}^2 / \psi_{\text{solute}}^2 \quad (10b)$$

with ψ_i and m_i the refractive index increment and the molar mass of element i , respectively, and w_{μ} the weight fraction of components with molecular weight $M_{\mu} = (\sum m_i)_{\mu}$ and identical values of $(\sum \psi_i m_i)_{\mu}$, with $\psi_{\text{solute}} = \sum w_{\mu} \psi_{\mu}$. Here, the sums over i extend over all of the scattering elements in molecule (particle) μ .

If each component is compositionally homogeneous, i.e., has only one type of scattering element, then $(\sum \psi_i m_i)_{\mu} = \psi_{\mu} M_{\mu}$, and

$$M_{\text{LS}} = \sum_{\mu} w_{\mu} M_{\mu} \psi_{\mu}^2 / \psi_{\text{solute}}^2 \quad (11)$$

In the simplest case, for an optically isotropic, compositionally homogeneous solute, $\psi_\mu = \psi_{\text{solute}}$, and this reduces to the well-known relation^(10, 18, 31)

$$M_{LS} = M_w = \sum_\mu w_\mu M_\mu \quad (12)$$

where w_μ is the weight fraction of component μ with molecular weight M_μ . This simple relation applies to solutions or dispersions in a mixed solvent, provided that $(\partial n/\partial c)_\Pi$ is used, as stipulated above. If the refractive index $(\partial n/\partial c)_w$ determined at constant composition of the mixed solvent is used instead, then, to a good approximation^(10, 16, 18)

$$M_{LS} = [(\partial n/\partial c)_\Pi/(\partial n/\partial c)_w]^2 M_w \quad (13)$$

where $(\partial n/\partial c)_\Pi = (\partial n/\partial c)_w$ for a single-component solvent. The ratio $(\partial n/\partial c)_\Pi/(\partial n/\partial c)_w$ may be interpreted in terms of preferential solvation of the solute by a component of the solvent.^(10, 16, 18) Deviations of $(\partial n/\partial c)_\Pi/(\partial n/\partial c)_w$ from unity are usually most pronounced when the preferentially solvating component is present at low concentration in the mixed solvent.

The more complex relation given above must be used if the solute is optically heterogeneous, as with a copolymer or particles with a spatially varying refractive index. For the special case with only two types of elements, characterized by refractive index increments ψ_A and ψ_B , with $\psi_{\text{solute}} = w_A \psi_A + (1 - w_A) \psi_B \neq 0$,^(10, 36, 37)

$$M_{LS} = M_w + 2Y \sum w_\mu M_\mu \Delta w_\mu + Y^2 \sum w_\mu M_\mu (\Delta w_\mu)^2 \quad (14)$$

where $\Delta w_\mu = (w_A)_\mu - w_A = w_B - (w_B)_\mu$ and $Y = (\psi_A - \psi_B)/\psi_{\text{solute}}$. Thus, M_{LS} is expected to be parabolic in Y , with $M_{LS} = M_w$ for $Y = 0$. Since $\Delta w_\mu = 0$ for either a strictly alternating copolymer, or a copolymer with random placements of the monomers, $M_{LS} = M_w$ for these important cases. Similarly, $M_{LS} = M_w$ for a collection of particles with two kinds of scattering elements, provided that the composition of each particle is identical with the average composition.

2.2.2 Isotropic solute beyond the RGD regime. It should be recognized at the outset that the RGD approximation will almost always be adequate for (nonabsorbing) threadlike macromolecules (e.g., flexible or semiflexible coils, rodlike or helical chains, etc.). This is the case not only at zero angle and infinite dilution, but also for all angles, and dilute solutions, owing to the sparse density of the

macromolecule in the intramolecular "domain". Thus, the RGD approximation may be applied, even for a large macromolecule, with an appreciably different refractive index than that of the solvent. The failure of the RGD approximation arises for large particles, under certain conditions elaborated in the following. If the RGD approximation cannot be used, the $[\mathbf{R}_{V_V}(0,c)/K'\psi_{\text{solute}}^2]_{\mu}^0$ may still be computed using an appropriate model, but since the scattering may no longer be taken as a sum over independent Rayleigh scattering elements, $(\sum \psi_i m_i)_{\mu}$ for the μ -th scatterer must be replaced by a more complex function. For the discussion of M_{LS} , this can be done for compositionally homogeneous scatterers by including a factor $h(\tilde{n}_{\mu})$ in ψ_{μ} for the μ -th scattering component, and multiplication of the modified ψ_{μ} by a function $m(\tilde{n}_{\mu}, \lambda, M_{\mu})$. Thus, even for chemically homogeneous scatterers differing only in size, the contrast factor may depend significantly on λ , $\tilde{n}$, M_{μ} , and the shape of the scatterer. With this modification, $M_{LS} = [m(\tilde{n}, \lambda, M)]^2 M$ for a monodisperse solute (with M_{LS} calculated using ψ_{μ} including the factor $h(\tilde{n}_{\mu})$). For example, with the Mie theory for a homogeneous sphere $h(\tilde{n})$ is given by $h_{\text{sph}}(\tilde{n}) = 3(\tilde{n} + 1)/2(\tilde{n}^2 + 2)$,^(13b, 21b, 22d) and $m(\tilde{n}, \lambda, M)$ may be expressed as $m_{\text{sph}}(\tilde{n}, \alpha)$, and calculated as a function of $\tilde{n}$ and $\alpha = 2\pi R/\lambda$; $m_{\text{sph}}(\tilde{n}, \alpha)$ reduces to unity as the magnitude of the maximum phase shift $2\alpha|\tilde{n} - 1|$ in the particle becomes small.^(13d, 21d, 22e) Examples of $M_{LS}/M = [m_{\text{sph}}(\tilde{n}, \alpha)]^2$ for monodisperse spheres given in Figure 1 over a range of $\tilde{n}$ and α reveal the complex character of this function, with the possibility that M_{LS}/M may be either larger or smaller than unity. In the use of this figure, consistency is required between M obtained from the determined M_{LS} and the ratio M_{LS}/M and $R = (3M/4\pi\rho N_A)^{1/3}$ used to select α , where ρ is the density of the particle. Deviation of M_{LS}/M from unity is important, for example, in the analysis of the eluent from chromatographic columns by low angle light scattering for large particles, see the Examples below.

It may be noted that the Rayleigh ratio is often not mentioned explicitly in discussions involving the Mie theory, but rather, the theory is developed in terms of scattering amplitude functions $S_i(\vartheta)$, which are the components of the scattering tensor for the scattering from an individual scatterer;^(13e, 21f, 22f) $S_i(\vartheta)$ is not to be confused with the structure factor $S(\vartheta, c)$ defined above. Reduced intensity functions are computed from the $S_i(\vartheta)$, e.g., for nonabsorbing, optically isotropic scatterers, $i_{V_V}(\vartheta) = |S_1(\vartheta)|^2$ and $i_{H_H}(\vartheta) = |S_2(\vartheta)|^2$, with $[\mathbf{R}_{V_V}(\vartheta, c)/V]^0 = N_A i_{V_V}(\vartheta)/k^2$, etc., where $k = 2\pi/\lambda$. For example, $i_{V_V}(\vartheta) = i_{V_V}(0)P_{V_V}(\vartheta, 0)$, with $i_{V_V}(0) = \alpha^6 \{2(\tilde{n} - 1)h_{\text{sph}}(\tilde{n})/3\}^2 [m_{\text{sph}}(\tilde{n}, \alpha)]^2$ for spherical particles in the nomenclature used here, which reduces to the expected result $[\mathbf{R}_{V_V}(\vartheta, c)/c]^0 = K'\psi_{\text{solute}}^2 M_{LS}$ for this case (including the factor $h_{\text{sph}}(\tilde{n})$ in ψ_{solute}).

For isotropic spheres, functions in the Mie theory may be expanded for $\tilde{n}\alpha \leq 1$ to give a result^(22g) that may be cast in the form

$$m_{\text{sph}}(\tilde{n}, \alpha) = 1 + j_{\text{sph}}(\tilde{n})\alpha^2|\tilde{n} - 1| + \dots \quad (15a)$$

$$j_{\text{sph}}(\tilde{n}) = (\tilde{n} + 1)(\tilde{n}^4 + 27\tilde{n}^2 + 38)/[15(\tilde{n}^2 + 2)(2\tilde{n}^2 + 3)] \quad (15b)$$

for nonabsorbing monodisperse spheres, where $j_{\text{sph}}(\tilde{n})$ approaches 44/75 as $\tilde{n}$ tends to unity. As may be seen in Figure 1, this expression provides a useful fit to $m_{\text{sph}}(\tilde{n}, \alpha)$ for small $\alpha^2|\tilde{n} - 1|$, but is generally limited to $\alpha^2|\tilde{n} - 1| < 0.1$ and $\alpha < 1$. In principle, in this range, the deviation from the RGD approximation could be taken into account using the above in expressions for M_{LS} discussed below for the scattering from spheres heterogeneous in M .

For nonabsorbing spheres with $\alpha \gg 1$, $i_{\text{v}}(0) = k^2[\mathbf{R}_{\text{vv}}(0, c)/v]^0/N_A$ is closely approximated by $\{(\alpha^2/4)Q_{\text{sca}}(\tilde{n}, \alpha)\}^2$,^(21d, 38) where $Q_{\text{sca}}(\tilde{n}, \alpha)$ is the extinction efficiency for scattering for spheres at infinite dilution, i.e., $\exp(-\tau vb)$ is the fraction of the incident light transmitted through a sample with turbidity $\tau = Q_{\text{sca}}(\tilde{n}, \alpha)\pi R^2$, thickness b and concentration v . Numerical calculations show that the approximation is quite reasonable for $\tilde{n} > 1.3$ and $\alpha > 4$, with the minimum value of α for which the approximation is useful decreasing with increasing $\tilde{n}$. The abundant literature on the extinction efficiency provides a means to compute $m_{\text{sph}}(\tilde{n}, \alpha)$ in this range and has itself been discussed as a means to characterize size heterogeneity among spherical solutes.^(21e, 39) For example, $Q_{\text{sca}}(\tilde{n}, \alpha) = (32/27)\alpha^4|\tilde{n} - 1|^2$ for Rayleigh scattering, increasing to $Q_{\text{sca}}(\tilde{n}, \alpha) = 2$ in the Fraunhofer scattering regime ($\alpha \gg 1$ and $\tilde{n} > 1.1$) discussed more extensively in the following,^(22h)

For a polydisperse nonabsorbing solute, with all components having identical $\tilde{n}$,

$$M_{\text{LS}} = \sum_{\mu} w_{\mu} M_{\mu} [m(\tilde{n}, \lambda, M_{\mu})]^2 \quad (16)$$

Similar expressions could be obtained for particles of other shape for which the RGD approximation cannot be used. For a spherical solute, use of $m(\tilde{n}, \lambda, M_{\mu}) = m_{\text{sph}}(\tilde{n}, \alpha_{\mu})$ gives $M_{\text{LS}} \geq M_{\text{w}}$, but M_{LS} cannot generally be reduced to an expression involving standard average molecular weights. In the limited range with $\tilde{n}\alpha_{\mu} < 1$ discussed above, the approximate expression for $m_{\text{sph}}(\tilde{n}, \alpha)$ may be applied, with the result (for particles of homogeneous refractive index)

$$M_{\text{LS}} \approx M_{\text{w}} + 2(2\pi R/\lambda M^{1/3})^2 j(\tilde{n})|\tilde{n} - 1| M_{(5/3)}^{5/3} \quad (17)$$

where $M_{(5/3)}^{5/3} \approx M_z^{2/3} M_w$ is defined in Table 2 (for $\varepsilon = 2/3$). In principle, the dependence on λ embodied in the parameters α_μ provides a means to interpret M_{LS} (or equivalently, Q_{sca}) in terms of w_μ from the variation of M_{LS} with λ using the Mie theory to compute $m_{sph}(\tilde{n}, \alpha)$, after accounting for any dispersion in the refractive indices of solute or solvent. Such a procedure has been the basis of some methods proposed in the literature to characterize the size of spheres by transmission measurements,^(13f, 21g, 39) but these have been largely superseded by methods discussed in the following involving measurements over a range of scattering angle.

2.2.3 Anisotropic solute. For a solute with anisotropic scattering elements, in the RGD regime $[R_{Hv}(0,c)/K'\psi_{solute}^2 c]^0$ gives the light scattering averaged mean-square molecular anisotropy δ_{LS}^2 (with $\psi_{solute} \neq 0$):^(10, 40, 41)

$$[R_{Hv}(0,c)/K'\psi_{solute}^2 c]^0 = (3/5)M_{LS}\delta_{LS}^2 \quad (18)$$

For solute with identical, but optically anisotropic scattering elements, $M_{LS} = M_w$, and

$$\delta_{LS}^2 = \sum_{\mu} w_{\mu} M_{\mu} \delta_{\mu}^2 / M_w \quad (19)$$

Since δ_{LS}^2 arises from orientational correlations among the scattering elements, it cannot be interpreted in the absence of a structural model for the scatterer. An example is included below. The expression for $[R_{Vv}(0,c)/K'\psi_{solute}^2 c]^0$ for this case becomes⁽¹⁰⁾

$$[R_{Vv}(0,c)/K'\psi_{solute}^2 c]^0 = M_{LS} \{1 + 4\delta_{LS}^2/5\} \quad (20)$$

2.3 Scattering at small angle and infinite dilution

2.3.1 Isotropic solute in the RGD regime. The ambiguous term "small angle" indicates that ϑ is small enough that the parameter $(R_G^2)_{LS}$ defined by the equivalent expressions

$$(R_G^2)_{LS}/3 = \{[c/R_{Vv}(0,c)]^0\}^{-1} \partial [c/R_{Vv}(\vartheta,c)]^0 / \partial q^2 = \partial \ln([R_{Vv}(\vartheta,c)/c])^0 / \partial q^2 \quad (21)$$

may be determined in the limit as ϑ goes to zero, where the superscript "o" indicates that the data are extrapolated to infinite dilution. Thus, for optically isotropic scattering elements, the expansion give above for $P_{iso}(\vartheta, 0)^{-1}$ may be applied, so that at infinite dilution (averaged over all orientations of the berry

scatterers), in the RGD approximation^(1, 10, 18)

$$(R_G^2)_{LS} = \sum_{\mu} w_{\mu} M_{\mu}^{-1} (\sum_{ij} \sum \psi_i m_i \psi_j m_j \langle r_{ij}^2 \rangle)_{\mu} / 2 M_{LS} \psi_{solute}^2 \quad (22)$$

where $\langle r_{ij}^2 \rangle$ is the mean-square separation of scattering elements i and j , and $\psi_{solute} \neq 0$. In this expression, w_{μ} is the weight fraction of a component with molecular weight M_{μ} and common $(\sum \sum \psi_i m_i \psi_j m_j \langle r_{ij}^2 \rangle)_{\mu}$, as scatterers with a given molecular weight may differ in composition and/or shape.

For a solute comprising optically identical scattering elements in all components (in the RGD approximation),

$$(R_G^2)_{LS} = \sum_{\mu} w_{\mu} M_{\mu} (\sum_{ij} \sum \langle r_{ij}^2 \rangle)_{\mu} / 2 M_w = \sum_{\mu} w_{\mu} M_{\mu} (R_G^2)_{\mu} / M_w \quad (23)$$

where again, the ensemble may include chains with identical M_{μ} but different $(R_G^2)_{\mu}$, as for a collection of branched and linear chains, all with the same molecular weight. The similarity of this with the expression for the z-average molecular weight (obtained by replacing $(R_G^2)_{\mu}$ by M_{μ}) often motivates the notation $(R_G^2)_z$ for $(R_G^2)_{LS}$ (or Φ_z for any property Φ similarly averaged), but that notation may be misleading if $(R_G^2)_{\mu}$ is not proportional to M_{μ} , and is not employed here. The parameter R_G^2 may be related to the characteristics of the scatterer in this RGD regime, such as the contour length L and persistence length $\hat{a}$ of polymer chains, the radius R of spheres, etc., see Table 1, or in some cases, expressed as a power of the molecular weight of the scatterer. Thus, for a solute with the special property that $(R_G^2)_{\mu} = r M_{\mu}^{\epsilon}$ with r a constant, the summation gives^(1, 42)

$$(R_G^2)_{LS} = r M_{(\epsilon+1)/M_w}^{\epsilon+1} \quad (24a)$$

$$M_{(\alpha)} = \left(\sum_{\mu} w_{\mu} M_{\mu}^{\alpha} \right)^{1/\alpha} \quad (24b)$$

where expressions for $M_{(\alpha)}$ are given in reference 42 for a number of commonly used molecular weight distributions (e.g., although $M_{(-1)} = M_n$, $M_{(1)} = M_w$, $M_{(2)} = (M_w M_z)^{1/2}$, etc., such simple expressions are not possible if α is not an integer). Expressions for $(R_G^2)_{LS}$ are given in Table 1 for a few cases of interest. Values of the light scattering averaged hydrodynamic radius $(R_H)_{LS}$ determined by dynamic light scattering are included in Table 1 for comparison. For example, for a random-flight chain ($\epsilon=1$), $(R_G^2)_{LS}$

$= rM_z$, with $r = \hat{a}L/3M$, and for a rod ($\epsilon = 2$), $(R_G^2)_{LS} = rM_zM_{z+1}$, with $r = (L/M)^2/12$, where M_z and M_{z+1} are the z - and $z+1$ -average molecular weights. It may be noted that in general, the averages in $(R_G^2)_{LS}$ and $(R_H)_{LS}$ differ.

For an optically isotropic solute discussed above comprising two different types of scattering elements (with $\psi_{\text{solute}} \neq 0$, and in the RGD approximation),^(10, 36, 37)

$$(R_G^2)_{LS} = x(R_G^2)_A + (1 - x)(R_G^2)_B + x(1 - x)\Delta_{AB}^2 \quad (25)$$

for a sample monodisperse in molecular weight, with $x = w_A \psi_A / \psi_{\text{solute}}$, $(R_G^2)_A$ and $(R_G^2)_B$ the mean-square radii of gyration of the portions of the solute molecules (particles) comprising only type A and type B scattering elements, respectively, and Δ_{AB}^2 the mean-square separation of the center of mass for these portions. The possible dependence of the parameters $(R_G^2)_A$, $(R_G^2)_B$ and Δ_{AB}^2 on solvent is neglected herein; this would be expected to be less of an issue with particles than with polymer chains. Expressions are available for Δ_{AB}^2 for certain graft copolymers, and for a solute polydisperse in molecular weight.⁽³⁶⁾ In some cases Δ_{AB}^2 is zero, simplifying the expression for $(R_G^2)_{LS}$, i.e., alternating copolymers or copolymers with a random placement of monomers, or spheres with a uniform coating (or shell). For block copolymers comprising n blocks each of A and B chains (e.g., $n = 1$ for an AB-diblock copolymer), $\Delta_{AB}^2 = 2\{(R_G^2)_A + (R_G^2)_B\}/n$, showing that Δ_{AB}^2 decreases with increasing n , as expected since $(R_G^2)_{LS} = (R_G^2)_A = (R_G^2)_B$ for an alternating copolymer.⁽³⁶⁾ Inspection of these expressions shows that $(R_G^2)_{LS}$ may bear little resemblance to the geometric mean-square radius of gyration $(R_G^2)_{\text{geo}}$ of the chain, e.g., $(R_G^2)_{LS}$ may be negative, whereas $(R_G^2)_{\text{geo}} > 0$. For example, one could construct a diblock polymer or a coated sphere for which $(R_G^2)_{LS}$ is zero, or even negative, though $(R_G^2)_{\text{geo}}$ must be positive, see Examples below.

2.3.2 Isotropic solute beyond the RGD regime. The preceding expressions must be modified if the RGD approximation fails, as the basic assumption in the RGD model that the scattering from the elements may be added independently for a particle is no longer valid (the reader is reminded that as discussed above, the RGD approximation is almost always adequate for (nonabsorbing) thread like macromolecules). For a compositionally homogeneous scatterer (all particles with the same $\tilde{n}$),

$$(R_G^2)_{LS} = \frac{\sum_{\mu} w_{\mu} M_{\mu} y(\tilde{n}, \lambda, M_{\mu}) [m(\tilde{n}, \lambda, M_{\mu})]^2 (R_G^2)_{\mu}^{(\text{RGD})}}{\sum_{\mu} w_{\mu} M_{\mu} [m(\tilde{n}, \lambda, M_{\mu})]^2} \quad (26)$$

where $(R_G^2)_{\mu}^{(\text{RGD})}$ is the value in the RGD regime, $m(\tilde{n}, \lambda, M_{\mu})$ is defined above, and $y(\tilde{n}, \lambda, M_{\mu})$ tends to

unity as $\alpha|\tilde{n} - 1|$ tends to zero.

With the Mie theory for a compositionally homogeneous sphere, for which $(R_G^2)^{(RGD)} = 3R^2/5$, $y(\tilde{n}, \lambda, M)$ may be expressed as $y_{\text{sph}}(\tilde{n}, \alpha)$, and calculated as a function of $\tilde{n}$ and $\alpha = 2\pi R/\lambda$.^(13d, 21d, 22e) Consequently, for monodisperse spheres

$$(R_G^2)_{\text{LS}} = (3/5)y_{\text{sph}}(\tilde{n}, \alpha)R^2 \quad (27)$$

Examples of $(R_G^2)_{\text{LS}}/\{3R^2/5\} = y_{\text{sph}}(\tilde{n}, \alpha)$ are shown in Figure 2 over a range of $\tilde{n}$ and α , showing the complex character of this function. Expansion of $y_{\text{sph}}(\tilde{n}, \alpha)$ for $\tilde{n}\alpha \leq 1$ gives a result^(22g) that may be cast in the form, $y_{\text{sph}}(\tilde{n}, \alpha) \approx p_{\text{sph}}(\tilde{n}) = (\tilde{n}^2 + 2)(\tilde{n}^2 + 4)/[3(2\tilde{n}^2 + 3)]$, where $p_{\text{sph}}(\tilde{n})$ approaches unity as $\tilde{n}$ tends to unity, so that $(R_G^2)_{\text{LS}} = 3R^2/5$ as $\tilde{n}$ tends to unity and $\tilde{n}\alpha \ll 1$, as expected in the RGD regime. It may be noted that even if $\alpha \ll 1$, so that $m_{\text{sph}}(\tilde{n}, \alpha) \approx 1$ and $y_{\text{sph}}(\tilde{n}, \alpha) \approx p_{\text{sph}}(\tilde{n})$, $(R_G^2)_{\text{LS}}$ tends to $\tilde{n}^2 R^2/10$ for $\tilde{n} \gg 1$ (but $\tilde{n}\alpha \leq 1$). The dependence on $\tilde{n}$ for small α is most clearly seen in Figure 2a; the fit of this approximate relation is good for $\alpha < 1$. Since $(R_G^2)_{\text{LS}} = 3R^2/4$, independent of $\tilde{n}$, in the Fraunhofer scattering regime ($\alpha \gg 1$ and $\tilde{n} \gg 1$) discussed in the next section,^(21g, 43, 44) $y_{\text{sph}}(\tilde{n}, \alpha)$ tends to 5/4 in that limit; the values of α used in Figure 2 are too small to exhibit such behavior. Similar expressions could be developed for other particles to which the Mie theory has been applied, e.g., stratified spheres and related structures mentioned in the preceding.^(13g, 45, 46)

As may be seen in Figure 2, the transition from the behavior for $\tilde{n} \approx 1$ and $\tilde{n}\alpha \ll 1$ to that for $\alpha \gg 1$, for any $\tilde{n}$, is complex, prohibiting an analytic representation of $(R_G^2)_{\text{LS}}$ for a sample of unknown size distribution. Thus, although

$$(R_G^2)_{\text{LS}} = (3/5) \sum_{\mu} w_{\mu} M_{\mu} y_{\text{sph}}(\tilde{n}, \alpha_{\mu}) [m_{\text{sph}}(\tilde{n}, \alpha_{\mu})]^2 R_{\mu}^2 / \sum_{\mu} w_{\mu} M_{\mu} [m_{\text{sph}}(\tilde{n}, \alpha_{\mu})]^2 \quad (28)$$

for a collection of spheres of different size, but identical $\tilde{n}$, this cannot generally be reduced to an expression involving standard average molecular weights. In principle, presuming that both $(R_G^2)_{\text{LS}}$ and M_{LS} can be determined (which may be difficult for large particles), one could compare these with values of $(R_G^2)_{\text{LS}}$ and M_{LS} calculated with an assumed two-parameter distribution function of M as a means to characterize the size distribution, e.g., for spheres, using the Mie theory to compute $y(\tilde{n}, \lambda, M_{\mu}) = y_{\text{sph}}(\tilde{n}, \alpha_{\mu})$ and $m(\tilde{n}, \lambda, M_{\mu}) = m_{\text{sph}}(\tilde{n}, \alpha_{\mu})$. In essence, a similar strategy is adopted by methods that attempt to fit the scattering determined at two small scattering angles.^(21e, 44) In addition, in principle, the dependence on λ embodied in the parameters α_{μ} provides a means to interpret $(R_G^2)_{\text{LS}}$ in terms of w_{μ} from

the variation of $(R_G^2)_{LS}$ with λ using the Mie theory to compute $y_{sph}(\tilde{n}, \alpha_\mu)$ and $m_{sph}(\tilde{n}, \alpha_\mu)$, after accounting for any dispersion in the refractive indices of solute or solvent.

2.3.3 Anisotropic solute. An estimate for $(R_G^2)_{LS}$ may be obtained from the dependence of either $[K'c/R_{Vv}(\vartheta, c)]^0$ or $[K'c/R_{Hv}(\vartheta, c)]^0$ for the scattering from anisotropic solutes in the RGD regime. Thus, for a solute with identical scattering elements, expressions for semiflexible chains give,^(10, 41, 47-49)

$$P_{Vv}(\vartheta, 0)^{-1} = 1 + [J_{Vv}(\delta)R_G^2]_{LS}q^2/3 + \dots \quad (29)$$

$$P_{Hv}(\vartheta, 0)^{-1} = 1 + 3[J_{Hv}(\delta)R_G^2]_{LS}q^2/7 + \dots \quad (30)$$

Expressions for $[J_{Vv}(\delta)R_G^2]_{LS}$ and $[J_{Hv}(\delta)R_G^2]_{LS}$ are available for semiflexible chains.⁽¹⁰⁾ In practice, the expression for rodlike chains (i.e., $\hat{a}/L > 1$) may be used as a first approximation for any $\hat{a}/L$, since $[J_{Vv}(\delta)R_G^2]_{LS} \approx (R_G^2)_{LS}$ and $[J_{Hv}(\delta)R_G^2]_{LS} \propto (\delta^2 R_G^2)_{LS} \approx 0$ as $\hat{a}/L$ becomes small and δ tends to zero for flexible chains;⁽¹⁰⁾ see the section on Examples.

2.4 Scattering at arbitrary angle and infinite dilution

2.4.1 Isotropic solute in the RGD regime. The angular dependence of the scattering over a wide angular range provides additional information on solute structure and dispersity, at least in principle. In practice, the effects of these two attributes may frustrate analysis, e.g., even in the preceding case for small scattering angle, the dependence of $(R_G^2)_{LS}$ on average molecular weights depends on the solute structure, see Table 1. For an optically isotropic solute (averaged over all orientations) in the RGD approximation,^(1, 10, 18)

$$P_{Vv}(\vartheta, 0) = [R_{Vv}(\vartheta, c)/K'c]^0 / M_{LS} \psi_{solute}^2 \quad (31a)$$

$$P_{Vv}(\vartheta, 0) = \sum_{\mu} w_{\mu} M_{\mu}^{-1} \left(\sum_{ij} \psi_i m_i \psi_j m_j \langle \sin(q|r_{ij}|)/q|r_{ij}| \rangle \right)_{\mu} / M_{LS} \psi_{solute}^2 \quad (31b)$$

where each sum runs over the M/m scattering elements on a component, and the second form is written in the RGD approximation. Expansion of the factor in $\langle \dots \rangle$ brackets yields the relation in terms of $(R_G^2)_{LS}$ given above. For optically identical scattering elements with molar mass m ,

$$P_{Vv}(\vartheta, 0) = \sum_{\mu} w_{\mu} M_{\mu} [P_{Vv}(\vartheta, 0)]_{\mu} / M_w \quad (32a)$$

$$[P_{Vv}(\vartheta, 0)]_{\mu} = (m/M)_{\mu}^2 \left(\sum_{ij} \sum_{ij} \langle \sin(q|r_{ij}|) / q|r_{ij}| \rangle \right)_{\mu} \quad (32b)$$

where as above, the ensemble may include chains with identical M_{μ} but different $[P_{Vv}(\vartheta, 0)]_{\mu}$, with w_{μ} the weight fraction of each distinct component.

Expressions for $P_{Vv}(\vartheta, 0)$ for a number of widely used models in the RGD approximation are given in Table 2, and a selection are illustrated in Figure 3. The exponential form $P_{Vv}(\vartheta, 0) = \exp(-R_G^2 q^2/3)$ is included for comparison, as this relation is sometimes used as a convenient approximation; inspection shows that it is not usually a good approximation unless $R_G^2 q^2$ is small, providing the best fit for spheres among the examples in Figure 3. Given the availability of computational equipment, it is usually not necessary to resort to tabulated numerical values of $P_{Vv}(\vartheta, 0)$ for scatterers in the RGD approximation—an extensive compilation of formulae for $P_{Vv}(\vartheta, 0)$ for a variety of macromolecular and particle shapes to supplement the entries in Table 1 may be found in reference.^(21h) In most cases, $P_{Vv}(\vartheta, 0)$ may be expressed in terms of q in the RGD approximation, but with some structures, $P_{Vv}(\vartheta, 0)$ depends explicitly on ϑ , as well as on q , e.g., for a rodlike chain (see Table 2).

In some models, the summations in $P_{Vv}(\vartheta, 0)$ may be completed in terms of standard molecular weight averages (M_n , etc.) without specification of a particular expression for the distribution w_{μ} . For example, for random-flight linear chains (e.g., at the Flory theta temperature), using $P_{Vv}(\vartheta, 0)$ in Table 2,^(1, 42)

$$P_{Vv}(\vartheta, 0) = [2M_n/M_w u_n^2] \{u_n - 1 + \sum_{\mu} w_{\mu} (M_n/M_{\mu}) \exp(-u_n M_{\mu}/M_n)\} \quad (33)$$

where $u_n = (R_G^2/M) M_n q^2$, with R_G^2/M a constant for this model. Further analysis requires an expression for w_{μ} , and this would be the normal situation with most forms for $P_{Vv}(\vartheta, 0)$. For example, in this case, using the Schulz-Zimm (two-parameter exponential) distribution function,^(1, 31, 42) the remaining sum is equal to $(1 + u_n/h)^{-h}$, where $h^{-1} = (M_w/M_n) - 1$. For a most-probable distribution of molecular weight ($h = 1$), this reduces the expression to a simple form linear in q^2 :^(1, 31, 42)

$$P_{Vv}(\vartheta, 0)^{-1} = 1 + (R_G^2)_{LS} q^2/3 \quad (34)$$

exactly, with $(R_G^2)_{LS} \propto M_z$ for this model for a linear polymer.^(42, 50) The same result obtains for a randomly branched flexible chain polymer.⁽¹²⁾ An expression for $P_{VV}(\vartheta, 0)$ for rodlike chains with the same distribution of molecular weight is available in the form of a series to be summed over $h - 1$ terms.⁽¹⁰⁾ Examples of $P_{VV}(\vartheta, 0)^{-1}$ computed for the random-flight linear chain and the sphere models using the Schulz-Zimm distribution function are shown in Figure 4.

The expression for $P_{VV}(\vartheta, 0)$ given in Table 2 for linear flexible coil chains assumes random-flight chain statistics, and therefore is not strictly applicable to polymer chains in so-called "good solvents" (i.e., solvents for which $A_2 \gg 0$), for which excluded volume effects introduce a nonlinear dependence of $|r_{ij}|$ on the separation of scattering elements i and j , resulting in a dependence of R_G^2/L on L .^(20b, 51) In practice, the expression given in Table 2 may usually be used in good solvents for the range of $(R_G^2)_{LS}q^2$ of usual interest, provided that the observed $(R_G^2)_{LS}$ is used, as opposed to the value of $(R_G^2)_{LS} = \hat{a}M_z/3$ obtaining under Flory theta conditions ($A_2 = 0$) called for by the model. Treatments attempting to include excluded volume effects by calculation of $P_{VV}(\vartheta, 0)$ using a model for which $|r_{ij}| = |i - j|^{1+\beta}$, with $0 \leq \beta \leq 1$, have been developed as an alternative.^(18, 52) Similarly, although $[P_{VV}(\vartheta, 0)]_{BR}$ has been computed for a variety of branch chain configurations,^(12, 53, 54) the expression $[P_{VV}(\vartheta, 0)]_{LIN}$ for linear flexible chains provides a first approximation to $[P_{VV}(\vartheta, 0)]_{BR}$, provided $(R_G^2)_{BR}$ observed for the branched chain is used in place of $(R_G^2)_{LIN}$ appearing in $[P_{VV}(\vartheta, 0)]_{LIN}$. Examples of this are shown in Figure 5 for a range of comb-shaped branched chains with different fractions ϕ of monomers in the backbone and different numbers of branches f per molecule (e.g., ϕ is zero and unity for linear and star-shaped structures, respectively;⁽⁵³⁾ substantial deviations are noted between the approximation and the expected behavior for $(R_G^2)_{BR}q^2 > 3$. It may be noted that the ratio $g = (R_G^2)_{BR}/(R_G^2)_{LIN}$ of the R_G^2 for branched and linear chains of the same M is frequently used in discussions of branched chains, but that is a sufficient descriptor only for self-similar structures, such as star-shaped branched chains. For example, comb-shaped branched chains with different ϕ and f may have the same g , as exemplified by the relation

$$g \approx \phi + (1 - \phi)^{7/3}(3f - 2)/f^2 \quad (35)$$

which provides a useful approximation for this model.⁽⁵³⁾ A similar form applies with randomly branched polymers,⁽⁵⁵⁾ with $g_w \approx \phi_w$, where ϕ_w is M_w for the longest linear chain in the branched structure divided by the total molecular weight, and $g_w = (\sum_{\mu} g_{\mu} w_{\mu} M_{\mu})/M_w$. See further discussion in the Examples.

In the limit of very large $(R_G^2)_{LS}q^2$, for thread-like chains in the RGD approximation^(10, 18, 54)

$$\lim_{(R_G^2)_{LS} q^2 \gg 1} [P_{VV}(\vartheta, 0)]_{\mu}^{-1} \approx s_{\mu} (r_{\mu} q^2)^{1/\varepsilon} + i_{\mu} + O(q^{-2}) \quad (36)$$

for a solute with $(R_G^2)_{\mu} = r M_{\mu}^{\varepsilon}$ (e.g., see Table 1), where i_{μ} and s_{μ} depend on the solute structure. Thus, for a rodlike solute ($\varepsilon = 2$ and $r = (L/M)^2/12$, with L the chain contour length),^(10, 18, 56)

$$\lim_{(R_G^2)_{LS} q^2 \gg 1} [P_{VV}(\vartheta, 0)]_{\mu}^{-1} \approx (L_{\mu}/\pi)q + (2/\pi^2) + \dots \quad (37a)$$

$$\lim_{(R_G^2)_{LS} q^2 \gg 1} P_{VV}(\vartheta, 0)^{-1} \approx (L/\pi M)M_w q + \dots \quad (37b)$$

showing that data on $\mathbf{R}_{VV}(\vartheta, 0)$ in this limit will provide the length per unit mass, but not the molecular weight; this situation may be realized with certain large rodlike structures.⁽⁵⁶⁾ For a linear or branched flexible chain polymers ($\varepsilon = 1$ and $r = g\hat{a}L/3M$, with g the ratio of R_G^2 for branched and linear chains with the same M),^(10, 18, 54)

$$\lim_{(R_G^2)_{LS} q^2 \gg 1} P_{VV}(\vartheta, 0)^{-1} \approx r M_n q^2/2 + (M_w/M_n)C + \dots \quad (38a)$$

$$\approx (M_n/M_z)(R_G^2)_{LS} q^2/2 + (M_w/M_n)C + \dots \quad (38b)$$

where C is $1/2$ for linear chains, and dependent on chain structure for branched chains. Consequently, in principle, investigation of the limiting behavior at large and small q can provide values for M_n , M_w and M_z for linear flexible chain polymers (or for branched flexible chains for which C is known). In practice, the limiting behavior at large q is seldom observed in light scattering experiments with flexible chain macromolecules, but it is possible to observe such behavior with low angle x-ray or neutron scattering — it may, however, be difficult to observe the limiting behavior for large and small q in the same experimental arrangement. Moreover, short-scale chain features not included in the models used to compute $P_{VV}(\vartheta, 0)$ will introduce behavior not included in these asymptotic expressions for large $(R_G^2)_{LS} q^2$. A related behavior obtains with spheres, in which the value of $P_{VV}(\vartheta, 0)$ for successive maxima at large qR decay as $(qR)^{-4}$ in the so-called Porod regime.^(21i, 24b, 57, 58)

For a solute monodisperse in molecular weight, but comprising two types of scattering elements,^{(10,}

$$P_{V_V}(\vartheta, 0) = x[P_{V_V}(\vartheta, 0)]_A + (1 - x)[P_{V_V}(\vartheta, 0)]_B + x(1 - x)[Q_{V_V}(\vartheta, 0)]_{AB} \quad (39a)$$

$$[Q_{V_V}(\vartheta, 0)]_{AB} = 2[P_{V_V}(\vartheta, 0)]_{AB} - \{[P_{V_V}(\vartheta, 0)]_A + [P_{V_V}(\vartheta, 0)]_B\} \quad (39b)$$

where $x = w_A \Psi_A / \Psi_{\text{solute}}$ as above, and $\Psi_{\text{solute}} \neq 0$. Here, $[P_{V_V}(\vartheta, 0)]_A$ and $[P_{V_V}(\vartheta, 0)]_B$ are calculated by the expression given above, and $[P_{V_V}(\vartheta, 0)]_{AB}$ by a variation of this expression with one sum each over scattering elements of type A and B. The expressions for $P_{V_V}(\vartheta, 0)$ in Table 2 apply for $[P_{V_V}(\vartheta, 0)]_A$ and $[P_{V_V}(\vartheta, 0)]_B$, but $[P_{V_V}(\vartheta, 0)]_{AB}$ must be computed for each case. Expansion of $[Q_{V_V}(\vartheta, 0)]_{AB}$ gives the leading term $\Delta_{AB}^2 q^2 / 3$, with Δ_{AB}^2 as defined above, i.e., $[Q_{V_V}(0, 0)]_{AB} = 0$. Examples are available for random-flight linear chains.⁽³⁶⁾ Inspection shows that the initial tangent $\partial[P_{V_V}(\vartheta, 0)]^{-1} / \partial q^2$ may be negative, zero or positive, reflecting the possibility mentioned above that $(R_G^2)_{LS}$ may be positive, zero or negative, respectively, for such a solute. For a sphere with radius R_A and scattering elements of type A coated by a shell with outer radius $R_B > R_A$ and scattering elements of type B,^(21j)

$$P_{V_V}(\vartheta, 0) = \left(x[P_{V_V}(\vartheta, 0)]_A^{1/2} + (1 - x) \frac{R_B^3 [P_{V_V}(\vartheta, 0)]_B^{1/2} - R_A^3 [P_{V_V}(\vartheta, 0)]_A^{1/2}}{R_B^3 - R_A^3} \right)^2 \quad (40)$$

where the expressions for $[P_{V_V}(\vartheta, 0)]_B$ and $[P_{V_V}(\vartheta, 0)]_A$ are the functions for spheres with radii R_B and R_A , respectively (given in Table 2). This expression reduces to $P_{V_V}(\vartheta, 0)$ for a shell of thickness $\Delta = R_B - R_A$ filled with the solvent for $x = 0$, or to $P_{V_V}(\vartheta, 0)$ for a sphere of radius R_A if $x = 1$. In using this relation, it must be remembered that $w_A \propto \rho_A R_A^3$ and $w_B = 1 - w_A \propto \rho_B (R_B^3 - R_A^3)$. If $\Psi_{\text{solute}} = 0$, then $[\mathbf{R}_{V_V}(0, c) / Kc]^0 = 0$, but $[\mathbf{R}_{V_V}(\vartheta, c) / Kc]^0$ for $\vartheta > 0$ may be computed using Equation (40) with x and $1 - x$ replaced by $w_A \Psi_A$ and $w_B \Psi_B$, respectively. The result will exhibit a series of maxima for $\vartheta > 0$, with a superficial similarity to $\mathbf{R}_{V_V}(\vartheta, c)$ observed with charged spheres, arising from interactions among the scatterers, see Examples below.

2.4.2 Isotropic solute beyond the RGD regime. Although the accuracy of the RGD approximation varies with ϑ and $\tilde{n}$, deviations from the Mie theory are usually small if $\alpha|\tilde{n} - 1| < 0.25$ (but this depends on ϑ and both α and $\tilde{n}$ individually in detail).^(21k, 22h) With the RGD approximation, $P_{Hh}(\vartheta, 0) = P_{V_V}(\vartheta, 0) \cos^2(\vartheta)$, but this relation does not usually hold if the phase shift is not small. The Mie theory provides expressions for $P_{V_V}(\vartheta, 0)$, $P_{Hh}(\vartheta, 0)$ and $P_{Hv}(\vartheta, 0)$ for optically isotropic nonabsorbing spheres as

the square of sums over functions of ϑ and the relevant refractive indices.^(8, 13d, 21m, 22h) Examples shown in Figure 6 give $P_{V_V}(\vartheta, 0)$ as a function of $q^2(R_G^2)_{LS}$ for a particular value of $\alpha = 2\pi R/\lambda$, over a range of $\tilde{n}$, with $\lambda = \lambda_0/n_{\text{medium}}$ (e.g., the α chosen in the example would correspond to aqueous suspensions of spheres with $R \approx 300$ nm, with $\lambda_0 = 633$ nm). The extreme dependence on $\tilde{n}$ may be observed, emphasizing the need to know this parameter accurately in this regime, and showing that it would be impossible to analyze the size distribution for an ensemble of spheres with heterogeneity of both $\tilde{n}$ and R . The data in Figure 6 are shown as $P_{V_V}(\vartheta, 0)$ vs $q^2(R_G^2)_{LS}$ to emphasize the correspondence at small q , but the systematic variation of $q^2(R_G^2)_{LS}$ for the first minimum in $P_{V_V}(\vartheta, 0)$ with $\tilde{n}$. In this format, the minima in $P_{V_V}(\vartheta, 0)$ tend to occur near the values of $q^2(R_G^2)_{LS}$ for the minima in the RGD approximation. Similar behavior may be observed for other values of α , including α large enough to be in the Fraunhofer diffraction limit discussed below.

Numerical methods to compute $P_{V_V}(\vartheta, 0)$ are available for a number of particle shapes.^(8, 13h, 59, 60) Fortunately, electronic computation at the desktop can facilitate the use of these, although extensive table of the functions appearing in the Mie theory for the scattering from spherical particles are available⁽²¹ⁿ⁾ (the functions reported herein were calculated using MathCad, kindly provided by D. C. Prieve, of the Department of Chemical Engineering of Carnegie Mellon University, with the number of terms in the relevant sums terminated at the next integer larger than $\alpha + 4\alpha^{1/3} + 4$ (slightly larger than an expression advocated in the literature⁽¹³ⁱ⁾ for accessible α); data in published tables⁽⁶¹⁻⁶³⁾ are useful to confirm the methods used in such calculations). Comparable expressions are available in the Mie approximation for shells, stratified spheres and examples with a continuous radially symmetric variation.^(13g, 21p, 26, 64-66) cylinders and ellipsoids.^(21q, 67-69) The application of these for polydisperse systems requires the use of Equation (32a) to compute the observable $P_{V_V}(\vartheta, 0)$, usually by a numerical analysis.

For both $\tilde{n} \gg 1$ and phase shift magnitude $|\alpha\tilde{n} - 1| > 10$, the angular dependence reduces to a regime termed the Fraunhofer diffraction limit.^(11, 13j, 21r, 22i) In that regime, the angular dependence is independent of $\tilde{n}$, and the same for absorbing or nonabsorbing particles. For example, for a spherical solute, the angular dependence of the scattering (for a monodisperse solute at infinite dilution) is that for Fraunhofer diffraction from a circular aperture

$$\lim_{R/\lambda \gg 1} P_{V_V}(\vartheta, 0) = \{2J_1(\alpha \sin(\vartheta))/\alpha \sin(\vartheta)\}^2 \quad (41)$$

where $\alpha = 2\pi R/\lambda$, $J_1(\dots)$ is the Bessel function of the first kind and first order. For a polydisperse

spherical solute in this regime,

$$\lim_{R/\lambda \gg 1} [\mathbf{R}_{V_V}(\vartheta, c)/c]^0 \propto \sum_{\mu} n_{\mu} \alpha_{\mu}^6 \{2J_1(\alpha_{\mu} \sin(\vartheta))/\alpha_{\mu}^2 \sin(\vartheta)\}^2 \quad (42)$$

where n_{μ} is the number fraction of spheres with radius R_{μ} . As discussed below, the simplicity of this result can be exploited in methods to determine the size distribution from $[\mathbf{R}_{V_V}(\vartheta, c)/c]_0$. Similar results obtain for other particle shapes. For example, for cylinders with length L_{cyl} and radius R , in the same limit, and with $L_{cyl} \gg R \gg \lambda$,⁽²²ⁱ⁾

$$\lim_{R/\lambda \gg 1} P_{V_V}(\vartheta, 0) = \sin^2(\alpha \vartheta)/(\alpha \vartheta)^3 \quad (43)$$

Since the patterns of the extrema are similar for these two functions, it would not be possible to differentiate between solutes with these two shapes from the scattering in this limit. Nor can the expression for cylinders with $L_{cyl}/R \gg 1$ be used to determine the distribution of cylinder lengths.

It has been observed that in the regime for which Mie scattering theory applies for optically isotropic spheres, the angular dependence for small angle may be approximated by the expression for the Fraunhofer regime given above, even if R is not much larger than λ ;^(21e, 44) Although the discussion of $(R_G^2)_{LS}$ in the preceding shows that this cannot be accurate for small angle (and is inaccurate for the RGD regime), it may, nevertheless, be a useful approximation over most of the regime for which the Mie theory is needed, offering a substantial simplification in the analysis of the size distribution in such cases.

If $\alpha \gg 1$, but $\tilde{n} \approx 1$ (e.g., for a particle immersed in a solvent with closely matching refractive index), so that the phase shift $\alpha|\tilde{n} - 1|$ is small, the angular dependence differs considerably from that for Fraunhofer diffraction for larger ϑ , in a regime called anomalous diffraction^(21, 22j) giving what has been characterized as "a set of queer scattering diagrams".^(22j) So-called anomalous scattering approximations to the Mie theory have been obtained in this regime for spheres,^(22k) reported to be accurate for computation of $P_{V_V}(\vartheta, 0)$ in the regime $\tilde{n} - 1 < 0.1$, $2\alpha|\tilde{n} - 1| < 0.1$ and $\alpha > 1$.⁽⁷⁰⁾ Use of the Fraunhofer diffraction approximation would, for example, give an erroneous estimate of the size distribution, see the Examples. It is reported that depolarized scattering may result from isotropic spheres in this regime.⁽⁷¹⁾ The preceding discussion has been limited to scattering with the polarization of the incident and scattered beams either perpendicular or parallel to the scattering plane, the plane defined by incident and scattered beams. A more general notation is needed to discuss the anisotropic scattering for spheres since $P_{H_V}(\vartheta, 0)$

as defined above is zero for isotropic spheres. In a more general description, the scattering plane may contain the incident beam, and be at an azimuthal angle ϕ relative to the polarization of the incident light for vertically polarized light. Thus, $\phi = \pi/2$ for the scattering plane considered thus far. An alternative nomenclature lets Vv and Hv indicate parallel and crossed polars, respectively, as in the preceding, but supplements the description by adding the azimuthal angle, e.g., $P_{Hv}(\vartheta, \phi, c)$, so that $P_{Hv}(\vartheta, 0)$, $P_{Vv}(\vartheta, 0)$, and $P_{Hh}(\vartheta, 0)$ discussed above become $P_{Hv}(\vartheta, \pi/2, 0)$, $P_{Vv}(\vartheta, \pi/2, 0)$, and $P_{Vv}(\vartheta, 0, 0)$, respectively. It has long been known that $P_{Hv}(\vartheta, \pi/4, 0)$ is not zero for optically anisotropic spheres (see below), with a first maximum in $P_{Hv}(\vartheta, \pi/4, 0)$ occurring at an angle ϑ that may be used to estimate the size of the sphere, see below.⁽⁵⁾ Calculations in the R-G-D approximation and using the Mie theory reveal that a similar maximum occurs with optically isotropic spheres in the anomalous diffraction regime,⁽⁷¹⁾ in agreement with observations on spheres thought to be optically isotropic.⁽⁷⁰⁾

2.4.3 Anisotropic solute. With the exception of semiflexible chains with relatively large $\hat{a}/L$, anisotropic scattering may normally be neglected in the excess scattering for polymer solutions (note that many solvents will exhibit anisotropic scattering, which must be accurately determined to study the excess anisotropic scattering due to the solute). The functions $P_{Hv}(\vartheta, 0)$ and $P_{Vv}(\vartheta, 0)$ for rodlike chains are given in Table 2, and are discussed in more detail below in an Example, along with the anisotropic scattering from particles.

Expressions for $P_{Vv}(\vartheta, 0)$ and $P_{Hv}(\vartheta, 0)$ for optically anisotropic rodlike molecules in the RGD regime are given in Table 1, and discussed below in the section on Examples. The functions $P_{Hv}(\vartheta, \phi, 0)$ and $P_{Vv}(\vartheta, \phi, 0)$ defined above have been computed for optically anisotropic spheres and other particle shapes.^(5, 26, 72) A principal result for anisotropic spheres is that $P_{Hv}(\vartheta, \pi/4, 0)$ exhibits extrema as a function of qR for monodisperse spheres,^(5, 21s, 45, 70, 73-78), see the Examples below.

2.5 The size distribution from scattering data at infinite dilution

In the preceding, the characterization of the size distribution is through averages of M and R_G^2 . Thus, with a model relating R_G^2 to M , the different averages in M_{LS} and $(R_G^2)_{LS}$ can permit an estimate of the breadth of the size distribution. Two principal methods are used to estimate more detailed information on the size distribution: (i) comparison of experimental $P_{Vv}(\vartheta, 0)$ with that calculated with an assumed distribution of M (or some other equivalent size parameter, such as R for spheres), and (ii) inversion of $P_{Vv}(\vartheta, 0)$ to obtain the size distribution function. Neither is entirely satisfactory, each with its own set of limitations. In either case, it is necessary to have a model for $P_{Vv}(\vartheta, 0)$, and to assume that the model applies to all scatterers in the system. Further, as a practical matter, it must be assumed that all

components are identical in composition. In practice, data on $\mathbf{R}_{Vv}(\vartheta, c)/Kc$ are often used to estimate a size distribution, rather than $P_{Vv}(\vartheta, 0)$, or even $[\mathbf{R}_{Vv}(\vartheta, c)/Kc]^0$. As discussed in the next section, this practice may introduce distortions into the size estimate unless $2(A_2)_{LS}M_w c \ll 1$. Multiple scattering is an additional practical issue sometimes encountered, especially in the scattering from dispersions of particles for which $\mathbf{R}_{Vv}(\vartheta, c)/Kc$ is not extrapolated to infinite dilution. Some schemes have been introduced to account for this effect, especially in the scattering from large spheres,⁽⁷⁹⁻⁸³⁾ but in general, it should be avoided by reducing the solute concentration, though this can have a deleterious effect on the estimate of the population of very small scattering components in the presence of large particles.

In the first method, a model is used to compute $P_{Vv}(\vartheta, 0)$ for comparison with the experimental data, based on an (assumed) solute structure and an assumed two or three parameter molecular weight distribution function, e.g., one of the several functions given in reference 42 with parameters M_w/M_n , M_z/M_w , etc., or alternatively, for spheres, these functions expressed as a distribution in R with parameters R_w/R_n , R_z/R_w , etc. Estimates of M_w and $(R_G^2)_{LS}$ may be used to guide estimation of the parameters in the distribution function if these are available; in some cases, for a solute with very large M_w it may not be possible to obtain the reliable extrapolation to zero scattering angle needed to estimate these parameters. For example, experimental data on $P_{Vv}(\vartheta, 0)$ for linear flexible chains or spheres (in the RGD regime) could be compared with Figure 4, calculated using the two-parameter exponential function mentioned above, to estimate the molecular weight dispersion. Comparison with $P_{Vv}(\vartheta, 0)$ for semiflexible chains provides an example of the ambiguity in matching experimental and calculated $P_{Vv}(\vartheta, 0)$ unless a reliable model is available. A similar situation obtains with particles, e.g., deviations from spherical symmetry will result in distortions of the scattering function similar to those caused by a distribution of size in spheres.

There is a long history of attempts to implement a direct inversion of $P_{Vv}(\vartheta, 0)$ (or $[\mathbf{R}_{Vv}(\vartheta, c)/c]^0$) for polydisperse scatterers (usually particles with spherical symmetry) to obtain a size distribution of the scattering species, much of it demonstrating the difficulty of obtaining reliable results. Present-day treatments are facilitated by the availability of computational facilities at the desk top to implement the computations, with almost all applications being to the size distribution of particles owing to the nature and limited accessible span of $P_{Vv}(\vartheta, 0)$ for macromolecules. Two principal methods are used, depending on the size of the particles: numerical inversion of the data via iterative techniques,⁽⁸⁴⁻⁹⁰⁾ and evaluation of an integral expression based on Fraunhofer diffraction for particles with dimension much greater than the wavelength, $\tilde{n} \gg 1$.^(81, 91-101) The numerical inversions required are similar in kind to those applied to estimate size distributions from dynamic light scattering data, which involves a similar inversion

relation, with similar limitations. For example, inversion is frequently attempted for the normalized electric field correlation function $g_{LS}^{(1)}(\tau; q, c)$ of dynamic light scattering, given by^(1, 7a, 10, 17, 88, 102, 103)

$$g_{LS}^{(1)}(\tau; q) = \sum_{\mu} w_{\mu} M_{\mu} [P_{VV}(\vartheta, 0)]_{\mu} \exp[-\tau \gamma_{\mu}(q)] / M_w P_{VV}(\vartheta, 0) \quad (44)$$

in the limit of infinite dilution, with $\gamma_{\mu}(q)$ the relaxation rate of the component μ . The similarity of this to the expression

$$P_{VV}(\vartheta, 0) = \sum_{\mu} w_{\mu} M_{\mu} [P_{VV}(\vartheta, 0)]_{\mu} / M_w \quad (45)$$

of interest here is evident, with a principal distinction being that the range of τ may be made much larger than the corresponding range in ϑ (or q), to the advantage of accuracy in the inversion. On the other hand, data acquisition is usually more time consuming in dynamic scattering. In some cases, it is convenient to replace w_{μ} by the number fraction n_{μ} of species with molecular weight M_{μ} , with $w_{\mu} = n_{\mu} M_{\mu} / M_n$, but in either case, implementation of an inversion protocol requires a relation between M_{μ} and a size parameter appearing in $[P_{VV}(\vartheta, 0)]_{\mu}$, e.g., as in Table 1. Furthermore, the inversions are ill-posed for both static and dynamic scattering functions, and constraints must be imposed to obtain a stable inversion.

It may be noted that expressions of this kind have been used for many years in the analysis of x-ray scattering data on particles, often with $P_{VV}(\vartheta, 0) \approx \exp(-R_G^2 q^2 / 3)$, along with a model to express R_G^2 in terms of M , eg., $R_G^2 \propto M^{2/3}$ for a spherical particle.^(24c) The several difficulties that hamper the determination of the molecular weight (or size) distribution by an inversion of $P_{VV}(\vartheta, 0)$, include

- (i) the ill-posed character of the inversion
- (ii) the need to have a theoretical $P_{VV}(\vartheta, 0)$
- (iii) noise in the data
- (iv) the physical range of ϑ , and hence the limited accessible q
- (v) uncertainty in the relative refractive index $\tilde{n} = n_{\text{solute}} / n_{\text{medium}}$
- (vi) the effects of solute aggregation
- (vii) the effects of multiple scattering

Various procedures have been investigated to effect the inversion, including versions of the methods used to invert dynamic scattering data, such as the constrained regularization method called CONTIN,^(102, 103)

as well as other methods.^(7c, 85-89, 98, 99, 104-108) As discussed above, the RGD approximation is generally valid for nonabsorbing solute if the phase shift within the molecule or particle is small enough. Although this is generally met for a polymeric solute, a direct inversion of $P_{Vv}(\vartheta, 0)$ is seldom of interest in such cases owing to the limited range of $(R_G^2)_{LS}q^2$ typically accessible for the scattering for a polymeric solute, as well as the limitations due to noise in the experimental data, e.g., see the comments above on the difficulties of obtaining reliable behavior at large q . By contrast, with larger particulate solutes, $P_{Vv}(\vartheta, 0)$ may typically cover a wider range, and perhaps exhibit maxima and minima, for the accessible range of $(R_G^2)_{LS}q^2$. As discussed above, the RGD approximation may be used for a range of particle size, but in such cases, the range of $(R_G^2)_{LS}q^2$ may not be large, in which case the inversion may not be accurate, depending on the particle shape. For larger phase shift, M_w must be replaced by M_{LS} , and the Mie theory may be used for spheres to compute the $[P_{Vv}(\vartheta, 0)]_\mu$ needed in the inversion for particles with spherical symmetry, albeit with an increase in the computational time required. Similar treatments are available for other shapes, including spherical shells,^(13k, 45) spheroids of revolution⁽⁴⁶⁾ and rods,⁽⁶⁷⁾ but it is not possible to permit both the particle shape and the size distribution to be unknowns in an inversion of the scattering from a polydisperse sample. Inversions in this regime may be reasonably stable and accurate, but usually require an accurate estimate of $n_{\text{solute}}/n_{\text{medium}}$, along with the attention of one skilled in the art to avoid erroneous results, see the section on Examples below.

The expression for $[R_{Vv}(\vartheta, c)/c]^0$ given above in the Fraunhofer limit, with $R \gg \lambda$, may be used to obtain an integral equation for the number fraction spheres with a given radius, eliminating the iterative methods described above. Experimental instruments to acquire data for this purpose differ in their design, and in the form of the integral expression used.^(43, 81, 91-95, 98-101, 109-111) A systematic, consistent analysis of these given in reference⁽⁹²⁾ is discussed below in the section on Examples.

2.6 Extrapolation to infinite dilution

All of the preceding has presumed that $R_{\text{iso}}(\vartheta, c)/c$ and $R_{\text{aniso}}(\vartheta, c)/c$ may be reliably extrapolated to infinite dilution. For dilute solutions, as discussed in Section 2.1, $R_{\text{iso}}(\vartheta, c)/c$ may be expressed in the form

$$R_{\text{iso}}(\vartheta, c)/KMc = S_{\text{iso}}(\vartheta, c) = P_{\text{iso}}(\vartheta, c)/\{1 + c\Gamma_{\text{iso}}(c)P_{\text{iso}}(\vartheta, c)H_{\text{iso}}(\vartheta, c)\} \quad (46)$$

where $K = K'\psi_{\text{solute}}^2$, with a similar expression for $R_{\text{aniso}}(\vartheta, c)/c$. The function $H_{\text{iso}}(\vartheta, c)$, which is usually close to unity, is discussed below, as is the possible dependence of $P_{\text{iso}}(\vartheta, c)$ on c , the latter principally

reflects changes in the mean-square radius of gyration with c .⁽⁴⁾ Since $P_{\text{iso}}(\vartheta, c) \ll 1$ for $q^2(R_G^2)_{\text{LS}} \gg 1$, one can anticipate that $\mathbf{R}_{\text{iso}}(\vartheta, c)/KMc \approx P_{\text{iso}}(\vartheta, c)$, for any concentration in that limit. The range of $(R_G^2)_{\text{LS}}q^2$ required to observe this convergence depends strongly on the solute structure.

For $\vartheta = 0$, $P_{\text{iso}}(0, c) = H_{\text{iso}}(0, c) = 1$, and for dilute solutions, a virial expansion may usually be used to represent $\Gamma_{\text{iso}}(c)$, with the result^(4, 10, 20a, 31)

$$Kc/\mathbf{R}_{\text{iso}}(0, c) = M_{\text{LS}}^{-1} \{ 1 + 2(A_2)_{\text{LS}}M_{\text{LS}}c + 3(A_3)_{\text{LS}}M_{\text{LS}}c^2 + \dots \} \quad (47)$$

For systems with large A_2 ("good solvents"), the term in c^2 may introduce appreciable curvature, motivating the use of the relation^(4, 10)

$$[Kc/\mathbf{R}_{\text{iso}}(0, c)]^{1/2} = M_{\text{LS}}^{-1/2} \{ 1 + (A_2)_{\text{LS}}M_{\text{LS}}c + \alpha_3((A_2)_{\text{LS}}M_{\text{LS}}c)^2 + \dots \} \quad (48)$$

where $\alpha_3 = \{3(A_3)_{\text{LS}}M_{\text{LS}}/((A_2)_{\text{LS}}M_{\text{LS}})^2 - 1\}/2$; α_3 tends to be small for systems with large A_2 , making the extrapolation more nearly linear to larger $(A_2)_{\text{LS}}M_{\text{LS}}c$ than with the first form. Possible exceptions to the behavior given by these relations may obtain if the solute is charged and the solvent is of very low ionic strength.^(16, 32)

Although the behavior for more concentrated solutions is outside the scope here, it may be noted that expressions are available for moderately concentrated solutions, both in good solvents, and under Flory theta conditions, for which A_2 , but not A_3 , is zero. In the latter case, the expression given above terminated at the term in c^2 provides a good fit to the data, whereas with good solvents, power-law expressions in A_2Mc may be used to replace the factor in $\{\dots\}$ in Equation 47.^(4, 33)

The expression for $(A_2)_{\text{LS}}$ involves a double summation over components, and need not be elaborated here (however, see the Example on association below), except to note that for a polydisperse solute, $(A_2)_{\text{LS}}$ is not equal to the corresponding value $(A_2)_{\Pi}$ obtained by osmotic pressure.⁽⁴⁾ Further, it may be noted that for polymer chains, for monodisperse solute, A_2 may be expressed in the form^(2a, 4, 10, 20c, 51)

$$A_2 = (A_2)_{\text{ROD}} F(L/\hat{a}, z) \quad (49)$$

where $(A_2)_{\text{ROD}} = (\pi N_A L^2 / 4M^2) d_{\text{thermo}}^2$ is the second virial coefficient for a rodlike chain with thermodynamic diameter d_{thermo} , $z = (3 d_{\text{thermo}} / 16\hat{a})(3L/\pi\hat{a})^{1/2}$ is a thermodynamic interaction parameter, and $F(L/\hat{a}, z)$ is a function that depends on chain conformation, with $F(L/\hat{a}, 0) = F(0, z) = 1$. For

uncharged solute, d_{thermo} is zero at the Flory theta temperature, and increases to about twice the geometric diameter d_{geo} for uncharged solute in so-called "good solvents". In good solvents, $A_2M/[\eta] \approx 1$ for linear flexible chains, with $[\eta]$ the intrinsic viscosity.⁽⁵¹⁾ By comparison, for particles interacting through a hard-core potential,^(20d)

$$A_2 = 4N_A f V_{\text{particle}} / M^2 \quad (50)$$

where V_{particle} is the particle volume and f is a parameter that depends on the particle shape, e.g., $f = 1$ for a sphere, and $f = L/4d_{\text{geo}}$ for a rod of diameter $d_{\text{geo}} \ll L$; $A_2M/[\eta] \approx 16/5$ for spheres. The behavior with charged solutes or particles is discussed in the section on Examples.

Similar relations obtain for optically anisotropic polymers, but the coefficients are generally smaller, reflecting the origin of the scattering from fluctuations in the orientation of the scattering elements. Thus, for rodlike chains,^(4, 10, 20e, 112)

$$\Gamma_{V_V}(c) = \{2(A_2)_{LS} M_{LS} + \dots\} + (4\delta^2/5)\Gamma_{V_H}(c) \quad (51)$$

$$\Gamma_{V_H}(c) = (A_2)_{LS} M_{LS}/4 + \dots \quad (52)$$

or an eight-fold smaller leading term for depolarized scattering than obtains with polarized scattering.

The possible dependence of $P_{\text{iso}}(\vartheta, c)$ and $H_{\text{iso}}(\vartheta, c)$ on c may complicate the extrapolation of data to infinite dilution, or the interpretation of data at a single concentration. For example, the initial tangent, given by

$$\partial[Kc/\mathbf{R}_{\text{iso}}(\vartheta, c)]/\partial q^2 = M_{LS}^{-1} \{ \partial[P_{\text{iso}}(\vartheta, c)^{-1}/\partial q^2 + c\Gamma_{\text{iso}}(c)\partial H_{\text{iso}}(\vartheta, c)/\partial q^2 \} \quad (53)$$

$$\partial[Kc/\mathbf{R}_{\text{iso}}(\vartheta, c)]/\partial q^2 = M_{LS}^{-1} \{ \partial P_{\text{iso}}(\vartheta, 0)^{-1}/\partial q^2 + c\Gamma_{\text{iso}}(c)\partial W_{\text{iso}}(\vartheta, c)/\partial q^2 \} \quad (54)$$

may depend on c (the potential dependence of $P_{\text{iso}}(\vartheta, c)$ on c is subsumed in the function $W_{\text{iso}}(\vartheta, c)$ in the second form); Γ_{iso} may be expressed as a virial expansion in dilute solutions. For the range of $(R_G^2)_{LS}q^2$ normally accessible with polymer chains, plots of $KMc/\mathbf{R}_{\text{iso}}(\vartheta, c)$ vs q^2 are usually observed to be essentially parallel for dilute solutions over a range of c , suggesting that $\partial W_{\text{iso}}(\vartheta, c)/\partial q^2$ is small — exceptions may occur for chains with very large M , and the corresponding larger range of $(R_G^2)_{LS}q^2$. Note

that with the expression for $H_{\text{iso}}(\vartheta, c)$ for spheres given below, plots of $KMc/\mathbf{R}_{\text{iso}}(\vartheta, c)$ vs q^2 would not be expected to be parallel, unlike the experience with flexible chain polymers. For convenience, the ratio of the initial tangent for small ϑ to the intercept $Kc/\mathbf{R}_{\text{iso}}(0, c)$ at concentration c is denote $b(c)^2 = [c/\mathbf{R}_{\text{iso}}(0, c)]^{-1} \partial[c/\mathbf{R}_{\text{iso}}(\vartheta, c)]/\partial q^2$, so that

$$b(c)^2 = \frac{(1/3)(R_G^2)_{\text{LS}} + c\Gamma_{\text{iso}}(c)\partial W_{\text{iso}}(\vartheta, c)/\partial q^2}{1 + c\Gamma_{\text{iso}}(c)} \quad (55)$$

Consequently, even if $\partial W_{\text{iso}}(\vartheta, c)/\partial q^2$ tends to zero (leading to parallel plots of $KMc/\mathbf{R}_{\text{iso}}(\vartheta, c)$ vs q^2 over a range of c), $b(c)^2$ will not equal $(R_G^2)_{\text{LS}}$ unless $c\Gamma_{\text{iso}}(c) \approx 2(A_2)_{\text{LS}}M_{\text{LSc}} \approx 0$, as at very high dilution, or for a dilute solution with $(A_2)_{\text{LS}} = 0$.

For $\vartheta > 0$, the function $H_{\text{iso}}(\vartheta, c)$ may introduce an additional dependence on ϑ , and for polymer chains, $P_{\text{iso}}(\vartheta, c)$ may vary with c , reflecting principally changes in the mean-square radius of gyration with c .^(4, 33) The behavior for spherical particles interacting through a hard-core potential provides an example of this behavior. In that case,^(4, 24d)

$$H_{\text{iso}}(\vartheta, c) = [P_{\text{iso}}(\vartheta', c)]^{1/2}/P_{\text{iso}}(\vartheta, c) \quad (56)$$

where $\sin(\vartheta'/2) = 2\sin(\vartheta/2)$, and $P_{\text{iso}}(\vartheta, c) = P_{\text{iso}}(\vartheta, 0)$ for this model. Consequently, $P_{\text{iso}}(\vartheta, c)H(\vartheta, c) = [P_{\text{iso}}(\vartheta', 0)]^{1/2}$, and $\mathbf{R}_{\text{iso}}(\vartheta, c)/KMc \approx P_{\text{iso}}(\vartheta, 0)$ for large $(R_G^2)_{\text{LS}}q^2$ as expected.

For flexible chain polymers, the mean square radius of gyration $(R_G^2)_c$ at concentration c tends to its value $\hat{a}L/3$ obtaining under Flory theta conditions with increasing c , even in "good solvents" for which $(R_G^2)_c$ exceeds this value at infinite dilution.^(4, 33) A first-approximation to $P_{\text{iso}}(\vartheta, c)$ and $H_{\text{iso}}(\vartheta, c)$ for flexible chain polymers in this situation is to use the relation for $P_{\text{iso}}(\vartheta, c)$ for a random-flight chain with the observed $(R_G^2)_c$ at concentration c (as opposed to the value at infinite dilution), along with the above approximation for $H_{\text{iso}}(\vartheta, c)$;^(4, 113, 114) Although this provides a qualitatively useful approximation, it may not be quantitatively correct, and should not be relied on if accuracy is critical; in one alternative, the Flory-Krigbaum pair potential^(29b) has been used to estimate $H_{\text{iso}}(\vartheta, c)$.⁽¹¹⁵⁾ The effects of electrostatic interactions among charged spheres are discussed in the Examples.

3. EXPERIMENTAL METHODS

3.1 Instrumentation

Discussion of the instrumentation, alignment and calibration methods, and methods of treating data may be found in a number of places^(1, 7d, 10, 18, 116, 117) and only a brief account will be given here. Light scattering photometers with a variety of designs and special purposes are commercially available. These comprise several components, including:

- (1) the incident light source and its associated optics;
- (2) the light scattering cell;
- (3) the detector and its associated optics;
- (4) the electronic components associated with the detector.

In addition, the experiment could require specialized apparatus in special cases, e.g., filters to remove (most of) any fluorescence emission, means to control the temperature, etc.

Several factors are necessary in converting the response $G(\vartheta)$ from the detector to useful parameters in the analysis of static light scattering, including:^(1, 7d, 10, 18, 116, 118)

- (1) the dependence of the scattering volume on angle and solvent;
- (2) the effects of attenuation of the incident or scattered rays;
- (3) the polarization state of the incident and scattered rays;
- (4) the relation of the detected signal to the Rayleigh ratio.

Most light scattering photometers make use of laser light sources, ranging from a few milliwatts to a hundred milliwatts or so in output power. Usually this is a plane-polarized state with the electric vector in the direction vertical to the scattering plane (the plane containing the incident and scattered rays), see below. The plane of polarization may then be rotated by rotation of a half-wave plate placed in the incident beam, providing a convenient tool for optical alignment. The detector optics are designed to control the angular acceptance of the scattered light, and the horizontal and vertical dimensions of the scattering volume — the depth of the scattering volume is controlled by the width of the incident beam. One of a few optical designs is usually employed in the detector optics,^(1, 7d, 10, 18, 116, 117) and one of two general arrangements to make use of these relations may be found in practice: (i) the use of a single detector mounted on a goniometer for use over a range of scattering angles, and (ii) the use of a separate detector for each angle. The angular resolution and scattering volume must be known at each scattering volume to permit assessment of the Rayleigh ratio. In some designs this is facilitated by insuring that the scattering volume has a vertical dimension smaller than that of the incident beam,^(1, 18, 117) but other procedures may be adopted. It is usually advisable to place a band-pass filter with a high transmission

for the scattered light before the detector to minimize the effects of any fluorescence from the sample or stray light from sources other than the incident beam. Similarly, a band-reject filter may be used to assess the presence of fluorescence. It is also advisable to place a polarizing filter of some kind before the detector, and it is essential to do this if the anisotropic scattering is to be studied. Unfortunately, not all commercially available instruments provide the option to place filters in the scattered beam.

Specialized instruments to examine the scattering profile in the Fraunhofer diffraction limit (very small scattering angles) have been constructed, and are commercially available, e.g., see references 119 and 120 for a discussion of some of these. The instruments differ principally in the manner of data collection: measurement of the intensity at some angle ϑ (within a small span $\delta\vartheta$), or collection over an appreciable angular range $\Delta\vartheta = \vartheta_{\max} - \vartheta_{\min}$, over a range of values for $\vartheta_{\max}$, see the Examples for further discussion. In some cases, these small angle measurements are augmented by scattering measurements at larger angle (or angles), sometimes using light from a laser with excitation at more than one wavelength to provide scattering over a range of q .

3.2 Methods

The optical clarification of the scattering sample is of paramount importance in obtaining reliable results in light scattering. The clarification should remove extraneous motes ('dust'), undissolved polymer, gas bubbles, and any other scattering source not intrinsic to the sample of interest. At the same time, the clarification process should not cause unwanted removal of a portion of the sample. Often, in the final stages of clarification, the number of extraneous motes is very small, giving the appearance of a few widely separated bright spots in the sample when the scattering is viewed at a small scattering angle. In some instruments the scattering volume is made small in a strategy to reduce the number of extraneous particles in the scattering volume to zero or one for the most part owing to the wide separation of any remaining extraneous motes. Since the scattering will then normally be rather different for these two states, it is possible to discriminate against the scattering from the extraneous matter. A similar strategy is sometimes employed in computer-aided data acquisition, by collecting data over some time interval long in comparison with the time scale for normal intensity fluctuations, but shorter than the time scale for fluctuations due to diffusion of the extraneous matter. The stronger than normal scattered intensity due to the motes may then be discriminated against in the data collection.

In some cases, the experimental data encompass a limited range of angles (e.g., two or three), leading to the use of "dissymmetry methods" to analyze scattering data in the RGD regime, following a procedure introduced early in the use of light scattering to characterize solute dimensions. Often, one of

the scattering angles is taken to be 90 degrees. The dissymmetry $Z(\vartheta_1, \vartheta_2) = G(\vartheta_1)V(\vartheta_2)/G(\vartheta_2)V(\vartheta_1)$, with instrument response $G(\vartheta)$ and scattering volume $V(\vartheta)$ for $\vartheta_1 < \vartheta_2$, may be used to estimate $(R_G^2)_{LS}/\lambda^2$ (with $\lambda = \lambda_0/n_{\text{medium}}$) provided a model is available, including the effects of molecular weight heterogeneity. The dissymmetry method may not be applied beyond the RGD regime, as then $Z(\vartheta_1, \vartheta_2)$ is not generally a single-valued function of $(R_G^2)_{LS}/\lambda^2$.⁽²³⁾ The use of supplementary angles ($\vartheta_2 = \pi - \vartheta_1$) will usually make the scattering volumes equal at the two scattering angles, simplifying the analysis. Note that in general, $[\mathbf{R}_{Vv}(\vartheta_1, c)/c]^0/[\mathbf{R}_{Vv}(\vartheta_2, c)/c]^0 \neq \mathbf{R}_{Vv}(\vartheta_1, c)/\mathbf{R}_{Vv}(\vartheta_2, c)$, requiring extrapolation to infinite dilution to determine $Z(\vartheta_1, \vartheta_2)$. In the original dissymmetry method, ϑ_1 and ϑ_2 were equal to 45 and 135 degrees, respectively, so that $V(\vartheta_1) = V(\vartheta_2)$ in a convenient cell geometry (e.g., cylindrical), and $Z(\vartheta_1, \vartheta_2) = G(\vartheta_1)/G(\vartheta_2)$.^(21t, 23) The value of $(R_G^2)_{LS}/\lambda^2$ may then be used to estimate with $P_{Vv}(\vartheta_3, 0)$ for the assumed model with the correction needed to deduce $[\mathbf{R}_{Vv}(0, c)/c]^0$ from $[\mathbf{R}_{Vv}(\vartheta_3, c)/c]^0$ determined at some particular angle, e.g., $\vartheta_3 = 90$ degrees in the original method. In some cases, only two scattering angles are used, one being fairly small, and the other being 90 degrees, with due attention to the ratio $V(\vartheta_2)/V(\vartheta_1)$.^(119, 120) Tables to assist this treatment are available for a number of models,^(121, 122) or the needed relations may be readily calculated as required using a desktop computer. The use of $P_{Vv}(\vartheta, 0)$ for a linear chain to estimate $(R_G^2)_{LS}/\lambda^2$ by the dissymmetry ratio for a chain that is branched may introduce an error in the estimate for $(R_G^2)_{LS}$ if $(R_G^2)_{LS}q^2$ exceeds about 1. For example, the deviations shown in Figure 5 would lead to increasingly serious overestimation of $(R_G^2)_{LS}$ with increasing $(R_G^2)_{LS}q^2$. An example of this effect may be seen for $Z(45, 135)$ vs $(R_G^2)_{LS}/\lambda^2$ for monodisperse linear chains and regular four-arm star branched molecules for the random-flight model.⁽¹²¹⁾

Finally, other methods of data treatment may be found in the literature. Examples include Guinier plots of $\ln(\mathbf{R}_{Vv}(\vartheta, c)/Kc)$ vs q^2 , based on the approximation $P_{Vv}(\vartheta, 0) = \exp(-(R_G^2)_{LS}q^2/3)$,^(24e) Casassa plots of $Kc/\mathbf{R}_{Vv}(\vartheta, c)$ vs q for rodlike scatterers, based on Equation (37) above,^(18, 56) Porod plots of $q^2\mathbf{R}_{Vv}(\vartheta, c)/Kc$ vs q , based on $P_{Vv}(\vartheta, 0)$ for wormlike chains, see below,^(2b, 18, 52, 123) and plots of $(Kc/\mathbf{R}_{Vv}(\vartheta, c))^{1/2}$ vs q^2 , introduced by the author.⁽¹⁰⁾ These are useful for analysis of data on dilute solutions under special circumstances. Thus, the Guinier plot was devised for use with the scattering from particles polydisperse in size and shape, for which a more detailed treatment was not feasible; as seen in Figure 3, the actual scattering behavior is usually not represented by the exponential function over a range of q (unless $(R_G^2)_{LS}$ is very small); with the exponential function providing a useful approximation to larger $q^2R_G^2$ for spheres than for the other examples in Figure 3. The Casassa plot is only useful for very long rodlike solute for which the asymptotic behavior for large q may dominate the scattering for all accessible q , in which case the tangent provides length per unit mass. Similarly, the Porod plot is

designed to elucidate the behavior at large q , and may, for example reveal the persistence length of a semiflexible (wormlike) chain if large enough q can be attained; the Porod plot is usually of most interest with the scattering from x-ray or neutron radiation owing to the need to reach large q . The "square-root" plot is based on the observation that for a linear, monodisperse random-flight linear chain model, for which R_G^2/M is independent of M , the relation

$$P_{\text{iso}}(\vartheta, 0)^{-1/2} = 1 + R_G^2 q^2 / 6 + \dots \quad (57)$$

facilitates evaluation of the initial tangent⁽¹²⁴⁾ and hence R_G^2 , since in this case the coefficient of q^4 tends to be smaller in this expansion than in the expansion for $P_{\text{iso}}(\vartheta, 0)$. Clearly, the use of $P_{\text{vv}}(\vartheta, 0)^{-1/2}$ to facilitate data analysis should be applied only under appropriate conditions, e.g., it would be inappropriate for the polydisperse solute with a most-probable distribution of molecular weight, see below. Similarly, for monodisperse spheres, $P_{\text{iso}}(\vartheta, 0)$ is closely approximated by $\exp(-R_G^2 q^2 / 3)$ for $R_G^2 q^2 < 2$, with the deviations growing for larger $R_G^2 q^2$, see Figures 3 and 6; this fit is less satisfactory for spheres heterogeneous in size, as may be deduced from Figure 4.

4. EXAMPLES

4.1 Static scattering and size separation chromatography

The application of light scattering and differential refractometry in on-line analysis of the eluent in size exclusion chromatography that separates the eluent by size provides a powerful tool for analysis and characterization and has found wide application, e.g., see references 127 and 128. Examples include size exclusion chromatography (SEC) and flow field-flow chromatography (FFFC). Since the solute concentration is usually very low in the eluent, it is normally assumed that $c\Gamma_{\text{vv}}(c) \approx 0$ for all elution volumes, or a correction is made based on an estimate for A_2Mc . With optically isotropic homopolymers, the response h_e of the differential refractometer at elution volume V_e permits evaluation of the weight fraction $w_e = h_e / \Sigma h_e$ for each V_e (excepting possible end group effects low M). Then, the static (excess) scattering data $[\mathbf{R}_{\text{vv}}(\vartheta, c)]_e$ at each elution volume may be used to compute the molecular weight as $M_e \approx [\mathbf{R}_{\text{vv}}(\vartheta, c)]_e / K c w_e [P_{\text{vv}}(\vartheta, c)]_e$, given the concentration $c \propto \Sigma h_e$ and $\partial n / \partial c$. The factor $[P_{\text{vv}}(\vartheta, c)]_e$ may be evaluated using either an experimental estimate for $[P_{\text{vv}}(\vartheta, c)]_e$ from on-line measurements of $[\mathbf{R}_{\text{vv}}(\vartheta, c)]_e$ as a function of ϑ , or as $[P_{\text{vv}}(\vartheta, c)]_e \approx 1$ if ϑ is small enough. In addition, on-line measurements over a range of scattering angles allow determination of $(R_G^2)_e$ as a function of V_e .

In some instruments, $[\mathbf{R}_{\text{v}}(\vartheta, c)]_{\text{e}}$ is measured only at a single angle, e.g., 90 degrees, with the resulting need to estimate $[\mathbf{P}_{\text{v}}(\vartheta, c)]_{\text{e}}$ at that angle a possible source of inaccuracy. In other instruments, it is possible to measure the scattering at two or three angles, permitting the use of 'dissymmetry' methods to estimate $[\mathbf{P}_{\text{v}}(\vartheta, c)]_{\text{e}}$ based on an assumed functional form e.g., see the discussion of dissymmetry methods above. Comparison of $M_{\text{w}} \approx \Sigma w_{\text{e}} M_{\text{e}}$ calculated from the data on the eluent with M_{w} determined directly on the unfractionated polymer provides a self-consistency check.

An example of the use of multi-angle light scattering with SEC to study the dimensions of poly(*n*-hexylsilane), PDHS, and poly(phenyl-*n*-hexylsilane), PPHS, is given in Figure 7 (from references 1 and 129). The upper panel gives M_{e} and $(R_{\text{G}}^2)_{\text{e}}$ resulting from analysis of the multi-angle scattering data, and the lower panel gives the response from the differential refractive index detector, normalized to give the same peak response. As expected from the mechanism of SEC, the values of $(R_{\text{G}}^2)_{\text{e}}$ are the same at a given elution volume for the two polymers, but the values of M_{e} differ. If the elution volume increments are small enough, then $(R_{\text{G}}^2)_{\text{e}}/M_{\text{e}}$ is expected to approximate the value for a monodisperse chain. Analysis of these data permitted assessment of the difference in R_{G}^2/M for these polymers, revealing the substantially larger persistence length for PPHS, owing to the effects of the phenyl substituent.

Another example is provided by the analysis and characterization of branched macromolecules. Certain polymerizations are expected to produce a randomly branched chain structure, in which the number of branch nodes and their placements are randomly distributed among the chains in the ensemble.^(29c) In such a case, it is not possible to achieve a simultaneous separation by the number m of branch nodes and overall molecular weight M , as each molecule in the ensemble is distinct in this respect. One could conceive a separation by either p or M , with each separated component then narrow in one feature, and polydisperse in the other. Analysis of SEC of such a polymer suggests that although the polymer at each elution volume V_{e} is polydisperse in both p and M , the distribution in M is much narrower than that in p .⁽¹²⁵⁾ Consequently, on-line determination of M_{w} and $(R_{\text{G}}^2)_{\text{LS}}$ of the eluent as functions of V_{e} offers the possibility that an average g_{e} may be estimated for an ensemble that approximates monodispersity in M , with a random distribution in p , with $g_{\text{e}} = (R_{\text{G}}^2)_{\text{LS}}/[(R_{\text{G}}^2)_{\text{LS}}]_{\text{lin}}$, where $[(R_{\text{G}}^2)_{\text{LS}}]_{\text{lin}}$ is for a linear polymer with same molecular weight as the branched chain. In this approximation, theoretical expressions⁽¹²⁶⁾ for g for a polymer monodisperse in M , with a random distribution in p , would be used to estimate p ; the formula, involving summations, is readily calculated with a desk-top computer. An example of data of this type is given in Figure 8 for samples of linear and branched poly(methyl methacrylates).⁽¹²⁷⁾ According to the preceding, these data may be used to estimate g_{e} , and hence the branching frequency, as a function of molecular weight provided a reliable

estimate for $[(R_G^2)_{LS}]_{lin}$ is available. As demonstrated in Figure 8, the latter may not be readily available at the higher molecular weights encountered with branched chains. For the data in Figure 8, the dependence of $[(R_G^2)_{LS}/M_w]_{lin}$ on M_w is stronger than anticipated for the larger V_e , perhaps reflecting the effects of increased molecular weight dispersity with increasing V_e with the column set utilized. Two extrapolations have been presented and used to estimate g_e , with the true value likely somewhere between these estimates.

The size distributions in vesicle preparations similar to that described in the next section have been examined using flow field-flow chromatography (FFFC).⁽¹²⁸⁾ Although a procedure involving simultaneous determination of the scattering and the concentration of the eluent could have been followed, only an (excess) instrument response $G(\vartheta, c)$ proportional to $\mathbf{R}_{v_v}(\vartheta, c)$ was determined as a function of elution volume. Owing to the low concentrations used, such that $2A_2Mc \ll 1$, it was assumed that $c\Gamma_{v_v}(c) \approx 0$ in calculations of the number fraction distribution n_μ . Then, since $[\mathbf{R}_{v_v}(\vartheta, c)]_\mu = KM_\mu^2 P_\mu(\vartheta, 0) v_\mu N_A$ for each fraction in this approximation, with v_μ the number concentration, the number fraction was computed as

$$n_\mu = \frac{G_\mu(\vartheta, c)/M_\mu^2 P_\mu(\vartheta, 0)}{\sum G_\mu(\vartheta, c)/M_\mu^2 P_\mu(\vartheta, 0)} \quad (58)$$

In the analysis, $P_\mu(\vartheta, 0)$ was fitted to the expression for a hollow shell (the RGD approximation being adequate), to give the outer radius R_μ for each eluent fraction, on the assumption that the shell thickness Δ_{sh} was invariant with R_μ , and could be evaluated for the unfractionated polymer, as described in the next section. The expression given above was then used to compute M_μ , using R_μ , Δ_{sh} and v_2 , to permit evaluation of n_μ for each R_μ . As anticipated from the mechanism for FFFC, R_μ increased linearly with elution volume, except for early times, for which the weak scattering may have introduced error in the evaluation of R_μ .

4.2 Light scattering from vesicles and stratified spheres

Many unilamellar vesicles comprise a single closed shell bilayer.⁽¹²⁹⁾ They may be prepared with a spherical shape, and that shape may be further stabilized by a slight imbalance in the compositions of the vesicle interior and exterior, to create a (small) positive osmotic pressure on the interior. Such vesicles provide an example of a shell-like structure, with a shell thickness Δ_{sh} generally much smaller than the outer radius R of the vesicle. The thickness Δ_{planar} of an analogous planar bilayer may be computed as

$\Delta_{\text{planar}} = 2V_{\text{lipid}}/A_{\text{lipid}}$, where V_{lipid} and A_{lipid} are the volume and cross-sectional area of the molecules in the bilayer, respectively. It is expected that $\Delta_{\text{sh}} \approx \Delta_{\text{planar}}$ with increasing R . For a shell, Δ_{sh} may be calculated from the ratio of its volume v_2M/N_A to its surface area $4\pi R^2$, where v_2 is the specific volume of the shell:

$$v_2M/N_A = 4\pi R^2 \Delta_{\text{sh}} \{1 - (\Delta_{\text{sh}}/R) + (\Delta_{\text{sh}}/R)^2/3\} \quad (59)$$

Consequently, the ratio of v_2M to R_G^2 may be used to approximate Δ_{sh} for spherical, monodisperse vesicles. The relation $P_{\text{vv}}(\vartheta, 0)$ given above for a shell may be used to compute R_G^2 as

$$R_G^2 = R^2 \left(\frac{3}{5} \frac{1 - (1 - (\Delta_{\text{sh}}/R)^5)}{1 - (1 - (\Delta_{\text{sh}}/R)^3)} \right) \quad (60a)$$

$$R = (R_G^2)^{1/2} / \{1 + (1/2)\beta + (1/20)\beta^2 + \dots\} \quad (60b)$$

where $\beta = v_2M/4\pi N_A (R_G^2)^{3/2}$. Then,

$$\Delta_{\text{sh}} = \frac{v_2M}{4\pi N_A R_G^2} \{1 + (1/3)\beta^2 + 0.06\beta^3 + \dots\}^{-1} \quad (61)$$

Inspection shows that $\Delta_{\text{sh}} \approx v_2M/4\pi N_A R_G^2$ and $R \approx (R_G^2)^{1/2}$ to a good approximation for $\beta < 1$, with correction factors readily calculated using experimental data for β . Light scattering data on unilamellar vesicles of phosphatidylcholine prepared over a range of size were analyzed to obtain R and Δ_{sh} , after extrapolation to infinite dilution, with results which gave Δ_{sh} a weakly decreasing function of increasing R , tending to Δ_{planar} ($\Delta_{\text{sh}} \approx 3.5$ nm and $R \approx 34$ -40 nm for the several samples examined).^(130, 131)

Size distributions for vesicles with characteristics similar to those discussed above have been reported from inversion of $P_{\text{vv}}(\vartheta, c)$, using a nonnegative least squares fit over a predetermined selection of radii, using $P_{\text{vv}}(\vartheta, c)$ for a vesicle, and the assumption that $c\Gamma_{\text{vv}}(c) \approx 0$ in the analysis.⁽¹³²⁾ The authors report no significant difference between the use of the RGD approximation and the Mie theory for hollow vesicles, owing to the small radius (≈ 50 nm), and although the distribution functions obtained were reproducible, they did differ significantly from those obtained by inversion of dynamic light scattering data. The latter gave a broader distribution, especially for larger particle radii. Among

possible reasons cited for this discrepancy, it was noted that the experimental time required for dynamic data acquisition was much longer than that for static data (hours compared with minutes), and that interparticle aggregation may have intervened during that longer time to introduce errors in the dynamic data. Another example of an analysis on hollow polystyrene spheres dispersed in water⁽¹⁰⁷⁾ produced the results shown in Figure 9, again under the assumption that $c\Gamma_{vv}(c) \approx 0$. The spheres had a radius of about 0.23 μm , large enough to require the use of Mie theory in the analysis of the data at the larger q ; the difference between the use of Mie theory and the RGD approximation is shown in Figure 9. The size distribution obtained from dynamic light scattering was shifted to smaller sizes, see Figure 9b, for reasons not definitively understood.

Block copolymers may form a core-shell micelle in solution, with a resemblance to a vesicle or hollow shell, but with scattering from the core as well as the shell.⁽¹³³⁾ In these cases, for a system with micelles nearly monodisperse in size and structure, $P_{vv}(\vartheta, c)$ would be given by Equation (40) for a shell in the RGD regime (or an appropriate relation for the Mie regime,^(21p) with scattering similar to that for a vesicle, but with a core with a refractive index different from that of the solvent. For example, in this case, since $\Delta_{AB}^2 = 0$, for the centro-symmetric micelle, and

$$(R_G^2)_{LS} = (3/5)\{(xR_A^2 + (1-x)[R_B^5 - R_A^5]/[R_B^3 - R_A^3])\} \quad (62)$$

with the relation discussed above for a sphere of radius R_A coated by a shell of (outer) radius R_B and thickness $\Delta = R_B - R_A$, and $x = w_A\psi_A/[w_A\psi_A + (1 - w_A)\psi_B]$. Since the refractive increments ψ_A and ψ_B may be either negative, positive or zero, as may $(R_G^2)_{LS}$, which consequently does not bear any simple geometric significance. Owing to symmetry, $(R_G^2)_{LS}$ for a sphere with more complex, but spherically symmetric, distribution $\psi(r)$ of refractive index increment and density $\rho(r)$ about the center of mass may be expressed by converting the summations used above in the RGD approximation to integrals:⁽²¹⁾

$$(R_G^2)_{LS} = \int_0^R r^4 \psi(r) \rho(r) dr / \int_0^R r^2 \psi(r) \rho(r) dr \quad (63)$$

For example, the preceding expression results by separating the integrals into two parts, from 0 to R_A , and R_A to R_B .

4.3 Scattering from very large particles

As noted above, for very large spheres, with both $\tilde{n} \gg 1$ and phase shift magnitude $\alpha|\tilde{n} - 1| > 10$, $P_{Vv}(\vartheta, c)$ reduces to the form for Fraunhofer diffraction from a circular aperture (or opaque disk), with the result that an exact integral expression may be written for the inversion of $P_{Vv}(\vartheta, c)$ to obtain the size distribution in terms of the scattered intensities. Thus, in this treatment, use is sometimes made of the expression^(134, 135)

$$L(x_1, x_2) = \int_{x_1}^{x_2} s \{2J_1(s)/s\}^2 ds = J_0^2(x_2) + J_1^2(x_2) - [J_0^2(x_1) + J_1^2(x_1)] \quad (64)$$

In this regard, an apparatus is used with a series of concentric-ring photodiodes, with each photodiodes spanning successive angular increments. Thus, the forward scattering intensity is determined over a set of annular rings in this apparatus, rather than as a function of ϑ , with the function $L(\vartheta_1, \vartheta_2)$ representing the fraction of the intensity incident on a particle scattered between angles ϑ_1 and ϑ_2 . The function $L(0, \vartheta)$ exhibits a series of plateaus for values of ϑ for which $J_1(\alpha\vartheta)/\alpha\vartheta = 0$, the first three of these given by $\alpha\vartheta$ equal to 3.83, 7.02 and 10.17, e.g., see references 13m, 22m, 119 and 139. In practice, the available angular range is adjusted for the set of ring-photodiodes with fixed geometry by using a series of lenses of differing focal length f to manipulate the angular range, with $\vartheta \approx r/f$, where r is the radial position of the light on the photodiode. The maximum angle used should be large enough to encompass essentially all of the scattering, for example to avoid skewing the measurement to the larger components in a polydisperse mixture, a problem called "vignetting" in some of the specialized literature in this area;⁽¹³⁴⁾ however, see below for an example of a related problem if the minimum angle is too large. When applied to the analysis of a polydisperse sample (with $\sin(\vartheta) \approx \vartheta$),^(134, 135)

$$L(\vartheta_1, \vartheta_2) \propto \sum_{\mu} n_{\mu} \alpha_{\mu}^2 \{J_0^2(\alpha_{\mu} \vartheta_2) + J_1^2(\alpha_{\mu} \vartheta_2) - [J_0^2(\alpha_{\mu} \vartheta_1) + J_1^2(\alpha_{\mu} \vartheta_1)]\} \quad (65)$$

where n_{μ} is the number fraction of spheres with radius R_{μ} . In practice, the sum over μ is approximated by a small number of discrete "components", each of these actually representing an average over components in a "size class" determined by the mean radius of the detector ring and the focal length of the lens in use.⁽¹³⁵⁾

As mentioned above, a systematic, consistent discussion of measurements in the Fraunhofer diffraction regime may be found in reference 92 for the representative optics and inversion methods. Instruments collecting the scattered light over a small angular increment at a given ϑ are considered,

along with instruments collecting light from some small angle $\vartheta_{\min}$ through angles up to ϑ ; both types are used in practice. The forms of the integral expressions used in the inversion depend not only on the optical arrangement, but also on the number of times an integration by parts is used to develop the integral equation used, with consequent change in the way data are processed in the inversion. In the ideal case, the accuracy of the inversion would not depend on these factors, but with real data, containing noise, and limited to a range of ϑ by instrument design, these factors usually will affect the outcome. In addition, the method used to present the scattering medium (either as a dispersion in a fluid, or an aerosol) may affect the results. In this analysis, the expression for $\mathbf{R}_{V_V}(\vartheta, c)$ in the Fraunhofer limit is recast as an integral:⁽⁹²⁾

$$\vartheta^a \mathbf{R}_{V_V}(\vartheta, c) \propto \int_0^\infty k_{ab}(\alpha, \vartheta) \alpha^b n(\alpha) d\alpha \quad (66)$$

where $\alpha = 2\pi R/\lambda$, $n(\alpha)$ is the (number) fraction of spheres with radius between R and $R + dR$ (for fixed λ), the factors ϑ^a and ϑ^b account for possible variation of the aperture over which the scattering is collected, and the conversion to distributions in terms of particle volume ($b = 2$) or area ($b = 1$), respectively, and $k_{ab}(\alpha, \vartheta)$ is the appropriate scattering function for the particle. For spheres, (with $\sin(\vartheta) \approx \vartheta$)

$$k_{ab}(\alpha, \vartheta) = J_1^2(\alpha\vartheta)/\vartheta^{2-a} \alpha^{b-2} \quad (67)$$

This expression may then be inverted to obtain $\alpha^b n(\alpha)$ for each α as an integral over ϑ (from 0 to ∞) of a kernel comprising functions of $\alpha\vartheta$ and derivatives of $\vartheta^a \mathbf{R}_{V_V}(\vartheta, c)$. The result may be cast in several forms, depending on a , b , and whether use is made of integration by parts in obtaining the relation used in the inversion. The required range of ϑ is, of course, nonphysical, but as the kernel involved reduces to essentially zero with increasing ϑ , the effect of the nonphysical upper limit on ϑ is usually nil. The inversion of noise-free scattering data over a span in ϑ typical of commercially available photometers is considered in reference 92 for five different arrangements, and a range of particle sizes (mean diameters of 7 to 506 μm) over a certain distribution of sizes given by a log-normal function in the particle area. Several statistical measures of the fit of the inversion to the starting size distribution given by the authors were evaluated to arrive at the following principal conclusions in this idealized comparison: (i) the various methods are essentially equivalent over a relatively narrow range of particle size, but differ markedly for either small or large particles, (ii) none of the methods provide a satisfactory representation

of the distribution for the smaller particles, and (iii) the methods vary considerably in their performance for distribution of larger particles. These results suggest that whereas the response may be reproducible, and therefore of use as a quality control protocol, the absolute distribution should be accepted with caution.

An example of the comparison of the size distribution deduced for some aerosols using an apparatus of the type described above with $L(\vartheta_1, \vartheta_2)$ determined over a set of angles is shown in Figure 10, including results obtained by inversion of $\mathbf{R}_{V_V}(\vartheta, c)$, and by fitting $\mathbf{R}_{V_V}(\vartheta, c)$ with an assumed size distribution.⁽¹³⁶⁾ An example of the effect of the choice of the focal length f of the lens used on the analysis is illustrated in Figure 11 for the scattering from polydisperse glass beads with a size distribution (20–170 μm) calibrated by microscopic measurements on a large sample of the beads (NIST Standard Reference Material 1004).^(134, 137) Data were taken in the Fraunhofer regime ($\tilde{n} \approx 1.146$ and phase shift magnitude $\alpha|\tilde{n} - 1| > 40$) with both 100 and 300 mm focal length lenses. Whereas the latter fitted the reported size distribution well, except for the largest size, the data with the smaller focal length lens did not afford a measurement at small enough ϑ to permit a satisfactory assessment of the population of the larger beads.

As mentioned above, the scattering from large particles immersed in a solvent such that $\tilde{n} \approx 1$ may not be in the Fraunhofer regime, but rather may exhibit anomalous diffraction. The assumption that Fraunhofer diffraction applies may lead to serious error in the size distribution determined from the angular profile of the scattered light. An example of this is given in Figure 11, showing data obtained with the 100 mm focal length lens and dispersions in different liquids to provide two values of $\tilde{n}$ close to unity ($\tilde{n} \approx 1.02$ and 1.08).^(134, 137) The data on $L(\vartheta_1, \vartheta_2)$ exhibit the profound effect of $\tilde{n}$. The expressions for the anomalous scattering regime were used to compute $L(\vartheta_1, \vartheta_2)$ using the size distribution, with the results give to be a reasonable fit to the data for both values of $\tilde{n}$. Further, the data for $\tilde{n} \approx 1.02$ were inverted under two assumptions: the use of the relations for the Fraunhofer and anomalous scattering regimes. Whereas the latter was in reasonable agreement with the result obtained with data in the Fraunhofer regime ($\tilde{n} \approx 1.146$), the use of the expressions for the Fraunhofer regime gave erroneous results, as expected.

4.4 Intermolecular association

Intermolecular association is not uncommon in macromolecular solutions or dispersions of particles, especially in aqueous solvent. In general, two forms may be encountered in the extreme: association involving two or more components at equilibrium at any give concentration; and metastable association,

in which the components present depend on processing history, but do not change sensibly with concentration in the range of interest for light scattering. Of course, intermediate situations may also occur.

Aside from criterion imposed by the anticipated nature of the solute, the experimenter may have little reason to suspect association from the dependence of the scattering on concentration in the case of a metastable association. In some cases of metastable association, the molecular weight deduced from extrapolation of $Kc/R_{vv}(\vartheta, c)$ to zero q and infinite dilution will depend on temperature or solvent, revealing the association. An example of this sort in which the nature of intermolecular association of a solute with a helical conformation was elucidated by the use of static and dynamic light scattering as a function of temperature is given in reference.⁽¹³⁸⁾ In the cited case, the scattering at any given temperature exhibited 'normal' behavior, and could not have been analyzed to reveal association if taken alone. In a different and somewhat unusual, but not unique, example, it has been reported that $Kc/R_{vv}(\vartheta, c)$ is linear in q^2 , albeit giving a molecular weight that is much larger than the true value of M_w for the solute.⁽¹³⁹⁾ This was observed with a system that formed a gel at a higher solute concentration, suggesting that the observed scattering behavior reflects the anticipated $P_{vv}(\vartheta, c)$ for a randomly branched polymer.⁽⁶⁾ More frequently, with intermolecular association involving flexible chain polymers, $Kc/R_{vv}(\vartheta, c)$ exhibits enhanced scattering at small q . This is often taken as evidence for the presence of an aggregated species mixed with solute that is either fully dissociated, or much less aggregated. Although reasonable, it should be realized that such an interpretation is not unique.

A well defined analysis is possible, at least in principle, for a case with equilibria among otherwise monodisperse monomers, dimers, etc., e.g., the equilibria obtaining among monomers, dimers and tetramers for hemoglobin in solution.^(140, 141) Equilibrium association can lead to nonparallel plots of $Kc/R_{vv}(\vartheta, c)$ vs q^2 if the species are large enough. In the ideal situation, the ratio of R_G^2 for the aggregates to the unimer would be precisely known, as would be the effect of association on A_2 , permitting an assessment of the equilibrium constant for the association given a model.⁽¹⁴¹⁾ An illustrative example of the effects of association is given in Figure 12. The example was calculated on the assumption that a monodisperse linear flexible coil chain of molecular weight M may undergo end-to-end dimerization to create a linear chain of molecular weight $2M$, with equilibrium constant K_{eq} . Further, it was assumed that $\partial \ln R_G^2 = \partial \ln M = \epsilon$, and $\partial \ln A_2 = \partial \ln M = \gamma$, with $\epsilon = 2(2 - \gamma)/3$, following the usual approximation for flexible chain polymers.^(20f, 29d, 51) Finally, in addition to the expressions for $M_{LS} = M_w$, $(R_G^2)_{LS} = (R_G^2)_Z$, and $P_{vv}(\vartheta, c)$ given above, $(A_2)_{LS}$ was calculated as^(10, 18)

$$(A_2)_{LS} = \sum_{\mu} \sum_{\nu} w_{\mu} M_{\mu} w_{\nu} M_{\nu} (A_2)_{\mu\nu} / M_w \quad (68)$$

where $(A_2)_{\mu\mu}$ is A_2 for monodisperse component μ , and $(A_2)_{\mu\nu}$ is approximated by $\{(A_2)_{\mu\mu}(A_2)_{\nu\nu}\}^{1/2}$.^(10, 18) With these relations,

$$M_w = M(2 - \zeta) \quad (69)$$

$$(R_G^2)_z = (R_G^2)_M [\zeta + 2^{1+\varepsilon}(1 - \zeta)] / (2 - \zeta) \quad (70)$$

$$P_{Vv}(\vartheta, c) = \{\alpha[P_{Vv}(\vartheta, c)]_M + 2(1 - \zeta)[P_{Vv}(\vartheta, c)]_{2M}\} / (2 - \zeta) \quad (71)$$

$$(A_2)_{LS} M_w = (A_2)_M M \{\zeta + 2^{1+\gamma/2}(1 - \zeta)\}^2 / (2 - \zeta) \quad (72)$$

$$\zeta = (\tilde{K}_{eq} / 2(A_2)_M Mc) \{(1 + 4(A_2)_M Mc / \tilde{K}_{eq})^{1/2} - 1\} \quad (73)$$

where ζ is the degree of association, and $P_{Vv}(\vartheta, c)$ is given by the expression in Table 1, with u replaced by $2^\varepsilon u$ for $[P_{Vv}(\vartheta, c)]_{2M}$. The calculations were completed for $\varepsilon = 7/6$ ($\gamma = 1/4$), over a range of $(A_2)_M Mc$ and $\tilde{K}_{eq} = (A_2)_M M^2 K_{eq}$. It may be noted that for large $\tilde{K}_{eq}$, the extrapolation to obtain the true molecular weight M at infinite dilution ($\zeta = 0$) may not be possible, and the experimenter may erroneously assume that the molecular weight of the polymer at infinite dilution is $2M$. The effect of the association in producing nonparallel $Kc/R_{Vv}(\vartheta, c)$ vs q^2 for data at different concentration is illustrated in Figure 12.

The situation is usually more complex than the idealized equilibrium association, and analysis of such behavior is sometimes facilitated by an approximate representation with a few 'pseudo components' (often two), each of which dominates the scattering over a limited range of q , with M , A_2 and $P_{Vv}(\vartheta, c)$ replaced by their light scattering averages for each pseudo component. That is,

$$R_{Vv}(\vartheta, c) \approx \sum_{\mu} [R_{Vv}(\vartheta, c)]_{\mu} = K \sum_{\mu} \left(\frac{Mc}{P_{Vv}(\vartheta, c)^{-1} + 2A_2 Mc} \right)_{\mu, c} \quad (74)$$

where the subscript "c" indicates that the parameters M and A_2 , and the character of the function $P_{Vv}(\vartheta, c)$ may all depend on c through the dependence of the state of aggregation on c ; note that this form does not properly account for the averaging among scattering elements, but it can provide a useful approximation

if the components are few and widely separated in size. The analysis of the suspected association with this relation is similar to the determination of the size distribution discussed above in the absence of association, but is made more complex as it involves data over a range of c , with concentration dependent parameters, and the function $P_{vv}(\vartheta, c)$ may not be the same, or even known, for all of the aggregates present, and may depend on c . In some of the literature on small-angle x-ray scattering, it has been common to assume that $P_{vv}(\vartheta, c) \approx \exp[-(R_G^2)_{LS} q^2/3]$ for each pseudo component, and frequently to assume that $2A_2c \ll 1$ in an analysis to estimate $(M_w)_\mu w_\mu$ and $[(R_G^2)_{LS}]_\mu$ for the assumed pseudo components, as a function of the overall concentration c .^(24c) Similar treatments are applied with light scattering, often restricted to small enough q that the expansion of $P_{vv}(\vartheta, c)$ may be applied. The advent of dynamic light scattering has allowed some improvement in analyses of this type, since one can apply a similar expression for the dynamic scattering in terms of pseudo components:

$$g^{(1)}(\tau; \vartheta, c) \approx \sum_{\mu} r_{\mu}(\vartheta, c) \exp[-\tau \gamma_{\mu}(\vartheta, c)] \quad (75)$$

where $r_{\mu}(\vartheta, c) = [R_{vv}(\vartheta, c)]_{\mu} / R_{vv}(\vartheta, c)$. Analysis of $g^{(1)}(\tau; \vartheta, c)$ then provides information on $(M_w)_\mu w_\mu$ and a hydrodynamic length $[a_{LS}]_{\mu} = kTq^2/6\pi\eta_s\gamma_{\mu}(\vartheta, c)$ for each component, and some degree of consistency is expected among the estimates for $(M_w)_\mu w_\mu$ obtained in the two experiments. Further, comparison of $[a_{LS}]_{\mu}$ and $[(R_G^2)_{LS}]_{\mu}$ can provide insight on the nature of the component. In some cases, it may be reasonable to estimate $(M_w)_\mu$ for the component with smallest $(M_w)_\mu$ with the assumption that $w_\mu \approx 1$ for that component, i.e., the scattering at small q reflects a small fraction of a large component. An example of a treatment of this kind may be found in reference 146. In some cases, the depolarized scattering can be particularly useful if the association induces order in the aggregated species.^(142, 143)

4.5 Scattering with charged species

In some cases, the polymeric and colloidal scattering species may bear electric charge. Whereas synthetic polyelectrolytes usually bear either anionic or cationic charge, biological macromolecules are often amphoteric, with a chain bearing both positive and negative charges. Electrostatic interactions among the scatterers may have two effects with macromolecules: (i) they may cause an expansion of the chain dimensions of macromolecules by intramolecular interactions, and (ii) they may alter the scattering through the effects of intermolecular interactions. Only the latter effect is relevant with charged particles. In the extreme, these interactions may lead to interactions with a very long coherence length, making it impossible to apply the relations discussed in the preceding.⁽¹⁶⁾ Fortunately, for purposes of size

characterization, the effects of electrostatic interactions on $\mathbf{R}_{Vv}(\vartheta, c)$ and $\mathbf{R}_{Hv}(\vartheta, c)$ may be suppressed, or screened, by the presence of supporting simple electrolyte in the solution, thereby permitting application of the relations presented in the preceding, with one stipulation: the refractive index increment $(\partial n / \partial c)_{\Pi}$ must be determined for the solution in osmotic equilibrium with the solvent containing the supporting electrolyte.^(16, 18) Measurement $(\partial n / \partial c)_{\Pi}$ of can be achieved by equilibrating the solution with the mixed solvent through a membrane of the kind used in measurements of the osmotic pressure. The same procedure must be made with any mixed solvent with components of different refractive index, e.g., a mixed solvent comprising two organic liquids.

The Debye electrostatic length κ^{-1} provides an important measure of the spatial range of electrostatic interactions, with electrostatic interactions suppressed among charged species much further apart than distance κ^{-1} . Here (in the esu system of units, most often employed by physical chemists)

$$\kappa = (8\pi N_A L_B I_0)^{1/2} \quad (76)$$

with $I_0 = \sum z_{\mu}^2 m_{\mu} / 2$ the ionic strength derived from small molecule ions in the solution, m_{μ} being the molar concentration of species μ with charge z_{μ} , and $L_B = e^2 / \epsilon kT$ the Bjerrum length, with ϵ the dielectric constant (relative permittivity) of the solvent and e the charge on an electron. (It should be noted that variations of this expression with a factor $4\pi\epsilon_0$ multiplying ϵ appear if SI units are employed, with ϵ_0 the permittivity of free space). Thus, at 25°C, $L_B / \text{nm} \approx 57 / \epsilon$ and $\kappa^{-1} / \text{nm} \approx (4.57\pi N_A \sum z_{\mu}^2 m_{\mu} / \epsilon)^{-1/2}$, or $L_B \approx 0.7 \text{ nm}$ and $\kappa^{-1} / \text{nm} \approx 0.42 / (\sum \tilde{m}_{\mu} / \text{mol L}^{-1})^{1/2}$ for an aqueous solution of univalent charged simple electrolyte at 25°C. With polyelectrolyte macromolecules, it is often convenient to adjust the supporting electrolyte composition to a level such that κ^{-1} is comparable to the geometric dimensions of a chain element. In that case, the thermodynamic diameter d_{thermo} appearing, for example in expressions for A_2 , will not be dominated by the electrostatic interactions among chains, and the effects of intramolecular electrostatic interactions on the chain dimensions will be largely suppressed.^(16, 32, 51, 144) If this is not done, reliable extrapolation of $Kc / \mathbf{R}(0, c)$ to infinite dilution may be impossible if $\kappa^{-1} > (M / cN_A)^{1/3}$; an example of this effect for a rodlike chain is shown in Figure 13a.⁽¹⁴⁵⁾ A similar effect will obtain with charged particles in solutions, e.g., as is well known, inter-particle electrostatic repulsion among spheres can be strong enough to lead to an ordered mesophase with increasing c if the average separation of the spheres is less than κ^{-1} .⁽¹⁴⁶⁾ In addition, for macromolecules, the chain dimensions may expand with increasing κ^{-1} if $\kappa^{-1} > d_{\text{geo}}$, with d_{geo} the geometric diameter of the chain repeat unit; an example of this is shown in Figure 13b.

It should be realized that an aqueous solution of an organic solute is often close to intermolecular association, and that the addition of salt, and consequent suppression of electrostatic interactions, may induce association. Thus, with amphoteric proteins, it is often found that association will occur if the pH is adjusted to the isoelectric point, a condition for which appreciable numbers of anionic and cationic sites coexist on the chain.⁽¹⁶⁾ For a pH far from the isoelectric point, the amphoteric macromolecule behaves as either an anionic or cationic polyelectrolyte, and the net charge can help stabilize the solution against association.

The effects of electrostatic interactions among charged spheres dispersed in a medium of low ionic strength can lead to a striking effect on $\mathbf{R}_{\text{iso}}(\vartheta, c)/KMc$, resulting from large values of $c\Gamma_{\text{iso}}(c)$ from electrostatic repulsion among the spheres. Thus, in this regime,

$$\mathbf{R}_{\text{iso}}(\vartheta, c)/KMc = \frac{P_{\text{iso}}(\vartheta, c)}{\{1 + c\Gamma_{\text{iso}}(c)P_{\text{iso}}(\vartheta, c)H_{\text{iso}}(\vartheta, c)\}} \approx \{c\Gamma_{\text{iso}}(c)H_{\text{iso}}(\vartheta, c)\}^{-1} \quad (77)$$

where $H_{\text{iso}}(\vartheta, c)^{-1}$ is expected to exhibit a maximum associated with the distance of average closest approach of the spheres, e.g., the expression for $H_{\text{iso}}(\vartheta, c)$ given above for uncharged spheres. Data on several dilute dispersion of charged polystyrene spheres ($R = 45$ nm) are given in Figure 14.⁽¹⁴⁷⁾ Similar results are reported for solutions of polyelectrolytes and for other charged particles.⁽¹⁴⁴⁾ As mentioned above, these curves bear a qualitative similarity to those obtaining for coated spheres under some conditions with the zero average refractive index increment, but their origin is very different, as is their shape in detail. A first-approximation to $H_{\text{iso}}(\vartheta, c)$ might be obtained by using $\sin(\vartheta'/2) \approx (2L_{\kappa}/R)\sin(\vartheta/2)$ in the expression for hard spheres if $L_{\kappa} \gg R$, where L_{κ} is an electrostatic length, expected to be related to κ^{-1} .^(144, 148) This approximation gives far too sharp a maximum, and values of L_{κ} to match the position of the maximum that are far larger than κ^{-1} .⁽¹⁴⁷⁾ In addition to the weakness of the *ad hoc* model, at least a part of this discrepancy may reflect heterogeneity or fluctuation of the charge density, which may broaden the peak.

4.6 Scattering from optically anisotropic solute

Although the (excess) scattering from polymer solutions is usually too small to be of much interest, exceptions can arise for chains with a semiflexible, or rodlike, conformation, and with spheres comprising optically anisotropic scattering elements. It is often assumed that the refractive index tensor of the scattering elements has cylindrical symmetry, with refractive index $n_{\parallel}$ and $n_{\perp}$ parallel and

perpendicular to the cylinder axis, respectively.^(10, 49) For this model, the orientationally averaged refractive index is $\tilde{n}_{\text{solute}} = (n_{\parallel} + 2n_{\perp})/3$, $\psi_{\text{solute}} \approx (\tilde{n}_{\text{solute}} - n_{\text{medium}})/\rho_{\text{solute}}$, and $\gamma_{\text{solute}} \approx (n_{\parallel} - n_{\perp})/\rho_{\text{solute}}$, with ρ_{solute} the density of the solute, If $\psi_{\text{solute}} \neq 0$, it is convenient to define the optical anisotropy of the scattering element as $\delta_0 = \gamma_{\text{solute}}/\psi_{\text{solute}}$.

A macromolecular model of interest is that of the persistent, or wormlike chain of contour length L and persistence length $\hat{a}$, with a cylindrical polarizability tensor for the scattering elements, each having an optical anisotropy δ_0 . For this model, the mean-squared molecular anisotropy form factor is given by^(10, 40, 41, 48)

$$(\delta/\delta_0)^2 = (2/3Z)\{1 - (3Z)^{-1}[1 - \exp(-3Z)]\} \quad (78)$$

with $Z = L/\hat{a}$; the corresponding expression for R_G^2 is given in Table 1. In the limit with $\hat{a} \ll L$, as with a flexible chain polymer (e.g., vinyl polymers and most condensation polymers), $(\delta/\delta_0)^2$ tends to proportionality with $\hat{a}/L = \hat{a}M_L/M$, with M_L the mass per unit chain contour length. As a consequence $\mathbf{R}_{\text{Hv}}(0,c)$ is proportional to the molecular weight of a chain element of length $\hat{a} \ll L$, and is much smaller than $\mathbf{R}_{\text{Vv}}(0,c)$ for such chains, and may be neglected in consideration of $\mathbf{R}_{\text{Vv}}(0,c)$. In the opposite extreme with $L \ll \hat{a}$, as for a rodlike chain, $\delta \approx \delta_0$, and the anisotropic scattering must be taken into account to determine M_w from $\mathbf{R}_{\text{Vv}}(0,c)$. For chains with an overall rodlike character arising from helical structure, δ_0 may be so small that the anisotropic scattering may still be ignored in determination of M_w from $\mathbf{R}_{\text{Vv}}(0,c)$. Nevertheless, $\mathbf{R}_{\text{Hv}}(0,c)$ may be of interest itself to evaluate δ^2 for use in an estimation of the persistence length. An example of comparison of δ^2 as a function of L used to estimate δ_0^2 and $\hat{a}$ for a rodlike polymer is given in Figure 15.

As mentioned above, $P_{\text{Hv}}(\vartheta, \pi/4, 0)$ exhibits extrema as a function of qR for monodisperse spheres, For calculations in the RGD regime⁽⁷²⁾ and in the anomalous diffraction approximation⁽⁷⁰⁾, the values of qR for these first maxima and following minima may be used to estimate R . In addition, the effects on the scattering pattern of the distortion of the anisotropic sphere, as might occur under a deformation, have been studied, e.g., see the discussion and literature citations in reference 154.

5. FREQUENTLY USED NOTATION

$\hat{a}$	Persistence length for semiflexible chains.
A_2, A_3	The second virial coefficient, the third virial coefficient, etc.; see Equation 8.
$b(c)$	A correlation length obtained from the dependence of $\mathbf{R}_{V_V}(\vartheta)$ on ϑ ; see Equation 55.
c, c_μ	The solute concentration (wt/vol); concentration of solute component μ .
$F_{iso}(\vartheta, c)$	The intermolecular structure factor $\mathbf{R}_{iso}(\vartheta, c)/KcMP_{iso}(\vartheta, c)$; see Equation 4.
$g^{(1)}(\tau; \vartheta, c)$	The normalized electric field autocorrelation function, $g^{(1)}(\tau; \vartheta)$; see Equation 44.
$H_{iso}(\vartheta, c)$	The function $\{F_{iso}(\vartheta, c)^{-1} - 1\}/c\Gamma_{iso}(c)P_{iso}(\vartheta, c)$; see Equation 6.
k	Boltzmann's constant.
K	An optical constant relating intensities to the Rayleigh ratio.
L	Chain contour length.
LS	A subscript to indicate the average of a function or parameter obtained in light scattering.
M	Molecular weight.
M_L	The mass per unit length, M/L .
n_μ	Number fraction of solute component μ .
n_{medium}	Refractive index of the medium.
n_{solute}	Refractive index of the solute.
$\tilde{n}$	The ratio n_{solute}/n_{medium} .
N_A	Avagadro's constant.
$P_{iso}(\vartheta, c)$	The intramolecular structure factor; see Equation 4.
$P_{H_V}(\vartheta, c)$	The intramolecular structure factor for the horizontally polarized component of the scattering with vertically polarized incident light.
$P_{V_V}(\vartheta, c)$	The intramolecular structure factor for the vertically polarized component of the scattering with vertically polarized incident light.
q	The wave vector, with modulus $q = (4\pi/\lambda)\sin(\vartheta/2)$ for an isotropic medium.
$\mathbf{R}(\vartheta, c)$	The excess Rayleigh ratio.
$\mathbf{R}_{aniso}(\vartheta, c)$	The anisotropic component of $\mathbf{R}(\vartheta, c)$.
$\mathbf{R}_{iso}(\vartheta, c)$	The isotropic component of $\mathbf{R}(\vartheta, c)$.
$\mathbf{R}_{H_V}(\vartheta, c)$	The horizontally polarized component of $\mathbf{R}(\vartheta, c)$ for vertically polarized incident light.
$\mathbf{R}_{V_V}(\vartheta, c)$	The vertically polarized component of $\mathbf{R}(\vartheta, c)$ for vertically polarized incident light.
R_G^2	Mean-square radius of gyration.
R_H	Hydrodynamic radius, defined as $kT/6\pi\eta_s D_T$, with D_T the translational diffusion constant and η_s the solvent viscosity.
$S_{iso}(\vartheta, c)$	The total structure factor $\mathbf{R}_{iso}(\vartheta, c)/KcM$; see Equation 7.
w, w_μ	The solute weight fraction; weight fraction of solute component μ .

α	The parameter $2\pi R/\lambda$ for spheres of radius R .
$\Gamma_{\text{iso}}(c)$	The function $\{F_{\text{iso}}(0,c)^{-1} - 1\}/c$; see Equation 6.
δ^2	Mean-square molecular optical anisotropy; see Equation 9.
δ_o	The optical anisotropy of a scattering element with molecular weight m_o .
ϑ	The scattering angle.
λ	The wavelength of light in the scattering medium; λ_o the same <i>in vacuo</i> .
ν	The number concentration of the solute, equal to cN_A/M_n .
ρ	The density (wt/vol).
Ψ_{solute}	The contrast factor for optically isotropic solute.
Ψ_{μ}	The contrast factor for component μ for optically isotropic media.

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Table 1
Intramolecular Structure Factor for Several Models^(a)
(Rayleigh-Gans-Debye Approximation)

Model	$R_G^{2(b)}$		$P_{Vv}(\vartheta, 0)$
random-flight linear coil	$\hat{a}L/3$	$u = \hat{a}Lq^2/3$	$p_c(u) = (2/u^2)[u - 1 + \exp(-u)]$
persistent (wormlike) linear chain ^(c)	$(\hat{a}L/3)S(\hat{a}/L)$	$v = u\hat{a}/L$	$\exp(v)\sum_{i=0}^{\infty}(-v/i!)^{-1}p_c[(v+i)L/\hat{a}]$
disk ("infinitely thin") ^(d)	$R^2/2$	$y = Rq$	$(2/y^2)[1 - J_1(2y)/y]$
sphere	$3R^2/5$	$y = Rq$	$(9/y^6)[\sin(y) - y\cos(y)]^2$
shell ("infinitely thin")	R	$y = Rq$	$[\sin(y)/y]^2$
rod ("infinitely thin") ^(e)	$L^2/12$	$x = Lq$	$p_1(x) = (2/x^2)[x\text{Si}(x) - 1 + \cos(x)]$

- 5 With one exception, the original citations for the entries for $P_{Vv}(\vartheta, 0)$, along with expressions for a number of additional models may be found in reference 21h. All functions are for full orientational averaging.
- 6 $\hat{a}$ is the persistence length; $L = M/M_L$ is the chain contour length (mass per unit length M_L); R is the radius for a disk or shell.
- 7 $S(Z) = 1 - 3Z + 6Z^2 - 6Z^3[1 - \exp(-Z^{-1})] \approx (1 + 4Z)^{-1}$; the expression for $P_{Vv}(\vartheta, 0)$ is limited to $\hat{a}/L < 0.1$; a more complete representation may be found in reference 52.
- 8 $J_1(\dots)$ is the Bessel function of 1st order and kind.
- 9 $\text{Si}(x) = \int_0^x ds\{\sin(s)/s\}$ is the sine integral For rods with optically anisotropic elements:^(10, 18, 41)
- $$(1 + 4\delta^2/5)P_{Vv}(\vartheta, 0) = p_1(x) + \delta^2\{(4/5)p_3(x) - (2 - \delta^{-1})m_1(x) + (9/8)m_2(x) + m_3(x)\}$$
- $$P_{Hv}(\vartheta, 0) = p_3(x) + (5/8)\sin^2(\vartheta/2)m_2(x)$$
- $$p_2(x) = (6/x^3)[x - \sin(x)]$$
- $$p_3(x) = (10/x^5)[x^3 + 3x\cos(x) - 3\sin(x)]$$
- $$m_1 = p_1 - p_2$$
- $$m_2 = 3p_1 - p_2 - 2p_3$$
- $$m_3 = p_3 - p_2$$

Table 2

**Light Scattering Average
Mean-Square Radius of Gyration and Hydrodynamic Radius
(Rayleigh-Gans-Debye Approximation)**

	$(R_G^2)_{LS}$	$(R_H)_{LS}$
Exact Relation ^(a)	$(1/M_w) \sum w_\mu M_\mu (R_G^2)_\mu$	$M_w / \sum w_\mu M_\mu (R_H^{-1})_\mu$
Approximation for ^(b) $R_H \propto R_G \propto M^{\varepsilon/2}$	$(R_G^2/M^\varepsilon) M_{(\varepsilon+1)}^{\varepsilon+1}/M_w$	$(R_H/M^{\varepsilon/2}) M_w/M_{(1-\varepsilon/2)}^{1-\varepsilon/2}$
Random-flight coil ^(c) ; $\varepsilon = 1$	$(R_G^2/M) M_z$	$(R_H/M^{1/2}) M_w/M_{(1/2)}^{1/2}$ $\approx (R_H/M^{1/2}) M_w^{1/2} (M_w/M_n)^{0.10}$
Rodlike chain ^(c) ; $\varepsilon \approx 2$	$(R_G^2/M^2) M_z M_{z+1}$	$(R_H/M) M_w$
Sphere ^(c) ; $\varepsilon = 2/3$	$(R_G^2/M^{2/3}) M_{(5/3)}^{5/3}/M_w$ $\approx (R_G^2/M^{2/3}) M_z^{2/3} (M_w/M_z)^{0.10}$	$(R_H/M^{1/3}) M_w/M_{(2/3)}^{2/3}$ $\approx (R_H/M^{1/3}) M_w^{1/3} (M_w/M_n)^{0.10}$

(a) For optically isotropic solute, and with $\partial n/\partial c$ the same for all scattering elements

(b) $M_{(\alpha)} = \left(\sum w_\mu M_\mu^\alpha \right)^{1/\alpha}$ and $M_n = 1/\sum w_\mu M_\mu^{-1}$; $M_w = \sum w_\mu M_\mu$; $M_z = \sum w_\mu M_\mu^2 / \sum w_\mu M_\mu$

(c) Approximations are for a solute with a Schulz-Zimm (two-parameter exponential) distribution of M , for which $M_{(\alpha)} \approx M_w \{ \Gamma(1+h+\alpha) / \Gamma(1+h) \}^{1/\alpha} / (1+h)$, see reference 42.

Figure Captions

- Figure 1 The ratio $M_{LS}/M (= m_{sph}(\tilde{n}, \alpha)^2)$ of the light scattering averaged molecular weight M_{LS} for monodisperse spheres of radius R to the molecular weight M as a function of the relative refractive index $\tilde{n}$ for the indicated values of the size parameter $\alpha = 2\pi R/\lambda$. The dashed lines give the limiting behavior for small $\tilde{n} - 1$ (see Equation (15)).
- Figure 2 The ratio $(R_G^2)_{LS}/(3R^2/5) (= y_{sph}(\tilde{n}, \alpha))$ of the light scattering averaged mean square radius of gyration $(R_G^2)_{LS}$ for monodisperse spheres of radius R to the geometric square radius of gyration as a function of (a) the size parameter $\alpha = 2\pi R/\lambda$ for the indicated values of the relative refractive index $\tilde{n}$, and (b) the relative refractive index $\tilde{n}$ for the indicated values of the size parameter $\alpha = 2\pi R/\lambda$.
- Figure 3 Examples of $P_{VV}(\vartheta, 0)^{-1}$ versus $q^2 R_G^2$ for monodisperse model structures (see Table 1):
 (a) rodlike chains (R), random-flight linear chains (C), disks (D), spheres (S), shells (Sh) and the exponential function $\exp(-q^2 R_G^2/3)$ (E), included for comparison;
 (b) the persistent or wormlike chain, for the indicated values of the ratio of the persistence length $\hat{a}$ to the contour length L .
- Figure 4 Examples of $P_{VV}(\vartheta, 0)^{-1}$ versus $q^2 (R_G^2)_{LS}$ for model structures with a weight distribution given by the two-parameter Zimm-Schulz distribution function, with $h = 1/[(M_w/M_n) - 1]$ per the discussion in the text, for random-flight linear chains (a) and spheres (b), for the indicated values of h , with h decreasing from top to bottom in each set of curves (the uppermost curve for the monodisperse case is bold in each set). The dashed line in (b) is the initial tangent.
- Figure 5 Examples of $[P_{VV}(\vartheta, 0)]_{BR}$ vs. $q^2 R_G^2$ for comb-shaped branched chain polymers divided by $[P_{VV}(\vartheta, 0)]_{LIN}$ for linear chains with the same R_G^2 (not the same molecular weight). The number of branches is indicated, along with the fraction ϕ of mass in the backbone of the branched chain. From reference 53.
- Figure 6 Examples of $P_{VV}(\vartheta, 0)$ vs. $q^2 (R_G^2)_{LS}$ for spheres with size parameter $\alpha = 2\pi R/\lambda = 4$ for the indicated values of the relative refractive index $\tilde{n}$. The angular range is 0 to 180 degrees in all cases except for $\tilde{n} = 2$. The RGD limiting case for very small $\tilde{n} - 1$ is given by the dashed curve. The dashed line gives the initial tangent. Values of $(R_G^2)_{LS}/(3R^2/5)$ may be seen for this α in Figure 2.

Figure 7 An example of the use of multi-angle light scattering as an SEC detector in the analysis of poly(di-*n*-hexylsilane), PDHS, and poly(phenyl-*n*--hexylsilane), PPHS.

- (a) M_w and $(R_G^2)_{LS}$ resulting from analysis of the multi-angle scattering data;
- (b) The response from the differential refractive index, normalized to give the same peak response.

From reference 1.

Figure 8 An example of the use of multi-angle light scattering as an SEC detector in the analysis of randomly branched poly(methyl methacrylate), PMMA.

- (a) M_w and $(R_G^2)_{LS}/M_w$ for the eluent for heterodisperse linear (●) and branched polymers (○) resulting from analysis of the multi-angle scattering data, with the dashed line and solid curves giving power law and polynomial extrapolations, as discussed in the text;
- (b) The ratio $[(R_G^2)_{LS}]_{BR}/[(R_G^2)_{LS}]_{LIN}$ from the data in part (a), using the powerlaw (○) and polynomial (●) extrapolations to estimate $[(R_G^2)_{LS}]_{LIN}$.

Adapted from figures in reference 132.

Figure 9 An example of the scattering from an aqueous dispersion of heterodisperse hollow polystyrene spheres.

- (a) the scattering function and fits thereto using the RGD approximation and the Mie theory;
- (b) the number fraction distribution of particles with a give size deduced from the inversion of the scattering function using the RGD approximation and the Mie theory; an estimate determined from analysis of the dynamic light scattering is included for comparison.

From figures in reference 107.

Figure 10 An example of the scattering from an heterodisperse aerosol.

- (a) the scattering function (solid curve) and fits thereto using the Fraunhofer diffraction approximation and an assumed size distribution function;
- (b) the weight fraction distribution of particles with a give size deduced from the inversion of the scattering function using the Fraunhofer diffraction approximation (solid curve) and the function used in part (a) (dashed curve) Adapted from figures in reference 140.

Figure 11 An example of the scattering from heterodisperse glass particles dispersed in different solvents to span a range of $\tilde{n}$.

- (a) the scattering function (points and solid curve) obtained using a lens with a 100 mm focal length and solvents to give the indicated $|\tilde{n} - 1|$, and fits thereto using the Mie theory and the known size distribution function (dashed curves);
- (b) the cumulative weight distribution of particles with a give size deduced by several methods: filled squares, from microscopic measurements (the "known" distribution function), as reported by NIST (see text), unfilled squares and diamonds, from inversion of inversion of the scattering function using the Mie theory for $|\tilde{n} - 1| \approx 0.15$ and two lenses, with focal lengths 300 mm (squares) and 100 mm (diamonds), and circles, for solvents to give $|\tilde{n} - 1| \approx 0.02$ calculated with the assumption of Fraunhofer diffraction (filled and dashed line) or anomalous diffraction (unfilled and solid line) Adapted from figures in reference 141.

Figure 12 Scattering functions for an illustrative example of a flexible chain polymer undergoing end-to-end dimerization.

- (a) dependence on angle, calculated as discussed in the text for a reduced equilibrium constant $\tilde{K}_{eq} = 0.1$ and the indicated values of $(A_2)_M Mc$, with the constant equal to zero or 0.2 for the solid and dashed curves, respectively;
- (b) scattering extrapolated to zero angle as a function of $(A_2)_M Mc$, for the indicated values of $\tilde{K}_{eq}$.

Figure 13 Scattering from a semi-flexible polyelectrolyte chain in solvents with low and high ionic strengths (unfilled and filled circles, respectively).

Adapted from figures in reference 150.

Figure 14 The dependence of the structure factor on qR for polystyrene spheres ($R = 45$ nm) immersed in deionized water, with the number concentration $v/\text{particles} \cdot \mu\text{m}^{-3} = 2.53, 5.06, 7.59$ and 10.12 for the circles with increasing depth of the shading, respectively.

Adapted from figures in reference 152.

Figure 15 The dependence of $(R_G^2)_{LS}$ and $(\delta/\delta_0)_{LS}^2$ on the ratio of the weight average contour length to the persistence length for rodlike molecules with a distribution of contour lengths. Adapted from figures in reference 10.