Quasi-elastic light scattering: separability of effects of polydispersity and internal modes of motion

Walter Burchard
Institute of Macromolecular Chemistry, University of Freiburg, West Germany
(Received 8 August 1978; revised 29 December 1978)

The influence of a size distribution on the angular dependence of the quasielastically scattered light is studied for (i) large hard spherical particles and (ii) large flexible chain molecules. For the spherical particles the angular dependence is shown to depend solely on the size distribution and the particle scattering factor. Combination of conventional elastic light scattering with quasielastic light scattering allows the determination of the z-average radii moments $\overline{r_z^n}$ ($n = -1, 1, 2, \ldots$) which define the size distribution. Flexible chains – linear and branched ones – show in any case a linear dependence of the apparent diffusion constant $D_{app} = \Gamma/q^2$ on $q = (4\pi/\lambda)\sin\theta/2$, when q becomes large. This behaviour represents the flexibility of the spring-bead model with strong hydrodynamic interaction. The initial part on the other hand form a straight line when D_{app} is plotted against q^2. The intercept of this straight line is the z-average diffusion constant while the slope is proportional to the z-average mean square radius of gyration. Thus, the polydispersity can be estimated from D_z and $\langle S^2\rangle_z$ while the asymptote at large q-values is determined by the internal flexibility of the molecule.

INTRODUCTION

The line width broadening of scattered light from large Brownian particles in solution or the corresponding time correlation function is influenced by a number of different types of motion. There are three main sources (1) irregular translational motions of the centre of mass (slow), (2) irregular rotations of geometrically anisotropic particles around the centre of mass, (fast); and (3) internal modes of motion of sections of a flexible particle, (spectrum of slow to very fast motions). Each of these modes shows a single exponential decay such that the total correlation function is[1–8]

$$g_1(t) = \sum_j e^{-\Gamma_j t} \tag{1}$$

In this equation $g_1(t)$ is the normalized electric field correlation function

$$g_1(t) = \frac{\langle E(0)E^*(t)\rangle}{\langle |E(0)^2|\rangle} \tag{2}$$

which is related to the scattering intensity correlation function $G_2(t)$ that can be measured by means of special fast computers[5,6,8,9]

$$G_2(t) = \langle i(0)i(t)\rangle = A + B\,|g_1(t)^2| \tag{3}$$

$i(t)$ is the scattering intensity at time t and A and B are constants.

The problem in an actual system is even more complex than described by equation (1) since most of the Brownian particles show a certain size distribution. Thus, the correlation function is actually an average of the kind

$$g_1(t) = \frac{\sum_N \sum_j w_N M_N P_N(q)\,e^{-\Gamma_{jN} t}}{\sum_N w_N M_N P_N(q)} \tag{4}$$

Here w_N is the weight fraction of a particle of molecular weight M_N and N is a labelling index which in the case of a macromolecule is just the degree of polymerization. $P(q)$ is the particle scattering factor (static correlation function in space, or static structure factor) and q is the scattering vector

$$q = (4\pi/\lambda)\sin\theta/2 \tag{5}$$

with λ the wavelength of the light in the medium and θ the scattering angle.

The different modes of motion and the polydispersity appear in equation (4) to be closely mixed up, and the question arises whether the two effects can be separated by the choice of appropriate measurements. The purpose of the present paper is to show that under certain circumstances (hard spherical particles) the distribution function can in fact be determined from the combination of quasi-elastic with integrated (conventional) light scattering. In other cases (flexible chain molecules, linear or branched) the effects of internal modes and of polydispersity turn out to be well separated in the region of large q-values. The derived equations have not yet been checked experimentally, and the paper is meant mainly as a suggestion to experimentalists

0032–3861/79/050577–05$02.00

to plan their experiments such that the integrated and quasi-elastically scattered light can be recorded simultaneously.

HARD SPHERES

Shape of the correlation function

Because of the rigidity and the symmetry of hard spheres there is no effect of internal modes of motion and of the particle rotation. The correlation function has been solved rigorously[4,6]

$$g_1(t) = \frac{\Sigma w_N M_N P_N(q) e^{-D_N q^2 t}}{\Sigma w_N M_N P_N(q)} \qquad (6)$$

where D_N is the translational diffusion coefficient of spheres with molecular weight M_N. The validity of equation (6) has been checked experimentally by mixtures of two sizes of latex particles[10,11]. In this case the correlation function is composed of two exponentials, and the two decay constants $\Gamma_1 = D_1 q^2$ and $\Gamma_2 = D_2 q^2$ can in favourable cases be well determined by a fit of the experimental correlation function. For a distribution function this procedure is no longer feasible and instead of this it is more sound to consider the approximation[12,13]

$$g_1(t) \simeq e^{-\bar{\Gamma} t}(1 + \mu_2 t^2/2 \ldots) \qquad (7)$$

where the initial decay constant $\bar{\Gamma}$ and μ_2 are related to the first two cumulants defined by Koppel. For the first cumulant one finds from equation (6)

$$\bar{\Gamma} = q^2 \frac{\Sigma w_N M_N P_N(q) D_N}{\Sigma w_N M_N P_N(q)} \qquad (8)$$

At $q \to 0$ the particle scattering factors of the individual spheres become 1, and in that limit one has[14-22]

$$\left(\frac{\bar{\Gamma}}{q^2}\right)_{q \to 0} = \frac{\Sigma w_N M_N D_N}{\Sigma w_N M_N} = D_z \qquad (9)$$

which is the definition of the z-average of the translational diffusion coefficient. In general, however, $\bar{\Gamma}/q^2$ depends on the scattering angle and will be called, therefore, an apparent diffusion coefficient

$$\Gamma/q^2 \equiv D_{app}(q) = D_z \cdot f(q) \qquad (10)$$

The function $f(q)$ depends on the particle scattering factors of the individual particles and on the polydispersity. For monodisperse samples the sum in equation (8) consists of one term only and $P(q)$ cancels; Γ/q^2 is independent of q and now equals the translational diffusion coefficient D.

Recently Aragon and Pecora have calculated the correlation function $g_1(t)$ for compact and for hollow spheres which have a Schulz–Zimm distribution in size[23-25]. They found that the initial slope at a fixed angle is diminished as the polydispersity increases if $\log g_1(t)$ is plotted against $\bar{D}q^2 t$, where $\bar{D} = D_n$ is the number average of the translational diffusion coefficient. This behaviour is not in contradiction to equation (9) as the decay constant is actually $D_z q^2 t$ and not $D_n q^2 t$ (see equation (9)), and quite generally the inequality holds (see appendix)

$$D_z \leqslant D_w \leqslant D_n \qquad (11)$$

(The subscript n denotes the number average and should not be confused with the subscript N which is a labelling index in sums). The initial decay would not change by the use of D_z.

More relevant is the question to what extent the share of the correlation function is changed by a size distribution: Pecora[23] compared the exact correlation function with a least square single exponential fit. Significant deviations were found if $g_1(t)$ has decayed below 15% of its initial value. This means that polydispersity can be determined from the analysis of the experimental correlation function if the base line A in equation (3) can be measured sufficiently well. Since the intensity correlation function $G_2(t)$ is proportional to $|g_1(t)^2|$ a value of $g_1(t) = 0.15$ corresponds to a difference of $G_2(t) - A = 0.022$. This example clearly demonstrates that the base line should be measurable to an accuracy of at least 0.5% before quantitative conclusions can be drawn on the polydispersity. A much stronger deviation from a single exponential occurs, however, for the logarithmic normal distribution. (The properties of the Schulz–Zimm and the logarithmic normal distributions are given in the consecutive paper[26]). Still the limitation of applying Koppel's cumulants is clearly stressed by Pecora's calculation[23].

Angular dependence of the apparent diffusion coefficient

For small particles, i.e. if $\langle S^2 \rangle < (\lambda/20)^2$, the analysis of $g_1(t)$ is certainly the only possibility for an estimation of the polydispersity of the system. For larger particles, however, the angular dependence of the apparent diffusion coefficient gives far more detailed information on the polydispersity than the shape of the correlation function. This information on the polydispersity and on the type of the size distribution can be extracted from D_{app} as follows. A slight rearrangement of equation (8) gives

$$\bar{\Gamma}/q^2 = \frac{(\Sigma w_N M_N P_N(q) D_N)/(\Sigma w_N M_N)}{(\Sigma w_N M_N P_N(q))/(\Sigma w_N M_N} =$$

$$\frac{1}{P_z(q)} \frac{\Sigma w_N M_N P_N(q) D_N}{\Sigma w_N M_N} \qquad (12)$$

or

$$D_{app}(q) P_z(q) = \frac{\Sigma w_N M_N P_N(q) D_N}{\Sigma w_N M_N} = (DP(q))_z \qquad (12')$$

where $P_z(q)$ is the z-average of the particle scattering factor which is observed experimentally in conventional integrated light scattering. Now, the particle scattering factors of the individual particles $P_N(q)$ may be expanded in a power series in terms of q^2.

$$P_N(q) = 1 - a_1 r_N^2 q^2 + a_2 r_N^4 q^4 - a_3 r_N^6 q^6 + \ldots \qquad (13)$$

The first coefficients a_i are for *compact spheres*[27] $a_1 = 1/5$, $a_2 = 3/175$ and for *hollow spheres*[28,29] $a_1 = 1/3$, $a_2 = 2/45$, $a_3 = 1/415$.

According to Einstein and Stokes the diffusion coefficient is related to the sphere radius r_N

$$D_N = kT/(6\pi\eta_0 r_N) = A/r_N \qquad (14)$$

Insertion of the last two equations into equation (12′) gives

$$D_{app}(q)\,P_z(q) = A\,[(r^{-1})_z - a_1 r_z q^2 + a_2(r^3)_z q^4 - a_3(r^5)_z q^6 + \ldots] \tag{15}$$

Similarly the power expansion of $P_z(q)$ yields

$$P_z(q) = 1 - a_1(r^2)_z q^2 + a_2(r^4)_z q^4 - a_3(r^6)_z q^6 + . \tag{16}$$

where

$$(r^k)_z = \frac{\sum\limits_N w_N M_N \nu_N^k}{\sum\limits_N w_N M_N} \tag{17}$$

Since $D_{app}(q)$ can be measured by means of quasi-elastic scattering and $P_z(q)$ by conventional integrated scattering the even moments of $(r^k)_z$ can be determined from a fit of the angular dependence of the integrated scattered light while the odd moments can be determined from the product of quasi-elastic and integrated scattering curves: $D_{app}(q)P_z(q)$.

The full set of moments contains in principle all information on the size distribution, but in actual measurements only the first few members can be determined to a sufficient accuracy. Still the type of the size distribution and its width can be determined within certain limits if only the first three moments are known. This is shown in the consecutive paper[26].

FLEXIBLE CHAINS

Randomly coiled linear or branched chains have approximately spherical shape but also considerable internal flexibility which has now an effect on the line width in addition to the polydispersity. In the pioneering work by Pecora[2,3] the effect of the first two modes of motion on the correlation function was calculated on the basis of the spring-bead model neglecting hydrodynamic interactions between the beads (Rouse model). A complete solution enclosing the effect from all modes of motion was not possible. Büldt[30] on the other hand could evaluate the corresponding sum for the initial decay constant and he obtained the surprisingly simple result for the Rouse case.

$$D_{app}(q) = \Gamma/q^2 = D/P(q) \tag{18}$$

In dilute polymer solutions, however, the hydrodynamic interaction is strong and plays the predominant role, and instead of equation (18) a more complicated function arises for the angular dependence of D_{app}, which depends on the type of the molecular structure and the size distribution. Calculation of D_{app} has become possible recently by the application of the projection operator technique[31] in combination with cascade theory[32,33]. The angular dependence has been calculated for monodisperse and polydisperse linear chains[32] as well as for two types of branched polymers[33] which differ significantly in the width of their molecular weight distributions.

In spite of the vast differences in the molecule architecture and the molecular weight distribution some common features are observed. For *small* values of the scattering vector q one finds

$$D_{app}(q) \rightarrow D_z(1 + c_1\langle S^2\rangle_z q^2 - \ldots) \tag{19}$$

while for *large* q-values one has

$$D_{app}(q) \rightarrow c_2 D_z \langle S^2\rangle_z^{1/2} \cdot q = c_3 \frac{kt}{\eta_0}\, q^t \tag{20}$$

where

$$c_2 = c_1^{1/2} \tag{2}$$

Hence, a plot of D_{app} against q^2 gives in any case an initial linear increase which is proportional to the mean square radius of gyration. The coefficients c_1 depend on the molecular architecture and are 1/6 for linear chains and f-functional random polycondensates, and 1/12 for a branched molecule formed under restrictions[33]. The second equality in equation (20) results from the fact that D_z is proportional to $\langle S^2\rangle_z^{-1/2}$, where the proportionality factors depend on the polydispersity. Thus, the coefficients c_3 depend on both the molecular architecture and polydispersity. The coefficients are for the f-functional random polycondensates $c_3 = 0.053$, for the under restriction branched molecule $c_3 = 0.025$ and for linear chains $c_3 = 0.0462\,K(m)$ where

$$K(m) = 0.08\frac{m + 1.868}{m + 1.5} \tag{22}$$

The polydispersity parameter m is related to the weight and number average degree of polymerization

$$m = (P_w/P_n - 1)^{-1} \tag{23}$$

The simple q-dependence of D_{app} at large q-values was first derived by Dubois–Violette and de Gennes[34], and the fact that this asymptotic behaviour is obtained for all flexible molecules is obviously the result of the internal flexibility of Gaussian chains in the presence of hydrodynamic interactions. In other words this asymptotic behaviour represents the effect of internal modes of motion. The effect of branching and polydispersity is condensed in the slope which is the product of $D_z\langle S^2\rangle_z^{1/2}$ and a numerical factor which depends on the type of branching. The latter in turn can be determined from the initial slope of $D_{app}(q)$ against q^2. Hence, the two effects of polydispersity and of internal motions are separable in this simplest case of ideal flexibility. Note that the effect of excluded volume is not included in equations (19)–(22).

Information on the type of branching can be obtained when the quasi-elastic light scattering measurements are combined with the common integrated light scattering. As shown in a previous paper[32,33] a plot of D_{app} against $1/P_z(q)$ on a double logarithmic scale should give a straight line with a slope which is expected to lie in between 1/2 for randomly branched polymers and 1/4 for non randomly branched chains. *Figure 1* shows as an example such a plot for amylopectin where a slope of 0.39 is observed[35].

CONCLUSIONS

The question of separability of the two effects of polydispersity and internal modes of motion can now be answered

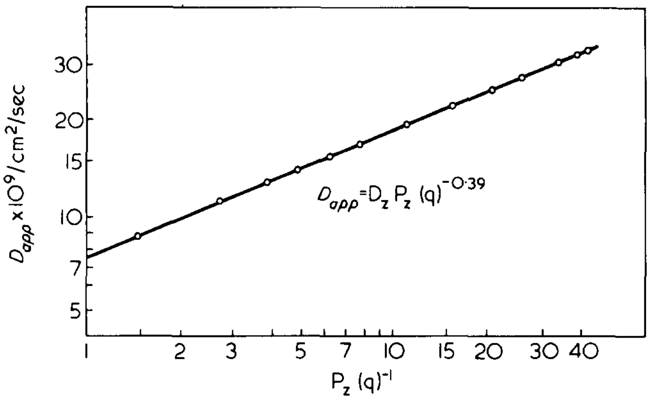

Figure 1 Plot of the apparent diffusion coefficient D_{app} obtained by quasi-elastic light scattering against the reciprocal particle scattering factor $P_z(q)^{-1}$ obtained by conventional integrated light scattering for Amylopectin β-limit dextrin in 1 N NaOH aqueous solution at 25° centrigades. $D_z = 7.4 \times 10^{-9}$ cm^{2}sec, $M_w = 500 \times 10^6$, $\langle S^2\rangle_z = 24. \times 10^4$ nm^2. The curve corresponds to measurements extrapolated to zero concentration. $D_{app} = D_z P_z(q)^{-0.39}$

for hard spheres and for flexible chain molecules. The polydispersity can for large Brownian particles at least be estimated if the shape of the individual particles is known. To this end, however, quasi-elastic and conventional light scattering should be combined, and for reasons of keeping the systematic errors low these measurements should be performed by the same instrument. Such simultaneous measurements are in principle feasible with the photo-counting technique although not yet possible with the commercially available instruments.

For *hard spheres* a non-linear least square fit of $P_z(q)$ and of $D_{app}(q)P_z(q)$ will give the moments $\langle r^k\rangle_z$, for $k = -1, 1, 2, \ldots$ which in turn will allow the reconstruction of the size distribution. For *flexible chains* the two moments $\langle 1/R_s\rangle_z$ and $\langle S^2\rangle_z$ can be obtained only because the asymptotic behaviour is here determined by the internal flexibility. For hard spheres the asymptotic region is determined by the higher moments. The Stokes radius R_s is given by the formal equation

$$D = kT/(6\pi\eta_0 R_s) \qquad (23)$$

Although these firm statements can be made only for the two limiting cases of hard spheres and ideal flexible chains it is tempting to speculate on the behaviour of fairly soft spheres. Probably the initial part at low q-values will be defined by the particle polydispersity but the range of larger q-values will reflect the influence of the internal mobility, because these modes comprise only parts of the molecule, and smaller dimensions correspond to larger q-values.

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APPENDIX

The number-(n), weight-(w) and z-averages of the diffusion constant are defined as

$$D_n \equiv \frac{\Sigma f_N D_N}{\Sigma f_N} \qquad (A1)$$

$$D_w \equiv \frac{\Sigma w_N D_N}{\Sigma w_N} = \frac{\Sigma M_N f_N D_N}{\Sigma M_N f_N} \qquad (A2)$$

$$D_z \equiv \frac{\Sigma M_N w_N D_N}{\Sigma M_N w_N} = \frac{\Sigma M_N^2 f_N D_N}{\Sigma M_N^2 f_N} \qquad (A3)$$

where f_N is the frequency distribution of particles with molecular weight M_N and diffusion constant D_N, and w_N is the corresponding weight distribution. According to the Einstein–Stokes relationship one has

$$D = \frac{kT}{6\pi\eta_0 R_s} \qquad (A4)$$

and the Stokes radius R_s can be assumed to increase with molecular weight as

$$R_s \sim M^\nu \qquad (A5)$$

(compact spheres: $\nu = 2/3$, hollow spheres: $\nu = 1$, random coils under theta-conditions: $\nu = 1/2$). Therefore

$$D_n = K\frac{\Sigma f_N(1/M_N^\nu)}{\Sigma f_N} \tag{A6}$$

$$D_w = K\frac{\Sigma(f_N M_N)(1/M_N^\nu)}{\Sigma f_N M_N} \tag{A7}$$

$$D_z = K\frac{\Sigma(f_N M_N^2)(1/M_N^\nu)}{\Sigma f_N M_N^2} \tag{A8}$$

where K is a constant which depends on the particle structure but which does not change with the particle weight. It is obvious from equations (A6)–(A8) that small values of $(1/M_N^\nu)$ are much stronger weighted in D_z than in D_w and D_n; thus

$$D_z \leqslant D_w \leqslant D_n \tag{11}$$