Quasielastic Light Scattering: An Experimental Study of Polydispersity

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ABSTRACT: The apparent diffusion constant $D_{\text{app}} = \Gamma/k^2$ defined as the autocorrelation decay constant, Γ, divided by $k^2 = (4\pi/\lambda)^2 \sin^2 \theta/2$, has been measured as a function of the scattering angle, θ, for mixtures of two sizes of polystyrene latex particles with diameters of $d_1 = 109 \pm 2.9$ nm and $d_2 = 481 \pm 1.6$ nm. The apparent diffusion constant is found to increase strongly at small scattering angles, to pass through a flat maximum at 75°, and to level off at a constant value at large angles. The behavior is shown to be caused by the polydispersity and the particle scattering factors of the two latex particles. Calculation of D_{app} from measured particle scattering factors and diffusion constants of the individual components results in a good agreement with the measured angular dependence. The autocorrelation function shows strong deviations from a single exponential. A fit of these curves with two exponentials allows the determination of the individual diffusion constants D_1 and D_2, of the mass fractions $B_1(k)$ and $B_2(k)$, and of D_{app}. In spite of a fairly large error in the determination of D_2 the apparent diffusion constant is found to agree well with the directly measured D_{app}.

In a recent paper Brehm and Bloomfield[2] reported on an analysis of polydispersity of polymer solutions by inelastic laser light scattering. The authors showed with examples of well-defined mixtures of latex particles that the autocorrelation function decay constant $\Gamma = k^2 D_{\text{app}}$ increases more strongly with the scattering angle than k^2, where $k = (4\pi/\lambda) \sin \theta/2$ and θ is the scattering angle. The apparent diffusion constant D_{app} was found to increase linearly with k^2. The purpose of the present study is to extend the work by Brehm and Bloomfield to particles of larger size and determine the dependence of D_{app} on scattering angle for systems of particles with diameters approaching the wavelength of light. Polydispersity has been the subject of many investigations.[3] In most cases, however, the influence on the shape of the correlation functions alone has been studied theoretically and experimentally while the influence on D_{app} has been mentioned only briefly.

A proper understanding of the effects of polydispersity has further significance in experiments designed to detect rotational diffusion[4-6] or intramolecular motion in flexible chain molecules. In general it is difficult to differentiate between these effects on the basis of light-scattering experiments alone.[7-9] In the present study, however, internal motion in a latex particle is much faster than in flexible coils and will occur at relaxation times well outside the range of measurements of common light-scattering instruments. Therefore the influence of polydispersity can be studied with these latex spheres unperturbed by internal modes of motion.

Theory

The angular dependence of the apparent diffusion constant is described by the following equation:[2,3]

$$D_{\text{z,app}}(k) = \frac{\Sigma w(M_i)M_iP_i(k)D_i}{\Sigma w(M_i)M_iP_i(k)}. \qquad (1)$$

In this equation D_i is the diffusion constant of particles with molecular weight M_i, weight fraction $w(M_i)$, and particle scattering factor $P_i(k)$. We have added the suffix z to the apparent diffusion constant since for $k \to 0$ eq 1 becomes

$$\lim_{k\to 0} D_{\text{z,app}}(k) = D_z = \frac{\Sigma w(M_i)M_iD_i}{\Sigma w(M_i)M_i} \qquad (2)$$

which is the definition of the z average of the diffusion constant.

According to eq 1 the angular dependence of the apparent diffusion constant is due to the particle scattering factors of the individual components and can be detected only for particles sufficiently large that $P_i(k)$ has a significant angular variation. A monodisperse sample will exhibit no angular dependence as the particle scattering factor cancels in eq 1.

Experimental Section

Apparatus. The measurements reported here were made using a Malvern Model 4300 Photon Correlation Spectrometer and a Malvern 48 channel digital correlator operated in the single clipped mode. The signal was optimized by making careful adjustments to the optical components shown in Figure 1 as follows: First, the incident laser beam was focused in the center of the cell by adjusting lens L_1 while observing the focused beam with a 10× eyepiece placed at the position of the photomultiplier. Second, the distance f_{22} was adjusted until the image of the scattering volume was focused on the entrance slit to the photomultiplier. Finally, the correct horizontal positions of lenses L_1 and L_2 were determined with the aid of the special fixture consisting of a thin copper wire carefully centered in a cylindrical cell shown in Figure 2. By adjusting the positions of L_1 and L_2 so as to maximize the light detected by the photomultiplier we were assured that the optical axes of the incident and scattered light paths met in the center of the cylindrical cell. Consequently we were able to measure the scattering angle with an accuracy of ±0.2°.

The RCA 8852 photomultiplier as supplied by the Malvern Co. was found to have a dark current that increased from 900 pulses/s at the beginning of measurements to 5000 pulses/s after several hours of measurements. The increase occurred because the temperature of the photocathode had increased due to resistive heating in the dynode resistor chain. The large dark current, which seriously diminished the signal-to-noise ratio of the measurements, was reduced to a fairly constant value of about 500 pulses/s by circulating cold water in rubber tubing wrapped around the photomultiplier housing.

Data Analysis. A comprehensive discussion of the various methods for the data analysis was given recently by Chu et al.[10] For the purposes of the present investigation we found it appropriate to apply somewhat different techniques for the data handling which depend on the special problem and the particular shape of the correlation function.

The first step in the data analysis was to determine the value of the correlation function at very large delay times. In all cases the baseline was obtained by taking the average value of the last 13 channels. This procedure requires a sample time long enough to ensure that the correlation function from channel 35 onwards has decayed to the baseline within the noise level. After subtracting the baseline from the raw data, the square root was taken, the amplitude was normalized, and the resulting quantity was fit in various ways as described below. Thus, the fitted quantity is

$$g_1(\tau) = [(G_2(\tau) - A)/(G_2(0) - A)]^{1/2} \qquad (3)$$

where $G_2(\tau)$ is the experimentally measured correlation function and A is the baseline.

For the determination of the z average of the apparent diffusion constant from the initial slope of the correlation function, two different methods were applied.

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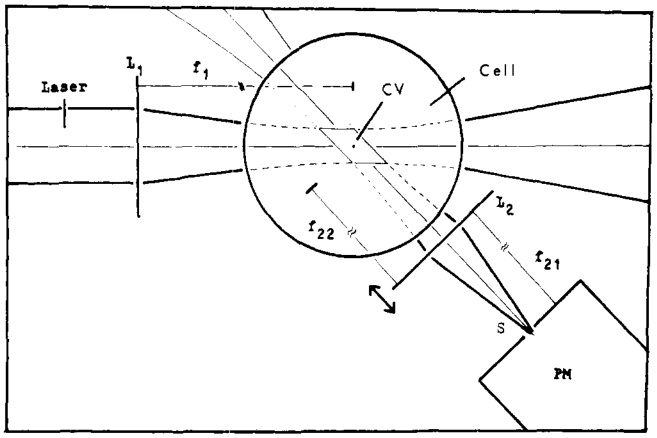

Figure 1. Sketch of the optical system in the Malvern 4300 photon correlation spectrometer. CV is the correlation volume; L_1 and L_2 are lenses of focal lengths f_1 and f_2; PM is the photomultiplier.

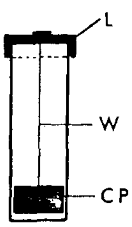

Figure 2. Special cell for adjustment of the optical axis in the center of the correlation volume. L is the lid; CP is the center piece; W is a thin wire of 0.1-mm diameter.

(a) Monodisperse samples yield straight lines when the logarithm of the correlation function is plotted as a function of time. Thus the diffusion constant was obtained by a linear fit of log $g_1(\tau)$ using the data of the first ten channels. (b) As described below (Figure 4) polydisperse samples, e.g., the latex mixtures, show a curvature in the logarithmic correlation function. To obtain the initial slope, the logarithm of the correlation function was fitted by a quadratic function $\ln (g(\tau) - g(\infty)) = a + b\tau + c\tau^2$ using again the first ten channels. The relation $b = -k^2D_{z,\mathrm{app}}$ gives $D_{z,\mathrm{app}}$.

A quite general fit of the data to two exponentials with variable amplitudes and time constants was unsuccessful. The results presented in this paper were obtained by the following procedure. The sample time was chosen such that the tail of the measured correlation function is essentially determined by the high molecular weight latex. The logarithmic correlation function $y = \log g_1(\tau)$ was then partitioned into two parts ranging from channel 1 to 15 and from 16 to 48. The part from channel 15 to 30 was fitted linearly, the slope of which was taken as D_2. The function $y_2 = \log B_2 - D_2K\tau$ was subtracted from the measured logarithmic correlation function y to yield $y_1 = y - y_2$. This residual curve represents nearly the logarithmic correlation function of the low molecular component, i.e., the high diffusion constant D_1, and was fitted by a straight line using again the first ten channels to yield D_1.

Sample Preparation. Solutions of polystyrene latex spheres with diameters of 109 ± 2.7 nm and 481 ± 1.6 nm in solutions of 10% concentration were purchased from Dow Chemical and diluted with clean distilled water to the working concentrations (c = 0.05 g/L). The samples were freed of dust by filtering through a 0.45 μm Millipore filter (small latex) or a 0.8 μm Sartorius filter (large latex). Within the limits of error (±5%) the resulting monodisperse samples showed no angular dependence of the diffusion constant over the range in scattering angle of 25 to 120°.

Results

Solutions of latex spheres having diameters of (1) 109 ± 2.7 nm and (2) 481 ± 1.6 nm were measured separately. The diffusion constants were found to be $D_1 = 4.1 \times 10^{-8}$ cm²/s and $D_2 = 8.9 \times 10^{-9}$ cm²/s, respectively, independent of scattering angle. These values agree well with the diffusion constants calculated by Stokes' equation when using the known diameters, $D_{1\mathrm{cal}} = 4.00 \times 10^{-8}$ cm²/s and $D_{2\mathrm{cal}} = 8.89 \times 10^{-9}$ cm²/s. The diffusion constant D_1 was found to increase slightly with increasing scattering angle but all values lie within the limits of the experimental error of ±5%.

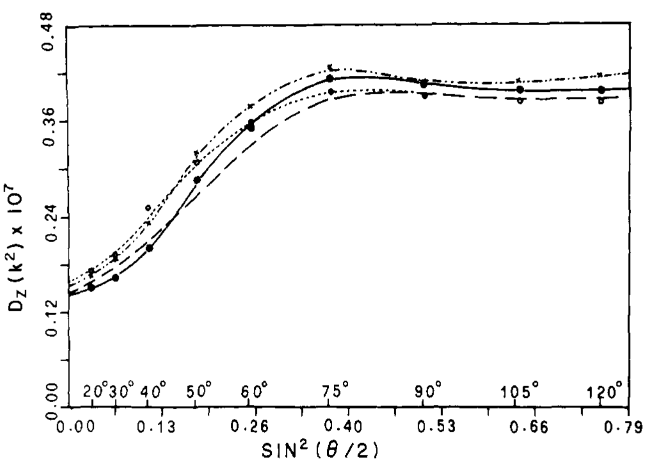

Figure 3. Variation of the apparent diffusion constant $D_z(k^2)$ with the scattering angle for a mixture of two lattices: (–●–) determined from the initial slope of the autocorrelation function; (- - -) calculated from the particle scattering factors and diffusion constants of the two components; (- - O - -) calculated from the correlation functions after fit with two exponentials and *unknown* diffusion constants of the components; (- X · · ·) calculated from correlation functions after fit with two exponentials and *known* diffusion constants.

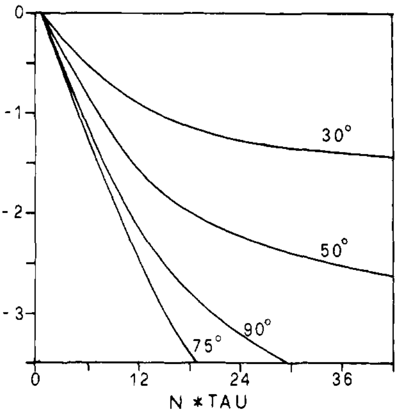

Figure 4. Correlation functions from a mixture of two latex particles at four scattering angles. N is the channel number; TAU = $k^2\tau$ is the reduced correlation time with τ being the real correlation time.

The results of measurements of a mixture of 97 ± 0.5% parts of the low molecular weight and 3 ± 0.5% parts of the high molecular weight samples are shown in Figure 3. In contrast to the findings of Brehm and Bloomfield[2] for smaller latex particles, a strong nonlinear dependence of D_{app} on $\sin^2 \theta/2$ was obtained. The experimental curve is situated between the limits of the diffusion constants of the two components. Most striking is the appearance of a flat maximum at a scattering angle of about 75°. A similar curve was found for a sample with a different ratio of concentration of the two components.

The logarithms of the normalized correlation functions for four different scattering angles are shown in Figure 4. It will be noticed that at larger scattering angles the initial portion of the correlation function is linear over a wider range than at small angles. The curvature of the logarithmic correlation function is caused by the bimodal size distribution of the latex mixture. In principle analysis of this curvature will give a complete determination of the mass fraction and the diffusion constants of the two components. The reliability of such analysis using the numerical analysis described in the last section is demonstrated in detail below.

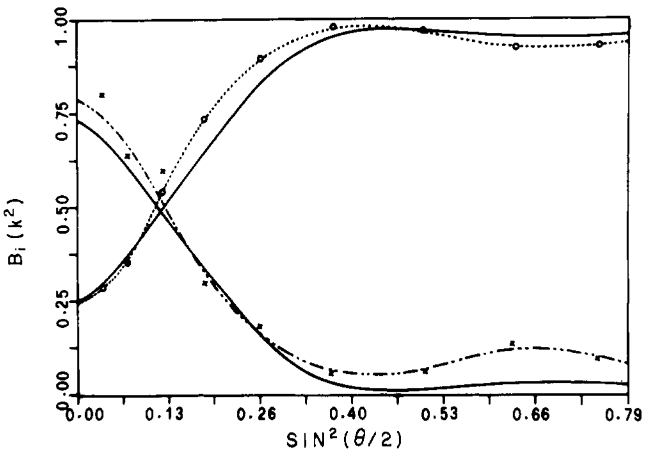

Figure 5. Variation of the coefficients $B_i(k^4)$, defined by eq 5 and 6, as a function of the scattering angle: (—) calculated from the particle scattering factors and known diffusion constants of the components; (· · O · ·) values obtained after fitting the correlation functions with two exponentials and unknown diffusion constants; (· · X · · ·) obtained after fits with two exponentials but *known* diffusion constants of the components.

Discussion

As outlined in the theoretical section the angular dependence of $D_{z,\mathrm{app}}(k)$ is caused by the angular dependence of the particle scattering factors of the individual components. For a bimodal size distribution eq 1 may be written explicitly

$$D_{z,\mathrm{app}}(k) = B_1(k)D_1 + B_2(k)D_2 \qquad (4)$$

where

$$B_1(k) = \frac{w(M_1)M_1P_1(k)}{w(M_1)M_1P_1(k) + w(M_2)M_2P_2(k)} \qquad (5)$$

$$B_2(k) = \frac{w(M_2)M_2P_2(k)}{w(M_1)M_1P_1(k) + w(M_2)M_2P_2(k)} \qquad (6)$$

with

$$B_1(k) + B_2(k) = 1 \qquad (7)$$

In these equations $w(M_i)$ and M_i are known, and $D_{z,\mathrm{app}}(k)$ may be calculated and compared with experiment if the particle scattering factors $P_i(k)$ are obtained by separate measurements. We determined the particle scattering factors using a Sophica elastic light-scattering photometer. While the low molecular latex particle showed only a weak angular dependence of $P(k)$, a very pronounced angular dependence was observed in the case of the large latex spheres. $P(k)$ had a minimum at 90° for the wavelength of the laser light. The calculated curves of $D_{z,\mathrm{app}}(k)$ using the measured particle scattering factors are shown in Figure 3. The good agreement with the experimental curve demonstrates that the strong nonlinear angular dependence is solely determined by the particle scattering factors. Our findings are not in disagreement with the results by Brehm and Bloomfield. These authors have used smaller latex particles and diameters which are closer together than in the present study. The less pronounced angular dependence of the particle scattering factors and the lower polydispersity result, also theoretically, in a linear angular dependence of $D_{z,\mathrm{app}}$ when plotted against $\sin^2 \theta/2$.

The angular dependence of the coefficients $B_i(k)$ calculated according to eq 5 and 6 are plotted in Figure 5. At the position where $D_{z,\mathrm{app}}$ has its flat maximum the coefficient $B_2(k)$ has its minimum, and this minimum appears at the same angle as the minimum of $P_2(k)$. Since at this minimum $B_2(k)$ is close to zero, $D_{z,\mathrm{app}}$ should become approximately D_1 because of the constraint of eq 7. This is in fact observed within the limits of the experimental error.

In principle, as already mentioned, it should be possible to determine the coefficients $B_i(k)$ and the two diffusion constants from the analysis of the correlation function

$$g_1(\tau) = \left[\frac{G_2(\tau) - A}{G_2(0) - A}\right]^{1/2} = B_1(k)\exp(-D_1k^2\tau) + [1 - B_1(k)]\exp(-D_2k^2\tau) \qquad (8)$$

As outlined in the section on data analysis the general fit was not better than 10% for D_1 and 20–30% for D_2. These large errors proved to be far too high to ensure a reliable determination of the coefficient $B_1(k)$.

However, if the diffusion constants from the measurements of the isolated components are used and inserted into eq 8 the one-parameter fit now yields the curves shown in Figure 5. A fairly good fit is obtained also when only D_1 is known.

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