Different Particle Sizes Obtained from Static and Dynamic Laser Light Scattering

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November 13, 2018

Abstract

Detailed investigation of static and dynamic laser light scattering has been attempted in this work both theoretically and experimentally based on dilute water dispersions of two different homogenous spherical particles, polystyrene latexes and poly(N-isopropylacrylamide) microgels. When Rayleigh-Gans-Debye approximation is valid, a new radius $R_s$, referred to as a static radius, can be obtained from the static light scattering (SLS). If the absolute magnitude of the scattered intensity and some constants that are related to the instrument and samples are known, the average molar mass for large particles can be measured. The size information obtained from SLS is purely related to the optical properties of particles, i.e., to $R_s$ and its distribution $G(R_s)$. The size information obtained from dynamic light scattering (DLS) is more complicated, the size distribution of which is a composite distribution that is not only related to the optical properties of particles, but also related to the hydrodynamic properties and the scattering vector. Strictly speaking, an apparent hydrodynamic radius $R_{h,app}$ is a composite size obtained from averaging the term $\exp(-q^2 D \tau)$ in the static size distribution $G(R_s)$, with the weight $R_s^6 P(q, R_s)$ that is also a function of both $R_s$ and the scattering vector $q$.

For colloidal dispersion systems, the light scattering is a widely used technique to measure the sizes of particles. During the last few decades, the standard method of cumulant is used to obtain the apparent hydrodynamic radius $R_{h,app}$ and its distribution $G(R_{h,app})$ of particles from the normalized time auto-correlation function of the scattered light intensity $g^{(2)}(\tau)$ [1–5] with the assistance of the Einstein-Stokes relation. The treatment of the static light scattering (SLS) spectroscopy is simplified to the Zimm plot, Berry plot or Guinier plot etc. to get the root mean-square radius of gyration $\left\langle R_g^2 \right\rangle^{1/2}$ and the molar mass of particles provided that the particle sizes are small [4, 6, 7].

The standard DLS techniques are not suited to accurately detect the polydispersities of less than about 10%. Pusey and van Megen [7] proposed a method to detect small poly-dispersities when the Rayleigh-Gans-Debye (RGD) approximation is valid, measuring the dependence of the effective diffusion coefficient obtained from the initial slope of the correlation function with respect to the
scattering angle. By definition, the effective diffusion coefficient is an intensity-weighted average diffusion coefficient. Meanwhile, when the standard method of cumulant was used, from the fit results of our samples, the values of second moment $\mu_2$ can have large differences even if the experimental data were measured under the totally same conditions. More importantly, the fit values of $\mu_2$ are often negative. It is a big contradiction with its definition and lets the second moment $\mu_2$ lose its physical meaning.

How the size distributions of particles were obtained directly from the SLS data has been researched by a few authors [9, 10]. In general, people think that the radius obtained using the SLS technique is the same as that obtained using the DLS technique if the effects of the different weights of particle sizes and the scattering vector are considered. From our results, a new radius can be obtained from the SLS data, namely static radius $R_s$. For simplicity, in this paper, the homogenous spherical particles are considered and the RGD approximation is thought to be valid. The average scattered light intensity of a dilute non-interacting poly-disperse system in unit volume can be obtained for vertically polarized light

$$\frac{I_s}{I_{inc}} = \frac{4\pi^2 \sin^2 \theta_1 n_s^2 \left(\frac{d\phi}{d\theta}\right)_{\theta=c}^2 c 4\pi \rho}{\lambda^4 r^2} \frac{\int_0^\infty R_s^6 P(q, R_s) G(R_s) dR_s}{3 \int_0^\infty R_s^8 G(R_s) dR_s}, \quad (1)$$

where $\theta_1$ is the angle between the polarization of the incident electric field and the propagation direction of the scattered field, $c$ is the mass concentration of particles, $r$ is the distance between the scattering particle and the point of the intensity measurement, $\rho$ is the density of the particles, $I_{inc}$ is the incident light intensity, $I_s$ is the intensity of the scattered light that reaches the detector, $R_s$ is the static radius of a particle, $q = \frac{4\pi}{\lambda} n_s \sin \frac{\theta}{2}$ is the scattering vector, $\lambda$ is the wavelength of the incident light in vacuo, $n_s$ is the solvent refractive index, $\theta$ is the scattering angle, $G(R_s)$ is the number distribution and $P(q, R_s)$ is the form factor of homogeneous spherical particles

$$P(q, R_s) = \frac{9}{q^6 R_s^6} (\sin (q R_s) - q R_s \cos (q R_s))^2. \quad (2)$$

The average molar mass is defined as

$$\langle M \rangle = \frac{4\pi \rho}{3} N_0 \int_0^\infty R_s^3 G(R_s) dR_s, \quad (3)$$

where $N_0$ represents Avogadro’s number.

Comparing with the Zimm plot analysis, the mean square radius of gyration for a poly-disperse system is

$$\langle R_g^2 \rangle_{Zimm} = \frac{3}{5} \int_0^\infty R_s^8 G(R_s) dR_s \int_0^\infty R_s^6 G(R_s) dR_s, \quad (4)$$
Here $G(R_s)$ is chosen to be a Gaussian distribution

$$G(R_s; \langle R_s \rangle, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{1}{2} \left( \frac{R_s - \langle R_s \rangle}{\sigma} \right)^2 \right),$$

(5)

where $\langle R_s \rangle$ is the mean static radius and $\sigma$ is the standard deviation relative to the mean static radius.

Two standard polystyrene latex samples from Interfacial Dynamics Corporation (Portland, Oregon) were used in SLS and DLS measurements. One is the sulfate white polystyrene latex with a normalized mean diameter of 67 nm and the other is the surfactant-free sulfate white polystyrene latex of 110 nm, as shown in Table 1. All values were provided by the supplier as obtained using Transmission Electron Microscopy (TEM) technique. The Latex 1 was diluted for light scattering to weight factor of $1.02 \times 10^{-5}$ and Latex 2 was diluted to $1.58 \times 10^{-5}$. The solvent is the fresh de-ionized water from a Milli-Q Plus water purification system (Millipore, Bedford, with a 0.2 µm filter). Because the sizes of polystyrene latex particles are small and the refractive index difference between the polystyrene latex and the milli-Q water (refractive index 1.332) is large, the $m-1$ is 0.19 and the “phase shift” $\frac{4\pi}{\lambda} R|m-1|$ [4,10] is equal to 0.21 if the sample Latex 2 is considered and the refractive index 1.591 of polystyrene at 590 nm and 20°C is used, so the mono-disperse model $G(R_s) = \delta(R_s - \langle R_s \rangle)$ was used to obtain the approximate values of the mean static radii $\langle R_s \rangle$ for the two commercial polystyrene latex samples respectively. The commercial values of the mean radii and standard deviations of the two samples shown in Table 1 were input Eq. 1 to get $I_s/I_{inc}$ respectively. In order to compare with the experimental data, the calculated and experimental values at $q = 0.01887 \text{nm}^{-1}$ were set equal. Figure 1.a shows the results of Latex 1.

In order to compare the expected values $\langle R^2_g \rangle_{cal}$ with experimental values of $\langle R^2_g \rangle_{Zimm}$, the commercial values of the mean radii and standard deviations also were input Eq. 4 respectively to obtain the expected root mean-square radii of gyration $\langle R^2_g \rangle_{cal}^{1/2}$. Meanwhile the root mean-square radii of gyration were measured using the Zimm plot respectively. Figure 1.b shows the fit results of Latex 1, $Kc/R_{av} = 1.29 \times 10^{-8} + 3.11 \times 10^{-6} q^2$. The DLS data of two standard polystyrene latex samples were measured under the same conditions as the SLS data respectively and the apparent hydrodynamic radii were obtained using the cumulant method. In order to conveniently compare with the values calculated using the size information obtained from the SLS data and avoid the contradictions of $\mu_2$, the values of apparent hydrodynamic radii were obtained using the first cumulant. For the two standard polystyrene latex samples, the values of apparent hydrodynamic radii at a scattering angle of 40° were chosen as the results obtained using the DLS technique since the values of apparent hydrodynamic radius almost do not depend on the scattering angle. All results are listed in Table 1.
Table 1: The commercial size information, \( \langle R_s \rangle \), values of \( \langle R_g^2 \rangle_1^{1/2} \), \( \langle R_g^2 \rangle_1^{1/2} \) and \( R_{h,app} \) at a scattering angle of 40°.

| \( \langle R \rangle (\text{nm}) \) (comm) | \( \sigma (\text{nm}) \) (comm) | \( \langle R_g^2 \rangle_1^{1/2} (\text{nm}) \) | \( \langle R_g^2 \rangle_1^{1/2} (\text{cal}) (\text{nm}) \) | \( \langle R_s \rangle (\text{nm}) \) | \( R_{h,app} (\text{nm}) \) |
|---|---|---|---|---|---|
| 33.5 (Latex 1) | 2.5 | 26.7 | 26.9 | 33.30 \( \pm \) 0.18 | 37.27 \( \pm \) 0.09 |
| 55 (Latex 2) | 2.5 | 46.8 | 43.2 | 56.77 \( \pm \) 0.04 | 64.48 \( \pm \) 0.56 |

For Poly(N-isopropylacrylamide) (PNIPAM) microgel samples, the synthesis of gel particles was described elsewhere [11, 12]. Equation 1 was used to fit the data of the PNIPAM microgel sample that the molar ratio of \( N, N' \)-methylenebisacrylamide over \( N \)-isopropylacrylamide is 5%. The data were measured at a temperature of 29°C. The concentration is \( 8.38 \times 10^{-6} \). The size information obtained using the SLS technique is \( \langle R_s \rangle = 216.7 \pm 0.3 \text{ nm}, \sigma = 18.3 \pm 0.5 \text{ nm} \) and \( \chi^2 = 1.07 \). The fit results at different scattering vector ranges are shown in Table 2.

Table 2: The fit results for PNIPAM microgel sample at different scattering vector ranges and a temperature of 29°C.

| \( q (10^{-3} \text{nm}^{-1}) \) | \( \langle R_s \rangle (\text{nm}) \) | \( \sigma (\text{nm}) \) | \( \chi^2 \) |
|---|---|---|---|
| 3.45 to 9.05 | 189.92 \( \pm \) 30.58 | 38.12 \( \pm \) 15.69 | 1.44 |
| 3.45 to 11.2 | 199.50 \( \pm \) 10.45 | 32.84 \( \pm \) 6.49 | 1.17 |
| 3.45 to 13.2 | 210.80 \( \pm \) 2.39 | 24.66 \( \pm \) 2.29 | 1.03 |
| 3.45 to 14.2 | 215.47 \( \pm \) 1.47 | 19.91 \( \pm \) 1.87 | 1.07 |
| 3.45 to 15.2 | 216.94 \( \pm \) 0.60 | 18.10 \( \pm \) 1.02 | 1.06 |
| 3.45 to 16.1 | 216.69 \( \pm \) 0.40 | 18.46 \( \pm \) 0.71 | 1.07 |
| 3.45 to 17.0 | 216.71 \( \pm \) 0.25 | 18.33 \( \pm \) 0.50 | 1.07 |
| 3.45 to 17.9 | 217.55 \( \pm \) 0.14 | 16.73 \( \pm \) 0.36 | 1.23 |
| 3.45 to 18.7 | 217.98 \( \pm \) 0.09 | 15.66 \( \pm \) 0.27 | 1.51 |
| 3.45 to 19.5 | 218.14 \( \pm \) 0.06 | 14.57 \( \pm \) 0.17 | 2.49 |
| 3.45 to 20.3 | 218.19 \( \pm \) 0.07 | 14.42 \( \pm \) 0.17 | 3.58 |

When Eq. 1 was fit to the data, it was found that the results for mean static radii \( \langle R_s \rangle \) and standard deviation \( \sigma \) depended on the scattering vector range being fit, as shown in Table 2. If a small scattering vector range is chosen, the parameters are not well-determined. As the scattering vector range is increased, \( \chi^2 \) and the uncertainties in the parameters decrease and \( \langle R_s \rangle \) and \( \sigma \) stabilize. If the fitting scattering vector range continues to increase, the values of \( \langle R_s \rangle \) and \( \sigma \) begin to change and \( \chi^2 \) grows. This is the results of the deviation between the experimental and theoretical scattered light intensity in the vicinity of the scattered intensity minimum. This minimum lies at about the scattering vector 0.0207 \( \text{nm}^{-1} \). In this range, most of the scattered light is cancelled due to the light interference. So many other characteristics of particles can show the effects on the scattered light intensity, for example: the particle number distribution deviates from a Gaussian distribution, the particle shape deviates from a perfect sphere and the density of particles deviates from homogeneity, etc. In order to avoid the effects of light interference, the stable fit results during the scattering vector range from 0.00345 \( \text{nm}^{-1} \) to 0.0170 \( \text{nm}^{-1} \) are chosen as the size information obtained using the SLS technique. The size information is \( \langle R_s \rangle = 216.7 \pm 0.3 \text{ nm}, \sigma = 18.3 \pm 0.5 \text{ nm} \) and \( \chi^2 = 1.07 \). The fit results in this range are shown in Fig. 2.
Using the standard method of cumulant, the apparent hydrodynamic radii can be obtained at different scattering angles from $g^{(2)}(\tau)$ measured under the same conditions as the SLS data. The values of apparent hydrodynamic radius $R_{h,app}$ are related to the scattering angle. The value is about 280 nm. Now using the light scattering techniques, different particle sizes for a same particle system can be obtained. This difference will not only influence the analysis of the physical quantities that are related to the particle sizes, but also, more importantly, it will bring one fundamental question: which size information is the better approximation of the particle sizes? For the two commercial polystyrene latex samples, the value obtained using the SLS technique is consistent with that measured using TEM. Further the effects brought by this difference to the standard method of cumulant also can be analyzed. From the process that $g^{(2)}(\tau)$ is obtained, it is determined by both the optical and hydrodynamic characteristics of particles. If the normalized time auto-correlation function of the electric field of the scattered light $g^{(1)}(\tau)$ is written out in detail for homogeneous spherical particles using the first cumulant, the following equation can be obtained

$$g^{(1)}(\tau) = \exp\left(-q^2 \langle D \rangle \tau\right) = \frac{\int R_s^6 G(R_s) P(q, R_s) \exp\left(-q^2 D \tau\right) dR_s}{\int R_s^6 P(q, R_s) G(R_s) dR_s},$$

where $D$ is the diffusion coefficient. From the Stokes-Einstein relation $D = \frac{k_B T}{6\pi\eta_0 R_h}$ and $\langle D \rangle = \frac{k_B T}{6\pi\eta_0 R_{h,app}}$, here $\eta_0$, $k_B$ and $T$ are the viscosity of the solvent, Boltzmann’s constant and absolute temperature, respectively and $R_h$ is the hydrodynamic radius of a particle. $R_{h,app}$ is the apparent hydrodynamic radius obtained using the cumulant method.

In Eq. 6 the quantity $\exp\left(-q^2 D \tau\right)$ is related to the hydrodynamic characteristics while $R_s^6 P(q, R_s)$ is determined by the optical features of particles. As a result, $g^{(1)}(\tau)$ is determined by both the optical and hydrodynamic features of particles but not purely determined by one of them. For an approximate mono-disperse system, equation $g^{(1)}(\tau) = \exp\left(-q^2 D \tau\right)$ is a very good method to obtain the hydrodynamic sizes of particles. When the distribution of particles needs to be obtained, exactly the distribution obtained using the cumulant method is a composite distribution $G(q, R_h, f)$, here $f$ represents the relationship between the hydrodynamic radius $R_h$ and the static radius $R_s$. For narrow distributions, we ever simply assumed that the relationship between the static and hydrodynamic radii is $a = R_h/R_s$, here $a$ is a constant. With the size information obtained using the SLS technique, the expected values of apparent hydrodynamic radius can be obtained using Eq. 6. The same PNIPAM microgel sample was measured at a temperature of 40°C. The fit results are $\langle R_s \rangle = 139.3 \pm 0.3$ nm, $\sigma = 12.4 \pm 0.6$ nm and $\chi^2 = 5.50$. When the constant $a$ was chosen to be 1.10, the five measured values obtained using the first cumulant and the expected results are shown in Fig. 3. In order to avoid the consideration for the large values of $\chi^2$, all fit results are chosen under this condition $\chi^2 \leq 2$.

The difference between the static and apparent hydrodynamic radii cannot be totally explained by the effects of the different weights of particle sizes and
the scattering angle. For other samples, we have obtained the same conclusion. The static radius and the apparent hydrodynamic radius are different physical quantities.

Eq. 1 provides a method to measure accurately the particle size distribution and makes it possible to measure the average molar mass of large particles. Comparing our method with the DLS technique, the simple particle size $R_s$ and size distributions $G(R_s)$ of dilute homogenous spherical particles can be directly obtained. The small poly-dispersities that cannot be measured using the cumulant method have been obtained. If the absolute magnitude of the scattered intensity and some constants that are related to the instrument and samples are known, the average molar mass for large particles can be measured. The apparent hydrodynamic radius $R_{h,app}$ obtained using the cumulant method is a composite size obtained from the average of $\exp(-q^2D\tau)$ in distribution $G(R_s)$ with the weight $R_s^6P(q, R_s)$. The simple sizes and distributions obtained using the SLS technique are the physical quantities that people really want to obtain from the experimental data. They let us avoid the other parameters’ effects when the effects of particle sizes are analyzed.

Fig. 1 The experimental and expected values of $I_s/I_{inc}$ and the Zimm plot analysis for Latex 1. (a) The circles show the experimental data and the line represents the expected values of $I_s/I_{inc}$. (b) The circles show the experimental data and the line shows a linear fit to the plot of $Kc/R_v$ as a function of $q^2$.

Fig. 2 The experimental and fit results for PNIPAM microgel sample at a temperature of 29°C. The circles show the experimental data, the line shows the fit results and the diamonds show the residuals: $(y_i - y_{fit})/\sigma_i$.

Fig. 3 The experimental and expected values of apparent hydrodynamic radii for the PNIPAM microgel sample at a temperature of 40°C. The circles show the experimental data, the diamonds show the expected results calculated using the size information obtained from SLS.

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