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Accurate measurement of small polydispersities in colloidal suspensions.

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Abstract

We demonstrate a simple method for the accurate characterization of the particle size distributions of colloidal particles with small polydispersities using a combination of dynamic light scattering and static light scattering. This method takes advantage of the variation in apparent radius observed using dynamic light scattering, as the scattering angle is increased through minima in the intensity form factor. Two-colour dynamic light scattering is used to ensure there are no contributions from multiple scattering. We demonstrate that the polymethylmethacrylate based particles used here have negatively skewed particle size distributions, and in many cases can be characterized by a two parameter Weibull distribution. The importance of the accurate characterization of the particle size distribution for studies of crystallization in hard sphere colloidal suspensions is discussed.

INTRODUCTION

Light scattering is a widely used technique for the characterization of particle size in colloidal suspensions. At the simplest level the basic data provided by both Dynamic Light Scattering (DLS) and Static Light Scattering (SLS) can be used to estimate average particle radius and polydispersity. At a more sophisticated level, a number of different analysis procedures allow the determination of the complex, possibly multimodal Particle Size Distributions (PSDs) of many industrial and scientific colloids. These procedures, which involve numerical Laplace inversion of light scattering spectra, have been reviewed in a number of articles (eg 1 and references therein). The ambiguity attendant to the ill-posed nature of such inversions can be reduced considerably when information from both DLS and SLS is taken into account (eg 2-7).

The above techniques are not necessarily suited to the accurate determination of narrow PSDs – particles with polydispersities less than about 10%. Pusey and van Megen (8) showed that one way of estimating these small polydispersities, in principle, is from DLS measurements of the effective diffusion constant, $D(q)$, (or equivalently the apparent particle radius) as a function of the scattering vector, q , whose magnitude is given by $q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the solvent refractive index, λ is the laser wavelength in vacuum, and θ is the scattering angle. The method is particularly accurate for particles large enough to have a form factor minimum accessible by light scattering. A deep form factor minimum scans an inverse window through the PSD with the result that the intensity weighted, effective diffusion constant varies with q in a manner that is sensitive to both the spread of the PSD (ie, polydispersity) and its skewness. For narrow PSDs of particles whose form factor can be described by Rayleigh-Gans-Debye (RGD) theory, Pusey and van Megen showed

that the amplitude of the swing of $D(q)$ about the value $D(q=0)$, when traversing a form factor minimum, is equal to twice the polydispersity. They also showed that the asymmetry of the swing relates, in principle, to the skewness of the PSD.

The main experimental disadvantage of the above technique is that information is most critical around the form factor minimum, where single scattering is weakest, and multiple scattering can distort the results. However, Segrè et al. (9) and Heymann et al. (10) showed that this disadvantage is obviated by using Two-Colour Dynamic Light Scattering (TCDLS). This technique extracts, from the total light scattered by the sample, only the light that has been scattered once.

In this paper we extend and improve on the original technique in a number of ways. First, experimentally we use TCDLS to measure both the scattered intensity, $I(q)$, and the effective diffusion constant, $D(q)$. From the latter we obtain apparent radius $R(q)$. Second, we use both $R(q)$ and $I(q)$ to determine the PSD, rather than one or the other. Third, we use a more general scheme for fitting the data which allows for distributions of arbitrary shapes and polydispersities, and use three different distributions to illustrate this. Finally, either RGD scattering or the full Mie theory can be used within this scheme, making the technique more broadly applicable to particles of all sizes and refractive indices.

Knowledge of the subtleties of very narrow PSDs is of direct import to fundamental studies of condensed matter for the following reason. Numerous studies have shown that systems of suspended particles have fluid, crystal and glass states that are analogous to those of atomic systems (eg articles in 11, or 12 for a recent paper) . In particular, a suspension of particles with hard-sphere interactions shows coexistence of colloidal fluid and crystal phases at volume fractions consistent with those predicted for a system of perfect hard spheres (eg 13-15). However, unlike the

freezing of a simple atomic liquid, crystallization of the colloidal system occurs slowly enough to be followed in real time. The potential this offers for enhancing our understanding of nucleation and growth of the crystal phase has motivated a number of experimental studies, by both microscopy (eg 16, 17) and spectroscopy. Since a fluid of hard spheres is considered as the reference system for real atomic liquids, most of these studies have used suspensions of particles having hard-sphere-like interactions.

One significant difference between the particles in a suspension and the atoms of a (one-component liquid) is that the particles, no matter how carefully prepared, have some inherent spread in their radii. While the polydispersity of these model colloids is small by the standards of those encountered more widely in colloid science, its significance has become apparent only relatively recently. The rate of crystallization is a strong function of polydispersity, as shown in recent experiments (18, 19). In the last few years the effect of polydispersity on phase behaviour has received a great deal of theoretical and computer simulation attention (20-24). These studies indicate that in addition to the rate of crystallization, the crystal structure and the propensity to vitrify are also very sensitive to small variations in the PSD.

THEORY

Static and Dynamic Light Scattering of Polydisperse Suspensions

Consider a suspension of particles with a normalized PSD, (i.e. the number of particles as a function of radius), $G(R)$. The intensity, $I(q)$, of light scattered by the suspension is given by the convolution of the PSD with the radius dependent form factor $P(q,R)$ (eg 8):

$$\overline{P(q)} = \int_0^{\infty} R^6 P(q, R) G(R) dR, \quad [1]$$

Analogous to Eq. [1], the effective, intensity weighted diffusion coefficient, $D_e(q)$ is expressed as :

$$D_e(q) = \frac{\int_0^{\infty} R^6 P(q, R) D(R) G(R) dR}{P(q)} \quad [2]$$

where the diffusion coefficient for a particular radius, R , is given by:

$$D(R) = \frac{kT}{6\pi\eta R} \quad [3]$$

where kT is the thermal energy and η is the solvent viscosity. $D_e(q)$ is obtained from the time auto-correlation function of the scattered intensity by the standard method of cumulants (eg 25).

A moment analysis by Pusey and van Megen (8) shows that

$$\begin{aligned} \left(\frac{D_e(0)}{D_e(q)} \right)_{\min} &= 1 - \sigma \\ \left(\frac{D_e(0)}{D_e(q)} \right)_{\max} &= 1 + \sigma \end{aligned} \quad [4]$$

where σ is the polydispersity (i.e. the relative standard deviation of the PSD). Eq. 4 says that the amplitude of the variation of the effective diffusion coefficient equals twice the polydispersity. This result applies universally, for any PSD, to first order in σ for optically homogeneous spheres in the RGD limit. Reference 8 also derives results for a skew symmetric PSD but, again, these are applicable only for a very narrow PSD.

In general, the PSD may not be sufficiently narrow for the analytical results of Reference 8 (eg. Eq. [4]) to be accurate or even applicable. We have, therefore, developed a general scheme that can be applied for any given PSD and particle form

factor. In this the parameters of a given PSD are adjusted until the best agreement is obtained between $I(q)$ and $D_e(q)$, numerically evaluated by Eq. [1] and [2], and the corresponding measured quantities.

The following three models for the PSD were used;

1) Gaussian – symmetrical distribution

$$G_g(R) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(R - \bar{R})^2}{2\sigma^2}\right) \quad [5]$$

where $\bar{R}$ is the mean radius and σ , as defined above, is the standard deviation relative to the mean radius.

2) Log-Normal – positively skewed distribution

$$G_l(R) = \frac{1}{R\sqrt{2\pi}\sigma_g^2} \exp\left(-\frac{(\ln(R) - \ln(R_m))^2}{2\sigma_g^2}\right) \quad [6]$$

where σ_g is geometric mean standard deviation and R_m is the median radius. These can be related to the mean and standard deviation via:

$$\sigma^2 = e^{\sigma_g^2} - 1$$

$$\bar{R} = \exp\left[\ln(R_m) + 0.5\sigma_g^2\right]$$

3) Weibull – negatively skewed distribution

$$G_w(R) = \alpha\beta R^{(\beta-1)} e^{-\alpha\beta R} \quad [7]$$

where α, β are the fit parameters and $\alpha, \beta, R > 0$. The variance and mean are given by:

$$\sigma^2 = \alpha^{-2/\beta} \left\{ \Gamma\left(1 + \frac{2}{\beta}\right) - \left[\Gamma\left(1 + \frac{1}{\beta}\right) \right]^2 \right\}$$

$$\bar{R} = \alpha^{-1/\beta} \Gamma\left(1 + \frac{1}{\beta}\right)$$

where Γ is the standard gamma function.

The above are respectively, symmetrical, positively skewed and negatively skewed PSDs and they are each determined by only two parameters. In principle, therefore, given two different measured spectroscopic properties, $I(q)$ and $D_e(q)$, the parameters obtained are unique. Details of these and other PSDs, that could equally well be considered, may be found in standard statistical texts (eg 26).

Two Colour Dynamic Light Scattering (TCDLS)

TCDLS has been described in detail elsewhere (9, 27, 28). Briefly, two different laser wavelengths from an argon ion laser (green (514 nm) and blue (488 nm)) are focused onto a small volume of the sample, and two photomultipliers detect the scattering green and blue light. The optics are arranged so that the detectors collect light at the same scattering wavevector q . In this arrangement only singly scattered light contributes to the cross correlation signal. The relevant equations for TCDLS are described below.

The cross correlation function of the singly scattered intensities $g_c^{(2)}(q, \tau)$ of the two lines is given by:

$$\beta_{ms}^2 = \frac{\langle I_B^s(q) \rangle \langle I_G^s(q) \rangle}{\langle I_B(q) \rangle \langle I_G(q) \rangle} \quad [8]$$

where I refers to scattered intensity, the subscripts B and G refer to blue and green light respectively, $f(q, \tau)$ is the normalized electric field autocorrelation function, τ is the delay time, and the angular brackets represent a time average. β is the usual

coherence factor and β_{ov} is an instrumental factor proportional to the ratio of the intersection and union of the scattering volumes of the blue and green colours. Both β and β_{ov} are sample independent quantities, and their product $\beta\beta_{ov}$ was determined by a separate measurement on a very dilute suspension of polystyrene particles of radius $R = 85$ nm, sufficiently small for their form factor to be only weakly dependent on scattering angle. This leads to an empirical equation $\beta\beta_{ov} = 0.1356 + 1.40 \times 10^{-3}q - 6.799 \times 10^{-5}q^2$.

The factor β_{ms} is given by:

$$\beta_{ms}^2 = \frac{\langle I_B^s(q) \rangle \langle I_G^s(q) \rangle}{\langle I_B(q) \rangle \langle I_G(q) \rangle} \quad [9]$$

which is the ratio of the average intensities of singly scattered light to total scattered light, and the superscript 's' refers to single scattering.

The cross correlation intercept (ie the zero time limit of Eq. [8]) is given by:

$$g(q, 0) = 1 + \beta^2 \beta_{ov}^2 \beta_{ms}^2 \quad [10]$$

As $\beta\beta_{ov}$ is known, the intercept of the cross correlation function can be used to calculate β_{ms} . From the latter and the intensities, $\langle I_B(q) \rangle$ and $\langle I_G(q) \rangle$, of the total scattered light, we obtain (Eq. [9]) the intensity,

$$I(q) = \sqrt{\langle I_B^s(q) \rangle \langle I_G^s(q) \rangle} \quad [11]$$

of the singly scattered light. In addition we obtain the effective diffusion coefficient, $D_e(q)$, by standard cumulant analysis of $g_c^{(2)}(q, \tau)$, and hence $R(q)$.

EXPERIMENTAL METHODS

The particles used in this study have been described in detail elsewhere (29). They consist of a core of a copolymer of methyl-methacrylate (MMA) and tri-fluoroethylacrylate (TFEA). In order to prevent coagulation, the particles were coated by an approximately 10 nm thick layer of poly-12-hydroxystearic acid. The particles used in this study are described in table 1. Particles were suspended in dodecane (Prolabo) at volume fractions sufficiently low to preclude the effects of particle interactions (of the order of 0.1% or less), and placed in cylindrical cuvettes of 8 mm path length.

All measurements discussed here were performed with an ALV TCDLS spectrometer. Cumulant fits were made using the in built ALV-5000 software. The dwell time at each angle in the range $20^\circ \leq \theta \leq 120^\circ$ was 60s or 180s. Between 6 and 20 repeat measurements were made at each angle, and the results averaged.

The results were analyzed in an in-house program written in MATLAB. Where Mie calculations are used, they were implemented in MATLAB based on the FORTRAN algorithm “BHMIE” of Bohren and Huffman (30). The PSD is constructed by dividing an appropriate radius range into one thousand bins. In general 1, 2, or any number of distributions can be added to give an arbitrarily complex PSD. The least squares fitting is done independently for the intensity form factor and apparent radius, and the results compared. The parameters which best fit overall lie somewhere between these two values. The final best fit is then determined by eye, taking into account the different experimental errors on these quantities. For all particles studied this was done using each of three unimodal distributions: Gaussian, Log-Normal and Weibull. Where none of the distributions gave a good fit, multimodal distributions

were used. For the larger particles both Mie and RGD scattering theory were used in the calculations. For smaller particles, only RGD scattering was used.

RESULTS

Figure 1 shows the measured and calculated results of (a) $R(q)$ and (b) $I(q)$ for XL63 particles. The best fits to these data, for the Gaussian, Log-Normal and Weibull PSDs are also shown, and the PSDs are shown in (c). The fit parameters are given in table 1. It is clear from Figure 1(a) that the apparent radius is very sensitive to the shape of the distribution, as the three distributions give noticeably different best fits. The Weibull PSD clearly allows the best fit, and the mean-square error of the optimum fits using Gaussian or Log-Normal PSDs is about five times that obtained for the Weibull PSD. Figure 1(b) shows that unlike the apparent radius, $I(q)$ is insensitive to the detailed shape of the distribution, as the three curves are indistinguishable. One infers, that for the small polydispersities of these particles, the intensity is insensitive to the skewness of the PSD.

Table 1 shows that the three PSDs yield essentially the same average radii and similar polydispersities. The main difference between the PSDs, seen in Figure 1c, is that the Weibull PSD is skewed to smaller radii. That the particles have a negative skew is consistent with the findings of electron microscopy on similar particles (19).

Results for a suspension of larger particles (XL60) are shown in Figure 2. Again, the intensity is insensitive to the functional form of the PSD and the Weibull distribution permits the best fit to the apparent radius. As for XL63 above, no discernable difference was found between optimum Gaussian and Log-Normal PSDs.

Fig 1: (a) Apparent radius, (b) Intensity form factors and (c) best fit PSDs for XL63 particles. Data points (filled circles). The fits shown are the best fits assuming RGD scattering and either a Gaussian distribution (thin line), a Log-Normal (dashed line) or a Weibull distribution (bold line). The best fit Log-Normal is basically a Gaussian.

Fig 2: (a) Apparent radius, (b) Intensity form factors and (c) best fit PSDs for XL60 particles. Data points (filled circles). The fits shown are the best fits assuming RGD scattering and a Weibull (thin line) or Gaussian distribution (dashed line), and Mie scattering using a Weibull distribution (bold line).

Table 1: Fit parameters for the fits shown in the figures.

Particle	Fit type	Scattering	α	β	R_m (nm)	σ (%)
XL63	Gaussian	RGD	--	--	186	7.9
	Log-Normal	RGD	--	--	184	8.0
	Weibull	RGD	13.19	0.192	185	8.6
XL60	Gaussian	RGD	--	--	309	6.6
	Weibull	RGD	17.80	0.315	306	6.9
	Weibull	Mie	18.35	0.309	300	6.7
XL64	Weibull	RGD	12.40	0.187	179	9.8
WVM7	Gaussian	RGD	--	--	223	10.4
	Weibull	RGD	13.10	0.236	227	9.3
WVM7 –	Gaussian A	RGD	--	--	245	4.0
2 component continuous	Gaussian B (wt 0.25)				140	60

Figure 2 also compares the best Weibull fits using the RGD approximation and the exact Mie form factor in Eq. [1] and [2]. The quality of the fit is the same for the two scattering theories. The parameters are shown in Table 1. The RGD approximation overestimates the average radius by a few nm, but the polydispersity and shape of the distribution are essentially the same. The error in R_m of 6 nm is small compared to the polydispersity of 6.7%, which corresponds to a half width of ~ 20 nm. Given these small differences and the fact that the other particles (Table 1) are smaller than XL60, for ease of computation RGD scattering has been used for the rest of the fits considered in this paper. For particles larger than XL60, Mie scattering should be used.

We have conducted these analyses for a range of particles of different sizes and composition (TFEA/MMA). In all cases we find that the Weibull distribution gives a better fit to the measured intensity and diffusion coefficients than either of the other two distributions. No systematic correlation was found as a function of MMA concentration in the particles.

However, although the Weibull distribution is always able to give a better fit to the data than Gaussian and Log-Normal distributions, it does not always produce a good fit. An example where the optimum fit is less than perfect is shown in figure 3 for XL64 particles. The fit shown is barely within the estimated errors, but it misses the average data points. This suggests that the PSD of this latex may be more skewed than is possible to represent with a single two parameter distribution.

A more extreme case is shown in Figure 4. For these particles (designated WVM7), none of the distributions tried could be made to fit the data. The figure shows fits optimized to fit the apparent radius (thin line) and the intensity (dashed line). The best fit for $I(q)$ gives a poor fit to $R(q)$. The PSD that best fits $R(q)$ fits both $I(q)$ and $R(q)$ poorly.

Clearly the particles considered here cannot be described by a simple 2 parameter distribution. They can, however, be described by a sum of two distributions. The obvious drawback in doing this is that with the introduction of five parameters, required to characterize the two PSDs, the results are no longer unique. Figure 4 also shows the optimum fits obtained to the data for two different combinations of two Gaussian PSDs. For simplicity we have used Gaussian distributions, though Weibull or other distributions could also be used and may give slightly improved fits. Both combinations are able to fit the data equally well. The PSDs corresponding to these fits are shown in figure 4(c), and the parameters are given in Table 1. One is a clearly

bimodal distribution, with a sharp spike around 70 nm, and the other is a semi-continuous distribution. Both combinations have the majority of the scattering produced by a component with radius around 225 nm. How to distinguish between these two extremes?

Common sense suggests that the bimodal distribution is unphysical. Such a distinctly bimodal distribution is unlikely to be the product of the polymerization procedure used to make the particles. To confirm this, two tests were used. First some preliminary electron microscopy was carried out, and no evidence was seen of these very small particles, which should be evident in large numbers if this distribution is correct. Second, a dilute sample was repeatedly centrifuged and the apparent radius and intensities were monitored at two angles as a function of centrifugation time. If the bimodal distribution were real, the smaller particles would in general not settle under centrifugation, so one would expect a substantial reduction in the apparent radius as the larger particles settle out of the scattering beam. This effect would be most noticeable in the form factor minimum (at 60°).

Fig 3: (a) Apparent radius, (b) Intensity form factors and (c) best fit PSD for XL63 particles using RGD scattering and a Weibull distribution. This was the best fit achieved.

Fig 4: (a) Apparent radius, (b) Intensity form factors and (c) best fit PSDs for WVM7 particles. Shown are the best fits to the intensity (dashed line) or the radius (thin line) assuming RGD scattering and a Weibull distribution. Gaussian and Log-Normal distributions gave worse fits (data not shown). The bold line shows the best fits using

two different two-component Gaussian distributions, a semi-continuous distribution, and a bimodal distribution. These two fits are indistinguishable on the graph. Only the two component PSDs are shown in (c).

Figure 5: Effect of centrifugation on (a) the intensity and (b) the apparent radius (a) (circles) and intensity (squares) at two different angles. Filled symbols are at 40° and open symbols are at 60°.

The results are shown in Figure 5. As can be seen, the intensity drops to about 10% of its original value after 70 minutes centrifugation, confirming that a good percentage of the particles have settled. However, there is no significant change in the apparent radius as a function of centrifugation time, either at the form factor minimum (60°) or at an angle away from the minimum (40°). Clearly these results show that the WVM7 particles do not have the bimodal distribution. All of the results combined are consistent with WVM7 having a highly skewed distribution which is well approximated by the semi-continuous fit shown in figure 4.

Discussion

This method presents a relatively simple way to obtain particle size distributions for dilute suspensions of colloidal particles. Using TCDLS to suppress multiple scattering is very important, particularly in the region of the form factor minimum, as has been shown previously (28). The use of this method to determine PSDs relies on accurate data particularly in the form factor minima (8). However, standard DLS/SLS could also be used, provided sufficient care was taken to ensure that there was no contribution to multiple scattering in the form factor minimum. This can be done by doing the measurements at 2 or more dilutions. If the results agree, then it can be assumed that multiple scattering is negligible.

An alternative method of PSD characterization is electron microscopy. However, it would be difficult to use electron microscopy to determine the distributions studied here to the same resolution, as many thousands of particles would need to be analyzed. For the distribution shown figure 4 for example, in order to measure a statistically viable number of particles in the long, low radius part of the distribution, one would need to measure say 10-20 particles in each 5 nm bin. This would require

the analysis of somewhere in the vicinity of 10000 particles. An analysis with only a few hundred particles would be likely to miss the skewness altogether. This is in addition to the potential complications brought about by sample preparation.

In many applications the levels of polydispersity discussed here would be considered small, and such particles would be considered monodisperse. Indeed in many applications the experimental difficulty is in determining the PSD of very broad, often truly multimodal distributions, and more advanced techniques combining both dynamic and static light scattering may be used to extract PSDs for these cases (1-7). The difference between the current approach and the previous methods is in this method physically reasonable continuous PSDs are assumed and fitted to the data. This is both computationally easier, and more transparent than the various Laplace inversion methods, and is more appropriate for the characterization of small polydispersities.

For some applications an accurate knowledge of both the shape and size of (small) polydispersities is critical. One such application is in the use of colloidal particles in the study of the fundamental nature of phase transitions. The gross effects of polydispersity on the crystallization behaviour of colloidal systems is well known. If particles have too high a polydispersity they will not crystallize, If on the other hand the polydispersity is too low, crystallization occurs too quickly to be studied. The bulk of crystallization studies have been carried out on samples with polydispersities in the range 3-8%, though the polydispersity is often not well characterized.

However, it is not widely recognized just how important polydispersity is, and how not only the polydispersity, but the detailed shape of the PSD is critical in determining the crystallization properties of hard-sphere colloidal suspensions. This is demonstrated clearly by recent crystallization studies of WVM7 (31).

Conclusions

We have demonstrated how small polydispersities of colloidal particles can be characterized using a simple combination of SLS and DLS measurements by assuming physically reasonable PSDs. We have shown that the PMMA based colloidal particles used here have negatively skewed distributions which can be characterized by Weibull distributions, or at worst, a combination of two Gaussian distributions. Given the emerging importance of the detailed shape of the PSD on the crystallization behaviour of hard sphere colloids, similar methods should be used to characterize the PSDs of all hard sphere particles used in crystallization experiments.

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