Determination of type and width of a size distribution from the z-averages of the radii moments r_z^n

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Relationships are given between the z-average radii moments $\overline{r_z^n}$ and the common moments $\overline{r^n}$ of a size distribution. Instructions are given for finding the type and width of a size distribution from measurements of the $\overline{r_z^n}$ moments.

INTRODUCTION

In the preceding paper[1] it was shown that the z-averages of the nth moments of the sphere radius $\overline{r_z^n}$ ($n = -1, 1, 2, \ldots$) can be obtained from the angular dependence of the elastically and quasielastically scattered light. These z-averages contain information on the width and the type of the size distribution. The purpose of the present paper is to show how the z-averages of the radius are related to the common average radius $\bar{r}$, and secondly how this information can be used to estimate the type and the width of the size distribution.

GENERAL RELATIONSHIPS

Let $h(r_N)$ be the frequency distribution of finding particles of sphere radius r_N. This distribution may be normalized $[\Sigma h(r_N) = 1]$, and, for instance, could be a normalized histogram determined by electron microscopy. A z-average of the nth moment of the radius is defined as:

$$\overline{r_z^n} = \frac{\Sigma w_N M_N r_N^n}{\Sigma w_N M_N} = \frac{\Sigma h(r_N) M_N^2 r_N^n}{\Sigma h(r_N) M_N^2} \tag{1}$$

where

$$w_N = M_N h(r_N)/\Sigma M_N h(r_N) \tag{2}$$

is the weight fraction of spheres with radii r_N and the molecular weight M_N.

Molecular weight and sphere radius are uniquely related. For *compact hard spheres* we have, for example:

$$M_N = \rho \frac{4\pi}{3} r_N^3 \tag{3}$$

while for *hollow spheres*:

$$M_N = \rho 4\pi r_N^2 d \tag{4}$$

where ρ is the constant particle density and d the shell thickness of the hollow sphere, which is assumed here to be constant and small compared with the sphere radius ($d \ll r_N$). For *compact spheres* it is easily verified on substitution of equation (3) or (4) into equation (1).

$$\overline{r_Z^n} = \frac{\Sigma h(r_N) r_N^{n+6}}{\Sigma h(r_N) r_N^6} = \frac{\overline{r^{n+6}}}{\overline{r^6}} \tag{5}$$

and for the *hollow spheres*

$$\overline{r_Z^n} = \frac{\Sigma h(r_N) r_N^{n+4}}{\Sigma h(r_N) r_N^4} = \frac{\overline{r^{n+4}}}{\overline{r^4}} \tag{6}$$

where

$$\overline{r^m} = \Sigma h(r_N) r_N^m \tag{7}$$

are the moments of the frequency distribution.

The two equations (5) and (6) show that the z-average moments $\overline{r_z^n}$ are uniquely related to the simple moments $\overline{r^n}$ if the relationship between the radius and the molecular weight is known, In any case the z-average moment is larger than the corresponding unweighted moments, i.e.

$$\overline{r_z^n} \geqslant \overline{r^n} \tag{8}$$

APPLICATION TO THREE TYPES OF SIZE DISTRIBUTION

Two types of size distributions are considered in the literature. These are the Schulz–Zimm distribution[2,3]:

$$h(r) = \frac{1}{m!} \frac{1}{r} (ry)^{m+1} \exp(-yr) \tag{9}$$

and the Logarithmic Normal distribution[4]

$$h(r) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \frac{1}{r} \exp\left[-\frac{(\ln r - a)^2}{2\sigma^2}\right] \tag{10}$$

Both distributions are defined by only two parameters. The Schulz–Zimm distribution has been found to be a good ap-

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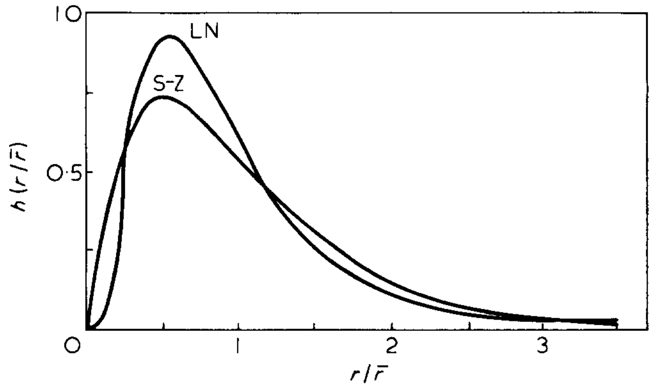

Figure 1 Schulz–Zimm distribution ($m = 1$) in comparison to the log–normal distribution of same mean radius and same width $\overline{r^2}/(\bar{r})^2 = (m + 2)/(m + 1) = \exp$. Note: the maximum width of a Schulz–Zimm distribution is obtained for $m = 0$ which corresponds $\bar{\sigma}^2 = 0.693$ for the log–normal distribution. For larger $\sigma^2 > 0.693$ the log–normal distribution has a pronounced skew shape with a long large radius tail

proximation for fractions of linear polymers while the log–normal distribution is utilized in characterizing the size distributions of emulsions or the corresponding latex particles which are formed in the course of emulsion polymerization.

The types of distribution quoted can differ immensely in shape (see *Figure 1*). In order to fill the large gap between these types of distribution functions Greschner[5] and Lechner[6] introduced the so-called three parameter distribution[7–10]:

$$h(r) = \frac{\nu y^{(m+1)/\nu}}{\Gamma\left(\frac{m+1}{2}\right)} r^m \exp(-yr^2) \tag{11}$$

This distribution is evidently a generalization of the Schulz–Zimm distribution. It has the remarkable property of including several well-known distributions as special cases. Some of these are listed in *Table 1*.

The square root distribution is highly unsymmetric and has a shape inbetween that of the Schulz–Zimm and the log–normal distribution. In a recent paper Lechner claims that also the log–normal distribution is well approximated by the three parameter distribution when $\nu = 0.1$ is chosen.

The moments of the three distributions (9) to (11) are easily derived. For the

Schulz–Zimm distribution:

$$\overline{r^n} = \frac{(m+n)!}{m!} y^{-n} \tag{12}$$

$$\overline{r^n_z} = \frac{(m+n+6)!}{(m+6)!} y^{-n} \quad \text{(compact spheres)} \tag{13}$$

$$\overline{r^n_z} = \frac{(m+n+4)!}{(m+4)} y^{-n} \quad \text{(hollow spheres)} \tag{14}$$

Log–normal distribution:

$$\overline{r^n} = \exp(na + n^2\bar{\sigma}^2/2) \tag{15}$$

$$\overline{r^n_z} = \exp[na + (n^2 + 12n)\bar{\sigma}^2/2] \quad \text{(compact spheres)} \tag{16}$$

$$\overline{r^n_z} = \exp[na + (n^2 + 8n)\bar{\sigma}^2/2] \quad \text{(hollow spheres)} \tag{17}$$

Three parameter distribution:

$$\overline{r^n} = \frac{\Gamma\left(\frac{m+n+1}{\nu}\right)}{\Gamma\left(\frac{m+1}{\nu}\right)} y^{-n/\nu} \tag{18}$$

$$\overline{r^n_z} = \frac{\Gamma\left(\frac{m+n+7}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)} y^{-n/\nu} \quad \text{(compact spheres)} \tag{19}$$

$$\overline{r^n_z} = \frac{\Gamma\left(\frac{m+n+5}{\nu}\right)}{\Gamma\left(\frac{m+5}{\nu}\right)} y^{-n/\nu} \quad \text{(hollow spheres)} \tag{20}$$

It is instructive to compare the z-averages of these moments with their common averages. In *Table 2* this is done explicitly for the first two moments. For the most probable (Schulz–Flory) distribution where $m = 0$ we find, for instance, an increase of the z-average radius by a factor of 7; for the 2nd moment the increase is a factor of 28. The corresponding increase for the log–normal distribution is much stronger. For instance, if $\overline{r_z}/\bar{r} = 7$ is assumed, the ratio $\overline{r^2_z}/\overline{r^2}$ becomes 49 instead of 28 for the Schulz–Zimm distribution.

More relevant in actual problems is the ratio $\overline{r^n_z}/(\overline{r_z})^n$, because this contains the moments which can be obtained from the fit of experimental scattering data. *Table 3* gives a list of the first members for the three distributions.

TREATMENT OF DATA

The characteristic data of a size distribution $h(r)$ are the mean radius, the width of the distribution, and, of course,

Table 1 Some distribution functions as special cases of the three parameter distribution given by equation (11)

Specification	$h(r)$	Name
$m = 0, \nu = 2$	$\left(\frac{y}{2\pi}\right)^{1/2} \exp(-yr^2)$	Gaussian
$m = 2, \nu = 2$	$2yr \exp(-yr^2)$	Maxwell
$m = 0, \nu = 1$	$\frac{(yr)^{m+1}}{m!r} \exp(-yr)$	Schulz–Zimm[2,3]
$m = 0, \nu = 1/2$	$\frac{1}{2} y^2 \exp(-yr^{1/2})$	Square root
$m = 1, \nu = 3$	$\frac{3}{\Gamma(2/3)} \frac{(r-r_0)}{\sigma^2} \exp\left[-\frac{(r-r_0)^3}{\sigma^3}\right]$	Stevenson[11]

Table 2 Ratio $\overline{r^n_z}/\overline{r^n}$ of the *z*-average to the common average moments of the sphere radius for three size distributions of compact spheres

	Schulz–Zimm	Log–normal	Three parameter
$\dfrac{\bar{r}_z}{\bar{r}}$	$\dfrac{m+7}{m+1}$	$\exp(6\overline{\sigma^2})$	$\dfrac{\Gamma\left(\frac{m+8}{\nu}\right)\Gamma\left(\frac{m+1}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)\Gamma\left(\frac{m+2}{\nu}\right)}$
$\dfrac{\overline{r^2_z}}{\overline{r^2}}$	$\dfrac{(m+8)(m+7)}{(m+2)(m+1)}$	$\exp(12\overline{\sigma^2})$	$\dfrac{\Gamma\left(\frac{m+9}{\nu}\right)\Gamma\left(\frac{m+1}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)\Gamma\left(\frac{m+3}{\nu}\right)}$
$\dfrac{\overline{r^n_z}}{\overline{r^n}}$	$\dfrac{(m+n+1)!\,(m!)}{(m+6)!\,(m+n)!}$	$\exp(6n\overline{\sigma^2})$	$\dfrac{\Gamma\left(\frac{m+n+7}{\nu}\right)\Gamma\left(\frac{m+1}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)\Gamma\left(\frac{m+n+2}{\nu}\right)}$

Table 3 Ratio $\overline{r^n_z}/(\bar{r}_z)^n$ for three size distributions of compact spheres

$\bar{r}_z/\bar{r}$	$\dfrac{m+7}{m+6}$	$\exp(\overline{\sigma^2})$	$\dfrac{\Gamma\left(\frac{m+8}{\nu}\right)\Gamma\left(\frac{m+6}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)^2}$
$\overline{r^2_z}/(\bar{r}_z)^2$	$\dfrac{m+8}{m+7}$	$\exp\ \dfrac{3}{2}\overline{\sigma^2}$	$\dfrac{\Gamma\left(\frac{m+9}{\nu}\right)\Gamma\left(\frac{m+7}{\nu}\right)}{\Gamma\left(\frac{m+8}{\nu}\right)^2}$
$\overline{r^3_z}/(\bar{r}_z)^3$	$\dfrac{(m+9)(m+8)}{(m+7)^2}$	$\exp(4\overline{\sigma^2})$	$\dfrac{\Gamma\left(\frac{m+10}{\nu}\right)\Gamma\left(\frac{m+7}{\nu}\right)^2}{\Gamma\left(\frac{m+8}{\nu}\right)^3}$
$\overline{r^n_z}/(\bar{r}_z)^n$	$\dfrac{(m+n+6)!}{(m+6)!\,(m+7)^n}$	$\exp\left[(n^2-1)\dfrac{\overline{\sigma^2}}{2}\right]$	$\dfrac{\Gamma\left(\frac{m+n+7}{\nu}\right)}{\Gamma\left(\frac{m+7}{\nu}\right)}\left[\dfrac{\Gamma\left(\frac{m+7}{\nu}\right)}{\Gamma\left(\frac{m+8}{\nu}\right)}\right]^n$

the type of distribution. Let us take $\overline{r^2}/(\bar{r})^2$ as a measure of the width. (Note that $[\overline{r^2}/(\bar{r})^2 - 1]\,r^2 = \sigma^2$ is the standard deviation of the distribution.) The corresponding width of of the *z*-weighted distribution is $\overline{r^2_z}/(\bar{r}_z)^2$ which determines the width $\overline{r^2}/(\bar{r})^2$ if the type of distribution is known. In principle a distributon is uniquely defined through its moments, but for numerical reasons the approximation is often unsatisfactory. In the following data handling scheme use is made of the effect that $\overline{r^n_z}/(\bar{r}_z)^n$ shows a dependence on $\overline{r^2_z}/(\bar{r}_z)^2$ which is characteristic for the type of distribution.

For compact spheres the quantities $\bar{r}_z\overline{r^{-1}}$ and $\overline{r^3_z}/(\bar{r}_z)^3$ are plotted against $\overline{r^2_z}/(\bar{r}_z)^2$ in *Figures 2* and *3* for the Schulz–Zimm and the log–normal distribution. It turns out that $\overline{r^2_z}/(\bar{r}_z)^2$ cannot become larger than 1.167 for the Schulz–Zimm distribution. Thus, if larger values are obtained experimentally the presence of a Schulz–Zimm distribution can be excluded. In the next step we have to check whether the log–normal distribution fits the other two moments $\overline{r_z^{-1}}$ and $\overline{r^3_z}$. If this is not the case we have to try to find a best set of parameters m and ν for the three parameter distribution (which, however, is cumbersome because of the unwieldy gamma functions). Once the type of distribution is found, the width and mean radius of the frequency distribution $h(r)$ is obtained from *Table 2*.

The question arises now as to whether in the region of low polydispersity a Schultz–Zimm distribution can be distinguished from a log–normal distribution. From *Figure 2* we see that this is certainly not possible from the values of the 3rd moments since almost identical curves are obtained

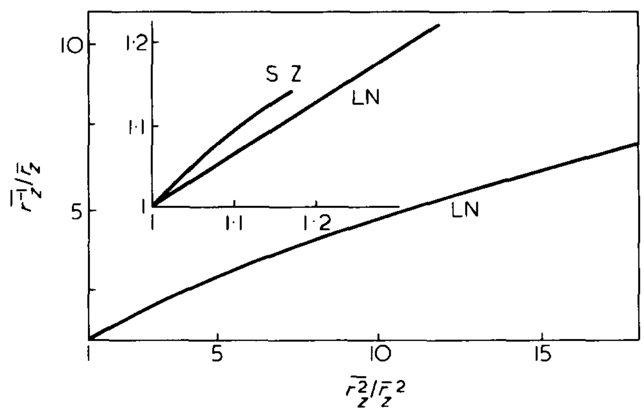

Figure 2 Product $\bar{r}_z\overline{r_z^{-1}}$ as a function of $\overline{r_z^2}/(\bar{r}_z)^2$

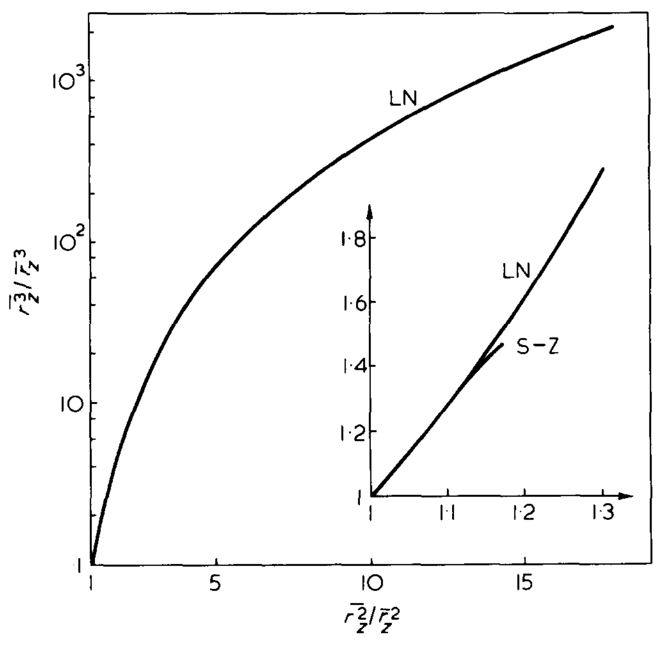

Figure 3 Ratio $\overline{r_z^3}/(\bar{r}_z)^3$ as a function of $\overline{r_z^2}/(\bar{r}_z)^2$

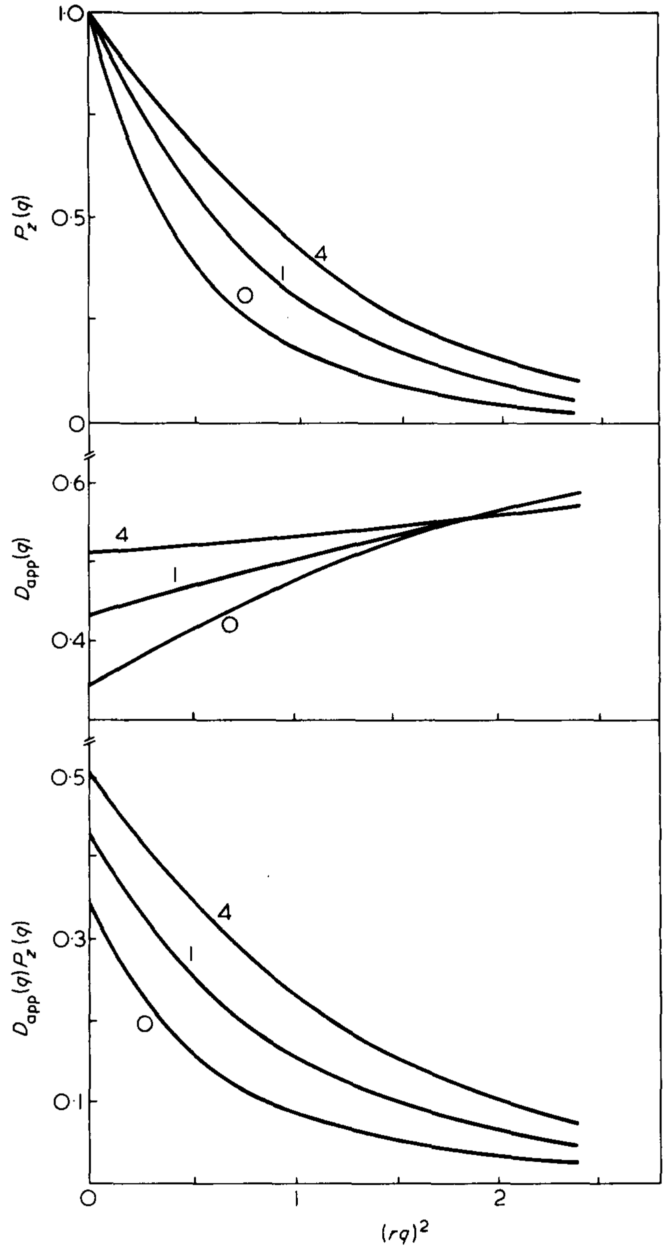

Figure 4 Effect of a Schulz–Zimm distribution on elastic and quasielastic light scattering. (a) Particle scattering factor (elastic light scattering) of compact spheres for distributions with m = 0, 1 and 4; (b) angular dependence of the apparent diffusion constant (quasielastic light scattering) for compact spheres; (c) the apparent diffusion constant multiplied by the particle scattering factor for compact spheres of different distribution width. Meaning of the figures as in (a) and (b)

for both distributions. Differentiation may be possible from the data of $\overline{r_z^{-1}}$ and $\bar{r}_z$, but requires a high accuracy of measurement.

In quasielastic light scattering the quantity $\bar{r}_z\overline{r_z^{-1}}$, for instance, is proportional to the product of the initial slope and the intercept of $D_{app}(q)P_z(q)$ plotted against q^2 while the $\overline{r_z^3}$ moment corresponds to the curvature of this plot. Finally, the second moment is proportional to the initial slope of the particle scattering factor $P_z(q)$ as a function of q^2 where $q = (4\pi/\lambda)\sin\theta/2$ and the other two quantities are defined in the preceding paper. The three curves for D_{app}, $P_z(q)$ and $D_{app}P_z(q)$ have been calculated for spheres of the same average radius r but different width of the Schulz–Zimm distribution and are plotted in *Figures 4a* to *4c*. The effects of polydispersity are large, and it is hoped, therefore, that the technique outlined here will be useful in estimating the size distribution from scattering experiments in cases where a suitable analytic centrifuge is not at hand. Certain success was achieved in the past by the analysis of the elastically-scattered light and without any doubt the accuracy in the determination of the size distribution is enhanced considerably by the combination of the quasielastic light scattering with the conventional elastic light scattering.

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