Macromol. Symp. ***145**, 1–7 (1999)*

Characterization of Nanoparticles

M. D. Lechner, W. Mächtle*[+]

*Physical Chemistry, University, Barbarastrasse 7, 49069 Osnabrueck, Germany

[+]Kunststofflaboratorium, Polymer Physics, BASF AG, 67056 Ludwigshafen, Germany

SUMMARY: Nanoparticles with diameters from 1 – 100 nm are used in large quantities for very different applications. A precise determination of the important physical quantities (which are responsible for the application properties) such as diameter, particle size distribution, and surface is therefore very essential. The most common methods for the determination of these quantities are analytical ultracentrifugation (AUC) and dynamic light scattering (DLS). The paper demonstrates the techniques of getting a precise characterization of nanoparticles and suggests a new method for the correction of the sedimentation coefficient and its distribution with respect to the diffusion coefficient.

Introduction

Nanoparticles are materials with diameters from 1 to 100 nm. They are produced in large quantities for very different applications such as lacquers, dyes, cosmetics, food, magnetic storage materials (tapes, disks, harddisks), catalysts, and print materials (toners, inks). The development of new nanoparticles and the modification of available nanoparticles with new properties need considerable scientific efforts. Important physical quantities of nanoparticles are the diameter d, the mass m, the molar mass M, the volume V, the density $\rho = m/V = M/V_m$ (V_m = molar volume), the specific volume $\upsilon = 1/\rho$, the surface O, the specific surface $o = O/m$ the differential mass and number distribution $w(d)$ and $x(d)$ and the integral mass and number distribution $W(d)$ and $X(d)$ of the physical quantities mentioned above. Nanoparticles have usually a spherical structure; therefore the relationships between the physical quantities are easy: $V = \pi\, d^3 / 6$, $O = \pi\, d^2$, $m = \pi\, d^3\, \rho / 6$, and $M = N_A\, \pi\, d^3\, \rho / 6$. For sophisticated nanoparticles e.g. core-shell materials the density gradient inside the particles may be also of interest. For catalysts the (specific) surface of the material is an important quantity and kinetic studies of the production of nanoparticles need number distributions of the physical quantities instead of mass distributions. The most reliable experimental methods for the characterization of nanoparticles are analytical ultracentrifugation (AUC) and dynamic light scattering (DLS). AUC has the advantage that the particles are fractionated; therefore different sizes of the particles may be detected with high precision.

CCC 1022-1360/99/$17.50+.50/0

Theoretical Considerations

Analytical ultracentrifugation (AUC)

In an analytical ultracentrifuge the diameter d of a nanoparticle and its distribution may be determined according to[1)]:

$$d = [18\eta_1 S/(\rho_2 - \rho_1)]^{1/2} \quad ; \quad S = (1/\omega^2)\mathrm{d}\ln r/\mathrm{d}t \qquad (1)$$

with η_1 = viscosity of the solvent, S = sedimentation coefficient, ρ_2 = density of the particle, ρ_1 = density of the solvent (dispersing agent), $\omega = 2\,\pi\,N$ = angular frequency of the rotor, r = distance from axis of rotation, and t = time.

For the experimental determination of the sedimentation coefficient of small particles and its distribution in an AUC it has to be taken into account that sedimentation and diffusion of the particles superimpose. The calculation of the diameter needs either to separate both effects or to calculate the diameter from combined sedimentation diffusion equations. This may be done in several ways:

- Extrapolation procedures. All kinds of extrapolation procedures takes into consideration that the sedimentation of a particle is proportional to the time t whereas the diffusion is proportional to the square root of the time $t^{1/2}$. That means extrapolation to t against infinity yields pure sedimentation and extrapolation to t against zero yields pure diffusion. The correct form of the differential distribution function of S, $g(S,C_0)$ or their integral function $G(S,C_0)$ could be derived by investigating the asymptotic behaviour of the boundary spreading equation[2)] for values of times reaching infinity. All extrapolation procedures exhibit true values of S together with its integral or differential distributions. From this the diameter d of the particle with its distribution and all other physical quantities may be calculated[2-5)].
- Correction of the apparent sedimentation coefficient with respect to the diffusion coefficient. The diffusion coefficient D may be calculated with the *Stokes-Einstein* relation:

  $$D = k\,T\,/\,(3\,\pi\,\eta_1\,d) \qquad (2)$$

  with k = *Boltzmann* constant, and T = temperature. Under the assumption, that the sedimentation of the particles is the dominant effect an approximate mean diameter of the particles may be estimated using eq. (1). The sedimentation curves may then be corrected with a calculated mean diffusion coefficient (using eq. (2)) by substraction of the concentration curve $C(r,t)$, the concentration gradient curve $(\partial C/\partial r)_t$ or the distribution curves $G(S,t,C_0)$ and $g(S,t,C_0)$ with the diffusion equation[6)]:

$$C(r,t)/C_0 = (1/2)\left\{1 - \mathrm{erf}\left[(r - r_\mathrm{m})/(4\,D\,t)^{1/2}\right]\right\} \;;\; \mathrm{erf}(x) = \left(2/\pi^{1/2}\right)\int_0^x \exp\left(-s^2\right)\mathrm{d}s \qquad (3)$$

$$(\partial C/\partial r)_t/C_0 = -\left[1/(4\,\pi\,D\,t)\right]\exp\left[-(r - r_\mathrm{m})^2/(4\,D\,t)\right] \qquad (4)$$

- Application of *Lamm's* equation. The problem has been solved with respect to monodisperse particles[2,7)]. Therefore this method is up to now not applicable to polydisperse particles.

Dynamic light scattering (DLS)

Dynamic light scattering measurements allow to determine the translational diffusion coefficient D according to[8)]

$$g_1(t) = \int_0^\infty G(\Gamma)\exp(-\Gamma\,t)\,\mathrm{d}\Gamma \;;\; \Gamma = D q^2 \;;\; q = (4\pi/\lambda)\sin(\theta/2) \qquad (5)$$

with $g_1(t)$ = autocorrelation function, t = time, λ = wavelength, and θ = observation angle. The relation of *Stokes-Einstein*, eq. (2) may be used to calculate the hydrodynamic diameter d from the diffusion cefficient D. Dynamic light scattering allows to determine the distribution of D and d according to eqs. (5) and (2) but the precision is not so high as those with the AUC; the reason is that the AUC fractionates the particles in contradiction to the DLS.

Results and Conclusion

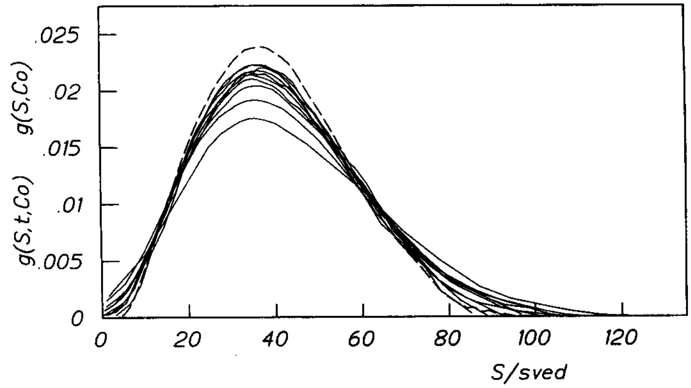

Fig. 1: Polystyrene latex in water, S – distribution, extrapolation (1 sved = 10^{-13} s)
C_0 = 3.015 g/L, ρ_1 = 0.9971 g/cm^3, ρ_2 = 1.055 g/cm^3, η_1 = 0.00891 g/(cm s), N = 25000 min^{-1}
——— = differential distribution functions at times t = 10 min to 60 min
– – – – = extrapolated differential distribution function at time $t = \infty$

Fig. 1 and 2 demonstrate the determination of the *S*- and *d*-distribution of a polystyrene latex measured in an analytical ultracentrifuge model E (*Beckman*, Palo Alto, CA, USA) equipped with *Schlieren* optics. The *Schlieren* curves $\mathrm{d}n/\mathrm{d}R = f(R)$ allow to determine the distribution function $g(S,t,C_0)$ and the sedimentation coefficient *S*. Extrapolation of $g(S,t,C_0)$ against $1/t = 0$ yields $g(S,C_0)$ and application of eq. (1) together with $w(d)\,\mathrm{d}d = g(S)\,\mathrm{d}S$ yields $w(d)$, $W(d)$, and d.

Fig. 3 and 4 demonstrate the new suggested diffusion correction procedure. Details of the procedure are given elsewhere$^{6)}$. Table 1 demonstrates that both extrapolation procedure and diffusion correction procedure give reliable results. For nanoparticles it would be better to use mass distribution based p-quantiles (preferably deciles) instead of number average, mass average, and z-average *d*-values. The reason is that they are more stable against outliers. In table 1 the following p-quantiles and range parameter are used:

d_{10} = 0.1-quantile = 1th decile
d_{50} = 0.5-quantile = 5th decile = median
d_{90} = 0.9-quantile = 9th decile
$(d_{90} - d_{10})/d_{50}$ = normalized interdecile range

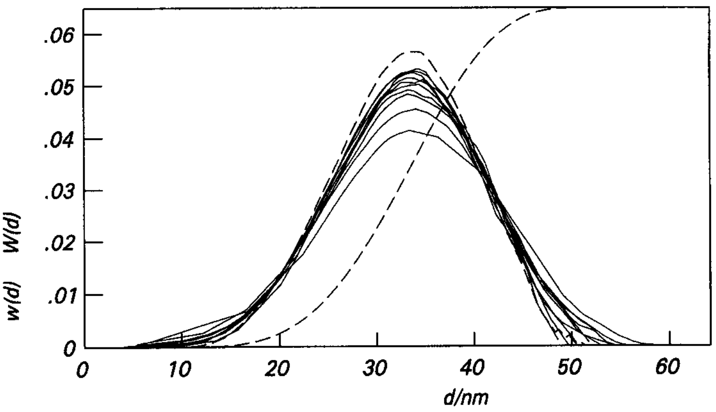

Fig. 2: Polystyrene latex in water, *d* – distribution, extrapolation (see fig. 1).
———— = differential distribution functions at times 10 to 60 min
– – – – = extrapolated differential distribution function at time t = ∞
– – – – = extrapolated integral distribution function at time t = ∞

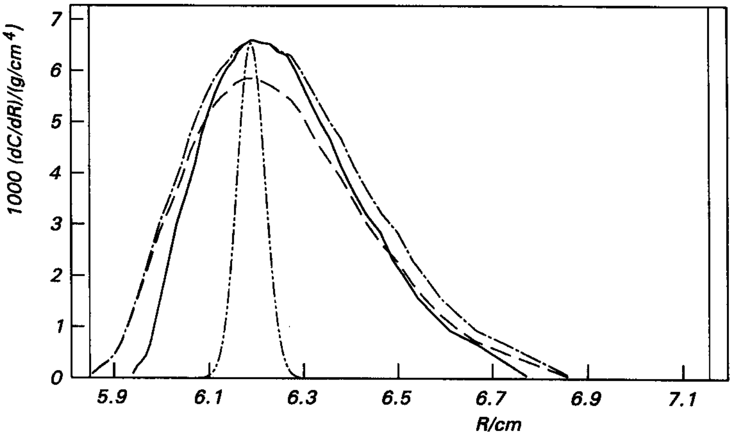

Fig. 3: Polystyrene latex in water, Schlieren optics curve at t = 45 min, correction method
— — — — — — = original curve ; — - — - — = correction for dilution
— - - — - - — = diffusion curve, eq. (4) ; ———— = correction for dilution and diffusion

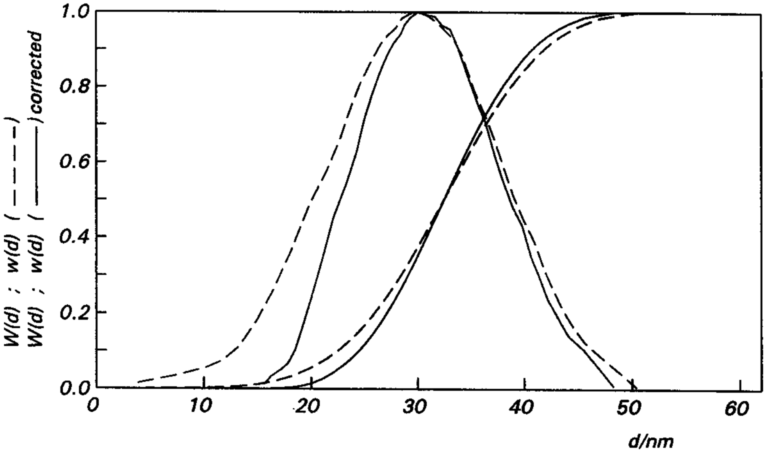

Fig. 4: Polystyrene latex in water, particle size distribution, correction method
— — — — — = without diffusion correction ; ———— = with diffusion correction

Table 1: Comparison of the calculated particle size distribution of polystyrene latex with the diffusion correction method and the extrapolation method.

Average values:	uncorrected	corrected new method	extrapolated ($1/t \to 0$) L.J. Gosting[3]
d_{10}/nm	22.0	24.3	23.7
d_{50}/nm	32.2	32.3	33.1
d_{90}/nm	41.8	40.6	41.5
$(d_{90} - d_{10})/d_{50}$	0.61	0.50	0.53

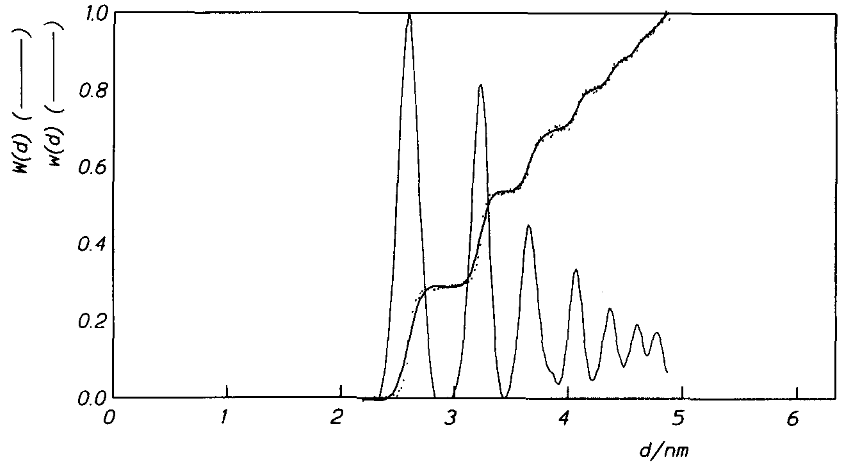

Fig. 5: ZnO in *iso*-propanol, integral and differential diameter distribution.
$C_0 = 0.766$ g/L, $\rho_1 = 0.781$ g/cm^3, $\rho_2 = 5.66$ g/cm^3, $\eta_1 = 0.021$ g/(cm s), $N = 25000$ min^{-1}

Figure 5 demonstrates that the AUC is able to resolve at least 6 different species[9]. The measurements were done with a *Beckman* Optima XL-A analytical ultracentrifuge (*Beckman*, Palo Alto, CA) with an absorption optics[9]. The absorption optics allows the direct determination of the concentration profile via *Lambert-Beers* law.

Figure 6 shows dynamic light scattering measurements on carboxymethylcellulose which was partially crosslinked. It is demonstrated that DLS is able to detect at least three different nanostructures: 1) the overall diameter ($d = 1720$ nm), 2) the distance of the network crosslinks ($d = 166$ nm), 3) the blob diameter ($d = 16.2$ nm).

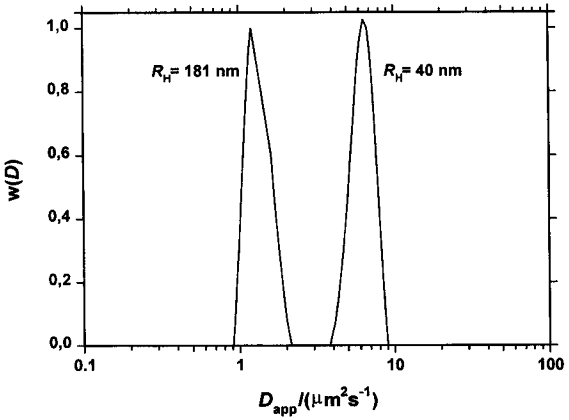

Fig. 6: Polystyrene latices in water. Diffusion coefficient distribution.

The examples show that the above described procedures work in order to determine physical quantities of nanoparticles. It depends on the special nanoparticle what kind of procedure gives the best results.

Particular thanks are due to the *BASF AG*, Ludwigshafen and to the *Fonds der Chemischen Industrie* for financial support.

References

1. W. Mächtle, Makromol. Chem. **185**, 1025 – 1039 (1984)
2. H. Fujita, Foundations of Ultracentrifugal Analysis, Wiley, New York 1975
3. L. J. Gosting, J. Am. Chem. Soc. **74**, 1548 – 1552 (1952)
4. N. Gralen, G. Lagermalm, J. Phys. Chem. **56**, 514 – 523 (1952)
5. K. E. van Holde, W. O. Weischet, Biopolymers **17**, 1387 – 1403 (1978)
6. M. D. Lechner, W. Mächtle, Prog. Coll. Polym. Sci., (1999), in press
7. P. Schuck, C. E. MacPhee, G. J. Howlett, Biophys. J. **74**, 466 – 474 (1998)
8. M. D. Lechner, K. Gehrke, E. H. Nordmeier, Makromolekulare Chemie, Birkhäuser, Basel 1996
9. H. Cölfen, T. Pauck, Coll. Polym. Sci. **275**, 175 – 180 (1997)