



Dynamic light scattering of dispersed fumed silica aggregates

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ABSTRACT

The characterisation of particle aggregates with dynamic light scattering yields an effective hydrodynamic diameter, which is dependent on the scattering angle. This dependency is partly due to polydispersity, but mainly caused by the aggregates' rotational diffusion. The paper examines this effect of rotation for suspensions of fumed silica by means of static and dynamic light scattering. A universal relationship between the hydrodynamic diameter and scattering angle was sought, as predicted by theory for DLCA aggregates (i.e. formed by diffusion limited cluster aggregation). The employed suspensions differed in BET of the powder (i.e. primary particle size) and state of dispersion.

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1. Introduction

Pyrogenic powders (e. g. fumed silica or carbon black) are important particle systems with various applications in liquid dispersions (e. g. as thickening agent). These powders are composed of relatively rigid, submicron aggregates from nanosized primary particles and possess a fractal-like structure that resembles that obtained in diffusion limited cluster aggregation (DLCA) simulations [1, 2]. The aggregates themselves may further agglomerate to large, supermicron clusters.

Dynamic light scattering (DLS) is a common characterisation method for suspensions of such powders. It probes the Brownian motion of particles and yields the particle diffusion coefficient or hydrodynamic particle diameter. There are several commercial DLS instruments, which differ in their optical set-up, signal processing and data evaluation. Of particular importance for the characterisation of aggregates is the variety of scattering angles θ (and wavelength), because the two types of diffusion, translational and rotational, contribute differently and as a function of θ to the scattering signal. As a result, the measured hydrodynamic aggregate size is a function of the scattering angle.

A previous study conducted by two of the authors [3] examined the structural and physical properties of commercial fumed silica powders. These powders differed mainly in the size distribution of the primary particles and in the distribution of the aggregation

number N and covered a wide range of fumed silica products with BET surfaces from 50 m²/g to 400 m²/g. One interesting result was, that the dependency of DLS results on the scattering angle θ or on the scattering vector q can be expressed in a dimensionless way ($D_{eff}/D_{eff,0}$ vs. qR_g), which seemed independent from the fumed silica grade—i.e. there is a master curve. This observation is in accordance with theoretical considerations for ideal fractal aggregates [4] and may be of potential benefit for the characterisation of such products.

The main objective of this paper is to explore if the master curve is affected by aggregate dispersion. This is of importance since there are as many dispersion procedures as there are research groups. The paper provides a detailed description on the theoretical background of the master curve and thoroughly discusses the procedures of analysing the measurement data. As a result of this discussion our previous experimental data were re-evaluated (mainly with regard to the radius of gyration) before being compared with the dispersion experiments.

2. Dynamic light scattering of fractal aggregates

Dynamic light scattering (DLS) probes temporal variations in the spatial arrangement of particles (= scattering objects) in the measurement cell. In a quiescent liquid such variations are caused by the Brownian motion of the particles. Thus, DLS can be employed to obtain the particle diffusion coefficient or the hydrodynamic particle diameter, respectively, if a sufficiently low particle concentration is preconditioned. However, Brownian motion possesses a translational and a rotational aspect. Commonly, only the translational diffusion coefficient is regarded in evaluating DLS data. This is correct for spheres. In the case of non-spherical particles or particle aggregates

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rotation causes an additional contribution to the light fluctuation. The significance of this contribution depends on the particle or aggregate size and the scattering angle. A further dependency of DLS results on the scattering angle is related to polydispersity.

2.1. Effect of polydispersity

In principle, scattering depends on the scattering angle. In the Rayleigh–Debye–Gans (RDG) limit this is related to the interference of the scattering waves which depends on the dimensionless inter-particle distance $q r_{ij}$, where q is the value of the scattering vector $q = 2k \sin(\theta/2)$. Besides, there may be an influence of the polarisation of the light wave. However, in most (dynamic) light scattering apparatus vertical polarised light is used ([5], p. 230), and we further assume monopole scattering from the primary particles.

DLS addresses the fluctuation of the scattered light intensity, which depends on the scattering angle θ or scattering vector q , respectively. The mean decay rate $\langle \Gamma \rangle$ of the light fluctuation of a polydisperse sample is given as:

$$\langle \Gamma \rangle = \int \Gamma dQ_{int} \quad (1)$$

where dQ_{int} is the relative contribution of the infinitesimal size fractions to the scattered light intensity. Evaluating DLS signals in terms of this mean decay rate is called the method of cumulants [6]. It is the most robust method for data interpretation and, therefore, commonly employed. The corresponding diffusion coefficient and particle size are the effective diffusion coefficient D_{eff} and the effective hydrodynamic diameter $x_{h,eff}$:

$$D_{eff} = \langle \Gamma \rangle / q^2 \quad (2)$$

$$x_{h,eff} = \frac{kT}{3\pi\eta} \cdot \frac{1}{D_{eff}} \quad (3)$$

For monodisperse particles of spherical shape the $x_{h,eff}$ and D_{eff} should be independent on the measurement technique. However, for polydisperse samples both parameters depend on the scattering angle θ or the scattering vector q . For a number weighted distribution the effective hydrodynamic diameter $x_{h,eff}$ is obtained from:

$$x_{h,eff} = \frac{\int C_{psca}(x) dQ_0}{\int x_h^{-1} C_{psca}(x) dQ_0} \quad (4)$$

where C_{psca} is the partial scattering cross section of particles of size x . In the Guinier limit of the RDG scattering the partial scattering cross section can be expressed as [7]:

$$C_{psca} = K \cdot V^2 \cdot \exp\left(-\frac{1}{3}(qR_g)^2\right) \approx K \cdot V^2 \cdot \left(1 - \frac{1}{3}(qR_g)^2\right) \quad (5)$$

with K being a constant and V the volume of the scattering object. If we further assume, that the radius of gyration is proportional to the hydrodynamic diameter ($R_g = \beta \cdot \frac{1}{2} x_{h,t}$) and that the particle volume is proportional to some power D of x_h we end up with:

$$x_{Cum} = \frac{\int x_h^{2D} \cdot \left(1 - \frac{1}{12}\beta^2 \cdot q^2 x_h^2\right) dQ_0}{\int x_h^{2D-1} \cdot \left(1 - \frac{1}{12}\beta^2 \cdot q^2 x_h^2\right) dQ_0} = \frac{M_{2D,0} - \frac{1}{12}\beta^2 \cdot q^2 M_{2D+2,0}}{M_{2D-1,0} - \frac{1}{12}\beta^2 \cdot q^2 M_{2D+1,0}} \quad (6)$$

where $M_{k,0}$ are number weighted averages (moments) of x_h^k . From this we obtain:

$$\lim_{q \rightarrow 0} \frac{D_{eff}}{D_t} = \frac{x_{Cum,q=0}}{x_{Cum}} = 1 + \frac{1}{12}\beta^2 \cdot q^2 \left(M_{2D+2,0}/M_{2D,0} - M_{2D+1,0}/M_{2D-1,0}\right) \quad (7)$$

At the same time the effective radius of gyration as obtained by static light scattering (SLS) is defined as:

$$R_{g,eff}^2 = \lim_{q \rightarrow 0} \int R_g^2 dQ_{int} = \frac{\beta^2 M_{2D+2,0}}{4 M_{2D,0}} \quad (8)$$

Without loss of generality we can explain the ratio of two moments $M_{k,0}$ and $M_{l,0}$ as the product of the $(k-l)$ -th power of $R_{g,eff}$ and a factor that depends on the polydispersity. However, for ideal aggregation processes (like DLCA) the polydispersity is independent from the aggregate size [8] and, as a first approximation, we will assume such a behaviour for all aggregate systems. Consequently, the moment ratios on the r.h.s. of Eq. (7) are proportional to the square of $R_{g,eff}$. Moreover, in a few examples we examined it appeared that the difference between these ratios is always positive as long as the distribution function obeys either a non-negative or a non-positive condition; that holds true for particle size distributions. Hence, we can state that:

$$\lim_{qR_g \rightarrow 0} \frac{D_{eff}}{D_t} = 1 + const. \cdot (qR_{g,eff})^2 \quad (9)$$

With a similar expression that will be derived for the rotational influence on the effective diffusion, this is a useful relationship for extracting the D_t from experimental data of fine particles, since DLS measurements are principally conducted at finite q -values.

2.2. Effect of aggregate rotation

The central idea behind DLS experiments is that the detector signal is caused by interference of the scattered fields originating from all illuminated particles. Thus, it depends on the position of the particles and each change of the particle arrangement coincides with a signal change. In the case of particle aggregates each primary particle acts as a scattering object. Consequently, the particle arrangement can be altered by translation or by rotation. Both are supposed to occur in Brownian motion and are quantified by the respective diffusion coefficients:

$$D_t = \frac{kT}{6\pi\eta R_{h,t}} \quad (10)$$

$$\theta = \frac{kT}{8\pi\eta R_{h,r}^3} \quad (11)$$

The impact of the rotational diffusion on the DLS of aggregates was studied by Lindsay et al. [4]. Their mathematical treatment is based on the assumption of RDG scattering and vertical polarisation. Moreover, they assumed, that the rotational and translational movements are decoupled—a reasonable approach when the aggregates show only moderate anisotropy (true for DLCA aggregates). Lindsay et al. derived analytical expressions for the field and intensity autocorrelation function and could prove that a Siegert relation [9] $G^{(2)}(\tau, q) \approx G_{Basis}^{(2)} + |G^{(1)}(\tau, q)|^2$ exists for a sufficiently large number of aggregates in the illuminated zone.

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