

Determination of dimensions of exfoliating materials in aqueous suspensions

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Abstract

A method for measurement of dimensions of platy particles of exfoliating materials, such as clays, in aqueous suspensions *in situ* is proposed. Equivalent spherical diameter (esd), measured by many common methods, depends more on the major (lateral) dimension of a particle, while it is less sensitive to changes of the particle thickness. Addition of the second method, which results are a function of the particle diameter and thickness too, would provide more accurate determination of the particle dimensions. The previous work [1] used a combination of low-temperature nitrogen adsorption (BET) and dynamic light scattering (DLS) methods for determination of specific surface area of dry powder of platy particles and their *esd* in suspension. While it is suitable for measurement of particle size for non-exfoliating materials, it gives incorrect results for exfoliating materials, which dramatically change their surface area when dispersed in liquid. We modify this method by substituting BET method with NMR relaxometry, which allows to measure wetted surface area of the dispersed material directly in suspension. The advantages of this method are:

- More accurate determination of diameter and thickness of platy, particularly exfoliating, materials directly in suspension
- Possibility of routine monitoring of particle size changes during the dispersing process

Method

The method is based on measurement of the specific surface area (S) of suspended particles by NMR relaxometry, and equivalent spherical diameter (esd) distribution of the particles by dynamic light scattering (DLS). Both measured values are functions of two particle dimensions d and t (lateral size and thickness), which can be then found from the system of two equations [1]:

$$\begin{cases} d = \arctan\left(\frac{d}{t}\right) \cdot esd_{50} \cdot e^{-\ln^2\left(\frac{esd_{84}}{esd_{50}}\right)} \\ S = \frac{2}{\delta} \left(\frac{1}{t} + \frac{2}{d}\right) \end{cases} \quad (1)$$

where δ - density of the particles; esd_{50} is the particle size where 50% of the particles are finer than this size and esd_{84} is the particle size where 84% of the particles are finer than this size, which are routinely determined from esd distribution by DLS method.

The measured parameters in NMR relaxometry are time of spin-spin (T_2) or spin-lattice (T_1) relaxation of hydrogen protons. The specific surface area of a material dispersed in water depends on the relaxation time according to the following equation:

$$S = \left(\frac{1}{T_i} - \frac{1}{T_{fi}}\right) \frac{T_{bi}}{l\rho C_0} \quad (2)$$

where T_i is the spin relaxation time of hydrogen protons in the dispersion, T_{fi} is the relaxation time of hydrogen protons in free (bulk) water, T_{bi} – spin relaxation time of hydrogen protons in water bound to the particle surface, i is 1 (spin-lattice) or 2 (spin-spin), l – thickness of the bound water layer, ρ is water density, C_0 – w/v concentration of the dispersed particles.

Measurement of T_{fi} and T_i is straightforward and requires simple measurement of the relaxation times of hydrogen in the particle-free water and the dispersion, respectively. At the same time the determination of the ratio T_{bi}/l is more elaborate, but **fortunately** needs to be found only once for a certain material. It can be determined in two ways:

1. Measurement of the relaxation time of hydrogen protons in water bound to the particle surface T_{bi} if the thickness of bound water layer l is known (it can be found from literature [2], for many clays l is about 1 nm [3]).
2. If a sample of dispersion with completely exfoliated material is available (calibration sample), the ratio T_{bi}/l can be calculated from the equation:

$$\frac{T_{bi}}{l} = \frac{S_c \rho C_c}{\frac{1}{T_{ci}} - \frac{1}{T_{fi}}} \quad (3)$$

where S_c – specific surface area, calculated from AFM measurements of the particles from the dried calibration sample; C_c – concentration of the particles in calibration sample; T_{ci} – relaxation time in the calibration sample.

As for the choice between measurements of spin-lattice (T_1) or spin-spin (T_2) relaxation time, T_2 is usually more suitable for the less concentrated suspensions as its dependence on the specific surface area is more pronounced [4], while measurement of T_1 may be required for measurements

of relaxation in hydrogen spins in bound water, because T_2 may be too small for such measurements [4].

As an example, we describe the detailed experimental procedure for this method for determination of geometrical dimensions of synthetic hectorite clay Laponite in aqueous dispersion. Laponite is a widely used model material for studies of exfoliating clays due to its high dispersibility in water, narrow size distribution and uniform shape of its individual disc-shaped platelets. Laponite powder consists of stacks, or tactoids, which exfoliate into platelets with diameter of about 20-25 nm and thickness of 1 nm, particle density $\delta = 2.53 \text{ g/cm}^3$ [5–7].

The 0.5% Laponite dispersion was prepared by slowly adding 0.1 g of Laponite powder (Laponite RD, BYK Additives & Instruments) to 20 ml of deionized water with pH adjusted to 10 with 1 M NaOH. The dispersion was stirred for 45 min by magnetic mixer at speed of 1000 rpm. Then the dispersion was filtered through Whatman syringe filter (pore size of 0.1 μm) to remove large agglomerates. The measurements were performed for 1 day old dispersion.

DLS measurements were carried out on Zetasizer Nano ZS instrument (Malvern) at backscattering angle of 175° and the laser wavelength of 632.8 nm. The autocorrelation function was automatically processed by cumulant method. The particle size distribution obtained by DLS is shown in Figure 1. Number particle size distribution was measured several times and for each distribution values esd_{50} and esd_{84} were calculated. Average value of esd_{50} was 14 nm and average value of esd_{84} was 18.4 nm.

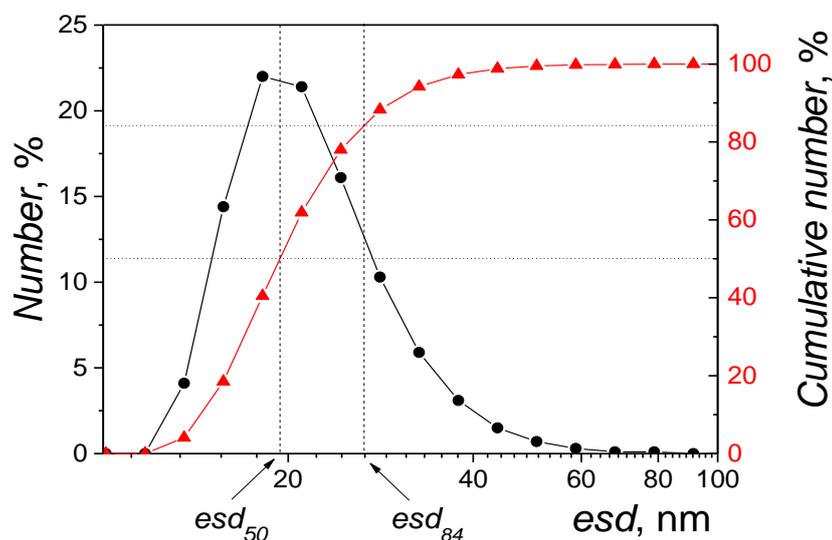


Figure 1. Particle esd distribution (black circles) and cumulative number (red triangles) particle esd distribution measured by dynamic light scattering for the Laponite suspension

^1H NMR-relaxometry was performed on a portable bench-top device Acorn Area particle analyzer (Xigo Nanotools), operating at the resonant frequency of 13.0 MHz. Measured spin

relaxation times were: $T_{f1} = 2.8$ s, $T_{f2} = 2.63$ s in Laponite-free water and $T_1 = 2.6$ s, $T_2 = 1.09$ s in Laponite dispersion.

The ratio T_{bi}/l was determined by two ways. The first approach is based on measuring the relaxation time of bound water T_{b1} using the powder with different amounts of adsorbed water and the second approach is based on calculation of T_{b2}/l using a calibration sample.

Method 1.

To measure spin-lattice relaxation T_1 of the hydrogen spins in water molecules adsorbed on the surface of Laponite powder, the powder was degassed for 5 hours at 350°C. Then the dried powder was placed into a sealed container filled with moist air for varied periods of time to adsorb different amounts of water, and then poured into the NMR tube, which was placed into the NMR relaxometer, where T_1 was measured. The amount of adsorbed water was determined by the mass difference between the wet and the degassed dry powders.

Figure 2 shows the dependence of T_1 on the water weight fraction in wetted powder. According to the two-phase fast-exchange model, the spin relaxation time T_i corresponds to T_{fi} and T_{bi} by the following equation [2,4]:

$$\frac{1}{T_i} = \frac{1}{T_{fi}} \frac{V_f}{V} + \frac{1}{T_{bi}} \frac{V_b}{V} \quad (4)$$

where V_f – volume of bulk water, V_b – volume of bound water, V – total water volume.

Equation (4) states that until all the water molecules belong to the surface bound water layer, T_1 changes minimally, but starts to grow when the surface layer becomes saturated and adsorption of molecules not bound to the surface begins. Thus, the point of inflection of the plot on Figure 2 corresponds to T_{b1} of 10.5 ms.

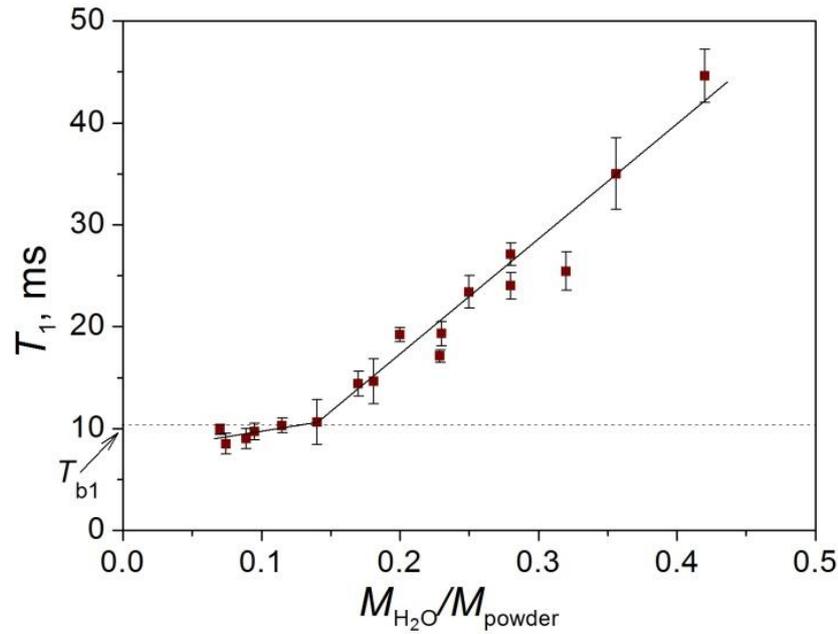


Figure 2. Dependence of spin-lattice relaxation time of hydrogen protons in powder with adsorbed water layer T_1 on the ratio of mass of water M_{H_2O} adsorbed on the powder to weight of the powder M_{powder} . T_{b1} – Spin-lattice relaxation time of protons in bound water molecules. The lines serve as a guide to the eye.

The thickness of the bound water layer $l = 1$ nm for Laponite particles in water [2,4]. However, on the surface of Laponite platelet there are pronounced centers of adsorption of water molecules, Na^+ ions, which have the energy of adsorption significantly greater than the surface oxygen atoms have [4]. Therefore, for Laponite we can only speak about the effective thickness of the layer of bound water l_{eff} . As Na^+ ions take only 10% place on particle surface [4], $l_{eff} = 0.1$ nm.

Considering $l_{eff} = 0.1$ nm and $T_{b1} = 10.5$ ms we get $T_{b1}/l = 0.1$ s/nm.

Method 2.

The second approach for calculating T_{b2}/l is to use to a calibration sample with known surface area. Laponite suspension (0.1 w/v %, 7 days old) was chosen for this purpose because particles completely exfoliate at this concentration [8].

The sample was diluted to 0.001% concentration and 10 μ l of this diluted sample was deposited on a mica substrate (1 cm^2) and dried at 150 $^{\circ}C$. Before measurements the substrate was placed in a water vapor for 1 hour to eliminate the charge influence and dried. Number average particle diameter measured by AFM in tapping mode (NTEGRA Aura scanning probe microscope, NT-MDT) was 19 nm, average thickness of a single particles was 1.05 nm.

Calculated from the AFM data, specific surface area $S_c = 840 \text{ m}^2/\text{g}$. Time of spin-spin relaxation of the calibration sample $T_{c2} = 1.9 \text{ ms}$. Using these values in the equation (3) T_{b2}/l is equal to $5.7 \cdot 10^{-3} \text{ s/nm}$.

Substituting the obtained values of T_1 , T_{f1} and T_{b1}/l from the first method, or T_2 , T_{f2} and T_{b2}/l from the second method to the equation (2), we get the values of the specific surface area of Laponite particles of 550 and 620 m^2/g , respectively, for the analyzed dispersion.

These values and esd_{50} and esd_{84} from DLS measurements were used in the equations (1) to calculate diameter and thickness of Laponite particles dispersed in water. The results are presented in Table 1.

Table 1

Method of determination T_{bi}/l	Specific surface area, m^2/g	Equivalent spherical diameter, nm		Diameter (d), nm	Thickness (t), nm
		esd_{50}	esd_{84}		
Method 1	550	14	18.3	19	1.4
Method 2	620	14	18.3	20	1.3

The difference of the calculated thickness value from the thickness of individual Laponite platelet (1 nm) indicates that the particles in the analyzed 1 day old sample didn't exfoliate completely, which is also demonstrated by smaller values of the specific surface area compared to the specific surface area of the calibration, completely exfoliated sample.

Acknowledgements

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