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SHORT COMMUNICATION

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Analysis of the morphology of hectorite by use of small-angle X-ray scattering

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Abstract An analysis of the three-dimensional correlation function of small-angle scattering is applied for the direct determination of stereological parameters of hectorite samples. Beside characteristic lengths and volume fractions the specific order distances are given. The samples can be described by homogeneous particles of different order magnitudes up to the size of the secondary particles, which were estimated to have maximum dimensions of about 450 nm. Beside traditional stereological formulas, including the interpretation of the derivatives of the small-angle correlation function, the so-called transformed correlation function is applied in order to detect distinctive characteristic lengths.

Key words Hectorite · Small-angle scattering · Aggregation · Primary particles · Secondary particles

Introduction

For the characterization of nanometric microparticles via scattering experiments, it must be taken into account that the information obtainable from a scattering curve, $I(h)$, is limited. The characterization of microparticles by use of the autocorrelation function of (electron) density (CF) of small-angle scattering (SAS) only "works" in a limited r interval, $r_{\min} < r < r_{\max}$. Here, $r_{\min}$ and $r_{\max}$ are the lower and the upper resolution limits of the SAS experiment, given in the optimum case by $r_{\min} = \pi/h_{\max}$ and $r_{\max} = \pi/h_{\min}$. The scattering vector is given by $h = 4\pi/\lambda \sin(\varepsilon)$, where the scattering angle is 2ε. The detailed interpretation and the explicit calculation of the CF $\gamma(r)$ from the experiment was analysed by several authors [1–3]. The determination of γ from $I(h)$ is a formal procedure, independent of the shape of the microparticles.

The scattering curve of a quasidiluted particle arrangement without long-range order is always band-limited [2, 3]; however also in cases of particle clusters or tightly packed particle arrangements, L has the meaning of a long order distance. Typical detectable values of L extend from 4 to 400 nm. L is a deciding parameter for all steps of data evaluation. An estimation should be known from other experimental data before starting the scattering experiments.

Theoretically, the position $r = L$ is clearly defined in the behaviour of the CF for large L. Coming from large r, L is obviously exactly the point on the r-axis where $\gamma(r)$ no longer equals zero. Because of the disappearance of a series of derivatives of $\gamma(r)$ at $r = L$, the idea to detect L directly from the CF cannot be used in most practical cases [4, 5].

In this study SAS is used for characterizing the arrangement of the primary and secondary particles of the clay mineral hectorite. Hectorite forms intercalated compounds with various organic and inorganic materials. This property is caused by the swelling behaviour of hectorite by water or polar organic molecules.

To understand the process of intercalation and to generalize the relation between structure and swelling properties of the minerals it is necessary to know the dimension and the arrangement of the hectorite layers of the primary and of the secondary particles and the pores formed between them.

Several authors used SAS to describe the swelling process in clay minerals [6–8], but in these studies the main aim was to characterize exclusively the arrangement of the silicate layers.

Experimental

Materials

Hectorite was synthesized under hydrothermal conditions at 200 °C using the gelation method. The following molecular ratio of the oxides represents the composition of reaction mixture used: 8 SiO_2/5.33 MgO/5.6 Na_2O/240 H_2O/0.67 Li_2O.

Silica sol, sodium hydroxide, lithium hydroxide, magnesium oxide and sodium aluminate solutions were used as starting materials to prepare the reaction mixture. The solid content of the reaction mixture amounted to about 20 wt%. After a crystallisation time of 24 h, the products were separated by filtration, washed with deionized water and air-dried at room temperature.

Methods

The SAS experiments were performed with the use of a Kratky camera and Cu K_α radiation in an h interval of $0.066/\text{nm} < h < 2.2/\text{nm}$.

Results and discussion

Basic properties of the transformed CF

The so-called transformed correlation function (TCF) is defined by [9]

$$\gamma_\mathrm{T}(r) = \frac{2}{\pi}\mathrm{arc}\ \sin(1 - [\gamma(r)]^{1/3}) \ . \tag{1}$$

Equation (1) can be applied to a wide class of geometric configurations. In principle, $\gamma_\mathrm{T}(r)$ represents the mean limiting angle, $\Theta(r)$, of linear erosion, which equals $\pi/2$, for the maximum chord, L, within the particle. $\gamma_\mathrm{T}(L) = 1$ holds and possible values exist in the interval $0 \le \gamma_\mathrm{T}(r) \le 1$.

This transformation was applied for several CFs of the right circular cones [5] and in some other cases, including the case of unlimited particles, $L \to \infty$, as well. Some general rules for the behaviour of $\gamma_\mathrm{T}(r)$ are explained later.

The linear extrapolation of $\gamma_T(r)$ yields L_{max}

In order to achieve an estimation for L in the form $L < L_\mathrm{max}$, the determination of the first two coefficients of series expansions of $\gamma_\mathrm{T}(r)$, Eq. (1), at $r = L$ was performed for a finite particle volume, V,

$$\gamma_\mathrm{T}(r) \approx 1 + \frac{2}{\pi}\sqrt{\frac{L-r}{w}}\left[1 - \frac{1}{24}\left(\frac{L-r}{w}\right) + \frac{3}{640}\left(\frac{L-r}{w}\right)^2 - \cdots + \cdots\right] \ . \tag{2}$$

If $\gamma_\mathrm{T}(r)$ is approximated in terms of L and γ, then, under certain presumptions in a special form including a representation for the coefficient, c_1, it follows that

$$\gamma_\mathrm{T}(r) \approx 1 + c_1(L-r) + c_2(L-r)^2 + \cdots$$

$$c_1 = \frac{2}{3\pi}\lim_{r\to L-}\left\{\frac{\partial[\ln\gamma(r)]}{\partial r}\frac{1}{\sqrt{2\gamma(r) - \gamma(r)^{4/3}}}\right\} \ . \tag{3}$$

c_1 is always negative. Lastly, $\gamma'_\mathrm{T}(L)$ has the property $\gamma'_\mathrm{T}(L) = -c_1 > 0$; therefore, the first derivative of the TCF at $r = L$ in each case is nonnegative and consequently

$$\lim_{r\to L-}\gamma'_\mathrm{T}(r) > 0 \tag{4}$$

holds near L. The L position itself is significantly marked by the strictly monotonically increasing behaviour, $c_1 < 0$, of $\gamma_\mathrm{T}(r)$, at least to the left of $r = L$, up to the limiting value $\gamma_\mathrm{T}(L) = 1$. Thus, based on these considerations, a linear extrapolation of the TCF always yields an estimation L_max for the largest particle diameter, $L_\mathrm{max} > L$.

$\gamma(r)$ follows from $I(h)$ by use of the transformation, including a careful reduction of the truncation errors,

$$\gamma(r) = \frac{\int_0^{h\max} h^2 I(h)(\sin(hr)/hr)\mathrm{d}h}{\int_0^{h\max} h^2 I(h)\mathrm{d}h} \ . \tag{5}$$

Equation (1) is applied in a second step. Based on this theory, the estimation of L_max is possible, operating with a linear extrapolation based on the biggest available $\gamma_\mathrm{T}(r)$ values, say at an r value which corresponds to $\gamma_\mathrm{T}(r) \approx 0.5$. These statements hold if the particle dimensions involve a finite V in the sense of the SAS experiment; however, the transformation Eq. (1) can be applied formally for any positive value of any CF, also in cases if $\gamma(r)$ is far from approaching the r-axis (e.g., if a particle with $L = 1000\,\text{nm}$ is sampled at $r = 200\,\text{nm}$).

For a simple application of $\gamma_\mathrm{T}(r)$ see Fig. 1. The mean chord length of the cone considered is $L_m = 0.55$ [5].

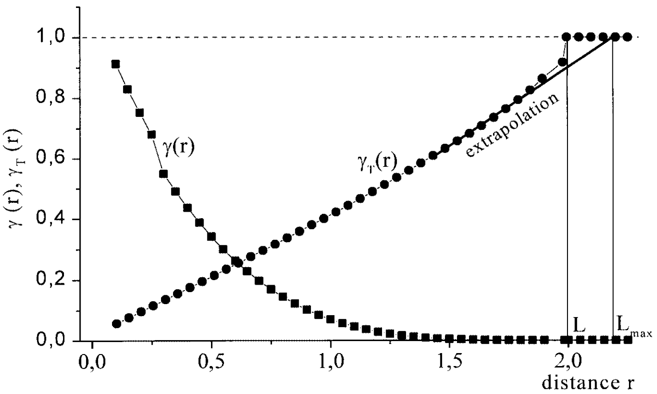

Fig. 1 Simulation of the functions $\gamma(r)$ and $\gamma_T(r)$ of a cone with the radius $R = 1$ and height $H = 1$. The largest particle dimension $L = 2$ is clearly marked by $\gamma_T(2) = 1$. L cannot be detected from $\gamma(r)$. An estimation $L_{max}, L_{max} > L$, can be calculated by use of an extrapolation of $\gamma_T(r)$.

$\gamma_T(r)$ in the case of an "infinitely extended" particle

There are some special models for particle systems with $L \to \infty$. In order to investigate the applicability of Eq. (1), the model case of an infinitely extended layer with constant height was considered in Refs. [9, 10]. $\gamma(r)$ asymptotically approaches zero. $\gamma(r) > 0$ and $\gamma_T(r) < 1$ hold for each r; thus, no L value is determinable.

The connection with an experimental case is the following. Independent of the sample under consideration, r_{min} and r_{max} clearly define the limits. Consequently, in cases $r_{max} < L$ no precise answer can be given concerning the distance L.

Two answers are possible based on a well-known r_{max}. On the one hand, in the case $L < r_{max}$, L can be determined absolutely reliably. On the other hand, in the case $r_{max} < L$, only the formal statement $r_{max} < L$ is correct. In the latter case, the experimental conditions are not tailor-made for the determination of L and thus should be optimized with respect to the L parameter of the sample. Similar problems were discussed by Damaschun et al. [3].

The case of separated particles having a systematic arrangement

The length L is well defined for separated or composite particles, see the example of a pair of spheres (two spheres with the same diameter $d = 1$, the centres of which are separated by a fixed distance s, $d < s$, e.g. $s = 2$) in Ref. [9]. L is $L = s + d = 3$. $\gamma(L) = 0$, $\gamma'(L) = 0$ and $\gamma''(L) = 0$ holds. L cannot be directly estimated from $\gamma(r)$, $\gamma'(L)$ or $\gamma''(L)$. It is demonstrated in Ref. [9] how this case can be handled via the TCF. The TCF assigns the exact position of L and it picks out the sphere diameter, d.

The case of nonconvex particles

This situation can be traced back to the case of several tightly packed convex particles. From the conditions in Ref. [4], it is clear that the shape of the particle surface near the maximum chord L exclusively influences the behaviour of the CF near $r = L$. Equation (1) is also applicable in such a case.

These theoretical foundations are now applied in addition to the whole theory of lineal analysis via $\gamma''(r)$. The characterization of a hectorite sample is performed with these methods.

Application of the CF for characterizing the structure parameters of the hectorite

Hectorite is an aluminium-free trioctahedral smectite clay. A schematic model representation of the structure of hectorite layers is shown in Fig. 2. It consists of coordinated tetrahedral–octahedral–tetrahedral sheets with magnesium ions placed at the octahedral positives. About every ninth magnesium ion is replaced by lithium. This replacement results in a negative layer charge of approximately 0.6 per unit cell (formula unit), typical for smectite-type minerals. The tetrahedral sheet contains only silicate tetrahedra. Foshag and Woodford [11], Strese and Hofmann [12] as well as Ames et al. [13] have found an ideal formula $(Mg_{5.33}Li_{0.67})^{VI}(Si_8)^{IV}O_{20}(OH,F)_4Na^+_{0.67} \cdot nH_2O$ for hectorite. The interlayer sodium cations, compensating the negative layer charge, are between the silicate layers. A specific number of silicate layers form multilayer arrangements, which are

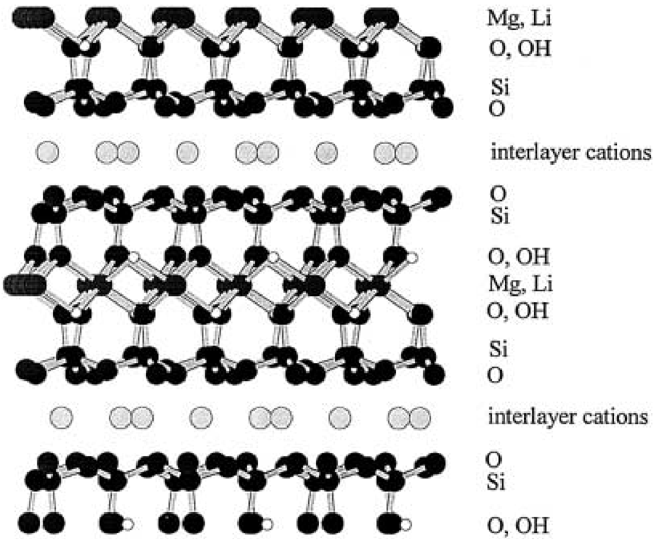

Fig. 2 Schematic structure of Hectorite

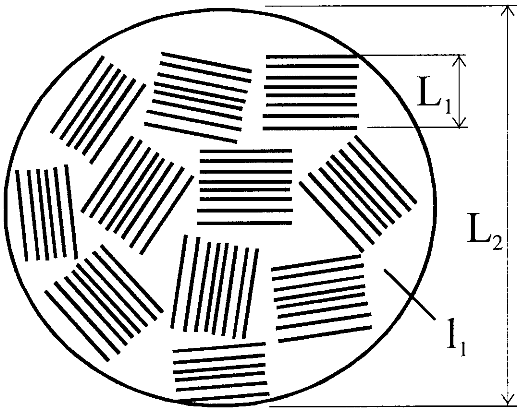

Fig. 3 Two-dimensional model of a primary particle L_1 : maximum dimension of the silicate multilayers,.L_2 : maximum dimension of the primary particle, l_1 : mean chord length of the mesopores

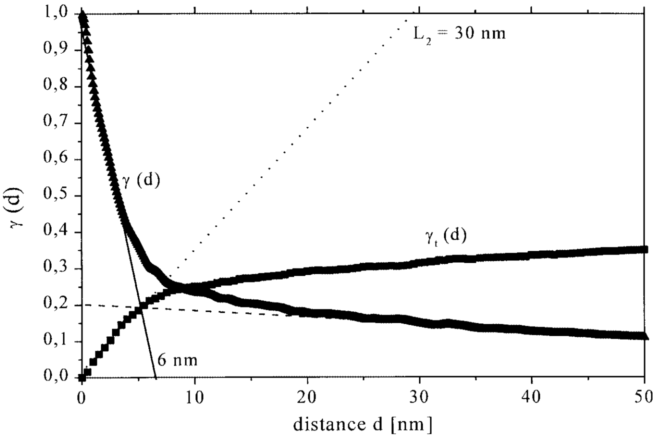

Fig. 4 Representation of the correlation function $\gamma(d)$ and the transformed correlation function $\gamma_T(d)$ of the hectorite

arranged in a specific way to each other and create the so-called primary particle (Fig. 3).

The main aim was to get information about the hierarchical buildup, i.e. the number and order of the silicate layers within the multilayers, of the multilayers within the primary particle as well as of the primary particle within the secondary particle.

From the SAS intensity of the hectorites the CF $\gamma(d)$ was calculated (Eq. 5) for the example of hectorite H/ 0.67 Li in the region from 0 to 50 nm, represented in Fig. 4. This CF contains all the geometrical information about the morphology of the silicate multilayers, the size of the primary particles and furthermore certain information about the secondary particles.

There is a general theory for the interpretation of the behaviour of $\gamma''(d)$ in terms of the corresponding chord lengths segments. In order to illustrate the curve behaviour of $\gamma(d)$ and $\gamma''(d)$ these functions are represented in Figs. 4 and 5.

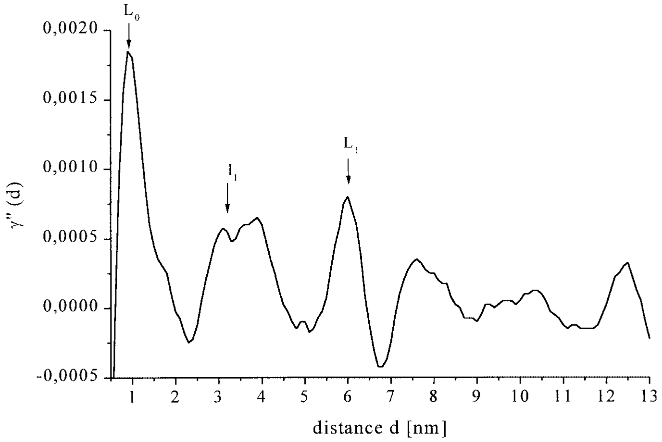

Fig. 5 Second derivative of the correlation function $\gamma''(d)$ to $\gamma(d)$, compare with figure 4

A value of $L_0 = 1\,\text{nm}$ follows from the analysis of the second derivative for the mean size of a single silicate sheet. For the multilayers $L_1 = 6\,\text{nm}$; for the extension of the mesopores, l_1, between the multilayers, a value of about 3–4 nm results from $\gamma''(d)$.

Consequently the volume fraction, c, of the multilayers within the primary particles is defined by $c = L_1/(L_1 + l_1)$; this yields approximately 60%. Consequently the mesopores involve 40%. Most of the peaks in Fig. 5 can be interpreted as sums of mean chord lengths.

From the extrapolation of the linear part of the TCF (Fig. 4, Eq. 1 [14]), $L_{\max} \approx 30\,\text{nm} < L_2$ was determined. Thus, $L_2 \approx 30\,\text{nm}$ is the maximum dimension of the primary particles. This is 5 times more than the calculated size of the silicate multilayers. This means, considering the volume part, a primary particle consists of a maximum of nine silicate multilayers.

Further, the extrapolation of $\gamma_T(d)$ based on the biggest available values of $d < r_{\max}$ (40–50 nm) can be used to estimate another order distance L_3 (greatest extension of the secondary particles). The extrapolation strategy (see earlier) yields a length of $L_3 = 450\,\text{nm}$.

From $\gamma'(0)$ the ratio of the particle surface to the volume of the mesopores within the primary particle can be determined. Using the extrapolation of $\gamma'(d)$ the following approximation can be obtained $|\gamma'(0)| = 1/7\,\text{nm} = S/[4\,V(c(1-c)][4,10]$, which with $c = 60\%$ leads to the result that the ratio of the particle surface to the particle volume for the multilayers in the primary particles is $S/V = 0.14/\text{nm}$. The ratio of the surface to the volume of the primary particles within the secondary particles cannot be estimated in detail more without further information. The volume fraction, p, of the primary particles within the secondary particles is unknown. With the help of $L_2 = 30\,\text{nm}$ and the linear extrapolation of $\gamma(d)$ it follows that $S/[4\,Vp(1-p)] = 0.2/30\,\text{nm}$. In this way, the relation of the surface to the

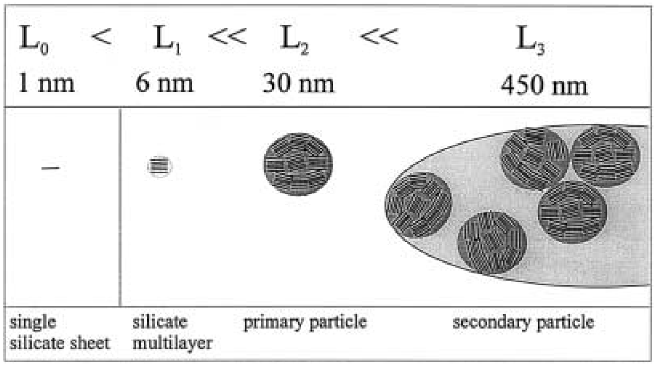

Fig. 6 Model of the determined parameters of the hectorite particle

volume is related as 1/150 nm. More precise statements cannot be made.

Conclusion

A method was developed based on the allowing the determination of the size parameters and volume parts for the individual building units of hectorite particles. In accordance with the determined parameters a model of the hierarchical construction of a hectorite aggregate is illustrated in Fig. 6.

The maximum height of a silicate sheet is 1 nm. The silicate multilayers consist of a maximum of six silicate sheets, because the maximum dimension of the multilayers is 6 nm. For the primary particles a maximum dimension of 30 nm was determined. The secondary particles were estimated to have a maximum dimension of about 450 nm.

In future, it is our aim to investigate these parameters for hectorites substituted isomorphically in order to examine and recognize a connection between the structure variation (different atomic occupation at the octahedral and tetrahedral sites) and the morphological parameters. The results show, that small angle X-ray scattering and the method according to Gille [9] are suitable to test also the influence of isomorphic substitution on the particle parameters. In addition, it should be possible in this way to investigate host–guest systems and the microstructure of porous glasses.

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