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Dynamic light scattering by rodlike particles: examination of the vanadium(V)-oxide system

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Abstract. The dynamics of a suspension of rodlike particles has been investigated using dynamic light scattering. The V_2O_5 sols investigated in this contribution are not monodisperse by nature and age with time. An evaluation of the first cumulant of the autocorrelation functions as a function of scattering vector is expected to yield the dimensions of the particles. While the data can be excellently fitted by the theoretical expressions for freshly prepared sols, we found that the theoretically expected interrelation of the (three) diffusion coefficients is not reproduced, which prohibits the unequivocal determination of the particle dimensions. Aged sols, on the other hand, cannot be described at all within the framework of the theory. While this partially may originate from the temporally increasing polydispersity of the V_2O_5 sol system, other factors like specific growth processes may have influence on our data.

PACS. 82.70.Dd Colloids – 78.35.+c Brillouin and Rayleigh scattering; other light scattering – 05.40.+j Fluctuation phenomena, random processes, and Brownian motion

1 Introduction

The dynamics of dilute colloidal suspensions of spherical particles is well-understood; a dynamic light scattering experiment, which reveals the diameter of monodisperse charged polystyrene latex spheres, is utilised as an experiment for the practical training of physics or chemistry students. On the other hand there are very few studies on the dynamics of rodlike particles. This might be due to the fact that their dynamics is more complex and the measured autocorrelation function is not a single exponential. Already in 1984 however, Maeda and Fujime published an exact theoretical result [1], which should enable to deduce the diffusion coefficients of a rodlike particle from dynamic light scattering data from a dilute suspension free of approximations regarding the coupling of translational and rotational diffusion. Since then, surprisingly few contributions utilised their result in order to investigate the dynamics of rodlike particle suspensions [2–4]. This might be due to the fact that only a limited number of monodisperse rodlike particle suspensions are known, above all the tobacco mosaic virus (TMV) and the fd virus suspensions. Therefore, it is of great interest to examine the validity of the theoretical approach for other colloidal systems to meet the growing general interest in the investigation of the dynamics of rodlike particles. Accordingly, the main aim of this study is to examine a colloidal system of rodlike particles, which is not naturally as ideal as the virus systems, as its exhibits a certain degree of polydispersity. We investigate the vanadium(V)-oxide sol system in order to find out whether the rods dynamics can be described by the theory mentioned. An additional feature of this system as compared with the viral systems is the possibility to observe a growth of the particles that changes their respective dimensions while keeping the ionic strength approximately constant. This might fruitfully be exploited in the construction of model systems for the liquid crystalline state of matter in the future.

2 Theoretical basics

The dynamics of colloidal suspensions is frequently investigated employing a homodyne light scattering experiment using a digital correlator. This device measures the (normalized) intensity autocorrelation function

$$g_I(t) = \frac{\langle I(0)I(t)\rangle}{\left\langle \left|I(t)\right|^2 \right\rangle} = 1 + \beta \left|g_E(t)\right|^2 \tag{1}$$

where stationarity has been assumed; β is a measure for the coherence of the optical setup. The field correlation function $g_E(t) = F_S(\mathbf{q},t)/F_S(\mathbf{q},0)$ is connected to the so-called "intermediate scattering function", which contains the information of the phase shift per particle

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in the (coherent) scattering experiment:

$$F_S(\mathbf{q},t) = \left\langle \exp\left[i\mathbf{q}\cdot\left(\mathbf{R}_j(t)-\mathbf{R}_j(0)\right)\right]\right\rangle$$
$$\text{with } \; q = |\mathbf{k}_i - \mathbf{k}_f| = \frac{4\pi n_M}{\lambda}\sin\frac{\theta}{2}\cdot \qquad (2)$$

Interactions between the particles are neglected; therefore, only the self-contribution is considered. The squared brackets indicate the ensemble average over the N particle positions. $k_f \approx k_i = 2\pi n_M/\lambda$ are the initial and final wave vectors of the scattering experiment under an angle θ in a medium with refractive index n_M using radiation with the vacuum wavelength λ.

$F_S(\mathbf{q},t)$, in turn, is the Fourier transform of the probability density $G_S(\mathbf{r},t)$

$$F_S(\mathbf{q},t) = \int \exp(i\mathbf{q}\cdot\mathbf{r})G_S(\mathbf{r},t)d^3r \qquad (3)$$

which is a measure for the conditional probability to find the particle j at $\mathbf{R}_j(t)$ after having found it at $\mathbf{R}_j(0)$; because the system is assumed to be homogeneous, the probability density depends only on $\mathbf{r} = \mathbf{R}_j(t) - \mathbf{R}_j(0)$.

$G_S(\mathbf{r},t)$ obeys the diffusion equation in the approximation of infinite dilution

$$\left(\frac{\partial}{\partial t} - D\nabla_r^2\right)G_S(\mathbf{r},t) = 0. \qquad (4)$$

The solution is easily obtained by Fourier transformation:

$$g_E(t) = F_S(\mathbf{q},t)/F_S(\mathbf{q},0) = \exp(-Dq^2t). \qquad (5)$$

Experimentally, one often fits the measured intensity correlation function to a cumulant expansion $\ln\left[1/\beta \times \left(g_I(t)-1\right)\right] = 2\ln\left[g_E(t)\right] = -K_1t + (1/2)K_2t^2 - \ldots$ For a single diffusing sphere one then obtains, as already shown,

$$K_1/2q^2 = D \;\text{ and }\; K_2 = 0. \qquad (6)$$

In order to determine the sphere's diameter from the diffusion coefficient, a hydrodynamic relation has to be known, which describes the reaction force of the viscous medium onto the movement of the particle. For an isolated sphere this is the well known Stokes-Einstein result

$$D = k_BT/3\pi\eta d \qquad (7)$$

where d is the sphere's diameter and η the solvent viscosity; for charged particles it is important to note that electroviscous effects are neglected [5].

Diffusing rods are more complicated to describe than diffusing spheres, because the rotational diffusion has to be taken into account. We follow the treatment of Doi and Edwards [6] in assuming that the rod j consists of N small beads of thickness d. $F_S(\mathbf{q},t)$ is then given by

$$F_S(\mathbf{q},t) = \frac{1}{N^2}\sum_{n,m=-N/2}^{N/2}\left\langle \exp\left[i\mathbf{q}\cdot\left(\mathbf{R}_{j,n}(t)-\mathbf{R}_{j,m}(0)\right)\right]\right\rangle$$
$$= \left\langle \exp\left(i\mathbf{q}\cdot\mathbf{r}\right)\frac{\sin\left(\mathbf{q}\cdot\mathbf{u}(t)L/2\right)}{\mathbf{q}\cdot\mathbf{u}(t)L/2}\frac{\sin\left(\mathbf{q}\cdot\mathbf{u}(0)L/2\right)}{\mathbf{q}\cdot\mathbf{u}(0)L/2}\right\rangle \qquad (8)$$

with $\mathbf{R}_{j,n}(t) = \mathbf{R}_j(t) + nd\mathbf{u}(t)$; $\mathbf{u}$ is the unit vector pointing from the center of gravity of the rod to its end; $L = Nd$ is the rod's length.

The suspension is again assumed to be homogeneous with respect to the centers of gravity of the rods, but also concerning their orientation with respect to the reference frame, which has to be taken into account explicitly while calculating $F_S(\mathbf{q},t)$ and results in the double sum of equation (8). The diffusion equation now reads

$$\left(\frac{\partial}{\partial t} - D_\parallel\left(\mathbf{u}\cdot\nabla_r\right)^2 - D_\perp\left\{\nabla_r^2 - \left(\mathbf{u}\cdot\nabla_r\right)^2\right\} - D_r\nabla^2_{\vartheta\varphi}\right)$$
$$\times\, G_S\left(\mathbf{r};\mathbf{u}(t),\mathbf{u}(0);t\right) = 0. \qquad (9)$$

The solution of this diffusion equation, which contains the coupling of translational and rotational motion implicitly, has been given by Maeda and Fujime [1]. From a slightly different starting point Wilcoxon and Schurr [7] obtained a result, which can be shown to be identical to that of Maeda and Fujime.

A complete expression for the autocorrelation function is only numerical possible, though the first cumulant can easily be derived:

$$\frac{K_1}{2q^2} = \bar{D} - \varDelta D\left[\frac{1}{3} - f_2\left(\frac{qL}{2}\right)\right] + \frac{L^2}{12}D_rf_1\left(\frac{qL}{2}\right) \qquad (10)$$

which has to be compared with equation (6). Note that here $K_2 \neq 0$. The functions $f_1(qL/2)$ and $f_2(qL/2)$ are numerically given by Maeda and Fujime [1] and were used in this work; an analytical expression for the first cumulant was given by Hammouda [8]. The combinations of the translational diffusion coefficients parallel and perpendicular to the rod's long axis, $D_\parallel$ and $D_\perp$ respectively, are given by $\bar{D} = (1/3)D_\parallel + (2/3)D_\perp$ and $\varDelta D = D_\parallel - D_\perp$. Note the following limiting behaviour: for $qL \ll 1$, $f_1(qL/2)$ and $f_2(qL/2)$ approach 0 and 1/3, respectively, whereas for $qL \gg 1$, $f_1(qL/2)$ and $f_2(qL/2)$ approach 1 and 0, respectively. Accordingly, in the low q limit, the first cumulant is dominated by the mean translational diffusion coefficient $\bar{D}$, while at large q the translational diffusion parallel to the rod's long axis ($D_\parallel$) does not contribute to the first cumulant any more.

This crossover behaviour can be observed in a light scattering experiment by changing the scattering angle when a wavelength comparable to the rod's long axis is used. In general, it is therefore possible to determine the three diffusion coefficients and hence the dimensions of rodlike particles from a dynamic light scattering experiment. To accomplish this, one needs expressions for the hydrodynamics of a moving rod, a problem, which treatment is by far more complicated than that of a diffusing sphere. Results for all three diffusion coefficients as a function of the rod's length L and its diameter d are given in [9–11]

$$\begin{aligned} D_{\|} &= \frac{k_B T}{2\pi\eta L}\left(\ln\frac{L}{d}+\gamma_{\|}\right) \\ D_{\perp} &= \frac{k_B T}{4\pi\eta L}\left(\ln\frac{L}{d}+\gamma_{\perp}\right) \\ \frac{L^2}{12}D_r &= \frac{k_B T}{4\pi\eta L}\left(\ln\frac{L}{d}+\gamma_r\right) \end{aligned} \tag{11}$$

and differ in the treatment of the hydrodynamic effects of the finite dimension of the rod, which are compiled in corrections $\gamma_i(L/d)$ for the rod ends. Note that the three diffusion coefficients depend (to a first order approximation) only on two geometrical parameters. This is a consequence of the necessary hydrodynamic coupling between an anisotropic translation and a rotation in a viscous medium.

Up to now we did not mention the influence of polydispersity on the data. As there is no general relation for the treatment of polydispersity, we defer the discussion of this effect to the last chapter.

Concluding this theoretical part, let us summarise the limitations of the theoretical result for the evaluation of the correlation function of a rodlike particle. Firstly, the rod's material is assumed to be optical isotropic, *i.e.* it consists of beads with a single refractive index n_P. Secondly, the Rayleigh-Debye-Gans condition is assumed to be valid by assuming small beads ($d < \lambda n_M/n_P$), which restricts the theory's validity to thin rods. An estimate for the range of applicability of the Rayleigh-Debye-Gans condition for rodlike systems is given by Buitenhuis *et al.* [12]. Both assumptions were used in the derivation of equation (10), so dynamics might be influenced if one of these does not hold. Third, no interactions between the rods are included in the theory, a consequence of treating only the self part of the intermediate scattering function. We will refer to these points later in the experimental section.

3 Experimental details

3.1 Sample preparation

Different preparation methods for a V_2O_5 sol have been described in literature [13]. We decided to utilise the method of Biltz [14] for the sake of its simplicity. In addition we aimed to exploit the reported instability of Biltz sols against particle growth (see below).

1 g NH_4VO_3 (Merck) was moistened with a small amount of water. 10 cm^3 of an aqueous solution of HCl containing 2 mol/dm^3 was added. The red precipitate formed was filtered through a glass filter crucible (grade 1 porosity) and washed with water, until the filtrate became reddish and turbid. The precipitate was then given into a volumetric flask and filled up with water to 100 cm^3. After shaking, an orange-red solution with pH > 4 is formed, which shows a strong Tyndall effect (light scattering cone). The water used in this procedure was demineralised by standard ion exchange resins and stored in plastic bottles. No care was taken to avoid air contact.

The suspension is unstable against added salt, which is expected for a charge stabilised system. If one increases the ionic strength up to 10 mmol/dm^3, first a gel phase is formed; still higher ionic strengths lead to flocculation. The colloidal particles are chemically dissolved completely in solutions with either pH > 10 or pH < 2.

3.2 Physical properties of the samples

The colloidal particles consist of red, rodlike V_2O_5 crystallites, which can be completely removed by filtration. The yellow filtrate contains polyvanadate ions like $V_{10}O_{28}^{6-}$ and so forth; consequently, a Debye-Scherrer X-ray scattering experiment reveals few peaks of the V_2O_5 crystals at comparatively large q values besides a broad, fluidlike structure at low q values. In suspension, the colloidal particles establish a chemical equilibrium with the vanadate ions, which leads to dissolution of the colloidal particles upon diluting the suspension.

A photometric determination of the total vanadium content of a typical suspension according to the method described by Wünsch [15] yields a vanadium concentration of about 15 mmol/dm^3. We roughly estimate that the described preparation process leads to a suspension which contains 50% of the total vanadium in the form of crystalline V_2O_5 and thereby estimate the particle concentration in the suspension to be typically 4 mmol/dm^3. If the colloidal rods are assumed to exhibit a length of $L = 500$ nm and a thickness of $d = 50$ nm, its volume fraction would be only about $\phi = 2 \times 10^{-4}$, or $c = 0.02c^*$ ($c^* = L^{-3}$). Electric conductivity measurements yield a typical value of $2.5 \times 10^{-2}\,(\Omega\mathrm{m})^{-1}$; assuming that only NH_4Cl contributes to this conductivity, a Debye-Hückel length of $1/\kappa \approx 8$ nm is obtained, which is two orders of magnitude smaller than typical particle distances. This result safely allows to neglect particle interactions and electroviscous effects; the low particle concentration allows for the neglect of multiple scattering contributions as well.

No attempt was made to verify the assumption of a structureless suspension by measuring the structure factor, because the particle form factor $P(q)$, which could be calculated in principle, cannot be measured by diluting the sample as the particle material dissolves. In addition, from a theoretical point of view, particle interactions complicate the evaluation of the scattered intensity, because the rods orientation correlations have to be taken into account explicitly. In this case, the scattered intensity can no longer be described as a simple product of a single-particle form factor $P(q)$ and a structure factor $S(q)$ [16,17].

Attempts to make electron micrographs of the crystalline particles failed, because we could not separate the particles from the amorphous salt background formed on evaporation. Electron micrographs can be found in the literature, however [13,18]. Both references report a strong growth of the length of the colloidal particles with time.

While agreement seems to exist on the strong influence of the ionic strength on the crystal growth, there is disagreement on the mechanism of the growth process. Huber and Zbinden [13] favour an aggregation process to dominate the needle growth, while Musić and Ljubešić [18] suggest that very effective conditions for the recrystallisation of V_2O_5 crystals in equilibrium with NH_4VO_3 in solution cause the observed growth. For the present contribution we only note that the Biltz sols are unstable against particle growth. Their polydispersity increases substantially with the ageing process. While freshly prepared sols of either preparation method show a polydispersity of about 10–20% in particle length, the distribution spreads considerably upon ageing, whereas the initial particle length remains the most frequent [13]. We note that according to electron micrographs, the growth process does not necessarily yield isometric particles.

V_2O_5 single crystals belong to the orthorhombic space group $P\,2_1/m\,2_1/m\,2/n$ with the lattice constants $a = 1.151$ nm, $b = 356$ pm, $c = 437$ pm [19]. An orthorhombic crystal in general is optical biaxial; one should therefore be able to observe the rotation around the rods long axis in a dynamic light scattering experiment, which is not possible for optical uniaxial particles with coinciding optical and geometrical main axes. Two of the refractive indices of the V_2O_5 crystal, however, are almost identical ($n_a = 2.89$, $n_b = n_c = 2.35$ at $\lambda = 633$ nm) [20]. We therefore do not expect this unusual dynamics to contribute to the light scattering correlation functions. Note, however, that the material is by no means optical isotropic. As geometrical and optical main axis coincide, this is of relevance for the quantitative determination of the rod's dimensions from static data only.

Light absorption and static light scattering of V_2O_5 sols were thoroughly investigated by Kerker *et al.* [21], who found a dramatic increase in absorption as well as scattering cross-section upon ageing of the sols. They report measurements, however, only up to $\lambda = 470$ nm; as we are interested in the scattering properties of the sols, we employ $\lambda = 633$ nm in this contribution, close to the minimum absorption of V_2O_5 sols at about $\lambda = 700$ nm. The transmission $T = I/I_0$ remains well above 25% at this wavelength. Kerker *et al.* obtained a refractive index for the particles of $n_P = 1.46$ at $\lambda = 546$ nm, in strong disagreement with the single crystal measurements from Parker *et al.* [20]. As compared to the data obtained at $\lambda = 633$ nm, they report still larger data ($n_a \approx 3$, $n_b = n_c \approx 2.5$) at $\lambda = 546$ nm, in accordance with a general optical dispersion trend. This disagreement unfortunately completely prohibits an assessment of the validity of the Rayleigh-Debye-Gans approximation following Buitenhuis *et al.* [12].

3.3 Light scattering apparatus

The light scattering set-up used was a non-standard experiment designed to perform heterodyne experiments on a wide angular range; the set-up is described in detail by Fromm [22]. However, the heterodyne capability provided no advantages for the systems under study and was therefore not utilised here. Accordingly, we employed the apparatus as a standard dynamic light scattering apparatus with a HeNe laser light source. Vertical polarisers in the transmitting as well as in the detection optics guaranteed a polarised (V_V) experiment. The incident light was focused by a lens with $f = 80$ mm into the cylindrical sample cuvettes with 15 mm diameter. No index matching bath was used. The detection optics comprised of a lens-pinhole optics in $2f$ geometry; the pinhole selecting the scattering volume had a diameter of 350 μm. The PMT (EMI 9863 KB-100) was supplied by Malvern together with the correlator, type K 7027, which offers 56 linear spaced channels plus four channels with a delay of 1024 times the sample time chosen. This enables the proof whether the correlation function has completely decayed in the time window chosen by the sample time.

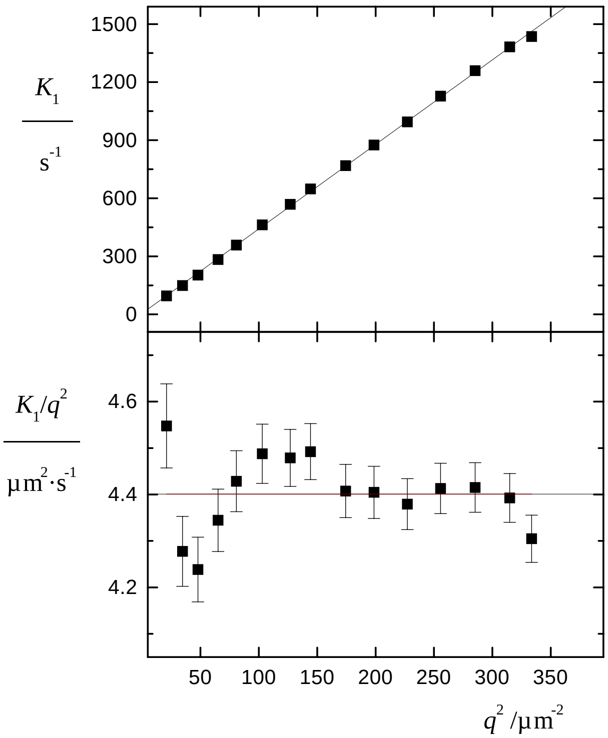

Fig. 1. (a) First cumulant K_1 of a suspension of polystyrene latex spheres as a function of q^2; (b) K_1/q^2 as a function of q^2. The nominal diameter of the spheres was $d = 234$ nm. The straight lines are linear fits to the data, resulting in $D = 2.19 \pm 0.02$ μm^2/s and $D = 2.21 \pm 0.02$ μm^2/s, respectively.

4 Dynamic light scattering results

We performed reference measurements with commercially available polystyrene latex spheres of nominal diameter $d = 234$ nm; no information was supplied about the method of determination of the diameter nor its standard deviation. The concentration of the reference sample was about $\phi \approx 10^{-3}$ with high salt content. Figure 1a

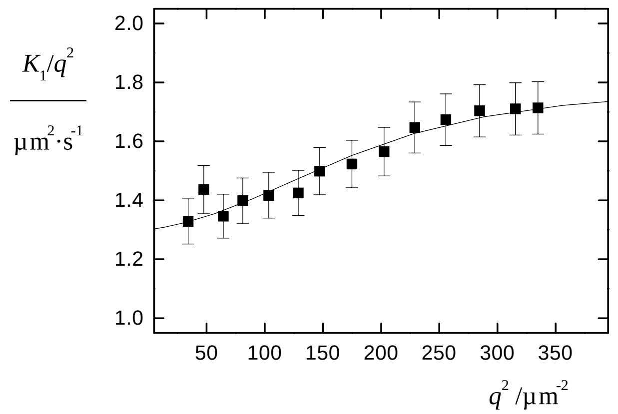

Fig. 2. K_1/q^2 as a function of q^2 of a V_2O_5 sol, aged 10 days. The drawn curve is a fit to the theory of Maeda and Fujime.

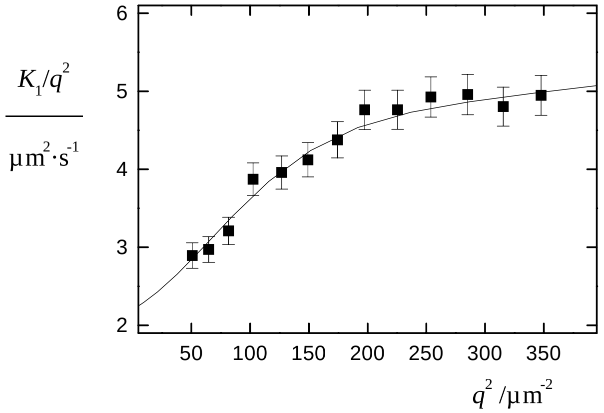

Fig. 3. K_1/q^2 as a function of q^2 of a V_2O_5 sol, aged 22 days. The drawn curve is a fit to the theory of Maeda and Fujime.

shows the obtained first cumulant K_1 as a function of q^2; in Figure 1b a plot of K_1/q^2 *versus* q^2 is shown. The respective straight lines yield diffusion coefficients, from which the diameter of the spheres can be obtained. We find $d = 222 \pm 2$ nm and 224 ± 2 nm, respectively, from the two different straight lines. Nominal and measured diameter agree within 5%; note, however, that usually the nominal diameter is found to be the lower one, as the spheres shrink in the vacuum of an electron microscope. A comparison of Figures 1a and 1b leads to the observation that a careful examination of deviations from the simple diffusion of a sphere is only possible when the data are plotted according to Figure 1b, *i.e.* as K_1/q^2 as a function of q^2.

Figures 2 and 3 show corresponding plots of the first cumulants of V_2O_5 sols, which were aged 10 and 22 days, respectively. The drawn lines are fits to the result of Maeda and Fujime, equation (10). Table 1 shows the fit parameters obtained. Note that the length of the particles is a fitting parameter, too, as the tabulated theoretical results are functions of qL. The fitting session therefore consists of first finding a window, in which the theoretical step-like curve approaches the data, thus obtaining the parameter L, and then altering the remaining three fit parameters until the result seems likely. The fit was performed by eye, which is possible because the fitting function is very sensitive upon slight variations of the (four) fit parameters (*cf.* Fig. 4). The errors given in Table 1 originate from these variations. The agreement between the data and the fitted curves is excellent, as visible from Figures 2 and 3, which might be expected for a four-parameter fit. However, we note that the general shape of the curve is quite insensitive to the parameters chosen. This means that even a four-parameter fit may not approach the data sufficiently, which will become obvious for an older sol. In addition, it is in general not possible to separate the influence of the individual fit parameters on the curve. Whereas, crudely speaking, the "baseline" of the curve is determined by $\bar{D}$ and the position of the step-like curve by L, the height of the step and its width are both determined by a combined influence of L, ΔD and D_r. This effect is visible in Figure 4, where model calculations for different sets of parameters are presented.

While the measurements of the younger sols can be fitted to the theory very well, this aim fails for the older ones. Figure 5 shows the result for one representative example, a sol which was aged 42 days. It is not possible to fit the measured linewidths to the theory unequivocally. The data of Table 1 should therefore only be regarded as an estimate for the relevant parameters. In addition, the measurements yield a tiny mean diffusion coefficient as compared to the data shown in Figures 2 and 3 for the younger sols.

5 Discussion

From the electron microscopy results the particles are expected to grow and to increase in polydispersity upon ageing. In order to explain the observed failure of the theory to describe the dynamics of the older sols, we performed model calculations in order to reveal the influence of polydispersity onto the data by averaging discrete functions according to equation (10) for different particle sizes. As an illustrative example, we added the theoretical curves for five different particle lengths $L = \{450 \ldots 550\}$ nm, but constant L/d, with equal weight. The calculation shows that even this strong, but symmetric polydispersity of 20% does not change the curve to a noticeable extent as compared to the monodisperse case for $L = 500$ nm. On the other hand, the presence of larger particles (*e.g.* $L = 2500$ nm) decreases the mean diffusion coefficient, as expected and experimentally observed. However, the height of the step of the curve decreases only slightly and the position of the step shifts to smaller q in addition, which is not in accordance with our measurements. We therefore conclude that no simple polydispersity model can be adopted in order to describe the data for the older sols. On the other hand, we regard the very small mean diffusion coefficient in these data as an indication for the presence of significantly longer particles than the length parameter L obtained from the fit. A quantitative

Table 1. Fitting parameters of Figures 2–4 according to the theory of Maeda and Fujime, equation (10).

Sol age (days)	L (nm)	$\bar{D}$ (μm^{2}s^{-1})	ΔD (μm^{2}s^{-1})	$(L^2/12)D_r$ (μm^{2}s^{-1})
10	530 ± 10	0.65 ± 0.01	0.9 ± 0.1	0.7 ± 0.1
22	650 ± 10	1.10 ± 0.05	3.5 ± 0.1	3.3 ± 0.1
42	500	0.05	1.2	1.0

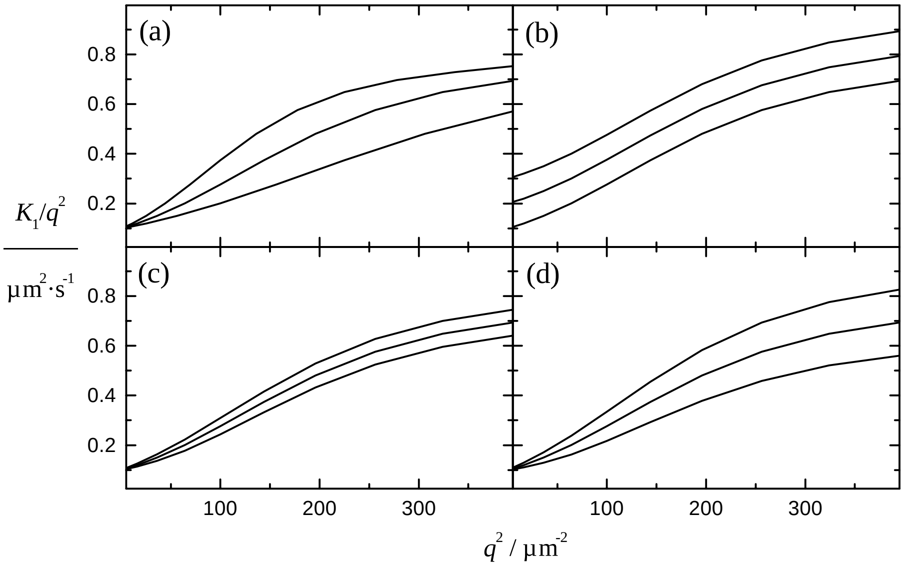

Fig. 4. Calculated curves according to the theory of Maeda and Fujime with the fitting parameters varied from bottom curve to top curve as follows: (a) $L\,(\mathrm{nm}) = \{400, 500, 600\}$; $\bar{D} = 0.05$ μm^{2}s^{-1}; $\Delta D = 0.9$ μm^{2}s^{-1}; $(L^2/12)D_r = 0.8$ μm^{2}s^{-1}; (b) $L = 500$ nm; $\bar{D}\,(\mu\mathrm{m}^2\mathrm{s}^{-1}) = \{0.05, 0.10, 0.15\}$; $\Delta D = 0.9$ μm^{2}s^{-1}; $(L^2/12)D_r = 0.8$ μm^{2}s^{-1}; (c) $L = 500$ nm; $\bar{D} = 0.05$ μm^{2}s^{-1}; $\Delta D\,(\mu\mathrm{m}^2\mathrm{s}^{-1}) = \{0.8, 0.9, 1.0\}$; $(L^2/12)D_r = 0.8$ μm^{2}s^{-1}; (d) $L = 500$ nm; $\bar{D} = 0.05$ μm^{2}s^{-1}; $\Delta D = 0.9$ μm^{2}s^{-1}; $(L^2/12)D_r\,(\mu\mathrm{m}^2\mathrm{s}^{-1}) = \{0.9, 0.8, 0.7\}$.

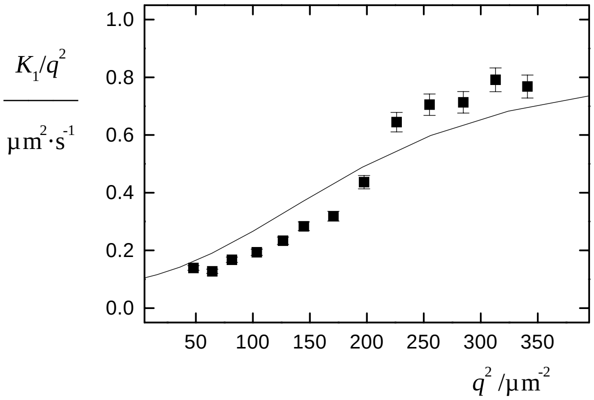

Fig. 5. K_1/q^2 as a function of q^2 of a V_2O_5 sol, aged 42 days. The drawn curve is a fit to the theory of Maeda and Fujime.

description, however, would require the knowledge of the particle dimensions distribution in the suspension under study.

The experimental situation for the younger sols seems to be more promising, as the length of the particles increases upon ageing as expected. However, closer examination of the data shows that there is an additional feature present which inhibits a conclusive determination of the particle dimensions even from the younger sols. We already mentioned in the theoretical section that the three diffusion coefficients $\bar{D}$, ΔD and D_r are not independent from each other, but interrelated by equation (11). In this respect we find deviations from the expected relations. In order to demonstrate this, we combine equation (11) to obtain

$$\frac{6\Delta D}{L^2 D_r} = \frac{\frac{1}{2}\ln(L/d) + \gamma_{\parallel} - \frac{1}{2}\gamma_{\perp}}{\ln(L/d) + \gamma_r},$$
$$\frac{9\bar{D}}{L^2 D_r} = \frac{\ln(L/d) + \frac{1}{2}\left(\gamma_{\parallel} + \gamma_{\perp}\right)}{\ln(L/d) + \gamma_r}\,. \qquad (12)$$

If the corrections for the end effects $\gamma_i(L/d)$ from Tirado *et al.* [11] are used, our results given in Table 1 are always in excess of their limiting values. For the sake of simplicity, we will not present details, as the discrepancy can be seen easily, if the end effect corrections $\gamma_i(L/d)$ are neglected with respect to $\ln(L/d)$. This assumption is valid for $L/d \geq 10$ and yields

$$\frac{6\varDelta D}{L^2 D_r} \approx \frac{1}{2} \qquad \Leftrightarrow \qquad \varDelta D \approx \frac{L^2 D_r}{12}, \tag{13}$$

$$\frac{9\bar{D}}{L^2 D_r} \approx 1 \qquad \Leftrightarrow \qquad \frac{3}{4}\bar{D} \approx \frac{L^2 D_r}{12} \cdot \tag{14}$$

While the first relation holds quite well with our data (*cf.* Tab. 1), our results disagree with the second relation. For the younger sols we find that the mean diffusion coefficient is too small by a factor of two approximately, while for the older sol the discrepancy is more than one order of magnitude. No data for the diameter of the particles are given in Table 1 because of this lack of correlation.

The observed disagreement between the diffusion coefficients cannot be due to the neglect of particle interactions. Following the argumentation of Weyerich *et al.* [23], a possible electrostatic interaction between the charged rods should lead to an increase of $\bar{D}$ with increasing interaction, in contrast to observations. This can, in turn, be regarded as an experimental hint that particle interactions play no dominant role in the dynamics, as claimed before.

On the other hand, polydispersity is to be expected to decrease the mean diffusion coefficient with decreasing scattering angle as, roughly speaking, larger particles contribute with increasing weight. This may explain the observed incompatibility, despite the fact that no simple modification of the theoretical functions seems feasible which does, on the same time, fit the experimental data and reduce the mean diffusion coefficient due to polydispersity effects. In this respect, the applicability of the theory of Maeda and Fujime to polydisperse rodlike systems remains uncertain. Note, however, that it is not self-evident that the theoretical curves fit the data at all (*cf.* the result for the older sol). In addition, a small but noticeable incompatibility of the diffusion coefficients was also observed by Wilcoxon and Schurr [7] for TMV suspensions, which they attribute to a failure of the hydrodynamic relations of Tirado *et al.* [11]. Therefore, there is still the necessity for further investigations of V_2O_5 sols or similar rodlike systems in order to resolve the discrepancies observed here.

As the data presented in Figures 2, 3 and 5 were obtained from individually prepared suspensions, no conclusion about the temporal development of a single sample can be drawn. According experiments are on their way, which should help to resolve the origin of the incompatibility of the diffusion coefficients. In addition, we attempt to reduce and to stabilise the polydispersity of freshly prepared suspensions by chemical means. Those suspensions will reveal more clearly the expected growth process by dynamic light scattering.

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