Stability Analysis of Emulsions and Suspensions with Photon Cross-correlation Spectroscopy

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ABSTRACT

The well established Photon Correlation Spectroscopy (PCS) probes the Brownian motion of colloidal particles, thus allowing the determination of their particle size distribution (PSD). The theory behind is valid for single scattered light only. Therefore PCS is limited to very low particle concentrations. A cross correlation setup [1] guarantees that only single scattered light contributes to the measured cross-correlation function. Hence Photon Cross-Correlation Spectroscopy (PCCS), overcomes the concentration restrictions of the PCS. A 3D-Cross-correlation setup [2] can be realised in an easy-to-handle instrument that is capable of measuring the PSD of opaque nano-sized suspensions and emulsions.

Cross-correlation is a filter for single scattered light and the intercept of the measured cross-correlation function is proportional to the ratio of single and multiple scattered light. Multiple scattering is closely connected to the absolute number of particles. Therefore, the intercept of the cross-correlation function is very sensitive to changes of the number of particles due to agglomeration, nucleation or desagglomeration. Combined with the estimated PSD the intercept of the cross-correlation function is a good indicator for changes within the sample giving an additional benefit for the user.

The measurement technique as well as selected applications are presented. Special emphasis will be placed on the stability analysis of suspensions and emulsions.

1 INTRODUCTION

Photon Correlation Spectroscopy (PCS) is a widely used technique for the particle size analysis of nano-sized particles. Analysing the fluctuations of the light scattered by the particles, multiple scattering falsifies the results and must be avoided.

There are several possibilities to suppress the influence of multiple scattered light. The classical way is to reduce the particle concentration and therefore the probability for multiple scattering. In practice most samples have to be highly diluted in order to get a nearly transparent sample.

Fig. 1: Setup of a 3D-Cross-correlation spectrometer

Another way is the Cross-Correlation Spectroscopy (PCCS) that realises two identical PCS-measurements in exactly the same measurement volume. The two signals correlate only with regard to the single scattered light from the particles in the measurement volume, whilst the multiple scattered light originating from different particles is completely uncorrelated.

Several attempts have been made in order to realise a cross-correlation setup [1,2]. The 3D-Cross-correlation (Fig. 1) is realised in a commercially available instrument (NANOPOHOX, Sympatec GmbH). A Laser beam is split into two partial beams and focussed with help of a lens into the sample vial. The crossing region forms the measurement volume. Two photo-detectors receive the scattered light under the scattering angle θ. The time resolved intensities measured by the photo-detectors are cross correlated.

The physics of the scattered light fluctuations are given by the electric field ($\vec{E}$) correlation function:

$$g_{AB}^{E}(\tau) = \frac{\left\langle \vec{E}_A(0) \cdot \vec{E}_B(\tau) \right\rangle}{\left\langle \vec{E}_A \right\rangle \cdot \left\langle \vec{E}_B \right\rangle} \tag{1}$$

which is connected with the measurable intensity (I_A, I_B) correlation function

$$g_{AB}^{I}(\tau) = \frac{\left\langle I_A(0) \cdot I_B(\tau) \right\rangle}{\left\langle I_A \right\rangle \cdot \left\langle I_B \right\rangle} \tag{2}$$

by the Siegert relation

$$g_{AB}^{I}(\tau) = 1 + \beta \cdot \left| g_{AB}^{E}(\tau) \right|^2 . \tag{3}$$

In (1) and (2) $\langle ... \rangle$ represents the ensemble average, whilst the factor β in (3) is called the intercept or the

amplitude of the correlation function. It is the product of two components:

$$\beta = \beta_{App} \cdot \beta_{MS} \qquad (4)$$

In (4) β_{App} is an apparatus constant depending on the scattering geometry, the quality of alignment and other parameters [3]. The factor β_{MS} considers the reduction of the intercept due to multiple scattering. The intensity correlation function g^J_{AB} is normalised to the intensity of scattered light measured in total. The multiple scattered light gives no contribution to the correlation and thus the intercept is reduced by the ratio of single scattered to multiple scattered light.

The amount of multiple scattered light depends on the number concentration and the mean distance between the particles. It is therefore very sensitive to changes due to sedimentation or aggregation. The intercept of the cross correlation function provides information on the structure of a suspension or emulsion and helps to detect changes of these parameters.

2 INTENTION

The aim of this contribution is to show, that the stability of a nano-sized suspension or emulsion can be observed by means of photon cross-correlation measurements. The intercept of the measured cross-correlation function is directly influenced by the internal structure of the suspension. Hence we expect this parameter to reflect suspension stability more reliably than indirect measures like the zeta-potential. Furthermore a stability analysis based on PCCS is not restricted to charge stabilised systems as an analysis by means of zeta-potential measurements.

3 STABILITY OF COLLOIDAL SUSPENSIONS

The DLVO theory [4] explains the stability of colloidal systems by the combined effect of van-der-Waals and electrostatic particle interactions. Hence, the decisive parameter for colloidal stability is the electric surface charge or more precisely: the electric surface potential. A relatively weak decay of the electric potential with distance from the surface favours stabilisation. This situation prevails for low electrolyte concentration (< 0.01 M). At high electrolyte concentrations the surface charge is completely screened within the immediate vicinity of the surface, what facilitates a close contact of particles and eventually coagulation.

The surface potential can not be probed by experiment. Instead the electrokinetic or zeta-potential is measured, which is considered as the electric potential at a conceptual shear plane. The zeta-potential is often used as an indicator for the suspension stability, assuming that a zeta-potential of at least 30 mV [4,5] is necessary for colloidal stability.

The zeta-potential is usually determined as function of the pH and/or the concentration of electrolytes, ionic surfactants or polyelectrolytes. The pH or concentration, at which the zeta-potential, thus the electrostatic repulsion, vanishes, is called isoelectric point (iep).

Note, that the DLVO theory accounts only for two effects, that affect the suspension stability. Furthers are: steric interaction, solvation forces, hydrophobic interaction, depletion flocculation, bridging flocculation etc [6]. If one of these effects becomes significant, the zeta-potential is not directly related to the stability any more. A well-known example is the remarkably good stability of colloidal silica at its iep, which is due to a repulsive hydration layer on the silica surface [7].

In contrast to zeta-potential measurements PCS/ PCCS probes the suspension stability directly. The particle diffusion coefficient, which is obtained from PCS experiments, is highly affected by interparticle forces and by particle coagulation. In particular, PCS can detect changes in the microscopic structure of slowly gelling systems or colloidal systems at the stability-instability border before they are reflected by significant changes in the macroscopic suspension properties [8].

4 MATERIALS AND METHODS

4.1 Particulate System

Experiments were conducted with aqueous suspensions of colloidal alumina, which was supplied as powder (NanoDur, Nanophase Technologies). According to the manufacturer the crystal composition is 70 % δ-Al_2O_3 to 30 % γ-Al_2O_3, the particle density is 3600 kg/m³ and the specific surface (BET) is specified with 42 m²/g, what corresponds to a sphere diameter of 40 nm. Scanning electron micrographs of the powder showed spherical particles in the size range from less than 20 nm to 500 nm.

Due to the relatively high polydispersity it is rather difficult to determine the "true" volume weighted size distribution. Figure 2 shows the results from three different characterisation methods: photon correlation spectroscopy (PCS), centrifugal sedimentation (Sed) and ultrasonic attenuation spectroscopy (US).
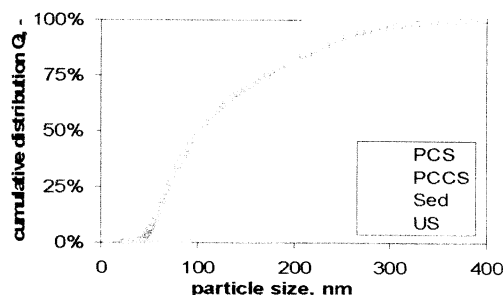

Fig. 2: Size distribution of the alumina powder; Photon Correlation spectroscopy (PCS), Photon Cross Correlation Spectroscopy (PCCS), Centrifugal Sedimentation (Sed), Ultrasonic attenuation spectroscopy (US)

4.2 Solvent

As aqueous phase we used solutions of potassium nitrate at different molar concentrations. The pH was adjusted with either potassium hydroxide or nitric acid. Solutions were prepared with distilled and deionised water.

4.3 Sample Preparation

Suspensions with approximately 2 wt.% solid content were prepared by dispersing the alumina powder in the electrolyte solution with a rotor-stator system (Ultra-Turrax T50, IKA, Germany) and pulsed high power ultrasound (VibraCell VCX600, Fisher Bioblock Scientic, France). Preliminary experiments had shown that the chosen procedure ensured best dispersion.

From the raw suspensions we prepared the measurement samples with pH values in the range between 2 and 11. The samples were stirred for at least twelve hours, then we recorded the pH and the conductivity.

Measurements of the zeta-potential were conducted at the original concentration. However, for the PCCS measurements the samples were diluted with supernatant in a ratio of 1:4 (solid content 0.4 wt.%). The supernatant was obtained by centrifugation.

4.4 Zeta-potential

The zeta-potential of the suspensions were measured electro-acoustically using the probe DT-300 (Dispersion Technology, USA). This instruments determines the dynamic electrophoretic mobility μ^* of charged particles from the *colloid vibration current* (CVI), which is the electric response of a suspension to an ultrasonic wave [9].

Calculation of the zeta-potential from the raw signals requires the knowledge of the particle density, the permittivity ($\varepsilon_r = 7$) and the size distribution, which was taken from ultrasonic attenuation spectroscopy (Fig. 2). Furthermore, it was assumed that the double layer is small compared to the particle size ($\kappa a \gg 1$). For an ionic strength of 10^{-3} mol/l the reciprocal of the Debye-Hückel-parameter κ is 10 nm, which is approximately the radius a of the smallest particles.

4.5 PCCS-measurements

Since the accurate knowledge of the sample temperature and the avoidance of convective flow are rather critical for PCCS experiments, we placed the samples in the temperature controlled sample holder of the NANOPHOX at least five minutes before starting the measurements. From each sample six cross correlation functions (CCF) were measured over periods of 300 seconds. The laser intensity and cuvette position was adjusted such as to ensure an average count-rate at the detectors of 300 kcps. However, when the intercept of the CCF fell significantly below 1 % we increased the count rate by a factor of four. The CCFs were analysed by the methods of cumulants [10], which provides a mean particle size x_{cum} and a polydispersity index (PDI). Besides, the intercept CCF(0s) of the cross correlation function was employed in the evaluation of the suspension stability.

5 RESULTS

5.1 Zeta-potential

The dependence of the zeta-potential from the pH value and the electrolyte concentration is shown in Fig. 3. The shift of the isoelectric point (iep) from approximately pH 8.4 for 0.001 M KNO_3 to pH 9.0 for 0.01 M

KNO_3 implies a specific influence of the electrolyte. Besides one can observe a weak decline of the maximum zeta-potential values with increasing electrolyte concentration.
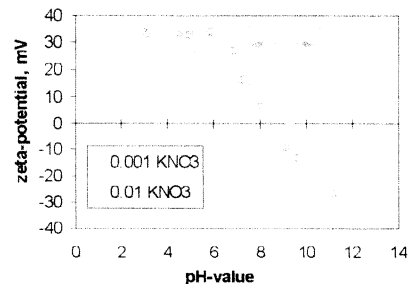

Fig. 3: Zeta-potential of employed samples, dashed lines mark the pH range of destabilisation

5.2 PCCS

Around the iep rapid agglomeration and sedimentation of the dispersed phase occurs. The measurement volume contained either a translucent supernatant (for pH values very close to the iep) or a slightly milky suspension with a clearly visible sediment (Fig. 4).
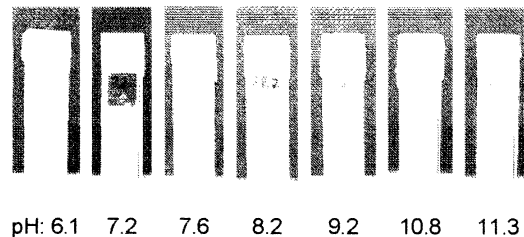

pH: 6.1   7.2   7.6   8.2   9.2   10.8   11.3

Fig. 4: PCCS samples with different pH (0.01 M KNO3) directly after the measurement

The intercepts of the CCF of the destabilised samples show either relatively high values (translucent supernatants) or very small values (milky suspensions). The pH ranges of visible coagulation are marked in the diagram by dashed lines (Fig. 5).
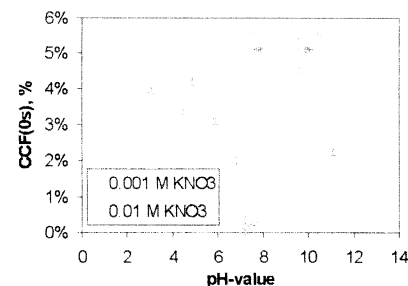

Fig. 5: CCF-intercept, dashed lines mark the pH range, in which destabilisation was observed

In Figs. 6 and 7 the calculated mean particle size x_{cum} and the PDI are shown. Generally, for the destabilised suspensions large particle sizes in the micrometer

range and very large PDI are observed. For the stable suspensions only a weak influence of the pH and the electrolyte was seen (mean particle size 140 nm).

Deviating from this general behaviour the destabilised sample 0.01 M KNO_3, pH 7.6 shows a very small particle size (due to the very low intercept of the CCF, which strongly hampers the analysis) and the seemingly stable suspension at 0.01 M KNO_3, pH 11.3 has very large particle sizes.
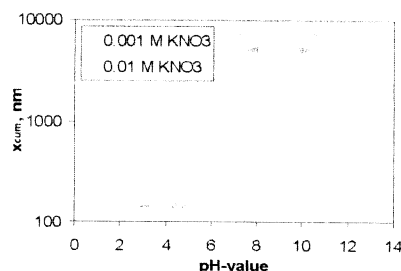

Fig. 6: Mean particle size from methods of cumulants, range of destabilised samples is marked
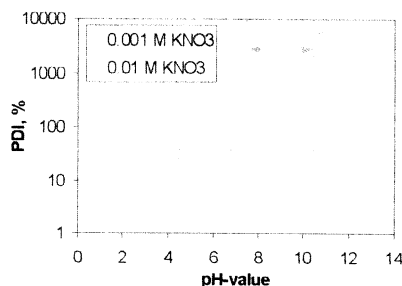

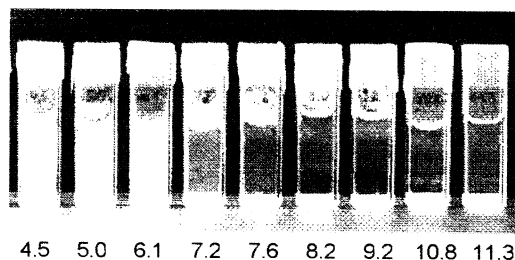Fig. 7: Polydispersity index from methods of cumulants

4.5   5.0   6.1   7.2   7.6   8.2   9.2   10.8   11.3

Fig. 8: PCCS samples at different pH (0.01 M KNO_3) after four days

The latter case was rather interesting, because we did not expect such a PCCS result from visual impression (Fig. 4). Even more exiting was, that after four days the alumina had completely settled down like in the other destabilised samples (Fig. 8). It is noteworthy that the microscopic destabilisation is not only reflected by the x_{cum}, but by the intercept of the CCF as well. A similar observation we made with the sample 0.001 M KNO_3, pH 7.2. For this sample the cross correlation function was hardly interpretable because of the low intercept

(0.17 %), but no indication of phase separation could be observed over 12 hours.

6 DISCUSSION

From the results presented above it can be concluded, that there is a strong correlation between the PCCS-results and the stability of a suspension. Figure 5 shows a clear descent of the cross-correlation for pH-values > 5. This corresponds with a descent of the measured zeta-potential (Fig. 3) and a slight increased mean particle size (Fig. 6). The descent of the cross-correlation intercept can be explained by a reduction of the mean free path length for the scattered light due to the beginning formation of a microstructure. This corresponds to the slight increase of the measured particle size, which is related to a hindered diffusion of the particles.

It is possible to detect changes in the structure of the suspensions although the resulting aggregates are not big or dense enough to settle.

7 CONCLUSION

PCCS can be used for particle size and stability analyses of nano-sized suspensions and emulsions. For the stability analysis it allows for a more direct access to the structure of a destabilised suspension than the zeta-potential. Furthermore the stability analysis is not only restricted to charge stabilised systems but for all kinds of stabilisation mechanism. For slowly gelling systems at the stability border PCCS allows for time resolved measurements resulting in an access to the kinetics of such processes.

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