Measurement of Particle Size and Stability of Nanoparticles in Opaque Suspensions and Emulsions with Photon Cross Correlation Spectroscopy (PCCS)

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ABSTRACT

PCCS is a novel technique allowing for simultaneous measurement of precise particle size and stability in the range of about 1 nm to some µm in opaque suspensions and emulsions. The key principle of PCCS is a 3D crosscorrelation technique. In a special scattering geometry, the crosscorrelation of the scattered light is calculated allowing for precise filtering of the single scattered fractions from the scattered intensity. This filtering is of decisive importance, as the well established theory for the evaluation of Photon Correlation Spectroscopy (PCS) data is only valid for light being scattered once. Any contribution of multiple scattered light to the detected signals would lead to erroneous results and misinterpretations. As a consequence, the former PCS required highly diluted suspensions in order to avoid multiple scattering. PCCS overcomes this limitation and extends the field of application to opaque suspensions and emulsions. This simplifies strongly sample preparation and handling. Clean room environments for sample preparation, as usually requested for the well established PCS, is no longer necessary. This broadens the field of applications, and many samples can be investigated even in the original state without dilution, now. As an additional benefit, the stability of the sample can be investigated simultaneously, showing if the sample is in a stable state or a sedimentation, growth, or flocculation process is taking place. Basing on this 3D cross correlation technique, a novel instrument has been developed and optimized for industrial use. Housed in a small table top unit it contains all necessary parts such as light source, detectors, the correlator and the sample containing vial and is ready four routine measurements in any laboratory. The operation is much simpler than with a conventional PCS system, because the samples are not diluted or at the utmost diluted moderately. Costly cleaning and sample preparation effort is avoided.

1 INTRODUCTION

PCS is widely used for the measurement of particle sizes in the nanometer regime. Typically the particles are illuminated by laser light which is focused into a cuvette with the sample suspension. The scattering pattern contains both: the scattering of the individual particles and the scattering of the particle arrangement, which is modified in time by the Brown's motion of the particles. The recorded intensity I at a certain scattering angle Θ varies with time t, as shown in Fig. 1.

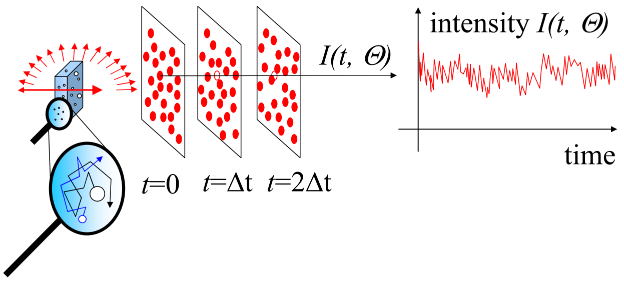

Figure 1: Scattered intensity in a typical PCS set-up.

The diffusion D of the particles of hydrodynamic diameter x can be described with the well known Stokes-Einstein relation using the Boltzmann's constant k_B and the dynamic viscosity of the liquid η in Eq. (1):

$$D(x) = k_B T/3\pi\eta x \tag{1}$$

For single scattering the autocorrelation function $G(\tau)$ of the intensities I^S can be expressed as

$$\begin{aligned} G(\tau) &= \langle I^s(\theta,0)\, I^s(\theta,\tau)\rangle = \\ &= \langle I\rangle^2 \,(1 + exp(-2\, D(x)\, q^2\, \tau)) = \\ &= \langle I\rangle^2 \,(1 + exp(-2\, q^2\, k_B T\, \tau/3\pi\eta x)) \end{aligned} \tag{2}$$

with scattering vector q and the temporary average expressed by the symbol $\langle\ldots\rangle$.

Equation (2) allows the evaluation of the particle size x with known η at temperature T from the slope of $ln(G(\tau)-1)$, which is commonly used in PCS. This simple evaluation is restricted to non-interacting spherical particles and single scattered light. Any contribution of multiple scattering, e.g. in opaque or concentrated suspension, gives erroneous results which become depending on concentration and the optical path, i.e. of the position of the cuvette. So usually the samples have to be strongly diluted. This results in low count rates, poor statistics or long measuring times.

The strong dilution makes the instrument sensitive to contamination with large (dust) particles which scatter proportional to x^6. For any successful PCS measurements clean conditions are obligatory.

2 PHOTON CROSS CORRELATION SPECTROSCOPY (PCCS)

Many attempts have been made to overcome the limitations of PCS, e.g. the “90° cross correlation” of Phillies (1981) [1], the “two colour cross correlation” of Schätzel (1989), FQELS of Horn (1991) [2], or the “one specle cross correlation” of Nobbman (1997) [3].

2.1 3D Crosscorrelation

The 3D crosscorrelation was introduced in 1990 by Schätzel [4] and improved 1996 by Aberle et al. [5]. In this set-up two lasers are focused to the same sample volume creating two sets of speckle (scattering) patterns as demonstrated in Fig. 2.

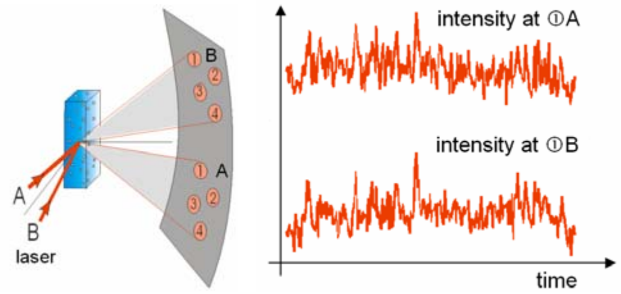

Figure 2: Set-up for PCCS, two lasers illuminate the same scattering volume creating two sets of scattering patterns

Both intensities are measured using the same scattering vector $\vec{q}$, as demonstrated in Fig. 3.

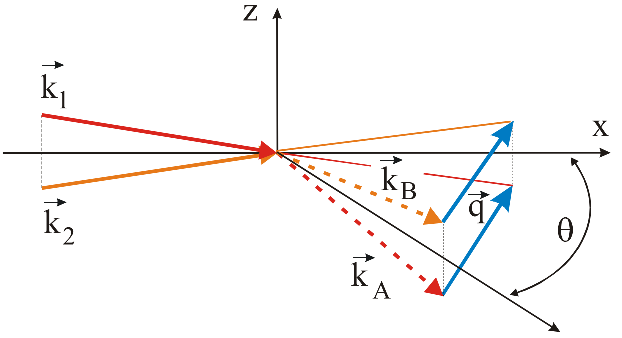

Figure 3: Scattering geometry for PCCS

Under these conditions, e. g. Aberle [4] showed that the crosscorrelation completely eliminates any contribution of multiple scattering. Corresponding to $G(\tau)$ for PCS, the crosscorrelation function $G2(\tau)$ has a direct relation to the particle size as displayed in Eq. (3).

$$In(G2(\tau)-1) \propto Diffusion\ D(x) \propto \frac{k_B T}{3\pi\eta x} \qquad (3)$$

So again, with known temperature T only the dynamic viscosity η is necessary for the evaluation of the absolute (hydrodynamic) particles size x. As the multiple scattering is completely eliminated, now concentrated or opaque suspensions can be measured. The results become independent of concentration and the position of the cuvette. The maximum concentration is only defined by the fact that the detectors still need to receive sufficient single scattered light for statistical relevant results. The additional benefits of measuring at high concentrations are: measuring at original concentrations of the sample, high count rates and thus short measuring times, the influence of contaminating particles is strongly reduced, so especially clean liquids and clean room conditions are avoided. The handling is strongly simplified.

As for PCS two restrictions are conserved for PCCS: the particles have to be spherical and non-interacting. But in contrast to PCS which cannot distinguish between the influences of multiple scattering or interacting particles to the results, PCCS allows for the studying of the interaction with a simple dilution series (as the influence of multiple scattering is eliminated).

2.2 Realization

Fig. 4 shows the optical set-up of the 3D crosscorrelation instrument.

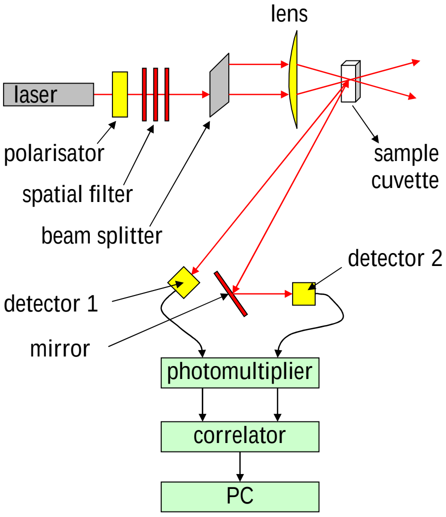

Figure 4: PCCS schematic of measuring set-up

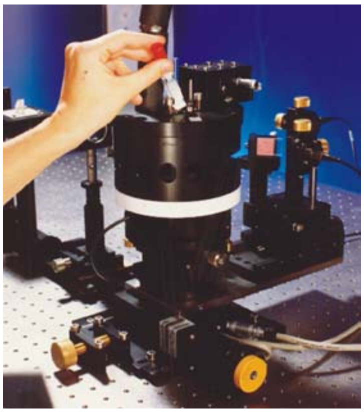

Figure 5: Experimental 3D-MALS-System (Multi Angle Light Scattering) using PCCS

Fig. 5 shows the experimental system used. The illuminating laser comes from behind. The two detecting fibers and the mirror are seen on the right.

As mentioned above, special care has to be taken that the scattering vectors $\vec{q}$ are identical for both detectors. The used embodiment and procedure, which makes the alignment even independent of the refractive index of the liquid used, was patented. It created the basis for a commercial instrument, which is displayed in Fig. 6.

Figure 6: Commercially available PCCS instrument basing on 3D crosscorrelation: NANOPHOX™ (Sympatec GmbH)

2.4 Results

PCCS has been used for a large variety of applications. Fig. 7 shows the volume distribution of three materials covering the size range of 3 nm to 200 nm in comparison with transmission electron microscopy (TEM).

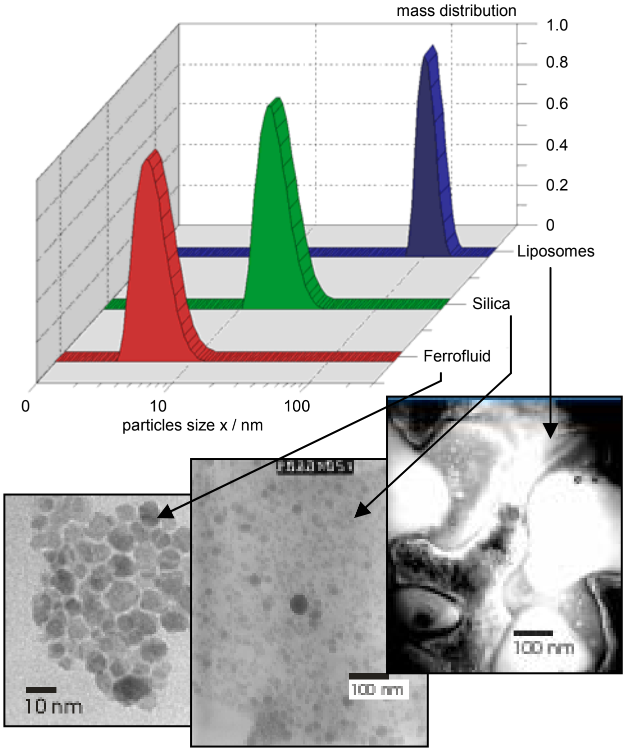

Figure 7: Comparison of PCCS results with TEM for three different materials

Even the liposomes, which are nearly destroyed in the TEM preparation, can be easily measured with PCCS.

Fig. 8 demonstrates the influence of the concentration to the results for monodisperse latex particles with a nominal value of $x = 107$ nm ± 10 nm. The autocorrelation function used by standard PCS shows the expected linear behavior for strong diluted suspension with a transmission T of 99.7%. The influence of multiple scattering in a high concentrated suspension with $T = 0.7\%$ creates a significant deviation from this linear behavior. For PCCS the multiple scattering is completely eliminated and the crosscorrelation function is strongly linear and independent of the concentration.

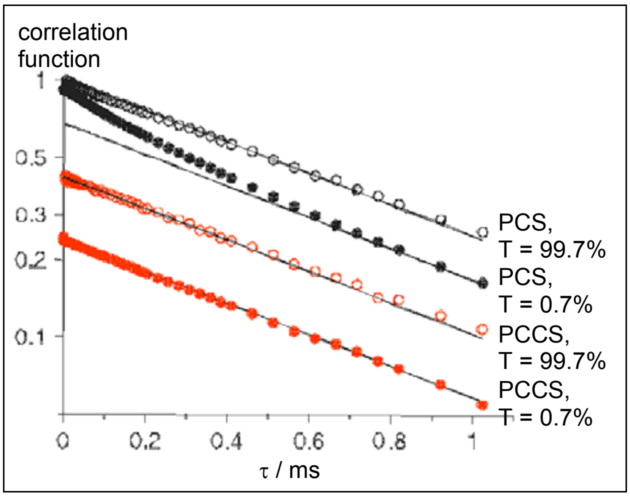

Figure 8: Latex in water with x = 107 ± 10nm (TEM). Autocorrelation function (PCS) and crosscorrelation function (PCCS) for transparent (T = 99.7%) and opaque (T = 0.7%) suspensions.

In Fig. 9 the calculated mass weighted diameter distribution is shown for a medium transmission.

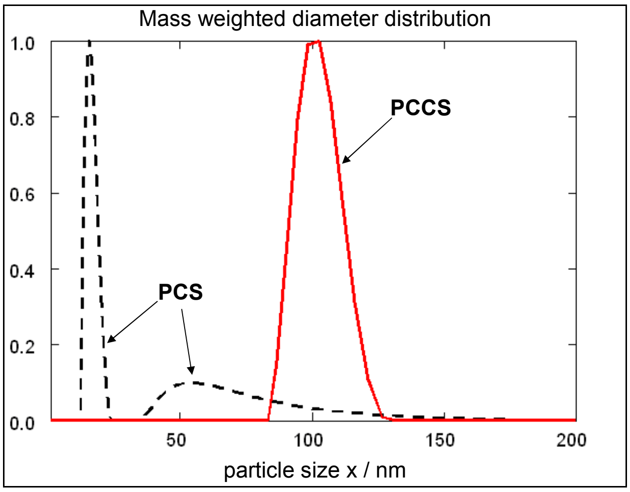

Figure 9: Latex in water with x = 107 ± 10nm (TEM). Calculated results for T = 36.5%.

While the 3D autocorrelation technique of PCCS reproduces a monomodal distribution with the expected x_{50} diameter of about 105 nm even at a very high concentration, the calculation for PCS creates as strange bimodal distribution even at a lower concentration. It has no relation to the measured material.

In addition to the size analysis PCCS offers parallel the analysis of the stability of the system. The amplitude of the crosscorrelation function for $\tau = 0$ is a direct measure of the amount of single scattered light. The lower transmission in Fig. 8 is equivalent to a higher concentration creating stronger multiple scattering. So the fraction of single scattered intensity is reduced which results in a reduced amplitude. The time dependency of the amplitude of the crosscorrelation function can now be used for a direct analysis of the stability of the sample. Only if the amplitude is constant, the sample is in a stable state. Otherwise sedimentation, growth or flocculation processes are taking place and can be monitored.

For further information please refer to [7], [8], [9]. [10], [11].

3 CONCLUSION

PCCS allows for simultaneous measurement of particles size and stability of opaque suspension in the range of 1 nm to about 10 µm. For absolute values the evaluation requires only the knowledge of the dynamic viscosity η. The crosscorrelation completely eliminates any contribution of multiple scattering to the results. So an adaptation of the theory for multiple scattering is no more necessary. This enables the measurement of opaque and colored samples. The results are independent of the concentration and the position of the cuvette. Measurements can be performed at high concentrations, usually without any dilution. High count rates result in short measuring times with minimum statistical uncertainties. No special precautions for cleanness are necessary, as with former PCS. This strongly simplifies the handling.

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