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Dynamic light scattering by preserved skimmed cow milk: A comparison of two-colour and three-dimensional cross-correlation experiments

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Abstract We investigate the dynamic light scattering of preserved skimmed cow milk and compare the performance of a standard two-colour (2C) cross-correlation setup with the recently developed three-dimensional (3D) cross-correlation setup. Undiluted milk could only be investigated using the 3D setup because of too low signal-to-noise ratio of the 2C setup. A tenfold diluted milk, however, could be investigated by both setups, and comparable results for the dynamics of the sample were obtained thus demonstrating the equivalence of the decorrelation schemes. On the other hand, we found that the dynamics of the milk is strongly altered upon dilution. This finding elucidates the benefits of the new 3D setup for the investigation of highly turbid samples.

Key words Dynamic light scattering – multiple scattering – cross-correlation – cow milk

Introduction

Currently, there is a growing interest in dense suspensions of colloidal particles where different direct interactions combine with hydrodynamic interactions to result in relevant influences on structure and dynamics. Related topics range from crystallization kinetics to the microscopic understanding of rheological behaviour. However, in dense samples, light scattering experiments are complicated due to multiple scattering events, which may even dominate the scattered intensity. Only in some rare cases can the turbidity of the samples be reduced by a certain match of the refractive index of the particles and the suspension medium. Dynamic light scattering (DLS) measurements have been performed by decorrelation of multiple scattering applying setups with a different degree of complexity [1–4]. Here we compare the performance of two state-of-the-art setups, both realized in our laboratory, i.e. the two-colour (2C) and the three-dimensional (3D) setup. As an illustrative example we investigate the dynamics of cow milk, because of its high reproducibility and its close relation to possible industrial applications of cross-correlation methods.

Experimental details

The experimental setup of the 2C experiment follows closely the description given in the original publication [2] and a recent performance report [5], respectively, while the setup of the 3D experiment has been already described elsewhere [6]. Consequently, we give here only a very short summary of the working principles. Both experiments measure the sample dynamics by two independent light scattering experiments, though applying the same scattering vector $\mathbf{q}_1 = \mathbf{q}_2$. While in the 2C setup the two experiments are distinguished by two different colours, the 3D setup switches to the third dimension thereby separating the light paths. These basic principles may be understood from Fig. 1, which shows a wavevector scheme for the respective DLS arrangements. Decorrelation of multiple scattering is performed by cross-correlating the signal fluctuations of both experiments [7]. The main

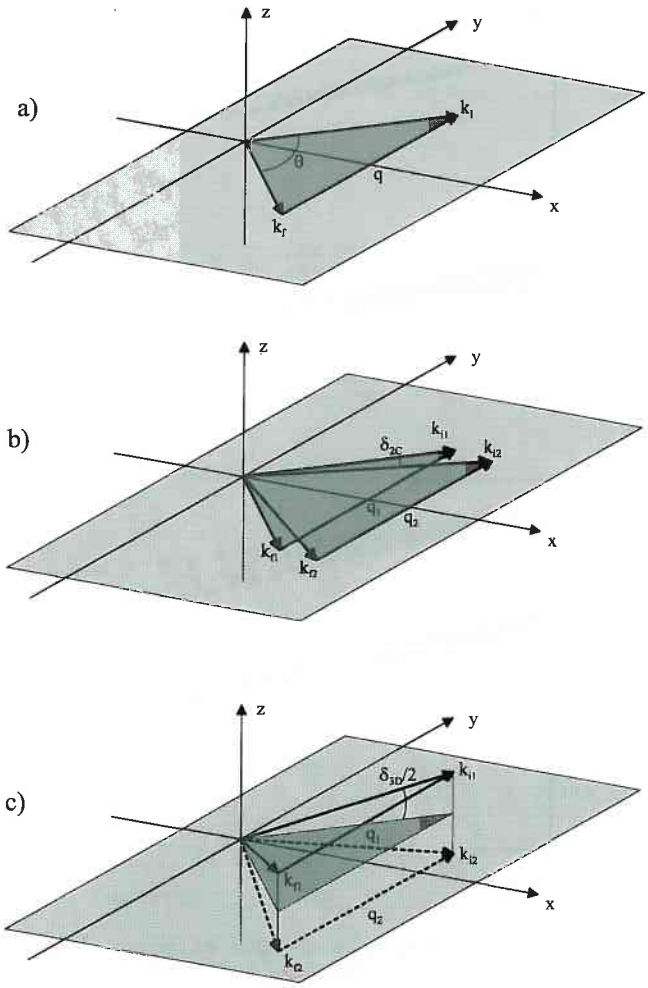

Fig. 1 "Evolution" of dynamic light scattering: (a) Conventional setup, with incoming and scattered wavevectors $\mathbf{k}_i$ and $\mathbf{k}_f$, respectively. (b) 2C setup; the incoming and scattered wavevectors both include a difference angle δ_{2C}; $\lambda_1 = 514.5$ nm, $\lambda_2 = 488.0$ nm. (c) 3D setup; the wavevectors include a difference angle δ_{3D} and share the common wavelength $\lambda = 790.0$ nm

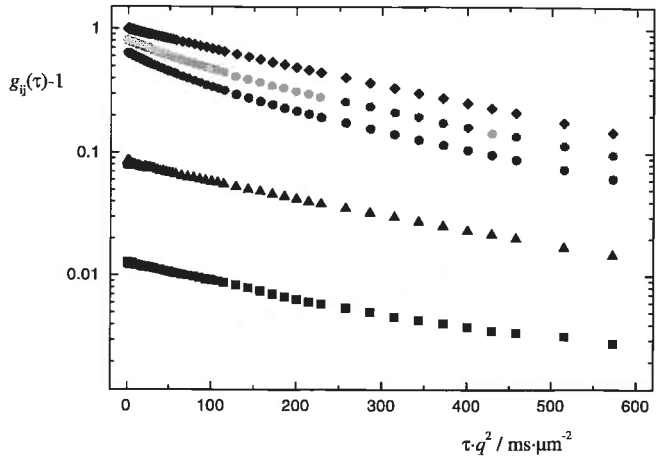

Fig. 2 Comparison of 3D and 2C DLS correlation functions applying a sample with $c/c_0 = 0.1$. An identical value of the scattering vector, $q = 16.7\ \mu m^{-1}$, is obtained by choosing $\theta_{2C} = 60°$ and $\theta_{3D} = 104°$. Auto-correlation: 3D (diamonds, $\lambda = 790.0$ nm); 2C (circles; $\lambda = 514.5$ nm: light grey, $\lambda = 488.0$ nm: dark grey). Cross-correlation: 3D (triangles); 2C (squares)

performance difference of the 2C and the 3D setup stems from the different wavelengths used. The mean wavelength of the 2C experiment is $\lambda = 501.3$ nm, whereas the 3D setup works at the longer wavelength of $\lambda = 790.0$ nm. As the scattering cross section in the Rayleigh–Debye–Gans limit varies as $1/\lambda^4$, the turbidity of the samples differs by a factor of six approximately, meaning a ratio of transmission coefficients $I_{2C}/I_{3D} \approx 2 \times 10^{-3}$. Utilising the 3D experiment one is therefore able to investigate samples of higher turbidity compared to the 2C experiment.

The milk under study was given by happy Hessian cows and, following a certain treatment, supplied by Schwälbchen Molkerei Jakob Berz AG, Bad Schwalbach, Germany, in tetragonal packages. We used the skimmed supply with a fat content of 0.3%; the original milk (c_0) was diluted by demineralised water in order to obtain samples with different concentration c and turbidity. No care was taken to prevent air contact. The milk has been stored in a refrigerator for approx. 24 h after dilution before starting the measurements, which were performed at room temperature.

Results and discussion

Let us first discuss differences and similarities of both setups for one chosen sample. Figure 2 shows auto-correlation functions $g_{11}(\tau)$ and cross-correlation functions $g_{12}(\tau)$ obtained from a tenfold diluted milk sample ($c/c_0 = 0.1$), measured with both setups under a scattering vector of $q = 16.7\ \mu m^{-1}$. Multiple scattering contributions to the auto-correlation function increase with decreasing wavelength, as clearly seen in the wavelength sequence of the $g_{11}(\tau)$ data in Fig. 2. The higher signal-to-noise ratio (i.e. the intercept β of $g_{ij}(\tau)$) of the 3D experiment in auto-correlation as well as in cross-correlation is both due to small multiple scattering contributions and an excellent signal-to-noise ratio obtained by using single-mode fibres [8].

Figure 3 shows only the cross-correlation results for both methods, now for four different sample concentrations as indicated. An increase in concentration is accompanied by a decrease in intercept, as expected. This behaviour is more pronounced for the 2C setup, still again due to the wavelength dependence, leading even to the "passing" of 3D by 2C. It becomes obvious that using the

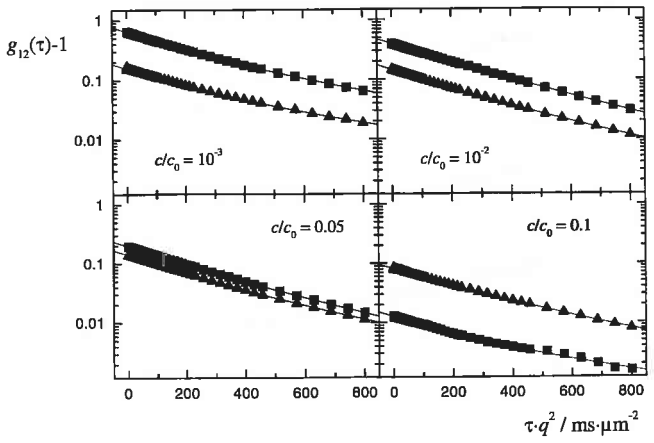

Fig. 3 Cross-correlation functions obtained from both, the 3D setup (triangles) and the 2C setup (squares) applying four samples with their concentration indicated in the plots. The drawn lines are fits to a second order cumulant expansion of the cross-correlation function. The droplet radii obtained from the first cumulant as determined by the 3D experiment are (in order of increasing concentration): $R = \{126, 116, 116, 127\}$ nm. The droplet radii determined by the 2C experiment are (in the same order): $R = \{119, 119, 118, 128\}$ nm

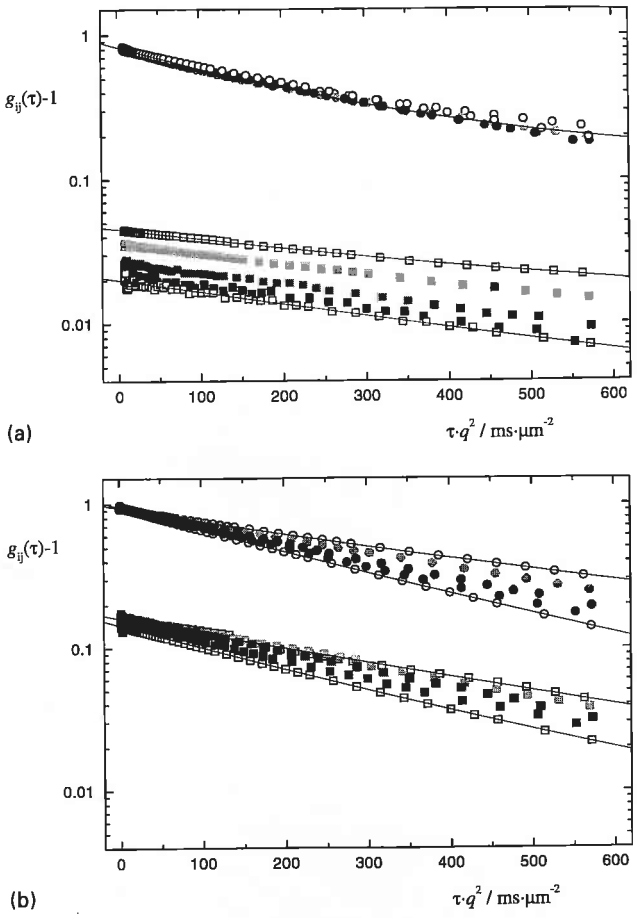

Fig. 4 (a) Correlation functions of undiluted milk ($c/c_0 = 1$) obtained with the 3D setup. Auto-correlation functions (circles) and cross-correlation functions (squares) are shown. Parameter is the scattering angle (36° and 104° (open symbols), 54°, 72° and 90° (increasing grey scale)). The drawn lines are fits to a second order cumulant expansion of the correlation functions; only the extremal values are shown. Droplet radii as obtained from the first cumulant of the cross-correlation function are (in order of increasing angle): $R = \{266, 252, 252, 266, 217\}$ nm; the experimental error is approximately 5%. (b) Correlation functions of diluted milk ($c/c_0 = 10^{-2}$) obtained with the 3D setup. Parameter is again the scattering angle, symbols are the same as in Fig. 4a. Droplet radii as obtained from the first cumulant of the cross-correlation function are (in order of increasing angle): $R = \{174, 171, 149, 124, 116\}$ nm; the experimental error is approximately 5%

3D setup we are able to investigate by far more concentrated samples than by using the 2C setup, thus confirming the expectation in the experimental section. The drawn lines are fits of a second order cumulant expansion to the data according to $\ln[g_{12}(\tau) - 1] = \ln\beta - K_1\tau + \frac{1}{2}K_2\tau^2$. We checked that a higher order cumulant fit does not change the results significantly. From the first cumulant, the droplet radii can be determined by using $R = k_B T q^2/3\pi\eta K_1$. The results are given in the legend of Fig. 3 and demonstrate very clearly the equivalence of both decorrelation methods, as the radii agree within the error of 5%.

Because of the signal-to-noise limitation mentioned we were not able to investigate undiluted cow milk with the 2C setup. However, with the 3D setup we employ rectangular cuvettes, the thickness of which we can make very small (approx. 1 mm). Multiple scattering contributions are reduced concomitantly as long as multiple scattering events take place outside the scattering volume, and the measurements can be extended to still more turbid samples. This method is by far more complicated if cylindrical cuvettes are employed, as is the in the two-colour scheme, because optical aberrations have to be considered in detail. This additional feature of the 3D setup enabled us to investigate even the dynamics of undiluted milk.

In Fig. 4 we present the data of angular dependent measurements obtained with the 3D setup for undiluted ($c = c_0$; Fig. 4a) and diluted ($c/c_0 = 10^{-2}$; Fig. 4b) milk. The undiluted milk shows a clear non-exponential behaviour in $g_{11}(\tau)$, which is almost absent in $g_{12}(\tau)$, indicating that the non-exponential behaviour in auto-correlation is due to multiple scattering. The decreasing intercept with increasing angle in cross-correlation is due to a methodical artefact. Note, that the droplet radii (approx. $R = 250$ nm) of the cross-correlation measurements are angular independent within the experimental errors.

In clear contrast, the diluted milk shows a strong angular dependence of $g_{11}(\tau)$ as well as $g_{12}(\tau)$. We interpret this finding as an increase in polydispersity of cow milk upon dilution. In addition, the droplet radii are found

significantly smaller (approx. $R = 150$ nm) than for undiluted milk. We conclude that cow milk cannot be diluted without significantly affecting its composition as measured by its droplet dynamics.

Conclusion

We reported measurements of the dynamics of preserved skimmed cow milk with two different methods to decorrelate multiple scattering. While we could demonstrate that both methods measure the dynamics without distortions due to multiple scattering, only by applying the recently introduced technique of the 3D setup using semiconductor lasers we were able to investigate undiluted milk. However, the dynamics of cow milk is drastically altered upon dilution. This finding might illustrate the importance of our development for the application of dynamic light scattering techniques to highly turbid samples.

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