

Investigation of evolution of surface layer of evaporating, single microdroplets of SDS/DEG colloidal suspension, the influence of micelle generation

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Abstract

We study experimentally the evolution of the mass of evaporating single microdroplets of sodium dodecyl sulphate (SDS) / diethylene glycol (DEG) mixture. First, we recognise a simple exponential decay of the evaporating droplet surface change rate. This enables us to study the influence of SDS concentration on the composite droplet evaporation. Next, we establish a simple relationship between the average SDS concentration and the droplet evaporation rate to enable the study of the evolution of SDS concentration at the droplet surface. The oscillatory nature of surface SDS concentration indicates cyclic changes in the surface monolayer associated with the cyclic creation of vesicles (micelles) at the surface. The model we developed, allows determination of SDS critical micelles concentration (CMC) in DEG as 60 ± 2 mM.

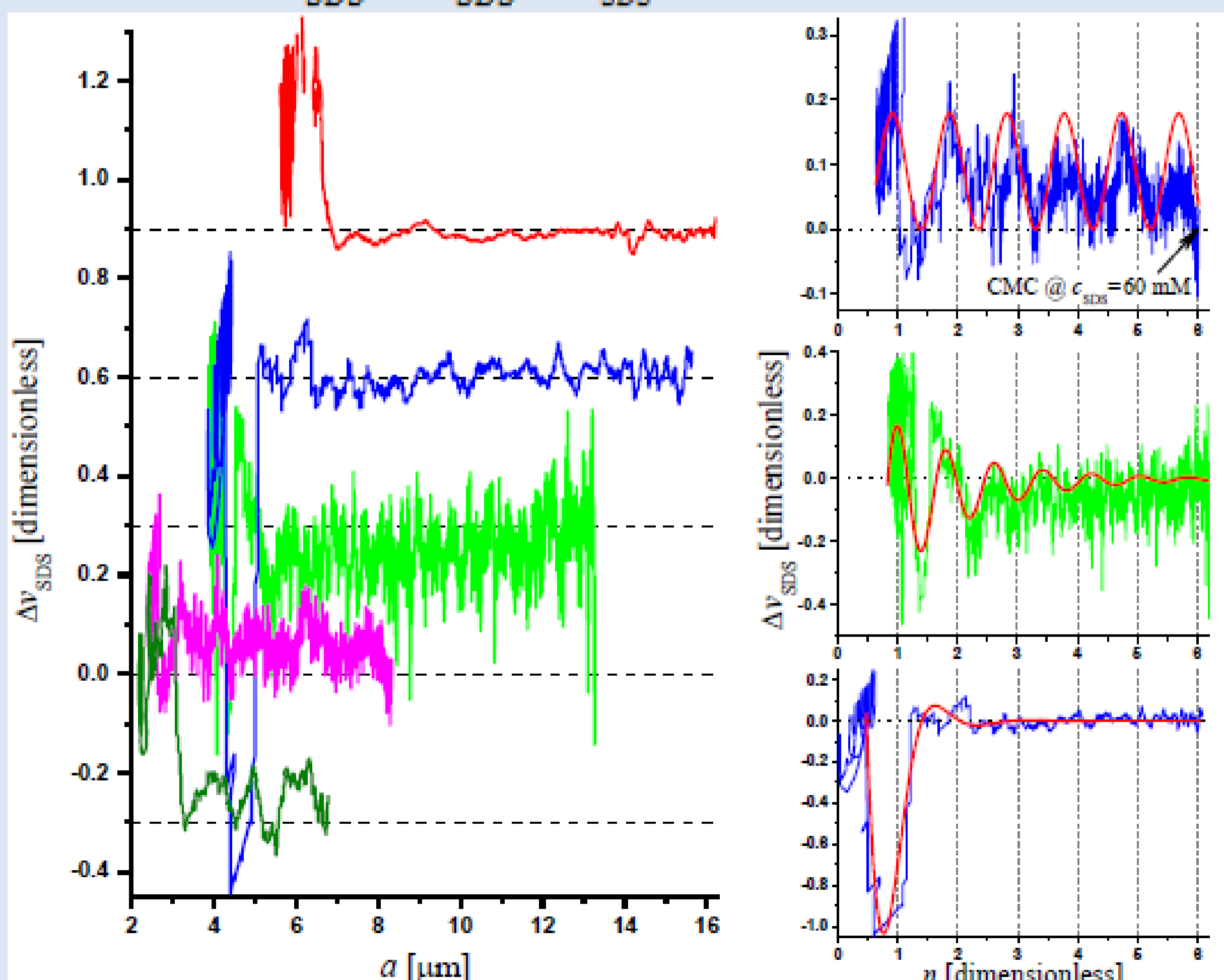
Single, charged microdroplets of solution were introduced into the 3D electrodynamic trap with a droplet-on-demand inject. The initial radius of a microdroplet was controllable with the injection driving pulse parameters (amplitude, shape, length and timing). Following the changes of this voltage enabled measuring the evolution of the droplet mass-to-charge ratio and finally finding the evolution of the microdroplet radius $a(t)$. The accuracy of electrostatic weighing is limited mainly by the discretization of the droplet position reading (with the CCD sensor) and is estimated at $\sim 1\%$. Since we did not observe any losses of the droplet charge, the radius was simply calibrated at the beginning of the evolution with MSLTM – radius of a nearly homogenous droplet was independently measured by analysing the scattered light intensity pattern with the help of Mie theory. Since SDS does not evaporate, it is possible, with the binary liquid evaporation model at hand [19] to find an exact radius value. The task was facilitated by the observation that the density of the solution can be assumed constant, as far as the density of DEG is 1.12 g/cm^3 , of SDS is 1.01 g/cm^3 , and of water is 1 g/cm^3 .

The droplet evaporation rate is dependent on the density of colloidal suspension at the droplet surface. Expressing densities with volume fraction of SDS v_{SDS}

$$a\dot{a} = -D_{\text{DEG}} \frac{\rho_{\text{sat}}}{\rho_{\text{L}}} \exp\left(-K \frac{v_{\text{SDS}}}{1 - v_{\text{SDS}}}\right) \quad v_{\text{SDS}} = -\frac{\ln \frac{a\dot{a}(t)}{a\dot{a}(t=0)}}{K - \ln \frac{a\dot{a}(t)}{a\dot{a}(t=0)}}$$

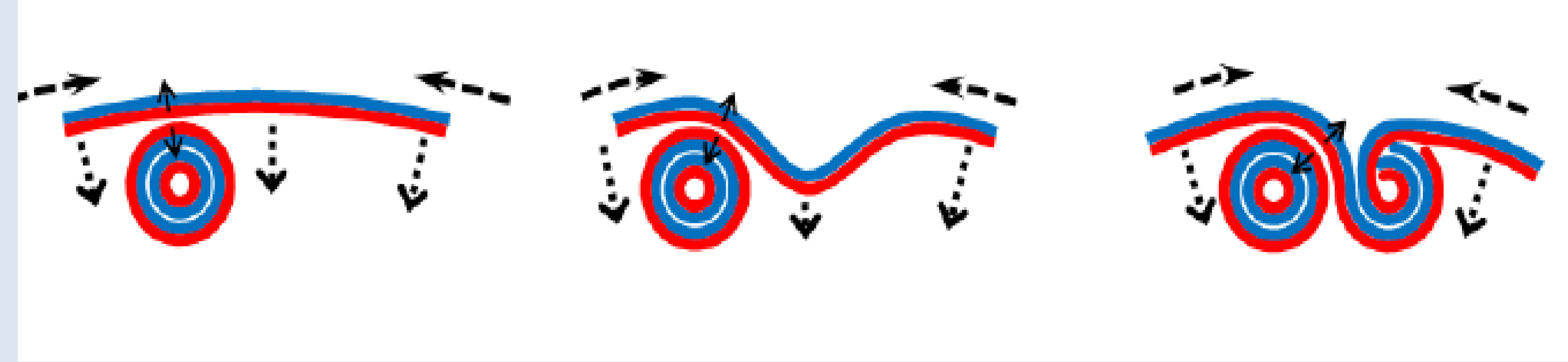
This equations made it possible determination of surface sds volume fraction

The evolution of the surface SDS concentration generally follows the mean concentration in the volume. Additionally significant oscillatory character appears, well visible in the excess of the surface SDS volume fraction over its mean volume value $\Delta v_{\text{SDS}} = v_{\text{SDS}} - \bar{v}_{\text{SDS}}$

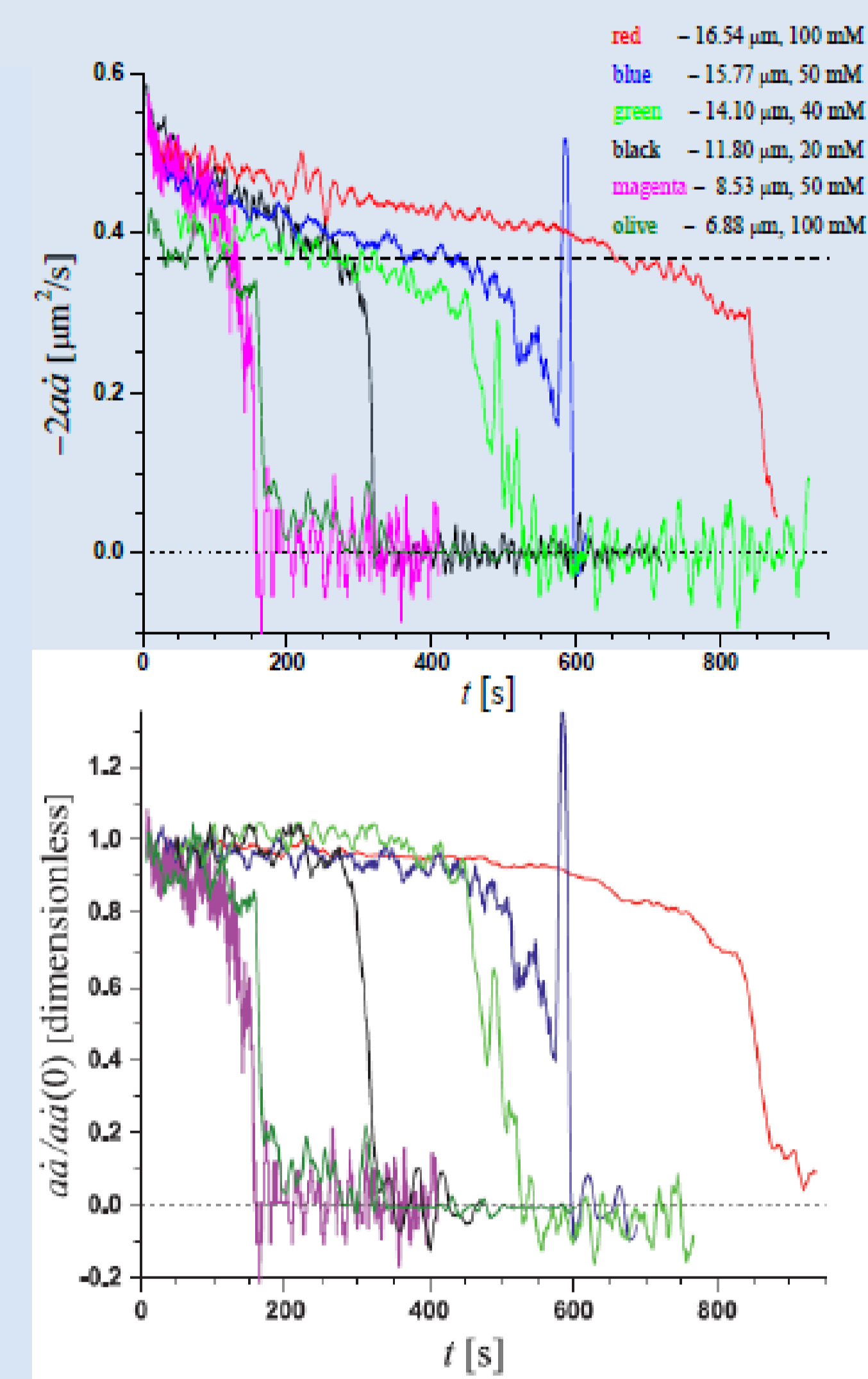
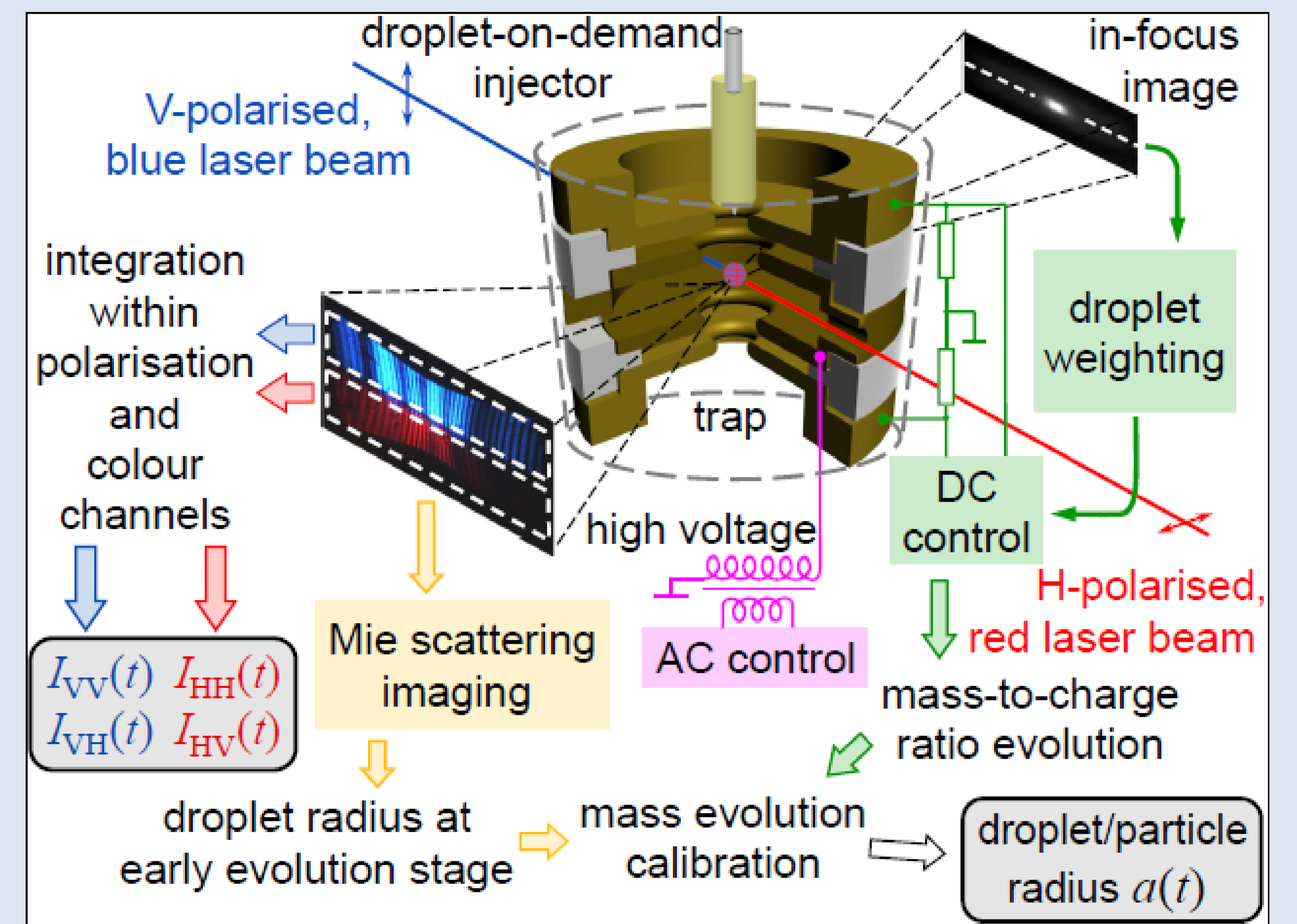


Evolution of the SDS volume fraction excess as the function of droplet radius (left panel) and of n – doubling of concentration (right panel). In the left figure, the zero levels were shifted by -0.3 (olive), 0.3 (green), 0.6 (blue) and 0.9 (red) to increase visibility. The red solid lines in the right figure are fits visualizing the (damped) oscillations.

Forming of a new generation of micelles at the surface of an evaporating droplet



Schematic diagram of the experimental setup, experiment control and data acquisition.



Evaporation rate $-da^2/dt$ (a – droplet radius) of the investigated droplets obtained from the measured droplet mass evolution. The pure DEG evaporation rate is indicated as the dashed black line. Initial values of the SDS concentration and the initial radii are shown in the legend.

Evaporation rate after subtraction of the influence of contaminating water and normalization

In order to explain oscillations of the surface SDS volume fraction we propose the following scenario:

- For SDS concentration smaller than CMC (Critical Micelles Concentration - practically outside the scope of our experiment) the surface film of SDS monomers behaves as a Langmuir monolayer compressed due to the droplet evaporation – shrinking of the droplet surface.
- At CMC, the surface monomer concentration saturates and further evolution of the surface film due to the droplet evaporation is possible only in radial direction. The surface film must buckle-in and form bulges evolving into vesicles, when the surface area continues to shrink. The process of formation of vesicles at the surface by buckling can be perceived as a nucleation due to the supersaturation of the surface SDS concentration. The process of (heterogeneous) nucleation should be initiated by nuclei of condensation