Dynamic light scattering on single levitated microdroplets of nanofluids

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ABSTRACT

We applied the dynamic light scattering (DLS) technique for studying single microdroplets of dispersions of SiO_2 and TiO_2 nanoparticles. The evaporating microdroplets were levitating in an electrodynamic quadrupole trap. Exponentially decaying autocorrelation functions (ACFs) were obtained for the light scattered by evaporating microdroplets as well as for microaggregates of nanoparticles formed at the end of the evaporation process. It was found that the temporal variation of the ACF generally reflects the evolution of the microdroplet of dispersion. At the initial stage of the evaporation, apart from the optical morphology resonances of the droplet (dielectric sphere), it was possible to identify the characteristic times corresponding to the Brownian motion of the dispersed nanoparticles. At the end of evolution, when the drying microdroplet transforms into a (non-rigid) microaggregate, the Brownian motion of the dispersed nanoparticles was masked by the rotational Brownian motion of the microaggregate as a whole.

EXPERIMENTAL SETUP

We've chosen electrodynamic levitation, since it enables trapping of (sub)microdroplets and causes smallest droplet deformation. A single droplet of a nanoparticle suspension injected into the trap was steadily kept at the desired location. For the detection of the fluctuations of the light scattered by a single micron-sized droplet, we used a fast photon-counting PMT (R649, Hamamatsu) with a thermoelectric cooler and an amplifier-discriminator (F-100T, Advanced Research Instruments Corporation) that sends the TTL level 10-ns pulses to the real-time digital correlator (Photocor- FC, Photocor Instruments). The autocorrelation functions were analysed with Alango DynaLS software to obtain the corresponding characteristic times by discrete component analysis. The sensitivity of the DLS setup was sufficient to get the signal level of 10^5—10^6 cps. As a result, we could obtain a high-quality autocorrelation function after a time of only 10 s.
A conventional DLS setup with a cuvette was used for reference particle size measurements for the given dispersion. It utilised a diode laser working at 405 nm wavelength.
All the experiments were performed at room temperature.

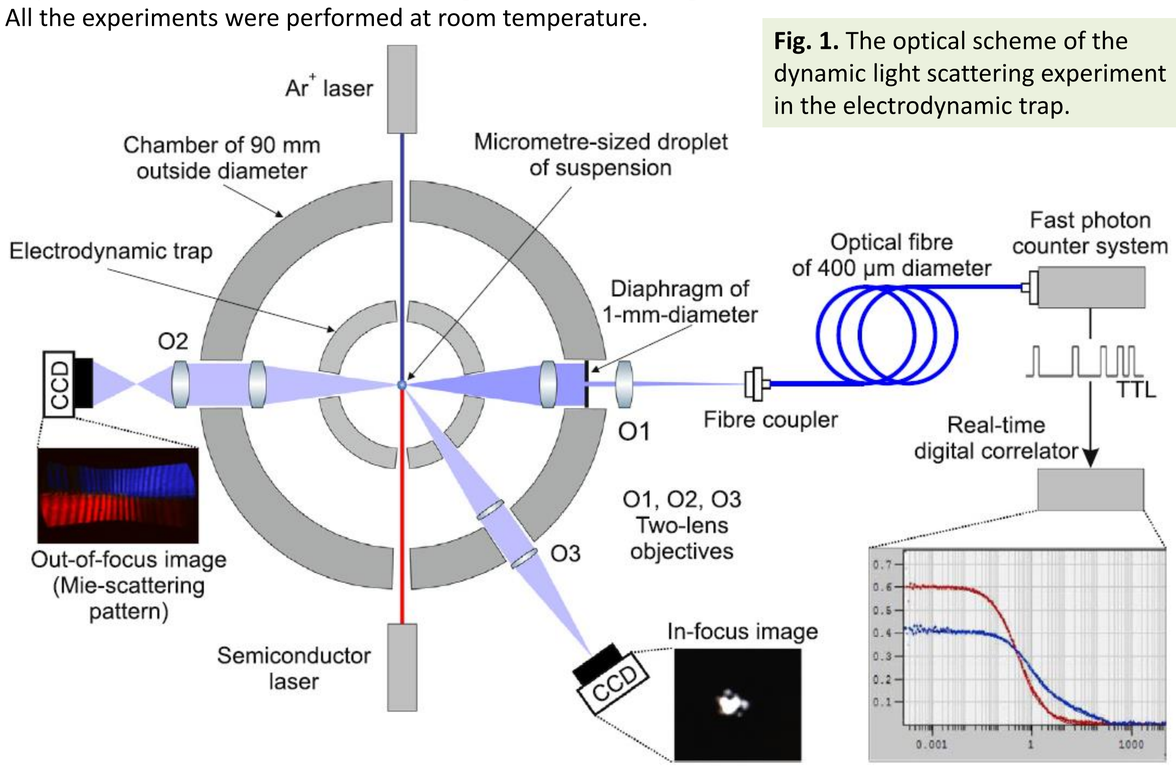

Fig. 1. The optical scheme of the dynamic light scattering experiment in the electrodynamic trap.

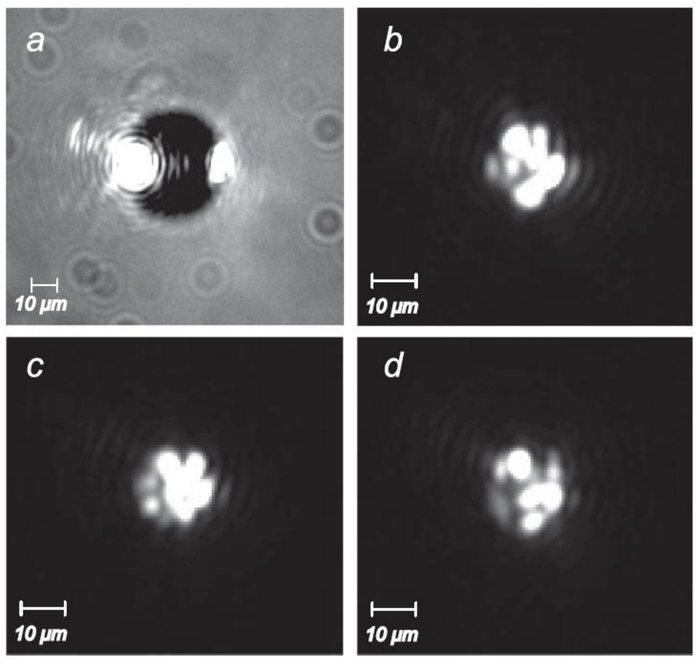

Fig. 2. (a) Experimental in-focus images of a levitated, pure tetraethylene glycol, ~40μm droplet. (b, c, d) Consecutive in-focus images of an aggregate – at the final stage of evolution – obtained from a water droplet containing ~300 TiO_2 nanospheres of 250 nm diameter. Image (a) was obtained with additional back-illumination with unpolarised white light, in order to visualise the droplet boundaries. It can be inferred that the random rotations of the microaggregate in the electrodynamic trap induce/facilitate changes of its shape. We haven't noticed any dependence of the rotational Brownian motion of aggregates upon the AC frequency. Thus we do not expect that they are significantly assisted by the AC field.

Autocorrelation function in DLS method

The random motion of particles in dispersion with the temperature T and the viscosity η is characterised by the diffusion coefficient D, which by means of the well-known Stokes-Einstein relation $D = k_B T/(6\pi\eta R_H)$ is linked to the so-called hydrodynamic radius R_H. In order to obtain the hydrodynamic radius with the DLS method it is necessary to measure the time dependence of the autocorrelation function G(τ) of the scattered light intensity $I(t)$. For a delay time τ, the normalised ACF is given by

$$G(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}. \quad (1)$$

For a monodisperse system of particles with Brownian motion the ACF exhibits the following exponential decay:

$$G(\tau) = A_0 + A_1 \exp(-2Dq^2\tau), \quad (2)$$

where A_0 is the baseline of the ACF for $\tau \to \infty$, and A_1 is the amplitude of the ACF at $\tau = 0$. The scattering vector

$$q = \frac{4\pi n}{\lambda}\sin(\theta/2) \quad (3)$$

is connected with the refraction index of the dispersion medium n, vacuum wavelength of the incident light λ and with the scattering angle θ. In many cases the intensity correlation function can be written in the form of the so-called Siegert relation, in which $A_0 = 1$ and $A_1 = \beta$ is the coherence factor, which is determined by the experimental conditions. The exponential time constant $\tau_0 = 1/(2Dq^2)$ can be easily found from the $G(\tau)$ curve for the monodisperse sample. This is the characteristic time of the considered diffusion process. However, in most cases the samples are polydisperse and the ACF becomes a sum of single exponential decay functions with different decay time constants (characteristic times) τ_i.

RESULTS AND DISCUSSION

The autocorrelation function for the accumulation time $t_{a1} = 10^4$ s (Fig. 3, curve (1)) exhibits a periodic character (with period T=296 s) due the morphology-dependent resonances (MDRs) of the droplet. In order to identify the Brownian motion of TiO_2 nanospheres we used a short-time part of this ACF obtained after subtraction the long-time A_0 level and normalisation. Such procedure was possible since the periodic part of the ACF changes very little over the first few orders of magnitude on a time scale.
The short-time part is represented in Fig. 3 by the curve (2). There are several characteristic times that can be identified in this part of the full ACF. The longest characteristic time of about 1 s is the remnant of the long-time part and should be associated with the MDRs. The shortest characteristic time (τ = 0.034 s) corresponds to the Brownian motion of titania nanospheres in the microdroplet.
The small local maxima that are present on the curve (2) correspond to the frequency of the AC field of the electrodynamic trap. In our experiment, the AC frequency varied from 200 Hz at the beginning of the droplet evolution to about 700 Hz at the final stage. The presence of such maxima in the ACF confirms the high sensitivity of the technique to small changes in the intensity of scattered light, such as those connected with the small droplet's oscillations at the AC frequency, relative to the equilibrium position – so-called micromotion. Since the droplet/aggregate was in the ground-state of the trap, there was no droplet macro-motion at the eigenfrequency of the trap. It is however expected that the frequency of free aggregate rotation would be independent and different from the AC frequency.

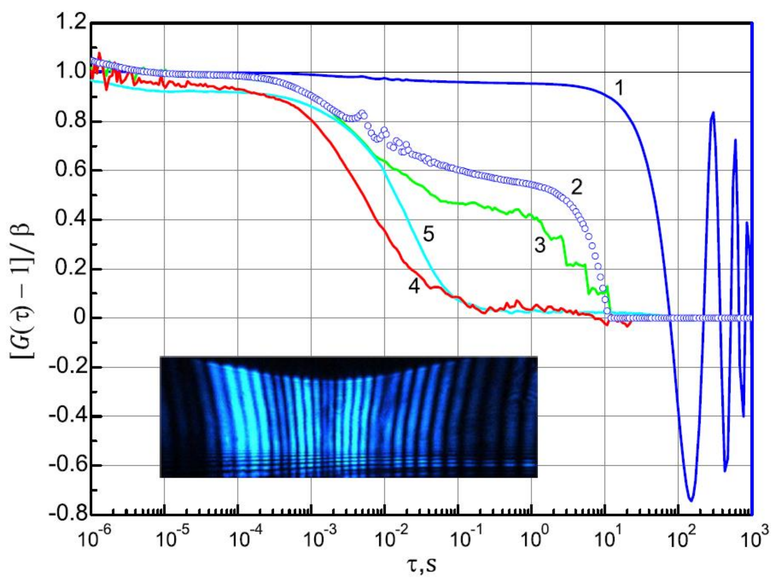

Fig. 3. Normalised ACFs for 250 nm TiO_2 nanospheres in tetraethylene gly-col. (1–4) pertain to the microdroplet and wavelength λ = 497 nm, while (5) pertains to the bulk sample in a cuvette and the wavelength λ = 405 nm. (1, 2): ACF with the accumulation time t_{a1} = 10^4 s, (3, 4): subsequent ACF with t_{a1} = 20.5 s and t_{a1} = 7.1 s respectively. The inset shows a typical snapshot of the Mie-scattering pattern for wavelength λ = 497 nm at the beginning of the droplet evaporation.

In accordance with relation (3), the characteristic times obtained from standard DLS experiments for the same conditions should be scaled with the wavelengths of the illumination source. For instance, for 497 nm and 654 nm, the exponential ACF decays with the characteristic times of 9.2×10^{-4} and 16.3×10^{-4} respectively can be expected. Then, $\tau(405) : \tau(497) : \tau(654) = 1 : 1.5 : 2.7$. However, in our DLS experiment with microdroplets (curves (3) and (4) in Fig. 4) we obtained $\tau_3(654) = 1.23\times10^{-3}$ s and $\tau(497) = 0.61\times10^{-3}$ s, which corresponds to the ratios of 1 : 2:2 : 4:4, significantly differing from the theoretical prediction for the Brownian motion. It can also be noticed in the inset in Fig. 5 (in ln-lin scale) that curves (3) and (4) exhibit a somewhat different character (curvature) than curve (5). As expected, the ACFs obtained for microaggregates exhibit properties, which do not correspond to the standard assumption of the Brownian motion of the nanoparticles. We expect that ACFs corresponding to different levitating aggregates (Fig. 4) reflect primarily the changes in the distribution of mass and charge in the aggregate and its random rotation rather than the parameters of the original dispersion.

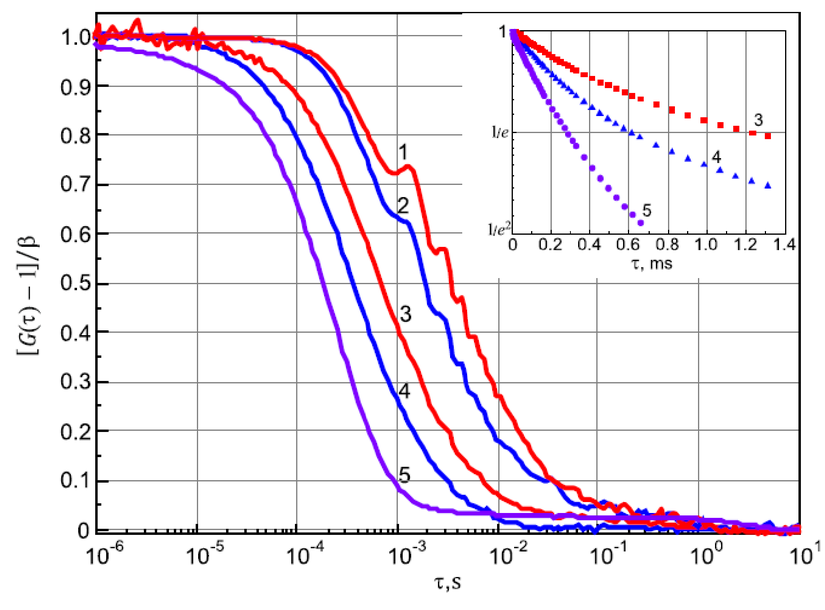

Fig. 4. A series of the ACFs that were measured for 0.004 wt% aqueous dispersion of 250 nm TiO_2 nanoparticles in droplets and in cuvette. Curves (1), (2) correspond to ACFs for a larger droplet, while curves (3), (4) correspond to a smaller droplet. Curves (1), (3) correspond to the wavelength of 654 nm, while (2), (4) correspond to the wavelength of 497 nm. Curve (5) corresponds to the measured in a cuvette at the wavelength of 405 nm. The inset presents the curves (3), (4) and (5) in ln-lin scale in a short range of delay time.

References

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