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Sizing of single evaporating droplet with Near-Forward Elastic Scattering Spectroscopy

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ABSTRACT

We have developed an optical setup and related numerical models to study evolution of single evaporating micro-droplets by analysis of their spectral properties. Our approach combines the advantages of the electrodynamic trapping with the broadband spectral analysis with the supercontinuum laser illumination. The elastically scattered light within the spectral range of 500–900 nm is observed by a spectrometer placed at the near-forward scattering angles between 4.3° and 16.2° and compared with the numerically generated lookup table of the broadband Mie scattering. Our solution has been successfully applied to infer the size evolution of the evaporating droplets of pure liquids (diethylene and ethylene glycol) and suspensions of nanoparticles (silica and gold nanoparticles in diethylene glycol), with maximal accuracy of ±25 nm. The obtained results have been compared with the previously developed sizing techniques: (i) based on the analysis of the Mie scattering images - the Mie Scattering Lookup Table Method and (ii) the droplet weighting. Our approach provides possibility to handle levitating objects with much larger size range (radius from 0.5 μm to 30 μm) than with the use of optical tweezers (typically radius below 8 μm) and analyse them with much wider spectral range than with commonly used LED sources.

1. Introduction

Understanding evaporation phenomenon is a highly challenging and important task. Despite that the evaporation has been studied for more than 130 years [1], some aspects of that phenomenon, still remain not fully explained [2]. As an example, we can mention a temperature jump at the liquid–vapour interface explained by Ward and Fang [3], does not predicted by the classical kinetic theory [4]. Understanding of evaporation, especially at micro- and nanoscale, leads to advances in many scientific disciplines such as atmospheric science [5,6] (e.g. formation of clouds or greenhouse effect), engine combustion [7,8] (to increase efficiency or for clean-burning), studies on the transpiration in plants [9] or drug delivery [10,11]. In most of the aforementioned applications one deals not only with pure liquids but also with suspensions of various nanoparticles. In order to effectively investigate evaporating droplets it is necessary to use a technique that provides non-invasive and non-contact means of droplet manipulation and characterisation. A well-established experimental technique that satisfies these requirements is the electrodynamic trapping [12–17]. If combined with non-contact characterisation technique, it can serve as a comprehensive tool for investigation of evaporating droplets. A variant of a quadrupole trap was developed in our laboratory (see e.g. [18] and references therein). By now, to characterise evaporating droplets on-line we have been using direct imaging of droplets for stabilisation and manipulation purposes and, more importantly, elastically scattered laser light [14,15,19]. In the latter method, scattering patterns recorded in the experiment are compared with numerically generated ones, usually calculated in advance with the use of the Mie theory [20]. Our solution is also based on the Mie scattering theory and therefore it was referenced to as the Mie Scattering Lookup Table Method (MSLTM) [18]. It provides high accuracy of ±10 nm in favourable cases and has been applied to several studies performed in our laboratory (see e.g. [2,18,21–23] and references therein). Unfortunately, the Mie scattering-based methods have significant drawback: they are limited to the homogeneous droplets. It is especially important when evaporation of droplet of suspension is observed. In that case aggregation process occurs and nanoparticles emerge on the droplet surface which manifests as fluctuations in the scattering intensities (speckles). Subsequently, scattering patterns become more and more distorted and cannot be analysed with the use of the Mie theory any more. That is why, for droplet sizing, commonly used are also Fourier Transform-based methods [24–26]. They are less accurate but seem to be applicable even to highly inhomogeneous droplets, or even solid corrugated particles. For our purposes,

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simultaneously with the MSLTM, as an auxiliary method, we have been using an electrostatic weighting. The method is based on the analysis of the constant electric signal U_{DC} used for the droplet stabilisation. As the stabilisation loop maintains the constant vertical position of the droplet in the trap by varying U_{DC}, the temporal evolution of droplet mass-to-charge ratio can be immediately obtained. If we know a composition of the droplet, we can easily derive a mathematical formula describing its radius. However, the absolute droplet charge remains unknown, therefore the weighting method requires calibration. Several approaches of resolving this issue have been shown in the literature [27–32]. For example, analysing of particle trajectories [27], analysing the dynamics of particle in the trap (spring point method [28,29], drag force method [30,31]) or controlled discharging of particle [32]. We however, utilised the calibration with our optical measurements [18]. It relies on the fitting of the two evolutions in the evaporation region where both methods can be unambiguously used. The elastically scattered laser light is not the only way to characterise evaporating droplets with optical methods. Also Raman scattering is widely used. Since Thurn and Kiefer first reported measurements of Raman spectra of optically levitated microspheres [33], the method became mature. In the following works Thurn and Kiefer showed structural resonances in the spectra for glycerol-water droplets and Deavis et al. for octadecane [13]. Smith et. al [34] reported that spontaneous Raman scattering can be effectively used to measure the temperature change due to evaporative cooling of a train of water droplet injected into vacuum. Similar investigation but for the droplet levitating within an electrodynamic trap in a nitrogen flow of variable velocity have been performed by Heinisch et. al [35].

Finally, also broadband scattering become a method interesting for consideration. As an example, Guillon and Stout [36] analysed droplets trapped optically in the air by scattered blue LED light at 90° with a spectral range ~60 nm. They determined both the droplet size and refractive index. Experimental results were compared with rigorous numerical calculations. Similar technique was used by Zardini et al. [37] in order to investigate the very low vapour pressure of substances in aqueous suspension. Similar as in our research, they utilised an electrodynamic quadrupole trap to levitate significantly larger droplets (radii range from 5 to 15 μm), however they used backscattered light of spectral range 560–610 nm. White LED of broadband spectra (480–700 nm) was used by Ward et al. [38] for accurate (±2 nm) droplet sizing and to determine the refractive index dispersion. However, utilisation of the optical trap limited the study to droplets within size range of 2–8 μm in radius. This method proves also its utility to determine the refractive index of solid polystyrene particles with astonishing accuracy of ±0.0005 over entire wavelength range 480–700 nm [39]. Due to technical limitations concerning available light sources, scattering spectroscopy of levitated objects had become much easier with appearance of supercontinuum laser sources. Tunable laser diodes, used previously for this purposes, were limited to narrow (<50 nm) spectral ranges, while white LED diodes or incandescent sources were not able to provide high spectral density. Obviously, LED diodes and incandescent sources had been hitherto successfully used for numerous applications concerning scattering spectroscopy of aerosols or clouds of nanoparticles (see e.g. [40,41]). The first application of the supercontinuum light source for both the optical trapping and the optical scattering spectroscopy was shown by Li et al. [42]. More comprehensive study concerning optical trapping and scattering spectroscopy with a supercontinuum laser was performed later on by Guillon et al. [43]. It is worth noticing that unlikely the monochromatic optical trapping, the broadband spectra covers several resonances of the first excited Mie coefficients.

In the current work we used a supercontinuum laser source for illumination and a droplet (aggregate) was levitating inside the electrodynamic quadrupole trap. Recorded scattering spectra was further analysed. Since the droplet was trapped in the electrodynamic quadrupole trap, significantly larger size range (radius from 0.5 to 30 μm) could be covered. Moreover, we can deal with highly-absorbing particles.

2. Experimental setup and sample preparation

2.1. Experimental setup

Detailed description of the electrodynamic trap used in this work can be found elsewhere [18]. However, here we present a brief description of the setup with emphasis on the optical part with supercontinuum light source and achromatic optics that was developed to perform the current study. The schematics of the experimental setup is shown in Fig. 1. The electrodynamic quadrupole trap (1) is kept in the small climatic chamber (volume ~10 cm^3) (2) with dry nitrogen atmosphere (humidity ~5%) at temperature of 25 °C. The trap and its auxiliary components are thermally regulated by a circulating liquid from an external gas–liquid heat thermostatic bath. An average temperature differences of less than 0.2 °C between the bath and the climatic chamber can be achieved. Single evaporating droplet of suspension (or fully dried aggregate) (3) levitates inside the trap, it's position being constrained by a combination of alternating (AC) and static (DC) electric fields. Droplets of pure liquids or suspensions are injected into the trap with the droplet-on-demand injector (placed above the trap, not shown in Fig. 1) and charged by charge separation in the outward field of the trap. Droplet is illuminated by two coaxial, counter-propagating laser beams: (4) an argon ion laser (476.5 nm) vertically polarized and a diode laser (657.5 nm) (5) horizontally polarized, with respect to the scattering plane. In-focus images obtained with CCD camera (6) are used to track and stabilize the droplet position with PID-type loop (using DC field), out-of-focus images recorded with another CCD camera (7) are scattering patterns used for the droplet sizing with the Mie Scattering Lookup Table Method [18]. The droplet is also illuminated by a polychromatic broadband light beam (SM-8-420 supercontinuum laser by Leukos) (8) collimated with achromatic collimator (9). Light beam directly passing through the trap is blocked by the beam blocker (10), while the scattering spectra of the droplet for the scattering angles between 4.3° and 16.2° pass through the achromatic optics (two aspheric doublets) (11), fiber coupler (12) and is recorded using the broadband spectrometer (USB 2000+ by Ocean Optics) (13). The spectrometer has a maximum spectral range of 345–1043 nm and a global half-height resolution 1.3 nm. Depending on the droplet size and therefore intensity of the scattered light, we used integration time from 50 ms up to 250 ms. The recorded spectra are the subject of the post-processing and further analysis.

2.2. Sample preparation

In the experiments discussed in this work we produced droplets of: (i) pure liquids: diethylene glycol (DEG) (Fluka, BioUltra, 99.0 GC area %) and ethylene glycol (EG) (Fluka, BioUltra, anhydrous, 99.8 GC area %), (ii) suspensions of 250 nm-diameter silica nanospheres (Corpuscular Inc.) in DEG and (iii) suspension of 50 nm-diameter gold nanospheres (BBI solutions) in DEG. The final suspension was prepared by mixing DEG with suspension of silica or gold nanospheres and sonication. The stabilizing agent introduced by the manufacturer was not removed. The bulk properties of substances used in the experiments are presented in Table 1. The table shows refractive index for the two wavelengths corresponding to lasers used for the droplet illumination, while,