

OPTICAL LATTICES AND STRUCTURAL TRANSITIONS IN MICRODROPLETS OF COLLOIDAL SUSPENSION PROBED WITH LUMINESCENT NANOPARTICLES.

Iaroslav SHOPA¹, Maciej KOLWAS², Izabela KAMIŃSKA², Gennadiy DERKACHOV², Kwasi NYANDEY²⁻³, Tomasz JAKUBCZYK⁴, Tomasz WOJCIECHOWSKI²⁻⁵ and Daniel JAKUBCZYK^{2,*}

¹ Faculty of Mathematics and Natural Sciences. College of Sciences, Cardinal Stefan Wyszyński University in Warsaw, Warsaw, 01-815, Poland

² Institute of Physics, Polish Academy of Sciences, Warsaw, 02-668, Poland

³ Laser and Fibre Optics Centre, Department of Physics, School of Physical Sciences, College of Agriculture and Natural Sciences, University of Cape Coast, Cape Coast, Ghana

⁴ Institute of Control and Computation Engineering, Warsaw University of Technology, Warsaw, 00-665, Poland

⁵ International Research Centre MagTop, Institute of Physics, Polish Academy of Sciences, Warsaw, 02-668, Poland

*Corresponding author: jakub@ifpan.edu.pl

Abstract

Luminescent nanoparticles (LNPs) were used as nano-probes to investigate possible evolution scenarios of slowly evaporating free microdroplets of (light-absorbing) suspension. Single microdroplets were kept in a linear electrodynamic quadrupole trap. It was found that intense ($\sim 50 \text{ W/mm}^2$) laser light may influence the distribution of light-absorbing nanoparticles in the microdroplet. Since the microdroplet acted as an optical spherical resonance cavity, the interaction of nanoparticles with light reflected the internal light field mode structure. Such interaction becomes nonlinear via positive feedback. It led, among others, to a very significant increase in modulation depth and narrowing of spherical cavity resonance maxima (of

whispering gallery modes observed both in luminescence and scattering. Though such nonlinear phenomena are not expected to be induced by solar light intensities, they should be considered for freely propagating laser beams at light intensities much lower than those usually associated with non-linear optical phenomena.

1 Experimental setup and procedures

The experiments were conducted in a linear electrodynamic quadrupole trap (LEQT) (compare [1]) equipped with two plate electrodes perpendicular to the trap axis (Figure. 1). The LEQT axis was kept in vertical position – an orientation/symmetry favourable for balancing the

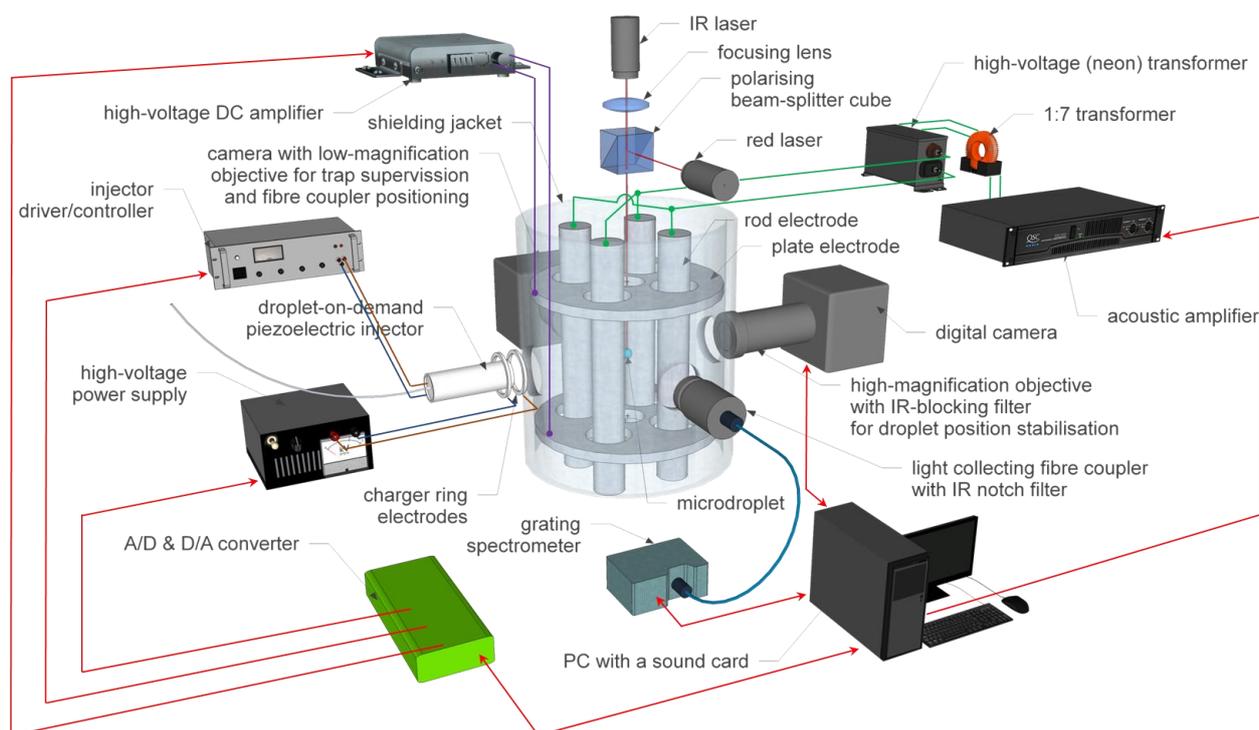


Figure 1 Experimental setup schematic visualisation.

levitated microdroplet weight and eventual other forces along this axis (see below). Electrically charged droplets were confined horizontally with the quadrupolar AC field of rod electrodes, while vertical confinement was achieved with the DC field of plate electrodes. The field between the plates electrodes in the presented configuration is not homogeneous but exhibits a gradient, which enables translating of microdroplets vertically by varying the applied voltage. The (vertical) position of the levitating microdroplet was observed with a digital camera (Smartek, GC651MP, equipped with IR filters) through a high-magnification microscope with the resolution of $\sim 1 \mu\text{m}/\text{pixel}$. This enabled setting up a stabilization loop and keeping the droplet at the desired vertical location – on the (horizontal) axis of the light-collecting optics. In order to find this point, an analogue camera with medium-magnification objective was placed in front of light-collecting optics. This camera also enabled supervision of the volume of the trap and detecting unwanted stray microdroplets/microparticles.

The trap had aluminium shielding jacket, which screened it from external (static) fields and minimized thermal gradients along the wall. The trap with shielding was kept in an air-tight chamber (not shown in the figure) with windowed ports.

Microdroplets were delivered to the trap with a droplet-on-demand piezoelectric injector equipped at the nozzle with annular electrodes for droplet charging. The charging high voltage was switched on only for the droplet injection while off directly afterwards, in order not to influence the trapping field during the stabilising loop operation.

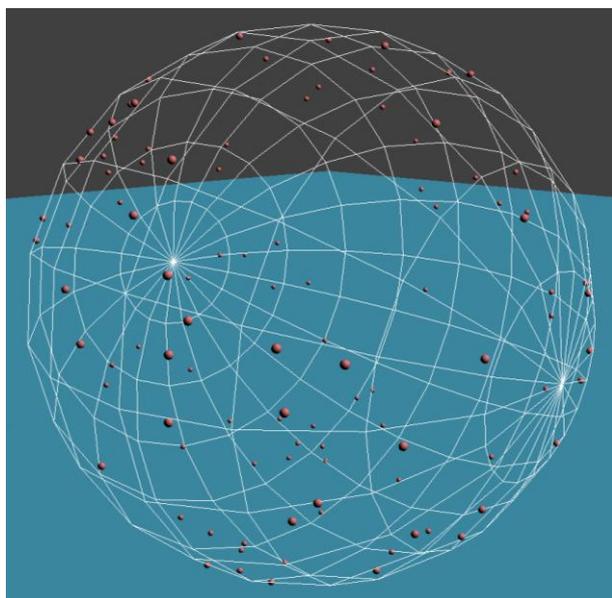


Figure 2 Visualization of a distribution of 102 LNPs in a microdroplet obtained with the evolution numerical model. The LNP and microdroplet radii were 435 nm and 39 μm respectively. Coulomb repulsion was taken into consideration, but no interaction with light.

In the presented experiments, the microdroplets were formed from a suspension of Gd_2O_3 : 1% Nd^{3+} LNPs in tetraethylene glycol. The LNPs were produced in-lab with the homogeneous precipitation method (compare [2]). 0.89 g of gadolinium nitrate $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 3.6 mg of neodymium chloride $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ were used for the synthesis. 3.6 g of urea $\text{CO}(\text{NH}_2)_2$ were used as the reducing agent. An aqueous solution (200 ml) of oxidants and reducing agent was prepared, which was heated to 85°C and shaken in a water bath for 4 h. The obtained nanoparticles were washed in distilled water four times and centrifuged in a laboratory centrifuge. Centrifugation parameters: 6000 rpm, 15°C , 15 minutes. A white powder was obtained which was dried overnight in a drying oven. Next, the nanoparticles were calcined in a laboratory furnace at 900°C for 3h. We used LNPs with the diameter of 870 ± 5 nm (compare Figure. 2). The dispersion medium was chosen for its very low volatility and high polarizability. Slow evaporation of the droplet enabled long integration time in light-detection scheme, while high polarizability ensures easy and stable microdroplet charging. The initial LNPs concentration in the prepared suspension was ~ 5 mg/ml (which corresponds to ~ 10 LNPs in a 12-nm-radius droplet). However, due to the density of Gd_2O_3 ($7.1 \text{ g}/\text{cm}^3$) being much higher than that of tetraethylene glycol ($1.1 \text{ g}/\text{cm}^3$), sedimentation readily manifests, leading to significant variation in the actual initial LNPs concentration in microdroplets. We tried to avoid this by conducting suspension preparation, injector loading and droplet injection (experiment) in quick succession.

The levitating microdroplet was illuminated with two perpendicularly polarized CW laser beams of two wavelengths: 805 nm (IR, 1.6 W) and 655 nm (red, 30 mW). Both beams were used for scattering measurements, while the IR was also used for luminescence excitation, and the red for droplet position stabilization.

For optical probing of the microdroplet we used Nd^{3+} luminescence at 5 close-lying spectral lines: 879, 892, 894, 911, 927 nm. In particular the 892-894 nm doublet presented a valuable sounding tool. The experiments on luminescence of $\text{Gd}_2\text{O}_3:\text{Nd}^{3+}$, were conducted with FT spectrometer (Bomem, DA8) equipped with PMT ($\Phi\text{ЭУ-62}$) covering the spectral range of 400-1100 nm, showed that the luminescence intensity of Nd^{3+} at the 5 lines mentioned above is comparable to the intensity at 1064 nm – usually the most prominent Nd^{3+} line. For the presented preliminary experiments we used a small grating spectrometer with a Si detector (Ocean Optics USB4000, 25 μm slit), which was much easier to integrate with the LEQT.

In order to obtain a measurable luminescence signal, the IR beam was (mildly) focused. In consequence, it exerted significant forces, both gradient and photophoretic – thus the choice of the trap type – LEQT and geometry/orientation. By following the stabilizing loop DC volt-

age, the forces could be balanced and measured, thus providing additional information.

The scattered light (red and IR) as well as the luminescence were collected with a dedicated objective with aspheric achromatic optics. The objective was equipped with a notch filter (805 nm, OD 6) and coupled to a multimode 600- μm -core fibre feeding the light to a grating spectrometer. Reasonable luminescence signals were obtained for exposition/integration times ~ 1 s, which set the luminescence and scattering signals temporal resolution. However, the temporal resolution of the vertical force measurement was limited only by the camera frame rate (~ 50 fps), which yielded ~ 20 ms. The evolutions of each spectral line intensity was extracted from obtained spectra sequences.

2 Experimental results

A very interesting phenomenon could be observed for a relatively low concentration of LNPs (compare [3–5]). For initial concentration of 1 mg/ml and a microdroplet of 39 μm radius, there are ~ 102 LNPs in the droplet (compare Figure. 2). When evenly distributed on the droplet surface, their average distance would be ~ 15 μm . Since the microdroplet was evaporating very slowly (~ 0.35 nm/s), many optical cavity resonances could be observed.

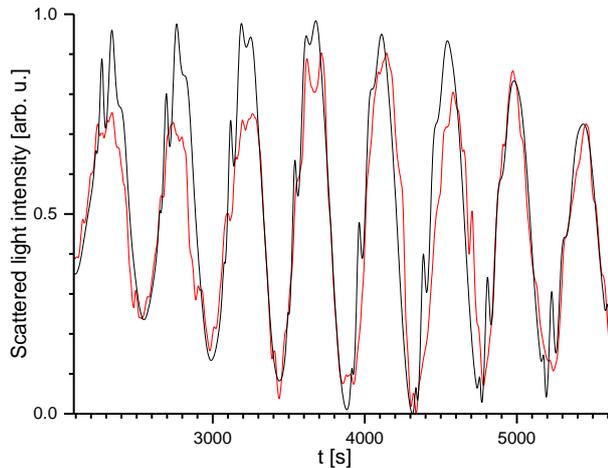


Figure 3 Evolution of scattered light intensity at 654 nm. Red – mildly smoothed experimental results (LOWESS, 19/3055 of range window), black – Mie theory prediction for a weakly absorbing sphere (see text).

Due to low LNPs concentration, the broad resonances of a microdroplet as a whole are plainly visible both in scattering as in luminescence all the time. The effective absorption of radiation by the droplet was small – the resonances modulation depth was generally high. Under closer scrutiny (Figure. 3), a fine resonance structure can also be detected, again, both in scattering and luminescence.

The broad resonance structure of scattered light intensity could be nicely fitted with Mie theory, while for the fine structure, only some of the peaks positions could be reproduced with a reasonable accuracy. This is only to be expected, since the field modes responsible for the narrow resonances are located close to

the microdroplet surface, where LNPs proceed to concentrate and the medium inhomogeneity is highest. The effective imaginary part of the refractive index $\Im(n)$ at 654 nm, estimated with the fitting was $5 \cdot 10^{-5}i$.

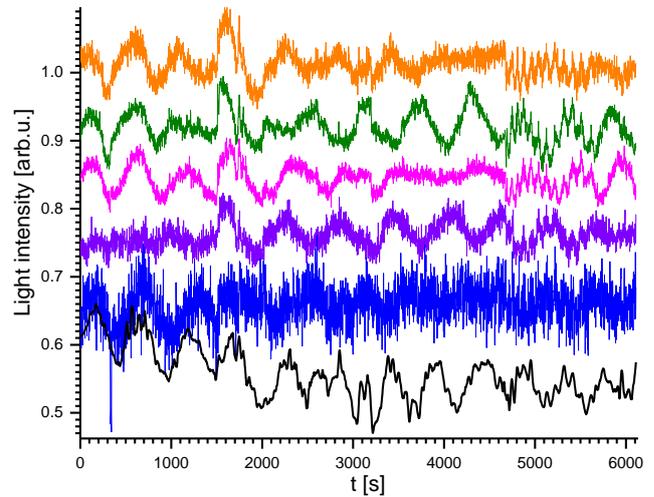


Figure 4 An evolution of light intensities representative for low LNPs concentration: black line – scattering near the excitation wavelength (805 nm), color lines – luminescence: orange – 879 nm, green – 894 nm, pink – 911 nm, violet – 927 nm, blue – 942 nm. The vertical scaling of each graph trace is independent.

The luminescence signal is more difficult to interpret as carrying more information and hence also more interesting. The exact shape of luminescence signal cannot be predicted at this stage of the model development (compare Figure. 6), since the details of coupling/interaction of luminescent nanoparticles with the internal light fields of the microdroplet (excitation and luminescence) is unknown. Interestingly, the fine resonance structure of the signal precisely corresponds such structure in the scattering signal. Since the resonances of the internal field correspond to those of scattering, it can be inferred that the correspondence results from absorption of 805-nm-wavelength internal field higher modes by near-surface LNPs. The slow oscillations visi-

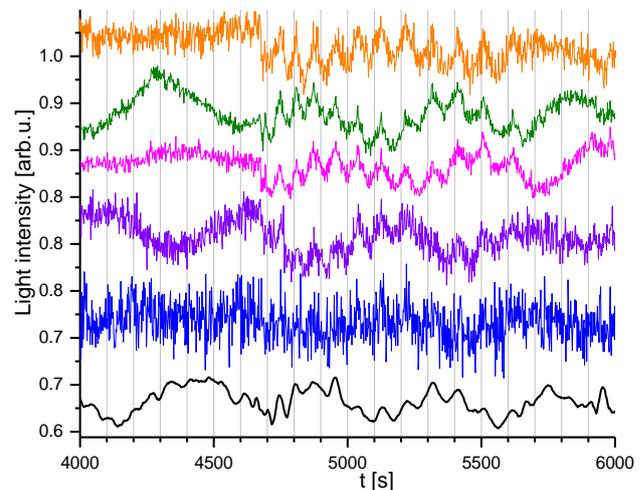


Figure 5 Magnification of ROI from Figure. 4: spherical resonator mode – LNPs lattice resonance.

ble in the signal correspond to lower modes of internal field – distributed more evenly in the droplet volume – and exhibit influence of microdroplet eigenmodes at the wavelength of the luminescence (compare Figure. 6). Some synchronization with the excitation field (805 nm) modes seems to persist, in particular when that field is stronger at the beginning of the droplet evolution. This may indicate some influence of strong excitation field modal structure, either via LNPs ordering (with photophoretic or gradient forces) or by creating an ordered distribution of refractive index via local heating due to absorption in the medium (for 805 nm $\Im(n)$ is over an order of magnitude higher than for 654).

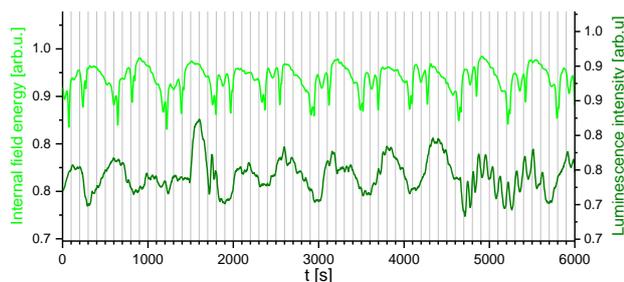


Figure 6 Dark green – mildly smoothed (Savitzky–Golay, 25/3055 of range window) luminescence signal at 984 nm (compare Figures. 4 and 5); light green – corresponding total internal field (energy) calculated with Mie theory for $\Im(n)$ found previously in NIR region.

For the most part of the observed microdroplet evolution the modulation depth of the fine structure seems in accordance with the $\Im(n)$ found (Figure. 6). However, at a certain moment (4675 s, see Figures. 4–6) the luminescence signal slightly but abruptly falls and the fine structure modulation depth becomes very significant. Furthermore, each constructive fine resonance peak exhibits a very narrow central maximum. Higher modulation depth is also visible in scattering at excitation wavelength. Again, the fine signal structure is in synchronicity with such structure of the excitation field, while the broad structure is not and corresponds to eigenmodes at luminescence lines. The proposed scenario is that the surface LNPs are ordered by the excitation field via photophoretic forces, which direct LNPs to local field minima – hence slight decrease of overall luminescence intensity – thus forming an LNPs lattice (near the droplet surface), which in resonance with the excitation field (modes). The process provides a positive feedback (stronger field – finer positioning in the node), which results in narrowing of resonance maxima. For some time the LNPs lattice follow the evolution of field nodes, but due to microdroplet movements/rotations the order is gradually lost. As can be seen in Figure. 2, forming of LNPs lattice by Coulomb forces is out of question for such a low concentration of LNPs.

The onset of the same phenomenon can also be spotted at 1749 s. However, the manifestation was much shorter.

3 Acknowledgement

This research was funded in whole or in part by National Science Centre, Poland, grant 2021/41/B/ST3/00069. For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

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