Collective Scattering of Light on Gold Nanospheres Dispersed in Diethylene Glycol Microdroplet

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Light scattering on a freely suspended, evaporating droplet of suspension of gold nanospheres (125 nm radius) in diethylene glycol is studied, revealing both local and nonlocal properties of the system. When the average distance between the nanospheres at the droplet surface matches the wavelength of light, a (broad) maximum, associated with the collective scattering on them, is observed. The number of nanospheres at the droplet surface can be found then. A fine modulation of the maximum is associated with the whispering gallery modes of the composite droplet. The Fano profile identified in the modulation is interpreted as an interference of collective scattering and whispering gallery modes. The ultra narrow enhancement-and-quench structure recognizable in the modulation is interpreted as associated with the creation and destruction of collective oscillation of plasmons of individual nanospheres. It is proposed that this phenomenon can be perceived as whispering gallery modes-assisted creation and destruction of a global plasmon.

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1. Introduction

Light scattering is often influenced by various resonances resulting from phase and frequency matching in its interaction with the scatterer. For example, the total intensity, as well as the intensity distribution of light scattered by a dielectric sphere shows a rich variety of structural resonances [1–5]. A particular class of these resonances, associated with the standing waves at the spherical surface, are referred to as whispering gallery modes (WGMs, see e.g. [6, 7]). For inhomogeneous or composite droplets, additional structural resonances resulting from the light wavelength matching to the characteristic lengths of the droplet internal structure (inhomogeneity) can also manifest. These additional structural resonances can be modified by the fundamental ones. For example, in case of droplets of dielectric suspensions, WGMs (of the entire droplet) can interact with the scattering on the surface inclusions [8]. The resonance conditions can enhance or decrease scattering significantly. In case of a coincidence of resonances of different origin, a significant enhancement/decrease can be expected. Such enhancement of scattering was studied in a layered, metal–dielectric structure of a sub-wavelength sphere [9, 10]. We expect that similar phenomena can manifest also in other complex metal–dielectric systems.

In this paper we studied light scattering on an evaporating microdroplet of suspension of gold nanospheres (GNS) in diethylene glycol (DEG). During DEG evaporation, the concentration of GNS at the droplet surface increases significantly faster than in the volume. It is also expected that GNS distribution at the surface becomes fairly regular with growing concentration, due to the electrostatic repulsion. This induces changes of the surface properties from dielectric-like to metal-like, and allows for the Bragg-like scattering on a lattice of surface GNS. The average distance between GNS favors certain WGMs (Bragg-like condition) and the arising scattering maximum can be perceived as the collective scattering (CS). In contrast to dielectric inclusions [8, 11], the high coupling between WGMs and scattering on the surface lattice of GNS can lead to synchronization of plasmons on individual inclusions. This can be perceived as the creation of a global plasmon [12].

The average distance between inclusions is controlled by their concentration and, in consequence, was scanned during the evaporation of the dispersion medium. Slow evaporation of DEG (slow droplet radius change) enabled a detailed study of various kinds of resonances as well as their interactions. We studied two slightly different systems: (A) a droplet with low initial concentration of GNS (≈ 60 GNS in a droplet of ≈ 16 µm initial radius) and (B) a droplet with 7.2× higher concentration of inclusions (≈ 125 GNS in a droplet of ≈ 10.6 µm initial radius). We identified and studied several phenomena:

1. manifestation of CS resonance, associated with the GNS at the surface,
2. modulation of CS maximum with WGMs and interference of WGMs associated with waves travelling in different media,
3. Fano interference of CS and WGM,
4. WGM-assisted synchronization of plasmons on individual GNS and formation of a global plasmon.

Some of the phenomena were observed in both systems, while the rest — only in one of them.

2. Measurement concept and experimental setup

The studied droplets of suspension were singly levitated in an electrodynamic quadrupole trap [13–16] built
in our laboratory [8, 17, 18]. A proper combination of alternating (AC) and static (DC) electric fields, in (nearly) quadrupolar configuration, enables constraining a charged particle to a very small volume, in practice to a point. The trap was kept in a small (∼10 cm³) thermostatic chamber with dry nitrogen at atmospheric pressure and 25°C. Single droplets were injected into the trap with the droplet-on-demand injector (built in our lab as well; similar to e.g. [19, 20]) kept at the chamber temperature. The droplets were charged by charge separation in the nozzle. Thus, the sign and, to some extent, the value of the charge was determined by the injection timing versus the phase of the trapping AC field. Our setup allows stable trapping of droplets of radius in the range from ∼ 35 μm to ∼ 0.5 μm. The average initial radius was several μm.

Two linear polarizers were used in the detection channel: H-polarizer (upper half of the field of view) and the V-polarizer (the lower half). Using a color camera allowed us to separate the scattered light spectrally and attribute it to appropriate incident beam polarization. We recorded temporal evolution of the scattered light intensity angular distribution. In post-processing, the spherical and chromatic aberrations introduced by the lens system were corrected and the distributions were integrated in appropriate detection channels over scattering angles θ = 90 ± 16.24° (azimuth) and Φ = 0 ± 5.33° (elevation). The scattered light intensities of the same polarization as the incident are denoted as \( I_{VV}(\Phi, \Theta; t) \) (red light) and \( I_{HH}(\Phi, \Theta; t) \) (green light). The, so called, cross-polarized scattered light intensities are denoted as \( I_{VH}(\Phi, \Theta; t) \) — red and \( I_{HV}(\Phi, \Theta; t) \) — green. For simplicity we denote intensity integrated over both Φ and Θ angles as \( I \), while integrated over Φ only, as \( I(\Theta) \).

The droplet radius evolution \( R(t) \) was determined by analyzing (mostly with the look-up table method in the framework of the Mie theory [21]) the scatterograms sequence (\( I_{VV}(\Theta, t) \) and \( I_{HH}(\Theta, t) \)) and by weighting with the help of the DC field of the trap [18]. The combination of these methods yields \( R(t) \) very accurately for a wide range of suspension concentrations.

3. Scattering of light on a droplet with low concentration of GNS

In this section, we study the light scattering on the droplet with low initial GNS concentration. The temporal evolution of the scattered light intensities, that we consider, is shown in Fig. 2. These are: \( I_{VV} \) (red light, polarization retained), \( I_{HH} \) (green light, polarization retained), \( I_{VH} \) (red, cross-polarized light) and \( I_{HV} \) (green, cross-polarized light). Fast oscillations of \( I_{VV} \) and \( I_{HH} \) signals — shown magnified in inset in Fig. 2 — are due to WGM of the droplet.

The cross-polarized intensities: \( I_{VH} \) and \( I_{HV} \) are small but substantial. Since scattering on a homogeneous spherical droplet practically does not lead to light depolarization near the equatorial plane, the \( I_{VH} \) and \( I_{HV} \) signals shall be associated with GNS. The electromagnetic (EM) field inside the droplet does not propagate along the incident light beam direction and the wave vector is only a local property. Scattering of such field on GNS (ensemble) in general does not retain the polarization of the incident wave and the cross-polarized (depolarized) scattered light appears.

During the suspension droplet evaporation, the concentration of the dispersed phase is growing nearly exclusively at the surface, where it accumulates from the evaporated dispersion medium volume. However, in case of a GNS suspension illuminated with a laser beam, the GNS interaction with EM field (photophoretic force, optical gradient force) should also be considered [22, 23]. For a droplet with low initial concentration of GNS, shown in Fig. 2, both mechanisms influencing their distribution...
with CS resonance is plainly seen in $I_{VV}$ signal at $\approx 500$ s of evolution.

In order to study the CS resonance in detail we have developed the following procedure: First, we extract the main evolution trends versus the droplet radius of intensity of light scattered by GNS independently: $I_{HV}^N(R)$ and $I_{VH}^N(R)$. This can be done, for instance, by fitting polynomials of lowest possible order (we found 3rd to be sufficient) to $I_{HV}(R)$ and $I_{VH}(R)$ with CS region ($420–540$ s) excluded.

Then, CS resonance can be emphasized by constructing the ratios $I_{HV}^N = I_{HV}/I_{HV}^0$ and $I_{VH}^N = I_{VH}/I_{VH}^0$ and presenting them versus the droplet radius (see Fig. 4). For each signal, a compound profile of the maximum is revealed then. It can be fairly well reproduced with a linear combination of two Gaussian profiles.

### 3.2. Modulation of CS maximum with WGMs and interference of WGMs associated with waves travelling in different media

In this section we show that $R$ and $L$ maxima are associated with the Bragg-like scattering of waves travelling below and above the (average) droplet surface and that the interference between WGMs associated with these waves can be observed as beating.
GNS participating in the scattering. The position of the maximum of the red scattered light intensity (at 8.5 µm) was used to estimate the number of inclusion as \( \approx 125 \pm 10 \). This is twice the number found for the low-concentration case. Due to a high number of inclusions the cross-polarized signal \( I_{\nu V} \) (blue line in Fig. 6) is only slightly lower than \( I_{\nu V} \) (red line).
4.2 Interaction of CS resonance with WGMs — Fano profile and beating of WGMs standing in different media

In order to study the details of CS we constructed $I_{VV}^N = I_{VV}/I_{HH}^N$ and $I_{HH}^N = I_{HH}/I_{VV}^N$ ratios and plotted them versus $R$ (see Fig. 7; it is worth noticing that $I_{VV}^N$ exceeds 2). The CS maxima in both signals can again be approximated with broad Gaussian profiles. However, it must be kept in mind that $I_{VV}^N$ signal still carries information on both scattering on GNS and on the entire droplet. The interference of these two modes of scattering results in a Fano profile, which can be observed near the center of $I_{VV}^N(R)$ maximum (compare: scattering of light on dielectric inclusions forming a surface layer in a droplet [11]). Simultaneously, an interference of two WGMs standing below and above the droplet surface can be identified, as the characteristic beating, in cross-polarized $I_{HH}^N$ signal (Fig. 7).

4.3 WGM-assisted synchronization of plasmons on individual GNS and formation of a global plasmon

It is worth noticing that a WGM minimum can entirely quench the CS maximum (e.g. at $R = 8.34 \mu$m in Fig. 7, $T_2 = 97.93$ s in Fig. 8). GNS scatter independently at WGMs minima, while at WGMs maxima (e.g. $R = 8.37 \mu$m in Fig. 7, $t = 100.7$ s in Fig. 8) they scatter collectively. This phenomenon of very strong coupling/decoupling between CS and WGMs manifests as dark and bright super-narrow (vertical dashed) lines (less than 40 nm wide) in $I_{VV}(\Theta, t)$ map in Fig. 8. Equivalently, it manifests as the revival/collapse of the interference fringes seen in $I(\Phi, \Theta)$ (movie frame in Fig. 8). When light is scattered on an ideally homogeneous droplet, only the interference fringes can be seen (frame $t_0$ in Fig. 8: no cross-polarized $I_{VV}$ at the very beginning of the droplet evolution). For light independently scattered on GNS (out-of WGM resonance) only speckles can be seen (in both $I_{VV}(\Phi, \Theta)$ and $I_{HH}(\Phi, \Theta)$, frame $t_4$ in Fig. 8). However, for WGM maxima coinciding with CS maximum, the interference fringes partly revive (frames $t_1$ and $t_3$ in Fig. 8). They sometimes seem to appear in cross-polarized light as well (frame $t_3$ in Fig. 8). This would signify that the polarization of the associated spherical cavity mode of entire droplet is skewed then. Since scattering of red light on 125 nm radius GNS has plasmonic nature, the WGM-CS coupling can be perceived as synchronization of plasmons on individual GNS and formation of a global plasmon. The phenomenon is
similar to the atomic/molecular dipole synchronization leading to creation of a macroscopic dipole [24].

5. Conclusions

An evaporating microdroplet of GNS suspension was used as a study of meta-material object with variable optical properties. The properties under study were modified due to the evaporation-driven changes of the GNS distribution in the droplet. The maximum of the distribution formed at the droplet surface. Several scattering phenomena associated with different resonant conditions corresponding to specific GNS distributions were also observed and identified. The resonant conditions for light scattering on a droplet of suspension are twofold. There are modes of the spherical resonator (the composite droplet as a whole) and resonances arising due to matching of the average distance between (surface) inclusions to the light wavelength. There are also very significant interactions between the two. During the droplet evaporation a variety of (consecutive) resonances was scanned. When the average distance between surface GNS was matching the wavelength of light, a broad maximum associated with the collective scattering (CS) on GNS was observed. A fine modulation of this maximum is associated with the whispering gallery modes (WGMs) of the composite droplet. WGMs associated with waves traveling below and above the (average) droplet surface can be recognized. The Fano profile identified in the modulation is interpreted as an interference of CS and WGMs. The ultra narrow enhancement-and-quench structure recognizable in the modulation is interpreted as associated with the creation and destruction of collective plasmon oscillation of individual GNS plasmons (WGM-assisted creation and destruction of a global plasmon).

Resonant phenomena are potential tools for precise measurements. We were able, for instance, to find the number of surface GNS with a fair accuracy. Engineering applications based on tuning the variable optical properties of the meta-material object seems also potentially feasible.

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References