LIGHT-GENERATED PLASMONIC NANO BUBBLE AND MICRO SURFACE BUBBLE IN GOLD NANOPARTICLE SUSPENSION

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Abstract

by

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Surface plasmonic heating effect is originated from the resonance oscillation of the free electrons in noble metal nanoparticles, i.e., plasmonic nanoparticles, when they are irradiated by the incident laser with resonance wavelength. The resonance wavelength of plasmonic nanoparticle can be tuned by engineering the materials, geometry and size of the nanoparticle. When surface plasmonic heating effect occurs in nanoparticle suspension, a large amount of heat is produced locally around the irradiated nanoparticles, which can vaporize the surrounding liquid and generate plasmonic bubbles. There are two major types of plasmonic bubbles, i.e., supercavitating nanobubble and surface microbubble. In this work, the coreshell gold/SiO₂ nanoparticle (120 nm diameter) and a near-infrared femtosecond pulsed laser (800 nm) are used to study the novel opto-thermo-fluidic behaviors and related applications of these plasmonic bubbles.

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Supercavitating nanobubble is a vapor bubble generated to encapsulate a single nanoparticle, i.e., supercavitating nanoparticle, which has a stabilized diameter of a few hundreds of nanometers. Supercavitating nanobubble can be detected by visualizing the magnification in the far-field cross section scattered probe light in pump-probe optical scattering imaging. The nanoparticles in a suspension can be driven by scattering optical force originated from the momentum exchange between incident photons and the nanoparticles. The photon stream in the laser beam usually exerts an optical pushing force that drives the nanoparticles to move in the light propagating direction. However, when a nanoparticle is encapsulated by a nanobubble, the moving speed of the nanoparticle can be ~ 2 orders of magnitude larger than a bare nanoparticle, since the nanoparticle moves in the vapor medium, that has a much lower viscosity, instead of liquid. Moreover, this supercavitating nanobubble can optically couple to the encapsulated nanoparticle to trigger the "negative" scattering optical forces on the nanoparticle, leading to an optical pulling force, depending on the position of a nanoparticle inside the nanobubble. Supercavitating nanobubble does not only influence the motions of suspended nanoparticles in bulk liquid, but also can disturb the capillary trapping force at the liquid/air interface and let supercavitating nanoparticles to move across the interface when driven by laser.

Using the optical pulling or pushing force, we can directly deposit plasmonic nanoparticles onto optically transparent substrates when they are immersed in nanoparticle suspensions. Once the nanoparticles deposited reach the critical number at a given laser power density, the surface heating effect can allow the substrate to reach a threshold temperature for the nucleation of surface microbubbles. This method eliminates the complicated surface plasmonic nanostructures pre-fabrication process in conventional surface microbubble generation methodology. Moreover, it is interesting that we observed much faster surface bubble growth rates in nanoparticle suspension compared to those in pure water with pre-fabricated nanostructures. Our analyses show that the volumetric heating effect around the surface bubble due to the existence of nanoparticles in the suspension is the key to explain this difference. Such volumetric heating increases the temperature around the surface bubble more efficiently compared to sorely surface heating which enhances the expelling of dissolved gas. In addition, the volumetric heating can also bring some hot nanoparticles to depin and extend the front three-phase contact line of the surface bubble enabling precise spatiotemporal light-controlled surface bubble movement. With this technique, we demonstrate that surface bubbles on a solid surface are directed by a laser to move at high speeds (>1.8 mm/s). Our findings are beneficial to a wide range of applications like combinatorial material development, microfluidic logic, catalysis, micropatterning, cell-level therapy and imaging, controlled drug delivery, and photothermal energy conversion.

This is for my FAMILY.

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CHAPTER 1:

INTRODUCTION

Plasmonic bubbles generated by photothermal effect are playing significant roles in a wide range of applications, such as microbubble logics,³ vapor generation,^{4–6} cancer therapy,⁷⁻¹¹ plasmon-assisted catalysis,¹²⁻¹⁵ and nanoparticle (NP) manipulation¹⁶⁻²¹ and deposition.^{22–24} To realize the photothermal effect, a light-absorbing substrate, such as silicon, thin-metallic, or conducting oxide layer, is usually immersed in liquid to convert optical energy into thermal energy.^{17,18,22,25} When the incident light intensity is sufficiently high to raise the temperature of the substrate to above a threshold, a surface bubble can nucleate and grow. However, for photothermal conversion, plasmonic metallic nanostructures are among the most efficient transducers, as they can support the surface plasmonic resonance (SPR) to amplify the light intensity at the metal/dielectric interface by orders of magnitude.^{5,26–29} As reported in previous works, surface plasmonic microbubbles can be generated on plasmonic nanostructures that predeposited on the surface subject to laser heating^{13,30–35}. In addition to predeposited nanostructures, generating surface bubbles directly by using the plasmonic heating effect of noble metallic NP suspension has also been demonstrated, and richer properties and novel bubble dynamics have been found during such bubble generation process.^{2,16,24,36,37}

The nucleation and growth of plasmonic surface microbubble in NP suspension relies on the optical-driven NP deposition process. The NPs in a suspension can be driven

by scattering optical force originated from the momentum exchange between incident photons and the NPs.^{38–47} The photon stream in the laser beam usually exerts an optical pushing force that drives the NPs to move in the light propagating direction. However, we found that a supercavitating vapor nanobubble can be generated to encapsulate a single NP, i.e., supercavitation.^{34,48–55} Supercavitating nanobubble, which has a stabilized diameter of a few hundreds of nanometers, can be detected by visualizing the magnification in the farfield cross section scattered probe light in pump-probe optical scattering imaging.¹ When a NP is encapsulated by a nanobubble, the moving speed of the NP can be ~ 2 orders of magnitude larger than a bare NP, since the NP moves in the vapor medium, that has a much lower viscosity, instead of liquid. Moreover, this supercavitation can optically couple to the encapsulated NP and alter the electromagnetic field profile around it. Such alteration can trigger the "negative" scattering optical forces on the NP, leading to an optical pulling force, depending on the position of a NP inside the nanobubble.^{1,56} Using the optical pulling or pushing force, we can selectively deposit NPs onto the backward-facing (BF) or forward-facing (FF) optically transparent substrates when they are immersed in plasmonic NP suspensions.² This technique can not only provide higher biocompatibility but also eliminate the complicated and expensive nanostructure pre-fabrication process to generate bubbles. In addition to influencing the motions of suspended NPs in bulk liquid, supercavitation can also disturb the capillary trapping force at the liquid/air interface and let supercavitating NPs to move across the interface when driven by laser.

The deposition of NP generally follows a Gaussian distribution, and once there are a critical number of NPs deposited at a given laser power density, the surface heating effect can allow the surface to reach a threshold temperature for the nucleation of surface microbubbles.^{5,31,35,51,52,57} The nucleation time of surface bubble is very short and usually less than 1 ms,³³ after which the bubble will move into the growth stage. As discussed in previous work,³² the growth of surface bubble can be generally divided into two phases, i.e., short-time and long-time growth phases. In the short-time growth phase (phase I), the surface bubble experiences an explosive nucleation due to the vaporization of the liquid surrounding NPs on the surface. In the long-time growth phase (phase II), the bubble growth is mainly because of the expelling of dissolved gas from the liquid surrounding the nucleated surface bubbles. The diameter of a phase-II surface bubbles is usually within a few hundreds of micrometers.^{32,36,37} It is interesting that we observed much faster surface bubble growth rates in NP suspension compared to those in pure water with pre-deposited surface plasmonic structures.³⁷ Our analyses show that the volumetric heating effect around the surface bubble due to the existence of NPs in the suspension is the key to explain this difference. Such volumetric heating increases the temperature around the surface bubble more efficiently compared to only surface heating which enhances the expelling of dissolved gas. We also find that the bubble growth rates can be tuned in a very wide range by changing the concentration of NPs, besides laser power and dissolved gas concentration.

In addition to the faster surface bubble growth due to the volumetric heating, NPs can also enable precise spatiotemporal light-controlled surface bubble movement. In ref. [³⁶], we demonstrate that the surface bubbles on a solid surface are directed by a laser to move at high speeds at least up to 1.8 mm/s, and we elucidate the mechanism to be the depinning of the three-phase contact line (TPCL) by rapid plasmonic heating of NPs deposited in situ during bubble movement. On the basis of our observations, we deduce a stick–slip mechanism based on asymmetric fore–aft plasmonic heating: local evaporation

at the front TPCL due to plasmonic heating depins and extends the front TPCL, followed by the advancement of the trailing TPCL to resume a spherical bubble shape to minimize surface energy. The continuous TPCL drying during bubble movement also enables welldefined contact line deposition of NP clusters along the moving path, which is very helpful to various microfluidics and pattern writing applications. Therefore, we believe our findings are beneficial to various biotechnologies and provide new excitements to the optonano-thermofluids field.

The following contents of this thesis are divided into seven chapters, which are: Chapter 2: Principles of experimental setups; Chapter 3: Introduction to the theoretical methods; Chapter 4: Optically driven gold nanoparticles seed surface bubble nucleation in plasmonic suspension; Chapter 5: Surface bubble growth in plasmonic nanoparticle suspension; Chapter 6: Light-guided surface plasmonic bubble movement via contact line de-pinning by in-situ deposited plasmonic nanoparticle heating; Chapter 7: Plasmonic supercavitation enables nanoparticle photo-ejection across air/water interface; Chapter 8: Future works.

CHAPTER 2:

PRINCIPLES OF EXPERIMENTAL SETUPS



Figure 2.1: The characterization of plasmonic bubble in NP suspension.

As shown in Fig. 1, in order to characterize and guide the movement of plasmonic nanobubble and surface bubble in NP suspension, we first need the Au coreshell (CS) NP suspension and contain it in a quartz cuvette. A femtosecond pulsed laser is directed to the cuvette and tightly focused on the interface between the suspension and the cuvette wall to generate plasmonic nanobubble and deposit NP onto the cuvette wall. The nucleation, growth and movement of the surface bubble are monitored and recorded by the high-speed videography with interferometry. The light deposited NPs can be visualized by optical and electron microscopies.

2.1 Sample Preparation

In this section, we will first discuss the Au NP suspension preparation, which includes the properties of the Au NP and the methods to degas and modify the concentration of the suspension. Then, the geometry and cleaning process of the quartz cuvettes used in the works of this thesis will be introduced.

2.1.1 Au NP Suspension Preparation

The CS Au NP used in these works consists of a ~50 nm silica core and a ~10 nm Au shell and are dispersed in deionized water produced by a Barnstead Nano Pure Diamond system with a purity of 18 MOhm (see figs. 2a and b). This type of so-called AuroShells NPs are made by Nanospectra Bioscience, Inc, which is designed to absorb specific wavelength and convert the photonic laser energy into heat sufficient to ablate the tumor.^{58,59} These CS Au NPs have the near-infrared surface plasmonic resonance wavelength (780~800 nm). This near-infrared resonance wavelength coincides with the wavelength of the pulsed laser we used in our lab (~800 nm), that can induce enhanced plasmonic resonance making the NPs produce enough heat locally to excite supercavitation and bubble nucleation. The CS Au NP is stabilized by electrostatically bonded carbonate ions from the growth process.

Another type of Au NP we used in these works is the solid Au NP, which has much shorter resonance wavelengths (NanoXact).^{60–62} This spherical solid Au NP has the surface plasmonic resonance wavelength of 563 nm, a diameter of 103 ± 10 nm, and the

concentration of $\sim 4.7 \times 10^{15}$ particles/m³ (see figs. 2c to e). The solvent of this solid Au NP is Aqueous 2mM Citrate and the NP surface is treated with Sodium Citrate. The colors of the CS and solid Au NP suspensions are blue and red, respectively, as shown in fig. 2f.



Figure 2.2: (a) The schematic of CS Au NP. The scanning electron microscope (SEM) images of a single CS Au NP (b) and solid Au NP (c). The measured size distribution (d) and optical absorption spectra (e) of solid Au NP. (f) The images of CS and solid Au NP suspensions.

To control the concentration of the Au NPs in suspension, we used centrifugation followed by solvent volume modification process. The new solvent we added is the Type I deionized water, which has a purity of > 18 Megaohm-cm (ChemWorld). The concentration of NP is measured by determining the optical absorption spectra with ultrafast optical spectroscopy. As shown in fig. 3a, the obtained optical absorption spectra of the suspension with modified NP concentration will be compared with the original suspension with known concentration. Since the NP concentration is proportional to the absorption, we can derive the modified NP concentration by the ratio of peak adsorptions to the original suspension.

The Au NP suspension is degassed in a sealed chamber pumped by an external mechanical pump. This is a physical way, which can pump out the dissolved oxygen and nitrogen simultaneously, given that the mass diffusivities of oxygen ($\sim 2.1 \times 10^{-5}$ cm²/s) and nitrogen (~ 1.9×10^{-5} cm²/s) are close in water. The concentration of oxygen in the suspension can be feasibly measured by an oxygen sensor. Then, we can use the ratio of dissolved oxygen to quantize the concentration of dissolved air in the suspension. The concentration of oxygen is $\sim 8.3 \text{ mg/L}$ in the suspension without degassing. After 3 h degassing, the concentration of oxygen becomes $\sim 60\%$ of the original concentration; after 24 h degassing, the concentration of oxygen drops to $\sim 25\%$. These three degassing levels are found to be stable and highly repeatable. During experiments, the quartz cuvette containing degassed suspension is kept sealed to slow down the air redissolving process. Based on of our tests, the concentration of oxygen increases less than 5% within 1.5 h while kept sealed in air (see fig. 3b). Because each of our experimental measurement normally lasts for less than 15 min, the concentration of oxygen in degassed suspension is considered to be constant.



Figure 2.3: (a) Measured optical absorption spectra for determining the CS Au NP concentrations in each suspension. (b) Oxygen concentration as a function of time of a degassed suspension as measured by using a Vernier Optical Dissolved Oxygen Probe.

2.1.2 Quartz Cuvettes

There are two types of quartz cuvettes have been used in my works. The first one is purchased from Sigma-Aldrich, Inc (fig.4 left). The dimension of this cuvettes is 45 mm \times 12.5 mm \times 12.5 mm with 4 polished transparent windows. It is made of optical glass with a parameter 320-2500 nm spectral range, pathlength 10x10 mm and chamber volume of 3500 µL. The second one (fig.4 right) is purchased from Alpha Nanotech. The materials, 4 windows and outer dimension of this cuvette is the same as the first one, but the inner channel pathlength is much narrower, only 1 mm (volume of 0.35 ml). The narrower pathlength is used to reduce the laser power attenuation by NP suspension inside the channel. The spectral range of this cuvette is 190-2500 nm. All quartz cuvettes are acid, base, organic solvent-resistant (not including chloroform), no leakage is found for these cuvettes containing hydrochloric acid, anhydrous ethanol, carbon tetrachloride, and

benzene for 24 hours. Temperature-resistant up to 600 °C / 1,112 °F for all cuvettes. Before filled with suspension, the quartz cuvette is cleaned in an ultrasonic bath and dried at 150 °C for 10 min. The wettability of BF and FF surfaces should be identical since the surface bubbles on the two surfaces have very similar contact angles, as shown in Fig. 4b. Here, $\theta_{BF} \simeq \theta_{FF} \simeq 18.5^{\circ}$, when the radius (R) of the surface bubbles on both surfaces are nearly the same in size, R ~ 27.6 µm.



Figure 2.4: (a) The images of two types of quartz cuvettes. (b) The optical images for the measurement of contact angles for the surface bubbles on BF (θ BF) and FF (θ FF) surfaces.

2.2 Optical Setups to Generate and Characterize Plasmonic Nanobubble and Surface Bubble

As discussed in the Introduction chapter, the pulsed laser is shown to function as both an optical force provider to drive NPs toward the cuvette inner surface and an exciter to intensely heat the NP to form a vapor nanobubble encapsulating the NP. In this section, we will introduce the experimental setups used to generate and characterize plasmonic nanobubble and surface bubble.

2.2.1 Optical Setups to Generate Plasmonic Bubbles

Figure 5a schematically shows the experimental setup used to generate plasmonic bubbles. A femtosecond mode-locked monochromatic pulsed laser (repetition rate of 80.7 MHz, pulse duration of ~94 fs and time intervals between each pulse of 10 ns) from a Ti:sapphire crystal in an optical cavity (Spectra Physics, Tsunami) is directed into a UV quartz cuvette (Alpha Nanotech Inc.) containing Au NP suspensions. The center wavelength of the laser is 800 nm with a full-width-half-maximum of ~10.5 nm. The laser beam is guided by a series of broadband dielectric mirrors and finally focused by a 20× objective lens (Edmund Optics, numerical aperture = 0.42, focal length = 10 mm) onto the inner walls of the cuvette with a $1/e^2$ radius of 6 µm (for a 10× objective lens, the $1/e^2$ radius is 22 µm). The laser power can be tuned continuously from 10 mW (1.76×104 W/cm2) to 1.05 W (1.85×106 W/cm2) using a continuously variable metallic neutral density filter (NDC-25C-4M, Thorlabs). An optical shutter controlled by a digital controller (KDC101, Thorlabs) is used to turn on/off the laser. We have also examined the effect of higher numerical aperture conditions but found that the 20× objective lens would be more advantageous for optical pulling or pushing (details will be discussed in the next chapter).

In fig. 5b, the plasmonic surface bubble nucleation and growth processes are occurred on the BF and FF surfaces. The forward- or backward-moving NPs driven by optical pushing or pulling force can be deposited on the surface and then act as surface photothermal plasmonic heaters on the transparent substrate. There is a critical number of deposited NPs at a given power density of the laser so that the surface heating effect can allow the surface to reach a threshold temperature for the nucleation of surface bubbles. Furthermore, bubble nucleation on the BF surface is only possible if the incident laser frequency coincides with the surface plasmonic resonance peak of the NP since intense plasmonic heating is needed to generate a supercavitation a necessity for optical pulling deposition.



Figure 2.5: (a) The schematic of the optical setups to generate plasmonic bubbles. (b) The optical images showing the nucleation of surface bubbles on BF and FF surfaces.

2.2.2 Pump-Probe Optical Scattering Imaging of Nanobubble

As reported in ref. [⁴⁹], these plasmonic nanobubbles have very short lifetime and the size of them are only within a few hundreds of nanometers, which means the traditional direct optical imaging method cannot capture them. In order to characterize plasmonic nanobubbles, the so-called pump-probe optical scattering imaging has been used in our works. As the schematic shown in fig. 6, a coherent probe laser source with a wavelength of 632.8 nm (HeNe, 2 mW, Thorlabs) is added into the original bubble generation setups. The probe laser beam is directed to have an angle, ~90°, to the imaging axis of the highspeed camera so that the probe laser cannot be seen by the camera directly, but the camera can capture the scattered probe laser light from the Au NPs in the suspension in the darkfield setting. An optical filter can be placed in front of the camera to filter out the pump laser light to ensure only the scattered light from probe laser can be seen by the camera. The far-field spatial intensity profile of scattered probe light from NP can be strongly enhanced, when the NP is near-field coupled to object (nanobubble) that is located within subwavelength length scale.



Figure 2.6: The schematic of pump-probe optical scattering imaging setups.

2.2.3 High-Speed Videography with Interferometry Characterization of Surface Bubble Dynamics

To characterize the plasmonic surface bubble nucleation, growth and movement, a high-speed digital camera (HX-7, NAC) with a $10 \times$ objective lens (Edmund Optics) and a white LED (300 lm) illumination source have been used (fig. 7a). The illumination source passes through the sample to enter the objective lens and is then focused onto the digital

camera, which is appropriately positioned to record the top view or the side view of the surface bubble. The motorized stage, the optical shutter, and the digital camera were electrically connected to a digital controller (KDC101, Thorlabs). To record the formation and motion of the surface bubble, the controller was controlled by predefined sequential parameters through a LabVIEW interface. The nucleation of surface bubble usually occurs with strong scattering light near the cuvette surface, as shown in fig. 5b. The growth rate of the surface bubble is determined by the variation of bubble size, which is fitted by a MATLAB code, over a certain amount of time converted from the imaging rate (normally 500 to 5000 frames per second). In order to characterize the depining motion of surface bubble movement, we employ a laser (632.8 nm, HeNe, 2 mW, Thorlabs) interferometry setup similar to ref. ^{[25}] to quantify the relative motion of the laser and the TPCL with a time resolution of 0.1 ms. The constructive and destructive patterns of a coherent light source (i.e., interference fringe patterns) in the microlayer under the surface bubble allows the identification of the TPCL. Figures 7b and c show the laser interferometry images and corresponding setups.



Figure 2.7: (a) Schematic experimental setup to characterize the motion of the surface bubble. (b) Optical interferometry images of a surface bubble. (c) Schematic of the experimental setup of high-speed videography with laser interferometry.

2.3 Deposition and Characterization of Au NPs

Benefited from the dispersive optical scattering pulling and pushing forces, a controlled amount of Au NPs can be deposited onto surfaces. The major difference between optical pulling and pushing depositions is pulling one requires the optical fluence of

incident laser to be above a threshold value, i.e., 7 mJ/cm² for our core shell Au NP,⁵² in order to generate supercavitating nanobubbles, but the push one does not need this. These deposited NPs are further used as the surface heating source for surface bubble nucleation and growth.

The optical and electron microscopies have been used to characterize these deposited NPs. As the scanning electron microscopy (SEM) image shown in fig. 8a, the deposited NPs will generally follow a Gaussian distribution as individual ones on the quartz surface, once the number density of them reaches a critical value a surface bubble will be generated. During the bubble growth stage, a large number of NPs can also be accumulated onto the surface through a contact line deposition process due to the thermocapillary flow around the bubble. Similar deposition mechanism can also be achieved while the surface bubble shrinkage and movement, which leads to the biocompatible functionalized NP concentration and 2D NP nano pattern writing applications.^{16,48} Since there are a large number of NPs deposited during surface bubble growth, the tremendous amount of heat generated will melt these deposited NPs and finally formed thin (of a few micrometers) metallic heating island on surface (fig. 8b). The back-scattered SEM imaging technique has been used here to characterize the deposited and melted NPs. Due to the different atomic numbers of Au shell and SiO_2 core, a clear contrast can be visualized in the backscattered SEM image shown in fig. 8c with the Au showing as brighter. Energy-dispersive X-ray (EDX) spectrum can also be used for the elemental analysis or chemical characterization of the sample. Figure 8d shows the EDX spectrum of the pre-deposited melted Au NPs. The Au peak is from the deposited Au clusters. The Si peak is from both the silica core of Au NPs and quartz substrate. The Ir peak is from the coating for SEM (2 nm thickness).



Figure 2.8: The SEM images of deposited NPs before (a) and after (b) surface bubble generation. The back-scattered SEM image (c) and EDX spectrum (d) of the predeposited melted Au NPs.

CHAPTER 3:

THEORETICAL MODELING AND SIMULATION METHODS

Plasmonic bubble dynamics is a very complex physics system that integrates optothermal, fluidic mechanics, bubble dynamics and electromagnetic theories. In order to capture these physical properties in our simulations, we employed finite element simulations using COMSOL Multiphysics together with some fluidic mechanics theoretical derivations and differential equation solving by MATLAB. In this chapter, I will introduce the modeling and simulation methods of plasmonic heating and bubble dynamics in details.

3.1 Full-Wave Electromagnetic Finite Element Simulations

As mentioned in the Introduction section, the plasmonic Au NP adsorbs incident light energy and converts it into heat, and when the NP suspends in liquid, it will also experience optical scattering forces. From the theoretical modeling point of view, both the plasmonic heating and optical forces are directly proportional to the optical energy used by the NP, which can be calculated as:

$$F_{eff} = F_{laser} \times \sigma_{abs} \tag{3-1}$$

where F_{eff} is the optical fluence (in the unit of J/m²) used by a NP, F_{laser} is the optical fluence of incident laser and σ_{abs} is the absorption cross section of NP. Therefore, we will first need to calculate σ_{abs} in order to know how much energy has been utilized by a NP. To obtain this, we used full-wave electromagnetic finite element simulations using COMSOL Multiphysics. As shown in fig. 9a, the simulation is set up as a core shell Au NP irradiating by the incidence of laser beam with the wave function as:

$$\varphi = E_0 \times e^{-ikz \cdot n_{water}} \tag{3-2}$$

where E_0 is the amplitude of electric field, *k* is the wavenumber and n_{water} is the refractive index of water, the wave is propagating in z direction. Then, the distribution of electric field can be derived by solving the Maxwell's equations of the system by finite element method (see fig. 9b). By integrating the electric field before and after the scattering by a NP, we can determine the power density loss by NP scattering. Then, we can divide this power density loss by incident power and calculate the adsorption cross section of a single NP, which is about 2.3×10^{-14} m².

As discussed in ref. $[^1]$, the dispersive optical scattering force on a NP by a pulsed laser is a function of time, which can be calculated by the Lorentz's force density (**f**) equation on a small object:

$$\mathbf{f} - \frac{\partial \mathbf{S}}{\partial t} = \nabla \cdot T \tag{3-3}$$

where *T* is the Maxwell's stress tensor and **S** is the electromagnetic momentum density.^{63–} ⁶⁵ While the incident light is a function of time, the Lorentz's force density (**f**) is also a function of time, *t*.

However, the oscillation of the amplitude of electromagnetic field at the optical frequency is convoluted by the duration of a pulse for our pulsed incident light with the duration of ~94 fs and the optical frequency of 3.7×10^{14} Hz (= a period of ~2.7 fs). It is obvious that these time scales are much faster than the mechanical response of a supercavitating NP, which suggests that the time-averaged optical force should be appropriate for analyzing the motion of NPs.^{66–68} By using equation (3-3), the time-averaged force **F**_t on a NP can be written as:

$$\mathbf{F}_{t} = \frac{1}{t_{2} - t_{1}} \{ \int_{t_{1}}^{t_{2}} \oint T \cdot dA dt - \int \mathbf{S}_{t_{2}} dV + \int \mathbf{S}_{t_{1}} dV \}$$
(3-4)

where A and V are the surface and volume of a NP, respectively.

Because the pulsed laser has a repetition rate of $v_0 = 80.7$ MHz, the last two volume integral terms in equation (s4) will vanish, if we pick t_1 and t_2 to integrate over one pulse, as they are identical. It means that the Maxwell's stress tensor alone is sufficient to determine \mathbf{F}_t without any momentum density terms from the perspective of the timeaveraged force calculation. Besides, as discussed in ref. [¹], we can use the optical force from a continuous wave laser with the same central frequency and intensity to approximate the time-averaged force on an Au NP by the a pulsed laser. Therefore, the time-averaged optical force on an Au NP (\mathbf{F}_t) can be estimated by the equation below:

$$\mathbf{F}_t \cong \bigoplus T_t \cdot \boldsymbol{n} \text{ da} \tag{3-5}$$

where T_t is the time-averaged Maxwell's stress tensor,^{41,47} and n is the normal vector of the surface of the Au NP. The time-averaged Maxwell's stress tensor is formulated with the electromagnetic field profiles of the simulation domain, which can be obtained by solving the Maxwell's equations at a frequency domain (i.e., at the central wavelength, 800 nm) with finite element method (*i.e.*, *COMSOL Multiphysics*). The normalized field profiles of complex electric field amplitude and the z-component of T_t of a NP (radius: 60 nm) with a nanobubble (radius: 130 nm) system are shown in figs. 9b and c. By integrating the time-averaged Maxwell's stress tensor over the whole surface of NP, we can estimate F_t . The z-component of F_t heads to the laser propagation direction. Note, the force on a bare NP is slightly larger than but of the same order of magnitude as a supercavitating NP (fig. 9d). In addition, the optical force on the NP does not change order of magnitude when the nanobubble size changes.¹


Figure 3.1: (a) The schematic diagram of the full-wave electromagnetic finite element simulations. The normalized field profiles of complex electric field amplitude (b) and the z-component of time-averaged Maxwell's stress tensor (c) profiles of a NP with a nanobubble. (d) The calculated total optical force of a bare CS NP (black), a pushed supercavitating NP (blue), and a pulled supercavitating NP (red) by the Gaussian beam.

3.2 Finite Element Thermofluidic Simulations

There are two major heating mechanisms for the plasmonic bubble dynamics, i.e., the volumetric and surface heating. The volumetric heating occurs when the suspended NPs are irradiated by incident laser and a large amount of heat is generated at the irradiation area due to the SPR effect. This is the major heating mechanism in plasmonic NP suspension, which follows a Gaussian heating profile according to the power density distribution of laser. The volumetric heating is dominant during nanobubble generation and NP movement stages. The surface heating happens when there are a large number of NPs have been deposited, and due to opto-thermal effect surface bubble can nucleate and grow on the deposition site. We found that the volumetric heating is much more efficient than surface heating for plasmonic surface bubble growth. Next, I will introduce the modeling and simulation to compare the efficiency of volumetric and surface heating on surface bubble growth in details.

We employ COMSOL Multiphysics to simulate the temperature and flow velocity profiles of the surface bubbles in the volumetric heating and surface heating geometries. Both the flow effect and thermal conduction are included in our simulations. Five conditions have been assumed in our simulations: (1) The liquid flow and heat transfer are at steady state. (2) In the liquid water, the flow is laminar and incompressible without body forces (note that gravity is perpendicular to the observed flow and thus is not considered to be important here), which satisfies the following momentum equation:

$$\rho(\vec{u} \cdot \nabla)\vec{u} - \nabla \cdot (\mu(\overleftarrow{\nabla u} + \overleftarrow{\nabla u}^{\mathrm{T}}) - p\vec{I}) = 0$$
(3-6)

, and continuity equation:

$$\rho(\nabla \cdot \vec{u}) = 0 \tag{3-7}$$

where ρ is the density of water, μ is the dynamic viscosity of water, \vec{u} is the velocity vector, p is the pressure, and \vec{l} is a 3x3 identity tensor. (3) The gas medium inside the surface bubble and quartz are considered as non-fluidic rigid materials, i.e., we are effectively modeling a single-phase liquid flow around a rigid bubble. Note, the purpose of these simulations is to understand how different heating geometries influence the temperature around the bubble, instead of modeling the bubble growth process itself. (4) The volumetric heating (Q_v) or the surface heating (Q_b) of the Au NPs is the only heat source in Case I or Case II, respectively, which supplies the heat to the liquid water with the following heat transfer equations:

In water,

$$\rho C_{\nu} \vec{u} \cdot \nabla T - k_{w} \nabla^{2} T = Q_{\nu} \text{ or } Q_{b}$$
(3-8)

where C_p is the heat capacity of water at constant pressure, *T* is the temperature, k_w is the thermal conductivity of water, Q_v and Q_b are the heat generation rates by the volumetric heating and surface heating, respectively, and in the medium of gas and quartz,

$$-k_s \nabla T = q \tag{3-9}$$

where k_s is the thermal conductivity of gas (or quartz), and q is the heat flux coming through the gas/water boundary (or gas/quartz boundary). (5) Finally, the surface of the bubble (gas/water boundary) has a slip boundary condition with the Marangoni effect as:

$$\left[\mu\left(\overleftarrow{\nabla u} + \overleftarrow{\nabla u}^{\mathrm{T}}\right) - \left(p + \frac{2}{3}\mu(\nabla \cdot \vec{u})\right)\vec{I}\right]\hat{n} = \gamma \nabla_{t}T$$
(3-10)

where \hat{n} is the normal outward vector to the surface of the bubble, γ is the temperature derivative of the water/gas surface tension, and ∇_t is the gradient of the tangent vector to the surface of the bubble. The models and boundary conditions used in our simulations are

illustrated in fig. 10. These mimic the real experimental structures. We use a finite element method to solve the \vec{u} , *p*, and *T* profiles using equations (3-6) to (3-10).



Figure 3.2: Schematic structures and boundary conditions for the simulations of the temperature profiles and the flow velocity profiles around the surface bubbles in the volumetric heating (a, b) and surface heating geometries (c, d). (b) and (d) zoom in the surface bubble regions of (a) and (c), respectively.

The heat generation rates of the volumetric heating and surface heating are as follow: In the volumetric heating simulation, as shown in figs 10a and b, the heating intensity follows a Gaussian distribution as the laser intensity profile with a heat generation rate of:

$$Q_{\nu} = \eta_{abs} \alpha \frac{P_0}{2\pi\sigma^2} exp\left[-\left(\frac{(r-d)^2}{2\sigma^2} + \alpha(z-h)\right)\right]$$
(3-11)

where P_0 is the source laser power, and $\eta_{abs} \sim 0.2$ is the optical absorption efficiency of Au NPs, which is determined by the ratio of the absorption quality factor and the extinction quality factor of the Au NP in DI water.³⁶ The optical attenuation factor of the NPs suspension α is ~ 262 m⁻¹, which is extracted from the absorbance spectrum³⁷ by the formulas:

Adsorbance(
$$\lambda$$
) = $log^{\frac{1}{T(\lambda)}}$ (3-12)

$$T(\lambda) = e^{-\alpha Z_0} \tag{3-13}$$

where λ is the resonant laser wavelength of Au NPs in DI water, which is ~780 nm. Adsorbance(λ) is the absorbance amplitude of the NP concentration of 2 × 10¹⁵ particles/m³ the resonant wavelength. $T(\lambda)$ is the transmission efficiency of laser at the resonant wavelength. Z_0 is the length of laser path in NPs suspension, which is 1 cm. For our 10× objective lens, $\sigma = 11 \,\mu\text{m}$ is the width of the Gaussian laser beam. *d* represents the distance from the bubble central axis, and *h* is the height of the bubble in the z-direction from the quartz surface at the distance *d* from the center. In the surface heating geometry (as shown in figs 10c and d), we use a thin layer of SiO₂ (10 µm-thick, 20 µm-width) sitting at the bottom of a surface bubble with a radius of 120 µm as the bottom heating source. The heat generation rate is:

$$Q_b = \frac{fP_0}{V} \tag{3-14}$$

where *V* is the volume of the thin film heater mimicking the deposited NPs, and *f* is the portion of laser power which is used to heat the bubble. To determine the value of *f*, we fit our experimental phase II bubble volume growth rate (K) in Case II with the theoretical model described in ref. [³²]:

$$K = \frac{1}{3} \frac{RT}{M_g p_{\infty}} \frac{C_{\infty}}{C_s} \left| \frac{dC_s}{dT} \right| \frac{fP_0}{c_w \rho}$$
(3-15)

where M_g is the molecular mass of air, and c_w is the specific heat capacity of water. The fitted value of *f* is ~ 0.2%.



Figure 3.3: (a) The mesh structure employed in the simulation of volumetric heating geometry. The total number of mesh elements is 134,812. (b) zooms in the surface bubble region of (a).



Figure 3.4: (a) The mesh structure employed in the simulation of surface heating geometry. The total number of mesh elements is 136,602. (b) zooms in the surface bubble region of (a).

In our simulations, an extremely fine mesh is used in both volumetric heating and surface heating geometries. The mesh structures of volumetric heating and surface heating geometries are shown in figs. 11 and 12, accordingly. Based on our convergence tests, as shown in fig. 13, the numbers of mesh elements used in the two geometries can provide sufficient accuracy. In addition, we also build a refined mesh structure for the volumetric heating geometry, which has 324,450 elements. As shown in fig. 14a, this refined mesh structure has densely distributed mesh elements at the locations adjacent to the bubble, the wall and in the volumetric heating region. Figure 14b shows the simulated bubble surface temperature using this refined mesh structure. Compared to our simulation using the extremely fine mesh, the average bubble surface temperature only changes by 0.7 K. Given that there is not any significant change in the temperature and flow velocity profiles of the surface bubble, we can confirm that using the extremely fine mesh is sufficient to understand the difference between volumetric heating and surface heating geometries in this work with reasonable computational cost.



Figure 3.5: The convergence tests of the mesh structures used in the simulations of both volumetric heating and surface heating geometries.



Figure 3.6: (a) The refined mesh structure employed in the simulation of the volumetric heating geometry. (b) The simulated bubble surface temperature from the top to the bottom of the bubble in the volumetric heating (black), volumetric heating with refined mesh structure (blue), and surface heating cases (red).

3.3 Monte-Carlo-Assisted Surface Temperature Field and Heat Flux Simulations of Optically Deposited Au NPs

To investigate the thermal threshold to enable surface bubble nucleation, we need to study the surface temperature profile and heat flux of the area enclosing the deposited CS NPs under laser irradiation using Monte-Carlo simulations with the following assumptions. The location of a deposited NP on the surface is given by a probability function proportional to the intensity profile of the focused laser spot (i.e., Gaussian profile). The quality factor of the optical absorption of each deposited NP is equal to that of a single isolated NP on the substrate. The heat flux generated by a deposited NP equals to the absorbed optical power by the NP, and the light intensity irradiating on this NP is given by the intensity profile of the laser spot at the location of the NP. The temperature profile on the surface around a deposited NP reaches steady state in a time scale $(10^{-6} - 10^{-10})$

⁸ seconds)³⁵ that is much shorter than the inverse of the deposition rate of the optically driven NPs (0.1~1 s). With the total numbers of CS NP needed for surface bubble nucleation in the corresponding laser power densities, we then move to analyze the surface temperature profile and heat flux at the NP deposition area under the irradiation of the incident laser. The incident laser is a Gaussian beam with a $1/e^2$ radius of 6 µm. The laser power density (*I*) at a given location (*y*, *z*) can be described by:

$$I(y,z) = I_0 \times e^{\frac{-y^2 + z^2}{2\sigma^2}}$$
(3-16)

where I_0 is the maximum laser power density which locates at the center of laser beam and σ is the standard deviation of the Gaussian laser beam which equals to 3 µm. By integrating equation (3-16) in the *y*-*z* space, we will obtain the incident laser power (P_L) as:

$$P_{L} = \iint_{-\infty}^{+\infty} I_{0} \times e^{-\frac{y^{2} + z^{2}}{2\sigma^{2}}} dy dz$$
(3-17)

Combining equations (3-16) and (3-17), we can calculate the maximum laser power density (I_0) and the expression of power density for a given laser power (the magnitude of laser power is measured by a laser power meter). A demonstration of incident laser power density profile with the laser power of 1 W is shown in next chapter. Then, the electric field strength (*E*) of the incident laser beam can be calculated from the power density (*I*) by:

$$E = \sqrt{\frac{2I}{nc\varepsilon_0}} \tag{3-18}$$

where *n* is the refractive index, *c* is the speed of light in vacuum and ε_0 is the electrical permittivity. The electric field strength (*E*₀) also locates at the center of laser beam, where has the highest power density (*I*₀). By inputting the value of *E*₀ as the amplitude of incident laser electric field expression, we performed full-wave electromagnetic calculations with finite element method to estimate the maximum dissipation power (*P*₀) of a single CS NP (see section 3.1 for details).

Here, since we are using the maximum electric field strength (E_0) in this simulation, the simulated dissipation power corresponds to the maximum power that can be dissipated by a single Au NP under a given laser power. Next, we employ finite element heat conduction simulation (convection is neglected at short time and length scales) to calculate the temperature profile on the surface of quartz cuvette due to the heating of a single Au NP. Since heating up a single NP by plasmonic effect is much faster than the heat conduction process, we thus choose to simulate the steady state temperature profile. The geometry used in our simulation is shown in fig. 15. A layer of water is sandwiched by two slices of SiO₂ substrates. A single NP is immerged inside the water layer. The dimensions of the system are large enough to eliminate the size effect (three orders of magnitude larger than the size of NP). The NP is the only heat source of the whole system, whose heat generation rate is calculated by:

$$Q_b = \frac{P_0}{V} \tag{3-19}$$

where P_0 is the simulated maximum dissipation power and *V* is the volume of a single NP. The NP sits on the surface of the bottom SiO₂ substrate with the NP/substrate contacting point shown in fig. 15a. Because of the heat transfer from the NP, the temperature of the surface of the bottom SiO₂ substrate will increase.



Figure 3.7: (a) The schematic diagram of the single Au NP-on-surface heat conduction simulations. (b) A sample simulated surface temperature profile with the incident laser power of 1 W. (c) Surface temperature profiles (in log scale) for laser powers of 0.1, 0.2, 0.4 and 0.8 W.

With all these simulations discussed above, we can finally calculate the temperature profile on the surface of quartz cuvette and heat flux generated by a single CS NP for a given laser power. A sample simulated temperature profile with the incident laser power equaling to 1 W is shown in fig. 15b. One thing to note is that this simulated temperature profile is the highest temperature can be generated by a single NP for a given laser power

(since we use the maximum dissipation power), which means this single NP is assumed to locate at the center of laser beam. Figure 15c plots the maximum surface temperature profiles generated by the single NP under different incident laser powers. It is interesting to see that the maximum surface temperature field is linear to the magnitude of incident laser power. With this linearity, we can quickly obtain the temperature profile and heat flux of the surface deposited with multiple NPs. We then calculate the entire surface temperature profile and heat flux of the many CS NP-deposited area prior to bubble nucleation under a given laser power: Firstly, we use Monte-Carlo simulations to randomly deposit many CS NPs on site according to the probability function of laser power density which follows a Gaussian distribution ($\sigma = 3 \mu m$). The total number of NP deposited in the simulation of a given laser power is determined from the experimental data, which is the total number of NP needed for each nucleation process. Secondly, the laser power density distribution and maximum surface temperature field generated by the single NP for an incident laser power can be obtained by the methods described above. Then, we can calculate the power density of each deposited NP according to the distance between this NP and the center of laser beam. Once we know the power density at the location of each NP, we can use the EM simulation as described above to calculate the dissipation power of the NP. The surface averaged heat flux is obtained by adding up the dissipation power of each individual NP and dividing the total dissipation power by the surface area of each circle with a different radius. Because the surface temperature field generated by individual NP is linearly related to incident laser power and power density, we can obtain the surface temperature field of each deposited NP from the maximum surface temperature field scaled by the ratio of the power density at the location of the corresponding NP to the maximum power density for this laser power. With the surface temperature field of each deposited NP calculated, we will finally be able to simulate the temperature profile of the entire NP-deposited area by the superposition of individual NP-induced temperature fields. Two samples showing simulated surface temperature profiles of the entire NP-deposited area are presented in next chapter. The temperature profile and heat flux are integrated over the circular region and then divided by its area. The area-normalized average temperatures and heat flux at different laser power densities are plotted as a function of the circle radius.

3.4 Theories of Surface Bubble Shrinkage

Figure 16 shows the bubble volume shrinkage plot. It is clear that the shrinkage is steady and linear, which agrees with the shrinkage behavior of gas bubbles. According to the theoretical model in ref. [³²], the volume shrinkage rate (K_{shrink}) of a gas bubble is:

$$K_{shrink} = \frac{6RTD\gamma_{W}}{p_{\infty}K_{H}}$$
(3-20)

where *R* is the gas constant, *T* is temperature, *D* is laser beam diameter, γ_w is surface tension of air/water interface, p_{∞} is ambient pressure, and K_H is the Henry coefficient of air in water. The volume shrinkage rate fitted in our study is about 420 µm³/s, which is of the same order of magnitude as the calculated one from equation (s1).



Figure 3.8: Bubble volume shrinkage (black) and the line fit (red) as a function of time. The bubble volume shrinkage rate is $\sim 420 \ \mu m^3/s$.

3.5 Calculating the Net Force at the Trailing TPCL

In the equilibrium system of the surface bubble in liquid, Young's equation at the TPCL at the azimuthal angle ϕ can be given by (see fig. 17 for the geometrical configuration):

$$\gamma_{SL}\hat{r} + \gamma_{LG}\cos\theta(\phi)\,\hat{r} + \gamma_{SG}(-\hat{r}) = 0 \tag{3-21}$$

where the equilibrium system depicts the center of the laser spot is at the center of the bubble (corresponding to the stage (i) in chapter 6), γ_{SL} is the surface tension at the solid-liquid interfaces, γ_{SG} is the surface tension at the solid-gas interfaces, γ_{LG} is the surface

tension at the liquid-gas interfaces, \hat{r} is the unit radial vector on the x-y plane where the TPCL is on, and $\theta(\phi)$ is the contact angle at the azimuthal angle of ϕ , which is defined as fig. 17. Here, $\theta(\phi)$ is $\theta_e \sim 11^\circ$ for all ϕ in the equilibrium system, which gives:

$$\gamma_{SL}\hat{r} + \gamma_{SG}(-\hat{r}) = -\gamma_{LG}\cos\theta_e\,\hat{r}.\tag{3-22}$$

As the laser spot moves along the y-direction and is overlapped with the front TPCL (corresponding to the stage (iii) in chapter 6), $\theta(\phi)$ is increased around the trailing. In this case, Young's equation can yield a non-zero net surface tension force $(f_{net}(\phi))$ at a certain ϕ and we can re-write equation (3-21) using (3-22) as:

$$f_{net}(\phi) = \gamma_{LG} \cos \theta(\phi) \,\hat{r} - \gamma_{LG} \cos \theta_e \,\hat{r} \neq 0 \tag{3-23}$$

where the direction of $f_{net}(\phi)$ is the negative \hat{r} since $\theta_e < \theta(\phi)$ for at the stage (iii). By integrating f_{net} along the trailing TPCL ($\pi < \phi < 2\pi$), we can evaluate the net force (F_{net}) at the trailing TPCL as:

$$F_{net} = \int_{\pi}^{2\pi} f_{net} (\phi) r_{TPCL} d\phi \qquad (3-24)$$
$$= r_{TPCL} \int_{\pi}^{2\pi} (\gamma_{LG} \cos \theta(\phi) \sin \phi \, \hat{y} - \gamma_{LG} \cos \theta_e \sin \phi \, \hat{y}) d\phi$$
$$= r_{TPCL} \gamma_{LG} \left(\int_{\pi}^{2\pi} \cos \theta(\phi) \sin \phi \, d\phi + 2 \cos \theta_e \right) \hat{y}.$$



Figure 3.9: Schematic of geometrical configuration for calculating the net force at the trailing TPCL.

CHAPTER 4:

OPTICALLY DRIVEN GOLD NANOPARTICLES SEED SURFACE BUBBLE NUCLEATION

Photothermal surface bubbles play important roles in applications like microfluidics and biosensing, but their formation on transparent substrates immersed in a plasmonic nanoparticle (NP) suspension has an unknown origin. Here, we reveal NPs deposited on the transparent substrate by optical forces are responsible for the nucleation of such photothermal surface bubbles. We show the surface bubble formation is always preceded by the optically driven NPs moving toward and deposited to the surface. Interestingly, such optically driven motion can happen both along and against the photon stream. The laser power density thresholds to form a surface bubble drastically differ depending on if the surface is forward- or backwardfacing the light propagation direction. We attributed this to different optical power densities needed to enable optical pulling and pushing of NPs in the suspension, as optical pulling requires higher light intensity to excite supercavitation around NPs to enable proper optical configuration.

4.1 Introduction

Surface bubbles generated by photothermal effects are playing significant roles in a wide range of applications, such as micro-bubble logics³, vapor generation^{4–6}, cancer therapy^{7–11}, plasmon-assisted catalysis^{12–15}, and nanoparticle (NP) manipulation^{16–20} and deposition^{22–24}. To realize the photothermal effect, a light-absorbing substrate, such as silicon, thin-metallic layer and conducting oxide, is usually immersed in liquid to convert optical energy into thermal energy^{17,18,22}. When the light intensity is sufficiently high to raise the temperature of the substrate above a threshold, a surface bubble can nucleate.

For photothermal conversion, metallic nanostructures are among the most efficient transducers, as they can support the surface plasmonic resonance to amplify the light intensity at the metal/dielectric interface by orders of magnitude^{26,27}. In addition, since the resonant wavelength of the surface plasmonic resonance can be tuned by properly designing the shape, spacing and size of the metallic nanostructures at the sub-wavelength scale, there have been systematic studies of surface bubble formation with surface plasmonic resonance (i.e., plasmonic surface bubble)^{13,30,32,36,37,69–71}. Fundamental studies have focused on the growth dynamics of the plasmonic surface bubbles, revealing interesting physics about bubble oscillation, vaporization, and gas expelling^{35,72}. With well-defined surface photothermal heat flux, bubble nucleation time is found to be inversely proportional to the concentration of dissolved air in liquid^{31,33,35}. On the periodic metal nanostructures (i.e., pillar or cylinder), it is observed that the laser power density threshold for bubble nucleation depends on the number density of the nanostructures^{30,73}. Overall, it has been known that the photothermal bubble generation process at a surface with plasmonic nanostructures is in principle similar to the conventional pool boiling, where the pre-decorated substrate is working as a heat source as well as providing nucleation sites for bubble nucleation^{13,25,30,31,33,35,72,74–78}.

However, it has been reported that surface bubble can be generated on optically transparent substrates when it is immersed in plasmonic NP suspensions^{23,24,36,79}. While the plasmonic NPs suspending in liquid can heat up the irradiated volume of liquid when

illuminated by a resonant light, there are no light-absorbing materials on the surface that convert optical energy into surface heating. The fundamental question here is how surface bubbles can be formed with the absence of direct surface heating source? In this work, we investigate the origin of surface bubble generation in plasmonic NP suspension on the transparent substrate. High-speed videography reveals that the light-guided NP deposition on the surface is a necessity for bubble nucleation, and it is the scattering optical pulling/pushing force that drives such deposition. Interestingly, the thresholds of laser power density to form a surface bubble by optical pulling force is much higher than the pushing force due to that a supercavitating nanobubble around the NP is required for optical pulling to happen⁵⁶. These results reveal interesting physics leading to photothermal surface bubble generation in NP suspensions.

4.2 Results and Discussions

We first demonstrate that surface bubbles can be generated in the core-shell (CS) NP suspension (concentration $\sim 2 \times 10^{15}$ particles/m³) when the laser at the wavelength of surface plasmonic resonance peak is focused on either the backward-facing (BF) or the forward-facing (FF) surface with the optical system^{36,37} shown in fig. 18. To shed light on the mechanism of bubble formation, we investigated the nucleation time as a function of laser power density. The laser power density we refer to in this work is the maximum of laser power density at the center of the Gaussian beam for a given laser power. We note that the nucleation time in this study is defined as the time between the moment of turning

on the laser and the onset of nucleation. In the experiments, the onset of surface bubble nucleation can be identified by observing the strongly scattered light at the surface where the laser beam is focused on. We note that the surface bubble nucleation in NP suspension includes a NP deposition stage after turning on the laser as discussed later. As a result, the time interval between turning on the laser and the observation of the strong scattered light is the total time including NP deposition and the nucleation of a surface bubble. We also note that how bubble nucleation time is defined may vary in different context. For example, on prefabricated plasmonic substrates,^{31,35} the nucleation time is the interval between switching on the laser and the onset of a giant vapor bubble. In these cases, the giant bubble collapses within ~200 μ s, followed by a subsequent oscillating bubble lasting for < 2000 μ s, which precedes the emergence of a stably growing vapor bubble. Since our measured nucleation times are on the order of 1~100 seconds, whether the onset of nucleation is chosen to be the start of the initial giant bubble or the subsequent stable bubble does not influence our analyses.



Figure 4.1: (a) Schematic of the experimental setup to characterize the surface bubble nucleation on the backward-facing (BF) or the forward-facing (FF) surface with respect to the laser propagating direction. (b) The nucleation time of surface bubble on the BF or FF surface as a function of the laser power density. The laser power density thresholds of the two cases are identified with vertical lines. (c and d) Representative optical images of nucleated surface bubble on (c) the BF surface and (d) the FF surface.

Our measurements show that the nucleation time can be shortened as the laser power density increases (fig. 18b). At the same time, however, it is found that at a certain power density, the nucleation times of bubbles on the FF surface are always shorter than those on the BF surface. We have also noticed that the thresholds of the power density to form a surface bubble in each of the two cases are drastically different. For nucleation on the FF surface, the threshold is $0.35 \sim 0.38 \times 10^6$ W/cm², but for the BF surface, the threshold is much higher, $1.00 \sim 1.04 \times 10^6$ W/cm².

One mechanism that can potentially contribute to the surface bubble formation in the NP suspension is volumetric photothermal heating³⁷, where the CS NPs in suspension absorb laser energy and heat up the laser-irradiated volume. However, if the bubble formation is such a purely thermal process, the nucleation dynamics would be similar for both the BF and FF surfaces when the laser is focused on them, respectively. Furthermore, if the surface bubble nucleation depends on the local temperature of the surface, as that in pool boiling, the threshold of laser power density for the bubble nucleation on the FF surface would be higher than that on the BF surface, since the laser energy is attenuated by the light-absorbing NPs in suspension while reaching the FF surface. Thus, the photothermal volumetric heating cannot explain the observed discrepancy in nucleation times on the BF and FF surfaces.

Upon detailed analysis of the side view high-speed videography, we observe that there are always CS NPs moving toward the surfaces leading up to every bubble nucleation (figs. 19a and b). In the experiments, we track the positions of the glowing dots as a function of time. As shown in the scanning electron microscope image in our previous work Ref. ⁴⁴], these CS NPs are deposited as isolated single NPs on the surface, which excludes the possibility of aggregated NPs during their motions. Therefore, one glowing dot corresponds to the diffraction-limited scattered spot from a single CS NP in the side view high-speed videography. When the laser power density is low ($< 0.35 \times 10^6$ W/cm²), such NP motion along the laser beam axis is not apparent, and there is no bubble formation. When the laser is focused on the FF surface, NPs moving towards the surface is observed when the laser power density is above $0.35 \sim 0.38 \times 10^6$ W/cm², and bubble nucleation follows. When the laser is focused on the BF surface, there are NPs moving towards the surface only if the laser power density is above $1.00 \sim 1.04 \times 10^6$ W/cm², following which bubble nucleation is also observed. Such NP movements along the laser beam propagation direction are observed within $\sim 50 \ \mu m$ from the surfaces, and they cannot be driven by thermal convective flow, since it is vertical near the walls of the upright cuvette. These

thus evident that NP moving toward the focused surface is a necessity for surface bubble nucleation. Then the question is what drives such NP movements?

Our previous studies have found that CS NPs in a suspension can be driven by scattering optical force originated from the momentum exchange between incident photons and the NPs ^{1,56,80}. The photon stream in the laser beam usually exerts an optical pushing force that drives the CS NPs to move in the light propagating direction. However, as reported in several previous works^{1,34,49–53,81}, plasmonic vapor nanobubbles can be formed around the heated CS NPs irradiated by a pulsed laser at the surface plasmonic resonance peak of the NPs. This supercavitation (i.e., nanobubble encapsulating the NP) can optically couple to the encapsulated NP to trigger the "negative" scattering optical forces on the NP, leading to an optical pulling force (fig. 19c), depending on the position of a CS NP inside the nanobubble^{1,56,80}. The initial location of CS NP inside nanobubble is stochastic due to Brownian motion⁸⁰ as well as the stochastic nature of nanobubble dynamics (nucleation and growth). As a result, only a portion of the NPs which have locations inside the nanobubble favoring negative optical force can achieve negative motion, as discussed in detail in Ref. $[^{1,56}]$. In these conditions, the laser beam can drive the CS NP to move against the photo stream, and this is why some NPs are seen moving against the light propagation direction towards the BF surface. We note, as discussed in ref. ^[1], since the supercavitating CS NP, which is intensely heated by laser, can evaporate the liquid instantaneously during its motion to ensure that the NP is always encapsulated in the vapor phase, the Marangoni stresses at liquid-vapor interface is not important in influencing the relative position of NP in nanobubble. Since such supercavitation needs relatively high laser power density to intensely heat the NP, the pulling motion is not observed until a laser power density

threshold is reached. It is worth noting that the fluence to create the supercavitating nanobubble for the CS NP used in this work has been known to be ~7 mJ/cm² ⁵², which is close to the threshold of the laser power density $(1.00~1.04\times10^{6} \text{ W/cm}^{2}, \text{ converted to fluence is 7.4~7.7 mJ/cm}^{2})$ to form the bubble on the BF surface. We also note that once the threshold is met, the generated nanobubble size does not change much as a function of NP temperature⁸⁰, suggesting that different laser powers will not significantly change the probability of achieving optical pulling forces. On the contrary, the CS NPs driven by the optical pushing force can occur without the need of supercavitation. Therefore, we see plenty of NPs moving toward the FF surface even with a laser power density of 0.37×10⁶ W/cm². These facts lead us to believe that it is such optical forces that drive the NPs to be deposited on the surfaces, which then serve as the heating source on the surface for bubble nucleation.



Figure 4.2: (a and b) Dark field optical images of optically driven CS NPs moving (a) against the light propagation direction by optical pulling force, and (b) along the light propagation direction by optical pushing force, as a function of time. The moving NPs are indicated by red arrows, and the yellow arrows show the trajectory of the NP between two frames. (c) Schematic of a supercavitating CS NP that has an optical condition enabling optical pulling motion ^{1,56}. (d) The deposition rate of CS NP, and (e) the average total number of CS NP deposited on surface prior to surface bubble nucleation as a function of the laser power density.

To quantitatively investigate the relationship between the optically driven CS NPs and the surface bubble formation, we analyze the number of CS NPs moving towards and reaching each surface prior to bubble nucleation with the high-speed videography. It is found that the number of CS NP deposited on the BF surface per unit time (i.e., deposition rate) is one order of magnitude lower than that on the FF surface (se fig. 19d). This observation is reasonable as enabling the optical pulling of a CS NP requires the presence of a encapsulating nanobubble, and even with the supercavitation, the NP can only experience optical pulling force when it is in a certain region inside the nanobubble as previously studied in Ref.¹. This is in sharp contrast to the cases of optical pushing motion that happens without the need of supercavitation. As a result, there is a higher possibility that CS NPs undergo pushing motion than pulling motion under laser irradiation, which leads to the higher NP deposition rates on the FF surface. Interestingly, the accumulated numbers of CS NPs deposited on the BF and FF surfaces prior to bubble nucleation are almost the same for a certain power density range (fig. 19e). This strongly indicates that the bubble nucleation is due to the surface heating provided by the deposited NPs via the photothermal energy conversion. It also suggests that the surface temperature history is not important to nucleation, but it is the instantaneous photothermal heat flux and the local temperature profile when sufficient NPs are deposited on surface that trigger the bubble nucleation.



Figure 4.3: (a) Simulated incident laser power density profile, with the laser power density of 1.76×10⁶ W/cm² (corresponds to the laser power of 1W). (b) Calculated surface temperature rise (from room temperature) profiles in the NP deposition area under the laser power densities of (top panel) 1.57×10⁶ W/cm² (corresponds to the laser power of 890 mW), and (bottom panel) 0.90×10⁶ W/cm² (corresponds to the laser power of 510 mW). (c) Left panel: the average surface temperature rise (with respect to room temperature), and right panel: the average surface heat flux of the NP deposition area with different radii from laser beam center under different laser power densities. The circular area radii equal to 4, 6 and 8 µm are depicted in (b).

To investigate the thermal threshold to enable bubble nucleation, we study the average surface temperature rise from room temperature and heat flux of the area enclosing the deposited NPs under a Gaussian laser beam irradiation (fig. 20a) using Monte-Carlo simulations. As shown in our previous work Ref. [⁴⁴], the NPs are deposited as isolated single NPs on the surface. In addition, based on the simulations in our previous work³⁶, the optical hybridization of these Au NPs, if any, does not significantly influence the heating efficiency. Thus, in the simulation, the NPs are modeled as single isolated ones. Taking the experimentally measured numbers of deposited NPs prior to surface bubble nucleation (fig.

19e) as the inputs, the Monte-Carlo simulation is used to produce 100 independent configurations of randomly deposited NPs for each laser power density. For each configuration, the resultant surface temperature profile and heat flux for this laser power are calculated. At the power density between $0.67 \times 10^6 \sim 1.57 \times 10^6 \text{ W/cm}^2$, it is found that there can be local hot spots with temperatures rise up to ~1000 K, if multiple NPs are closely deposited (se fig. 20b). However, we believe the observed bubble nucleation is not driven by these hot spots, which strongly depends on the configuration of deposited NPs, since the numbers of deposited NPs in each of the five runs of the same experiment do not differ more than 10%. On the other hand, when we pick five random configurations from the Monte-Carlo simulation, the chance to obtain such hot spots is very small. In another word, the emergence of the hot spot strongly depends on the spatial distribution of the deposited NPs. As a result, we believe the bubble nucleation we observed is more related to the average thermal condition of the surface.

We then investigate the average surface temperature and heat flux in circular areas with different radii, as shown in fig. 20c. The areas are defined as the circles centered at the origin of the Gaussian beam profile (fig. 20b). Both the calculated average temperature profiles and heat flux are within the error bars of each other for different laser power densities, and as the circle radius increases, the average temperature and heat flux from different laser power densities further converge. As seen in fig. 20c, the average surface temperature decreases as the surface area increases for any power densities. It was reported in ref. [³⁵] that the critical nucleation temperature of surface bubble on pre-deposited plasmonic surfaces is ~422 K in gas-rich deionized water, which is very similar to our case. In addition, ref. [³⁵] also showed that the diameter of a so-called giant bubble, based on

which nucleation was defined, is 10~20 µm in diameter. In fig. 20c, we can see that the average surface temperature above 422 K would be from a radius of 9~10 µm (i.e., a diameter of 18~20 µm), that is similar to the size of the reported giant bubble. This at least supports that the experimentally determined critical number of deposited NPs prior to bubble nucleation can lead to the surface temperatures high enough to form a surface bubble. These findings also indicate that it is the surface heating effect from the deposited NP that leads to the surface bubble nucleation in a NP suspension. For a given laser power density, it is necessary to accumulate sufficient NPs on the surface to reach the nucleation temperature before a surface bubble can be formed. When the laser power density is lower, more NPs need to be deposited to convert the laser energy into heat to raise the temperature to the critical value for bubble nucleation, and when the laser power density is higher, less NPs need to be deposited to reach the same effect.

As a comparison, we also studied surface bubble nucleation in a suspension of solid Au NP. Each of the spherical solid Au NP has a diameter of 103 ± 10 nm. The concentration of the solid Au NPs is ~4.3×10¹⁵ particles/m³, and dissolved air level is the same as the CS Au NPs suspension (i.e., air equilibrium). The higher concentration of this solid Au NP suspension than the previous CS Au NP suspension (~2.0×10¹⁵ particles/m³) can avoid extremely long nucleation time which may cause significant error in the results. We firstly focus the laser on the BF surface, but we cannot observe any pulling motion of the solid Au NPs or bubble nucleation even the laser power density is increased to 1.85×10^{6} W/cm², the maximum achievable in our experimental setup. Because of the mismatch between the surface plasmonic resonance wavelength of the solid Au NP (563 nm) and the incident laser wavelength (800 nm), there is no significant plasmonic heating effect, and thus it is very difficult for the NP to form supercavitation, which is essential for achieving the optical pulling effect ^{1,56}. However, we can still see robust optical pushing motion of NPs when the laser focal plane is on the FF surface (fig. 21a). This pushing motion again results in the deposition of NPs on the surface, and thus surface bubbles can still be formed and grow under the irradiation of the off-surface plasmonic resonance laser beam. The bubble nucleation time as a function of laser power density is plotted in fig. 21b. This experiment further confirms that the NP deposition is a necessity for photothermal surface bubble formation in plasmonic suspensions.



Figure 4.4: (a) Optical images of the optical pushing motion of a solid spherical Au NP indicated by the red arrow. The focal plane of the laser is on the FF surface. The time interval between each image is 20 ms. (b) Surface bubble nucleation time as a function of laser power density in the pushing case of solid spherical Au NP.

4.3 Summary

In conclusion, we have elucidated the mechanism of surface bubble formation on a transparent bare quartz surface immersed in plasmonic CS or solid Au NP suspension. The forward- or backward-moving NPs driven by optical pushing or pulling force can be deposited on the surface and then act as surface photothermal plasmonic heaters on the transparent substrate. There is a critical number of deposited NPs at a given power density of the laser so that the surface heating effect can allow the surface to reach a threshold temperature for the nucleation of surface bubbles. Furthermore, bubble nucleation on the BF surface is only possible if the incident laser frequency coincides with the surface plasmonic resonance peak of the NP since intense plasmonic heating is needed to generate a supercavitation – a necessity for optical pulling deposition.

CHAPTER 5:

SURFACE BUBBLE GROWTH IN PLASMONIC NANOPARTICLE SUSPENSION

Understanding the growth dynamics of the microbubbles produced by plasmonic heating can benefit a wide range of applications like microfluidics, catalysis, micropatterning and photo-thermal energy conversion. Usually, surface plasmonic bubbles are generated on plasmonic structures pre-deposited on the surface subject to laser heating. In this work, we investigate the growth dynamics of surface microbubbles generated in plasmonic NP suspension. We observe much faster bubble growth rates compared to those in pure water with surface plasmonic structures. Our analyses show that the volumetric heating effect around the surface bubble due to the existence of NPs in the suspension is the key to explain this difference. Such volumetric heating increases the temperature around the surface bubble more efficiently compared to surface heating which enhances the expelling of dissolved gas. We also find that the bubble growth rates can be tuned in a very wide range by changing the concentration of NPs, besides laser power and dissolved gas concentration.

5.1 Introduction

Plasmonic bubbles can be generated in noble metal plasmonic NP suspensions upon the irradiation of a pulsed laser due to the enhanced plasmonic resonance.^{4,5,28–30,82} Incident light at the surface plasmonic resonance can cause the strong oscillation of the free electrons in NPs. Due to electron-phonon coupling, the energy of these hot electrons is quickly transferred to the lattice to intensely raise the temperature of NP, which induces the nucleation of plasmonic bubbles. Micro-sized bubbles can play important roles in a wide range of applications, including biomedical imaging,^{83–86} healthcare diagnosis,^{10,51–} ^{53,87} microfluidic bubble logics,³ pulsed laser ablation in liquid (PLAL),^{88–94} and optothermal microbubble assisted manufacture.^{76–78} In recent years, studies on the growth dynamics of plasmonic surface bubbles have attracted significant attention.^{13,25,30,32,35,73,95,96} As discussed before,³² the growth of surface bubbles can be generally divided into two phases, i.e., short-time and long-time growth phases. In the short-time growth phase (phase I), the surface bubble experiences an explosive nucleation due to the vaporization of the liquid surrounding NPs on the surface. In the long-time growth phase (phase II), the bubble growth is mainly because of the expelling of dissolved gas from the liquid surrounding the nucleated surface bubbles.

Plasmonic metal nanoclusters on substrates and submerged in deionized (DI) water have been used previously to study the growth dynamics of plasmonic surface bubbles. In this type of experimental systems, surface bubbles usually have an extremely short (10 to hundreds of milliseconds) phase I (vaporization-dominated growth), in which the bubbles grows very fast (on average $10^6 \sim 10^7 \,\mu\text{m}^3$ /s), and the volume growth is proportional to \sqrt{t} , where *t* is time. Compared to phase I, phase II (dissolved air expelling-dominated growth) lasts much longer (e.g., bubbles can be stable for minutes or even more depending on the growth environment), and the volume growth of surface bubble is much slower and linear in time (~ $10^4 \,\mu\text{m}^3$ /s). Although the two growth phases are different, the fundamental cause is the same – plasmonic heating of metal nanoclusters on substrates. In addition to Ref. ³², different behaviors and mechanisms of plasmonic surface bubbles have been investigated

and proposed in other studies. For example, Wang et al. have revealed the giant and oscillating plasmonic surface bubble in the very early life phase. This is due to the composition of the surface bubble in the early life phase gradually changing from vapor to gas.³⁵ Baffou et al.¹³ and Zaytsev et al.⁹⁵ have studied the bubble shrinkage behavior. Since the surface bubble in the long-time growth phase is mainly made of dissolved gas, it displays a linear and slow diffusion-dominated volume shrinkage in air equilibrium water with turning-off the incident laser. Liu et al.³⁰ and Chen et al.⁷³ have studied the bubble growth dynamics on gold nano-arrays. They found that the volume growth rate of bubble is largely related to the density and geometry of these nano-arrays, which both influence the collective input heating power. Zhao et al.¹⁷ and Lin et al.⁷⁹ have shown the convective flow around surface bubble can be used to trap nano- or microparticles. This originates from the Marangoni flow surrounding the surface bubble. This Marangoni flow is attributed to the temperature gradient formed around the micro-size surface bubble.^{72,74,75,96,97} In addition to pre-deposited nanostructures, generating surface bubbles directly using the plasmonic heating of NP suspension has also been demonstrated.^{24,36,98} In Richardson et al.'s work,⁹⁸ the theoretical model of light-to-heat conversion efficiency in NP suspension is established from fitting the experimental data of a droplet on the millimeter-scale. The adsorption and conversion efficiencies highly depend on the concentration of NPs and input laser power. Armon et al.²⁴ have demonstrated that bubble movement in NP suspension can be used for micro-patterning. Compared to pre-deposited optically resistive nanostructures, plasmonic NP suspensions feature the advantages of simpler fabrication procedures, higher heating efficiency and potentially better compatibility with biological environments. Fundamentally, plasmonic NP suspensions are

subjected to volumetric heating wherever the excitation laser beam covers, instead of only surface heating as in the pre-deposited nanostructure cases. However, detailed investigation of the plasmonic surface bubble growth in NP suspensions has not yet been performed despite their importance for myriad potential applications.

In this paper, we systematically study the growth dynamics of surface bubbles in plasmonic NP suspensions via experiments accompanied with theoretical analyses. Microsized plasmonic surface bubbles are generated with both pre-deposited NPs clusters and NP suspensions under the irradiation of a pulsed laser at the SPR peak of the NP suspension. The growth dynamics of the surface bubbles in both conditions are investigated and compared using high-speed videography. It is demonstrated that under the same laser conditions (e.g., power density), the surface bubbles grow much faster in the NP suspensions than in DI water with pre-deposited NPs. Our analysis indicates that it is the volumetric heating in the NP suspension that leads to a higher heating efficiency, which results in higher temperature around the surface bubble and thus larger bubble growth rates. In addition, we also find that the bubble growth rate can be tuned efficiently by changing the concentration of NP in suspension, besides laser power and dissolved gas concentration.

5.2 Results and Discussions

We first study the plasmonic surface bubble growth dynamics in two comparing cases. In Case I, we generate micro-sized surface bubbles on a bare quartz surface
immersed in a NP suspension, as shown in fig. 22a. In Case II, the bubbles are generated on a quartz surface pre-deposited with NP clusters immersed in DI water, as shown in fig. 22d. In both cases, pulsed laser excitations are used, and the beams are focused on the quartz/suspension (or /DI water) interfaces. In case I, a surface bubble nucleates in a few seconds upon laser irradiation. During the short period before bubble nucleation, a small amount of NPs are found deposited on the quartz surface as shown in the SEM image in fig. 22b. The van der Waals interaction between the NPs and surface makes this deposition relatively robust.¹⁶ The NPs are deposited due to the negative optical scattering forces as recently revealed in Ref.¹. Generally, the femtosecond pulsed laser we used in our experiments allows us to generate nanobubbles formed around individual suspended NPs with much lower optical fluence.^{51,52} A femtosecond pulse in the laser train can deliver an amount of energy within ~ 100 fs (generally, the pulse duration is smaller than the electronphonon coupling time constant), so that the NPs can efficiently deposit the energy to increase the temperature while minimizing the dissipation of heat to the surrounding water. However, when the duration of pulse increases to ns, µs, or infinite (i.e., cw laser), the deposited energy on the NPs during a pulse can be dissipated into the surrounding medium while the duration of a pulse remains. As discussed in the Ref.¹, the nanobubble/water interface at the side of light propagation can redirect the photon flux into backward like a macroscopic optical mirror. When the NP is located in the nanobubble at the side of the light incident, the backward photon stream strikes the surface of NP and thus induces an optical scattering pulling force against the laser incident. Due to this optical pulling force, these NPs are finally deposited and work as opto-thermal heating sources and nucleation centers for the surface bubble generation. We notice that the area with deposited NPs on

the quartz surface is about ~ 100 μ m², comparable to the laser beam cross-sectional area. When using the 10x objective lens, the $1/e^2$ length of our Gaussian laser spot is ~11 μ m as determined from a beam profiler. This means that once the surface bubble nucleates and grows, these deposited NPs will be mostly in contact with the gaseous phase, which limits their effectiveness of heating up the liquid in the phase II growth due to the large thermal resistance of the gaseous phase.^{99–101} The volumetric heating in the irradiated area due to absorption of the suspended NPs acts as a second heating source in conjunction with the deposited NPs acting as a surface heater, as described in fig. 22a. These NPs can provide additional heat to the liquid around the surface bubble during the entirety of the growth period.



Figure 5.1: Schematic descriptions of micro-sized plasmonic surface bubble growth in (a) Au NP suspension (Case I) and (d) DI water with pre-deposited NPs on surface (Case II). Scanning electron microscope (SEM) images of pre-deposited Au NPs at the bubble nucleation site in (b) Case I and (e) Case II. Optical images from the side view of a plasmonic surface bubble under laser illumination in (c) Case I and (f) Case II. Scale bar is the same in (c) and (f). The bright regions in (c) and (f) are from the laser scattered by either pre-deposited or suspended Au NPs. On the other hand, the condition where a surface bubble grows in Case II (DI water with pre-deposited NPs on surface) has two major differences compared with Case I, as illustrated in fig. 22d. Firstly, Case II has a much larger amount of NPs pre-deposited on the surface, which can lead to stronger surface heating. As shown in fig. 22e, it is easy to see there are many more Au NPs pre-deposited on the surface in Case II than in Case I. Secondly, since the surface bubble is surrounded by DI water rather than NP suspension in Case II, there is no volumetric heating, leaving surface heating as the only heating source. This can be visually observed from the glowing spots in the optical images of surface bubbles under laser illumination, as shown in fig. 22c and f. These glowing spots correspond to the scattered light from the plasmonic Au NPs, either deposited on the surface or suspended in liquid. As seen from figs. 22c and f, there are glowing spots both on the surface and in the laser beam covered volume on top of the bubble in Case I, while there are only such glowing spots on the surface in Case II.

Since the two cases have distinct heating geometries, different bubble growth behaviors are expected. We record and compare the bubble growth dynamics in the two cases using high-speed videography when they are subject to the same laser irradiation conditions. Recall that surface bubble growth experiences two phases, i.e., the explosive vaporization (phase I) and gas expelling (phase II). As shown in fig. 23a, the bubble in Case II undergoes a very fast growth in phase I, with the duration of shorter than 500 ms. The reason of this fast growth is that the large amount of heat from the highly dense NPs pre-deposited at the surface in Case II can quickly lead to a high surface temperature to vaporize water. After the bubble contact line circle is larger than the laser spot size as the bubble grows bigger, the heated pre-deposited NPs can no longer maintain the liquid-vapor

interface of the bubble above the vaporization temperature due to the large vapor thermal resistance. This causes the bubble growth to slow down and transition into phase II, which is displayed as a kink in the volume growth plot (figs. 23a and b). On the other hand, in the NP suspension (Case I), the phase I bubble grows much slower than that in Case II, which can be attributed to the much fewer NPs on the surface as heating sources (see figs. 22b and e). However, it is interesting to see that in the NP suspension, the bubble has longer phase I growth (~ 3s) and reaches a larger size at the end of this period. This is likely due to that the volumetric effect in NP suspension can provide higher heating efficiency than surface heating, which is shown in later discussions. The higher heating efficiency can maintain the evaporation of the water surrounding surface bubble at a larger bubble size. During this longer phase I, the oscillations of the bubble volume are also observed, which is similar to the behaviors in Ref.³⁵.



Figure 5.2: (a) Surface bubble volume as a function of time in the two cases. Both are from liquids with 60% degassing level and the same laser power of ~ 1.1 W. (b) The plot shows a zoomed view of the range from 0 to 5 s in (a). (c) The averaged surface bubble volume growth rates of phase II in the two cases under different degassing levels (error bars are included).

Phase II growth usually lasts much longer than phase I. As shown in fig. 23a, both cases have linear volume growth in phase II, consistent with the growth behavior of phase

II gas bubbles in previous works.³² In our cases, the plasmonic surface bubble growth is resulted by the local gas oversaturation produced by the enhanced plasmonic heating effect of Au NPs. Unlike the diffusive bubble growth observed in the studies of microelectrode heating,¹⁰² the bubble volume growth induced by local gas oversaturation is linear in phase II.³² However, there is a clear difference between the growth rates in the two cases, with the NP suspension showing a much higher growth rate. Since phase II growth is due to dissolved gas expelling at elevated temperatures, we then have performed the same experiments but with different degassing levels. As shown in fig. 23c, the phase II bubbles always grow faster in the NP suspension (Case I) than in DI water with pre-deposited NPs (Case II) disregarding the degassing levels. When the dissolved gas is reduced to a very low level (e.g., ~ 25%), the surface bubble in Case I still maintains a significant growth rate, while that in Case II hardly grows.

To reveal the mechanism of the different phase II growth behaviors, we have first confirmed that the compositions of the bubble in both cases are dissolved gas rather than vapor. As the bubble shrinkage study in chapter 3 evidenced, the shrinkage of our plasmonic surface bubble in phase II is very slow, taking more than 30 mins. If it is a vapor bubble, it would collapse immediately (in milliseconds) when the thermal excitation is turned off.¹⁰³ Moreover, our bubble shrinkage is linear with a very slow bubble shrinkage rate (~ 420 μ m³/s). As discussed in⁹⁵, the linear bubble volume shrinkage in gas saturated water is due to the fact that we can take the limiting case with no gas concentration gradient in the system. In addition, this shrinkage rate is of the same order of magnitude as reported in Ref.¹³, and it is proved that the bubble shrinkage in our cases has a feature of expelled gas re-dissolving into liquid as the temperature around the bubble slowly decreases. With

this confirmed, we examined the difference in heating sources (i.e., surface heating and volumetric heating) that influences the dissolved gas expelling rates. Since the surface heating is different in the two cases given the drastically different NP densities on the surface (see figs. 22b and 1e), we studied a third case where we immersed the substrate with pre-deposited NPs in the NP suspension (Case III) to better quantify the role of volumetric heating. With the same laser power of 1.1 W, we observed a much faster phase II bubble growth rate in Case III than in Case II (fig. 24a). By taking the difference of the phase II bubble growth rates (**K**) of these two cases, the volume growth rate that can be attributed to volumetric heating in the suspension is ~ $4 \times 10^4 \,\mu \text{m}^3$ /s (the volume growth rate by solely surface heating. For a phase II bubble, the mass influx of dissolved gas into the bubble (dm_g) is proportional to the change in local oversaturation ($d\zeta$) by the following formula:³²

$$\mathrm{d}m_a = C_s V_w \mathrm{d}\zeta \tag{5-1}$$

where C_s is the local air solubility in water, and V_w is the volume of water contributing to the gas expelling for bubble growth, which depends on the thermal boundary layer thickness¹⁰⁴ at the bubble surface. d ζ is further proportional to the change in the local temperature surrounding the bubble (d*T*) by:

$$d\zeta = -\frac{c_{\infty}}{c_s^2} \frac{dc_s}{dT} dT$$
(5-2)

where C_{∞} is the gas saturation far away from the bubble. Combining equations (5-1) and (5-2) (note $\frac{dC_s}{dT}$ is negative), it is clear that the increase in the temperature of liquid water surrounding the surface bubble (boundary layer) will result in a positive local oversaturation, which further leads to the mass influx of dissolved air in the boundary layer expelling into surface bubble. This is the main cause of the phase II bubble growth.



Figure 5.3: (a) Surface bubble volume as a function of time in DI water (Case II) and NP suspension (Case III), both with the same amount of pre-deposited Au NPs and the same laser power of ~ 1.1 W. The volume growth rates (K) in phase II are shown in the plots. The simulated temperature profiles in the (b) volumetric heating and (c) surface heating cases. (d) The simulated bubble surface temperature from the top to the bottom of the bubble in the two cases. The simulated liquid flow velocity magnitude contours in the (e) volumetric heating and (f) surface heating cases.

To quantify the volumetric heating effect on the temperature around the bubble, we employ finite element simulations to investigate the temperature distribution under the two different heating geometries. The simulated temperature profiles of the two heating conditions are shown in figs. 24b and c. We can easily observe the difference in the locations and distributions of the hottest regions in the two cases as they are around the respective heating sources. The temperatures around the bubble surfaces are also different. Figure 24d shows the temperature at the bubble surfaces as a function of the arc length from the top to the bottom of the bubble. The overall bubble surface temperature in the volumetric heating case is higher than the one in the surface heating case, with the average temperature of the former 20 K higher than the latter. The reasons of this surface temperature difference are as follows: 1. In the surface heating case, there is significant heat loss from the heating source to the quartz substrate; 2. Most of the surface heater is in contact with the gas in the bubble, so the heat cannot be conducted to the bubble surface efficiently; 3. In the volumetric heating case, the thermocapillary flow of liquid near the surface of the bubble helps distribute heat around the bubble surface (see the velocity profile in figs. 24e and f). These simulation results indicate that volumetric heating is much more efficient in heating the surroundings of the bubble to a higher surface temperature, and this should be the main cause of the dramatically increased bubble growth rate.

The volumetric heating in the NP suspension provides additional means to control surface bubble growth via tuning the NP concentration in suspension, besides the conventional laser power control in surface heating methods. To study the effects of changing laser power, we tune the source laser power from 0.3 W to 1.12 W, which starts from the minimum laser power that can enable bubble nucleation to the maximum power achievable in our laser system. As plotted in figs. 25a and b, the volume growth rate has only been increased by less than two times in this laser power range which changed four times. To examine the effects of changing Au NP concentration, we prepare the Au NP suspensions with four different NP concentrations from ~ 1×10^{15} to 4×10^{15} particles/m³.

Other experimental conditions, like laser power (~ 1.1 W) and dissolved air concentration (100%), are kept the same in all experiments. The phase II bubble volume growth as a function of time for the four different NP concentrations are all linear, but with significantly different slopes, and the growth rates are shown in fig. 25d. As can be seen, the bubble volume growth rate is highly sensitive to the change of Au NP concentration, increasing by one order of magnitude with a 4-fold increase in NP concentration. Based on our comparisons, it is clear that NP suspension is able to provide a much more significant controllability on surface bubble growth compared to the effect from tuning the laser power. This will be beneficial for many microfluidics applications which desire widely tunable bubble sizes.³



Figure 5.4: (a) Phase II surface bubble volume growth as a function of time under different laser powers from 0.55 W to 1.18W. The dissolved air concentration is 100%, and the Au NP concentration is 1 × 10¹⁵ particles/m³ for all cases. (b) The averaged phase II surface bubble volume growth rates under different laser powers. (c) Phase II surface bubble volume growth as a function of time in the NP suspensions with different concentrations of Au NPs. The dissolved air concentration of 100% and laser power of ~ 1.1 W are held constant for all cases. (d) The averaged phase II surface bubble volume growth rates with different concentrations of Au NPs.

5.3 Summary

To summarize, the growth dynamics of plasmonic surface bubbles in two cases, NP suspension (Case I) and DI water with pre-deposited NPs on surface (Case II), have been systematically investigated in this work. Due to the special volumetric heating geometry, NP suspension enables much higher bubble volume growth rates compared to the more conventional surface heating conditions. This is mainly because that the volumetric heating geometry has higher heating efficiency and is able to maintain a higher bubble surface temperature under the same laser power. We have also demonstrated that NP suspension can provide greater bubble growth tunability via changing the NP concentration. These results may provide fundamental insights to surface bubble growth dynamics in plasmonic suspensions. They may also offer additional degrees of freedom to control surface bubbles for microfluidics applications.

CHAPTER 6:

LIGHT-GUIDED SURFACE PLASMONIC BUBBLE MOVEMENT VIA CONTACT LINE DE-PINNING BY IN-SITU DEPOSITED PLASMONIC NANOPARTICLE HEATING

Precise spatio-temporal control of surface bubble movement can benefit a wide range of applications like high-throughput drug screening, combinatorial material development, microfluidic logic, colloidal and molecular assembly, etc. In this work, we demonstrate that surface bubbles on a solid surface are directed by a laser to move at high speeds (> 1.8 mm/s), and we elucidate the mechanism to be the de-pinning of the threephase contact line (TPCL) by rapid plasmonic heating of nanoparticles (NPs) deposited in-situ during bubble movement. Based on our observations, we deduce a stickslip mechanism based on asymmetric fore-aft plasmonic heating: local evaporation at the front TPCL due to plasmonic heating de-pins and extends the front TPCL, followed by the advancement of the trailing TPCL to resume a spherical bubble shape to minimize surface energy. The continuous TPCL drying during bubble movement also enables welldefined contact line deposition of NP clusters along the moving path. Our finding is beneficial to various microfluidics and pattern writing applications.

6.1 Introduction

The ability to manipulate bubbles in liquids promises to greatly advance robotic handling of liquid, which has a wide range of applications such as high throughput genomics screening, combinatorial material development, healthcare diagnosis, microstructure assembly, microfluidic logic, and vapor generation.^{3-6,105-108} In a related field of liquid droplets manipulation, extensive research has been performed and different mechanisms have been thoroughly studied, such as electrostatic interaction, optical tweezers, and Marangoni effect.¹⁰⁹⁻¹¹¹ In contrast, the fundamentals of controlled bubble movement on a solid surface have been under-explored. The Marangoni effect has been commonly cited as the key mechanism driving gas bubble movement in liquids. In 1888, Quincke moved a surface air bubble in water using the solutal Marangoni effect enabled by an alcohol-induced surface tension gradient, which caused the bubble to migrate toward the alcohol-rich region (lower surface tension). Since surface tension is temperature-dependent, the Marangoni effect can also be realized by imposing a temperature gradient across the bubble, also called thermo-capillary convection. In 1959, Young et al.¹¹² leveraged such an effect to prevent the ascension of a bubble in a liquid column as the thermal Marangoni effect drives the bubble away from the colder end with higher surface tension.

To introduce a temperature gradient, the photothermal conversion process has been leveraged because a tightly focused light can precisely heat a specific location around a surface bubble and this allows more accurate manipulation of surface bubbles. There have been several demonstrations of using focused light to direct bubble movements on solid surfaces coated with optically resistive thin-films (e.g., metals, semiconductors, or metal oxides).^{17,22,23,79,113,114} In these studies, light is focused on the optically resistive thin-films to generate heat which creates a surface bubble, and various mechanisms have been proposed to manipulate the location of surface bubble. For example, Hu et al.^{113,114} have shown that a 200-µm air bubble can be actuated by pre-defined light patterns focused on

an amorphous silicon substrate that absorbs the light and generates heat. When the laser dislocates away from the surface bubble, it has been found that the surface bubble moves toward the new location of the laser spot. They attributed the bubble movement to the thermo-capillary flow generated around the bubble. In another two experiments, Fujii et al.²² and Lin et al.⁷⁹ have used pre-deposited Au film and indium tin oxide film, respectively, and proposed that, as the laser spot moves, a new vapor bubble was generated at the current laser spot and the old bubble collapsed, and such high rate phenomena exhibited as if a bubble was moving continuously. On the other hand, another strategy has been proposed by Zheng et al.²³, Zhao et al.¹⁷, and Zou et al.²⁵, where the de-pinning of the three-phase contact line (TPCL) of the surface bubble can trigger the bubble to move. In their experiments, the liquid at the front TPCL of a bubble can be rapidly evaporated by laser heating of the Au thin-film, leading to the de-pinning of the trailing TPCL and then the migration of the surface bubble toward the laser spot. While most of the abovediscussed works use an absorbing layer on the surface to transduce light into heat, Armon et al.²⁴ have shown that surface bubbles generated in a metallic nanoparticle (NP) suspension can be directed by a laser spot without any optically resistive thin-films on the surface, which can usually degrade light transmission efficiency or require multiple fabricating processes in vacuum. In their discussion, they attributed the interesting phenomenon of laser-guided surface bubble movement to the thermo-capillary convective flow. However, the underlying mechanism has not been clearly explained or indisputably confirmed, and a detailed study is needed.

In this work, we present evidence showing that the thermal evaporation-induced de-pinning of the front TPCL triggers the surface bubble movement in a plasmonic NP

suspension. In the NP-water suspension, thermo-capillary convection due to volumetric heating brings NPs to the TPCL, which then work as an intense heat source by plasmonic resonance to induce local evaporation to de-pin the front TPCL and extend it forward. This is followed by the advancement of the trailing TPCL in a sequential stick-slip mechanism involving the fore and aft positions of the bubble. During bubble translation, surface NP clusters are left behind by the de-pinned TPCL through contact line deposition. With predeposited NPs, bubble movement can reach a high speed of at least 1.8 mm/s. By comparing the stick-slip motion with the spatial distribution of the deposited Au NPs, we find that the bubble lags more on the Au NP-deficient region while it translates faster in the region with abundant Au NPs. Using high-speed videography with interferometry, we indeed observe that the front TPCL is pushed forward when the laser spot overlaps with the front contact line, which sequentially leads to the de-pinning of the trailing TPCL and eventually leads the bubble to slip forward within ~1 ms. Based on the interferometry, we find that the driving force to de-pin the trailing contact line is two order-of-magnitude larger than the force induced by the thermo-capillary convective flow surrounding the surface bubble. This confirms that the TPCL de-pinning due to the plasmonic NPs heating is the main reason for the laser-directed surface bubble movement. The results of this work hence elucidate the fundamental mechanism of laser-directed surface bubble movement in plasmonic NP suspensions. The possibility of high-precision bubble manipulation has useful practical implications for a wide range of microfluidic applications.

6.2 Results and Discussions



Figure 6.1: Characterization of moving surface bubbles. (a) Schematic experimental setup to characterize the motion of the surface bubble. (b) Optical images from the top view of the moving bubble on the quartz substrate in the NP suspension guided by the laser with a velocity (v_{laser}) of 100 µm/s and a power (P_{laser}) of 550 mW. The green arrows depict the direction of the laser translation. In (b), the black arrow depicts the formed Au NPs stain on the path of the moving bubble.

The experimental setup to generate, move, and monitor the surface bubble is schematically illustrated in fig. 26a. We disperse Au NPs (Nanospectra Bioscience, Inc) consisting of a silica core (~ 100 nm of diameter) and an Au shell (~ 10 nm of thickness) in deionized (DI) water and contain it in a quartz cuvette. A femtosecond pulsed laser (repetition rate of 80.7 MHz and pulse duration of 200 fs) with a Gaussian intensity profile with a $1/e^2$ radius of 20 µm and a center wavelength of 800 nm is directed to the cuvette and tightly focused on the interface between the suspension and the cuvette wall. The wavelength of the laser coincides with SPR peak of the used Au NPs. The laser heats up the Au NPs and a surface bubble can be generated at the laser spot. The bubble is allowed to grow to a certain size (radius, 20 µm < R < 50 µm), after which the laser spot starts to translate along the surface (y-direction, fig. 26a) with a certain velocity (v_{laser}). We note

that gravity is in the negative y-direction. A high-speed camera (NAC image technology, HX-7) is used to record the bubble generation and movement.

In experiments, it was observed that the generated surface bubble can follow the movement of the laser spot instantaneously and intimately, and fig. 26b shows representative optical images of a moving bubble from the top view at an interval of 200 ms. For more detailed analyses, the bubble movement is also recorded from the side view at a fine time resolution of 0.2 ms (fig. 27a). In fig. 27a, it is clear that the bubble is attached to the quartz surface, where a reflection image of the bubble is seen. The laser beam passes through the surface bubble from the bottom in the z-direction. It is observed that the laser beam coming out of the top of the bubble is skewed towards the laser moving direction. Such a distorted beam shape resulted by the light refraction at the top surface of the bubble suggests that the laser beam slightly precedes the center of the bubble during laser and bubble movement. After careful observation of the refracted laser beam shape, we see a gradual spreading of the beam leading edge towards the laser moving direction before it abruptly retracts (see figs. 27b and 2c). This implies that the laser beam moves away from the bubble center gradually (it is referred to as the "lag" motion in fig. 27b) and then the bubble suddenly displaces to center at the new laser location (it is referred to as the "advance" motion in fig. 27c), which suggests that the bubble moves in a lag-and-advance stick-slip manner.



Figure 6.2: (a) Optical images from the side view of the moving bubble on the quartz substrate in the NP suspension guided by the laser with a velocity (v_{laser}) of 100 μ m/s and a power (P_{laser}) of 550 mW. In (a), the magenta arrow indicates the scattered laser light from nano-bubbles with Au NPs in the suspension, which propagates towards the top of the surface bubble. (b and c) Refracted laser beam passing out of the top surface of the bubble by optical imaging (left) and schematic illustration (right) in (b) the 'lag' state and (c) the 'advance' state of the bubble movement.

In the NP-water suspension, the laser thermally excites the suspended NPs at the SPR, which leads to volumetric heating of the volume irradiated by the laser beam.^{49–52,81} The volumetric heating induces a thermo-capillary convective flow as schematically shown in fig. 28a. The flow can bring NPs in the suspension towards the TPCL of the surface bubble.^{115,116} This is evident by tracking the movement of the glowing dots, where the glowing dots correspond to the scattered light from the plasmonic Au NPs. In fig. 27a, we can clearly see that the glowing dots move towards the surface bubble (e.g., one dot indicated by the red arrows in fig. 27a). By tracking the NP motion, we estimate an average flow speed of ~ 30 mm/s in the laser irradiated region above the surface bubble. We reproduced thermal convective flow using a finite element method (FEM) simulation by

assuming volumetric heating (see fig. 28b). Figure 28b clearly shows that the induced flow direction is towards the surface bubble, which agrees with the migration direction of the NP in the experiments (fig. 27a). In addition, the calculated flow velocity is on the same order of magnitude of the observed result (see the scale bar in fig. 28b). This flow eventually brings the suspended NPs to the TPCL of the surface bubble. As the liquid at the TPCL dries out by the laser heating, clusters of NPs are left on the surface as stains, which can be seen from fig. 26b (black arrow). These immobilized NP clusters can serve as a heat source when subject to laser irradiation. However, the volumetric heating is found to be key to reproduce the experimentally observed thermo-capillary convective flow direction. If we assume surface heating to be dominated from the deposited NPs at the surface, the thermo-capillary convective flow would be in the opposite direction (see fig. 28c) as predicted and observed by a number of previous studies,^{17,22,23,79} which is apparently not consistent with our experimental observation.



Figure 6.3: Thermo-capillary convective flow surrounding the surface bubble. (a) Schematic of the vertical thermo-capillary convective flow direction when the suspension is subject to volumetric heating in the laser beam covered region. (b) Calculated thermocapillary convective flow around the surface bubble when the laser induces volumetric heating in the suspension. The shade area in the suspension depicts the volumetric heating region covered by the laser irradiation. The black arrows show the direction of the convective flow. The magenta solid lines are the isothermal contours of temperature. (c) Schematic of the thermo-capillary flow when the heat source is located at the surface of the substrate.

Although laser heating of the deposited NP clusters is not the main cause of the thermo-capillary convective flow, it is critical to bubble movement. Using the NP-water suspension, we vary the laser moving speed and find that the surface bubble can follow the laser instantaneously until the laser speed reaches 560 μ m/s (fig. 29a). Given that the thermo-capillary convective flow has a much higher speed (30 mm/s) than the laser moving speed (< 1 mm/s), this indicates that the thermo-capillary convective flow is not the likely culprit for surface bubble motion. As shown later, the viscous stress and pressure acting on the surface bubble solely induced by the thermo-capillary convective flow is much smaller than the driving force needed to move the bubble. Instead, we find that the density of the NP clusters stain left on the solid surface due to contact line deposition steadily decreases as the bubble moving speed increases, as seen in the dark-field optical microscope (fig. 28b) and SEM (fig. 29c) images. Therefore, we propose that it is the result of a lack of Au

NPs delivered to the TPCL that leads to too small a heating intensity to de-pin the TPCL, which makes the surface bubble to fail to follow the laser spot at high velocities. If so, this can be potentially overcome when the surface is pre-deposited with Au NP clusters. To confirm this, we create a path of the Au NP stain by generating and moving a surface bubble slowly ($v_{\text{laser}} = 100 \,\mu\text{m/s}$). We then generate a new surface bubble and move the laser along the pre-deposited Au NP path with a constant acceleration of 3 mm/s² for a total travel distance of 1 mm. The bubble is able to follow the laser spot instantaneously for the whole process (see fig. 29d) with speed up to 1800 μ m/s. This confirms that the deposited Au NPs is responsible for the surface bubble movement. We should note that 1800 µm/s is the largest speed our translation stage can reach, and thus it should represent the lower limit of the achievable speed of the laser-directed bubble movement. We also note that in the Au NP stain, there are aggregated NPs like dimers or trimers. While the scattering peak of these aggregated NPs is likely to be red-shifted,¹¹⁷ we find that their optical absorption efficiencies are similar to (or even higher than) that of the single NPs. Thus, the heating and the resultant depinning effect by these aggregated NPs should also be similar to that by single NPs.



Figure 6.4: Displacement, velocity, and the deposited Au NPs of moving surface bubbles on surfaces and the effect of the pre-deposited Au NPs. (a) The travel distance and velocity of the laser (solid lines) and the surface bubble (symbols) as a function of time in the NP suspension on pristine quartz surface. The laser moves with a constant acceleration (or de-acceleration) of $a_{laser.} = 1 \text{ mm/s}^2$ (b) Dark-field optical microscope image of the Au NPs stain deposited along the path of the moving surface bubble with $v_{laser} = 100 \text{ }\mu\text{m/s}$ (top), 300 $\mu\text{m/s}$ (middle), and 500 $\mu\text{m/s}$ (bottom). (c) Scanning electron microscope images of the deposited Au NPs stains from $v_{laser} = 100 \text{ }\mu\text{m/s}$ (top) and 500 $\mu\text{m/s}$ (bottom). (d) The travel distance and velocity of the laser (solid lines) and the surface bubble (symbols) as a function of time in the NP suspension with pre-deposited NP stain on the quartz surface; here $a_{laser} = 3 \text{ mm/s}^2$.

We also microscopically resolve a moving surface bubble from the side view with a time interval of 50 μ s, which displays a very interesting lag-and-advance bubble motion. From the video, we track and analyze the travel distances of the surface bubble along the

y-direction as a function of time. As seen in fig. 30a, the distance traveled by the bubble in any instance is shorter than that of the laser spot. In addition, the movements of the surface bubbles are not continuous, but are a series of lag-and-advance motions (see fig. 30a). We also find that the lag-and-advance motion is in general correlated with the density of the deposited NP along the moving path (e.g., fig. 30b). The lag state is prolonged when there are less NPs on the surface. When the NP density is low at the TPCL, the laser needs to move further so that the higher intensity portion of the Gaussian intensity profile overlaps with the lower NP density to generate sufficient heat to evaporate the fluid at the TPCL and de-pin it. We also note that the NP deposition during the bubble movement is stochastic (see fig. 30c) and it is possible that when the deposited NP density is too low, especially when the laser moves too fast, the de-pinning cannot happen. This is why the bubble can fail to follow the laser spot as previously shown (fig. 29a).

To further investigate the Au NP stain effect decoupled from the surrounding thermo-capillary convection in the suspension, we purged the NP-water suspension and filled the cuvette with DI water. After generating a surface bubble on the pre-deposited NP path, the laser is moved again with a constant acceleration of 3 mm/s² for a total travel distance of 1 mm, and it is seen that the bubble can follow the laser movement in the whole process. This additionally verifies that the bubble movement is driven by the deposited Au NPs stain since there should be very weak thermo-capillary convection on the surface bubble movement in the DI water. In addition, it is worth mentioning that the size of the bubble in DI water keeps decreasing during the movement since the bubble is being cooled by quartz substrate when moving to a new location, while that in NP suspension shows increasing radius. This should be related to the volumetric heating in NP-water suspension

which helps the dissolved gas in water expel into surface bubble during the moving process.³² After degassing the NP-suspension using a mechanical pump, the growth rate of the moving surface bubble in the suspension is significantly reduced in comparison to that of the pristine suspension.



Figure 6.5: Stick-slip motion of the surface bubble. (a) Travel distance of the surface bubble (color lines) and the laser (black lines) as a function of time when the laser moves with $v_{laser} = 100$, 200, and 300 μ m/s. (b) Travel distance of the surface bubble as a function of time corresponding to the time period indicated by the arrow in (a). The inset shows the optical image of deposited Au NPs on the corresponding travel path. The bottom axis shows the relative laser spot position in the y-direction. (c) Deposited Au NPs spot density along the laser moving path, which corresponds to the inset optical image in (b).

From the above results, we have found that the laser heating of the deposited Au NP clusters is the key to the moving bubble and its lag-and-advance stick-slip motion. The mechanism of this stick-slip motion is illustrated in fig. 31a. Before the laser beam moves, the TPCL of a surface bubble is pinned with an equilibrium contact angle (θ_{e}). When the laser beam moves forward slightly, the laser overlaps with the front contact line and heat up the deposited NP clusters there. The heating locally evaporates the liquid microlayer at the TPCL, pushing the contact line outward. This is also described as the "recoil force"^{99,118,119} from the rapid evaporation of the liquid at the TPCL. As the front TPCL is pushed outward, the effect of the vapor/water surface tension will result in a contact angle larger than the equilibrium one. The trailing TPCL will then also possess the similar contact angle as the bubble minimizes the vapor/water surface energy. In the meantime, the trailing contact line is still pinned, and the bubble movement lags behind that of the laser. As the front TPCL is further extended following the laser movement, the contact angles further increase until a critical angle (θ_c) is reached. Beyond this point, the pinning effect can no longer hold the trailing TPCL,^{120–122} it then retracts, and the whole bubble advances forward to follow the laser beam. Due to the pinning effect, the laser beam center will precede the center of the lagged bubble, leading to the asymmetric refraction of the beam coming out of the top of the bubble as previously discussed in figs. 27a and 27b.

To obtain more insights into the stick-slip motion and visualize the propagation of the TPCL during surface bubble movement, we employ a laser interferometry setup similar to Ref. [²⁵] to quantify the relative motion of the laser and the TPCL. The constructive and destructive patterns of a coherent light source (i.e., interference fringe patterns) in the microlayer under the surface bubble allows the identification of the TPCL. Figure 31b shows the laser interferometry images corresponding to each stage described in fig. 31a. Figure 31c illustrates the distance between the laser spot center and the bubble center as a function of time with a time resolution of 0.1 ms. At first, in stages (i) and (ii), the bubble lags behind the moving laser spot, and the distance between two centers increases gradually. Then, in stage (iii) the laser spot overlaps with the front TPCL and push it forward because of heating up of the deposited NP clusters at the contact line. The laser spot keeps drying the contact line and pushing it to result in a contact angle larger than θ_c . Finally, in stage (iv), after the pinning force can no longer hold the surface bubble, the bubble slips forward to "catch up" the laser spot. One point to mention here is that this "catch-up" motion of the surface bubble is extremely fast, which is finished within ~ 1 ms (fig. 31c).

The interference fringe patterns also allow us to estimate the contact angle on the trailing TPCL. In the interferometry images, the distance between two neighboring constructive rings (dashed lines in fig. 31d) in the radial direction (Δd) can determine the contact angle (θ) via the following relation¹²³:

$$\theta = \operatorname{atan}\left(\frac{\lambda}{2n\Delta d}\right) \tag{6-1}$$

where λ is the vacuum wavelength of the coherent light, and *n* is the refractive index of water (*n* = 1.33). Using this relation, we can estimate the contact angles at the trailing TPCL to be $\theta_e \sim 11^\circ$ at stage (i), and $\theta \sim 24^\circ$ at stage (iii). Two representative interferometry images in fig. 31d clearly shows the changes of fringe patterns from the equilibrium (i.e.,

stage (i)) to stage (iii), where it is evident that the shape of the TPCL is changed to an oval shape from a circle (solid white lines in fig. 31d) as the laser spot overlaps with the front end of the TPCL. In addition, our calculated contact angles match well with the reported values due to the TPCL de-pinning process of surface bubble on a hydrophilic SiO₂ surface²⁵, which uses optically resistive thin-films buried under the SiO₂ surface to induce the TPCL de-pinning.

The increased trailing contact angle at stage (iii) means that Young's equation will yield a non-zero net force, as the projected liquid-vapor surface tension at the trailing TPCL is weakened due to the increased contact angle. Here, it is reasonable to assume that the surface bubble can only move when this non-zero net force is larger than the pinning force that holds the surface bubble. Using Young's equation, the net force (F_{net}) at the trailing TPCL can be expressed as:

$$F_{net} = r_{TPCL} \gamma_{LG} \left(2\cos\theta_e + \int_{\pi}^{2\pi} \cos\theta(\phi)\sin\phi\,\mathrm{d}\phi \right)$$
(6-2)

where r_{TPCL} is the radius of the TPCL ($r_{TPCL} = 33 \ \mu\text{m}$) of the surface bubble (white solid line in fig. 31d), γ_{LG} is the water-air surface tension ($\gamma_{LG} = 72 \ \text{mN} \ \text{m}^{-1}$), ϕ is the azimuthal angle on the surface plane, $\theta(\phi)$ is the contact angle depending on ϕ at stage (iii). We assume that $\theta(\phi)$ is the equilibrium angle at $\phi = \pi$, and it linearly increases to 24° at $\phi =$ $2\pi/3$, and then linearly decreases to the equilibrium angle at $\phi = 2\pi$. We expect the assumption of the linear relation between the contact angle and the azimuthal angle to give the correct order of magnitude in force estimation. This leads to $F_{net} \sim 1.8 \times 10^{-7} \ \text{N}$ according to Eq. (6-2), which is the minimum force needed to de-pin the TPCL and allow the surface bubble to displace. We further compare this pinning force with force from the viscous stress and pressure induced by the thermo-capillary convective flow from the volumetric heating of the NP suspension. According to our calculation, it is found that the force on the surface bubble by the thermo-capillary convective flow is ~ 5×10^{-9} N when the laser spot overlaps with the front contact line. This is almost two orders of magnitude lower than the estimated pinning force. This reasonably leaves the front TPCL de-pinning due to plasmonic heating as the main reason for the laser directed surface bubble movement. We note that if the surface is super-hydrophilic, the pinning force will be smaller and thus the surface bubble may move faster as directed by the laser.

Finally, as a potential application, we leverage our finding to merge two surface bubbles. The surface bubble merging process is particularly important to chemical reactants or catalyst delivery on surface.^{12,124} Using a laser, we first generate a surface bubble with a radius of ~ 120 μ m (referred to as the "target bubble") on the quartz surface in the suspension. We then create another surface bubble with a radius of ~ 30 μ m (referred to as the "carrier bubble") at a remote location away from the target bubble and move the laser spot to deliver the carrier bubble toward the target bubble to let them merge together. It is clearly seen that the larger target bubble absorbs the smaller carrier bubble instantaneously as their vapor/liquid interfaces contact each other. The merging process occurs at a time scale of less than 200 μ s, which is due to the Ostwald ripening effect.^{125,126} We believe that the laser-guided merging process of two surface bubbles can enable potential applications beyond the demonstrated ones such as micro-pattern writting and micro-particle assembly.



Figure 6.6: De-pinning of contact line in Lag-and-advance motion of the surface bubble. (a) Schematic illustration of the lag-and-advance of the surface bubble. (i) The contact lines are pinned with the equilibrated contact angle ($\theta = \theta_e$) before the laser beam moves. (ii) When the laser moves slightly forward and the beam starts to overlap with the deposited Au NPs around the front TPCL, the NPs provide more heat for water evaporation at the contact line. This pushes the TPCL outward and leads to an increase of the front contact angle. To minimize the vapor/liquid surface tension, the trailing contact angle increases accordingly. The increased trailing contact angle is still smaller than a critical angle ($\theta_e < \theta < \theta_c$), and the trailing TPCL is still pinned. In this phase, bubble lags behind the translating laser spot. (iii) The laser continues moving forward, and the front contact line is further pushed outward (red arrow). This process eventually increases the trailing contact angle to reach critical angle, and (iv) finally, the trailing contact line overcomes the pinning effect and moves forward, which enables the surface bubble to advance forward. (b) Optical interferometry images of a surface bubble in lag-andadvance motion. Each stage from (i) to (iv) in (b) corresponds to that in (a). The brighter white dots show the locations of laser spot. Here, Plaser is 500 mW and 20x Objective lens is used to focus the laser. The light source for the interferometry has the wavelength of 630 nm and power of 2 mW. (c) The distance between the center of bubble and that of the laser spot as a function of time. The red arrows indicate the time corresponding to each stage in (b). (d) Optical interferometry images at stage (i) (left) and stage (iii) (right). The white solid lines indicate the TPCL and the area inside the white solid lines is the dry-out region. The periodic red and black rings outside the white solid lines correspond to the fringe patterns of coherent light source in microlayers, respectively. The white dotted lines indicate the first-three constructive interference rings on the side of the trailing contact line.

6.3 Summary

In conclusion, we present evidence showing that the surface bubble movement in an Au NP-water suspension is triggered by the thermal evaporation-induced de-pinning of the front TPCL, followed by the advancement of the trailing TPCL. The thermo-capillary convection brings NPs to the TPCL, which then works as a heat source to induce local evaporation to de-pin the TPCL and thus move the bubble. Meanwhile, NP clusters are deposited on the surface due to TPCL drying. Along the line-written path of pre-deposited NPs, bubble movement can reach high speeds of at least 1.8 mm/s. High-speed videography and the analysis of the diffracted laser light of the microlayer near TPCL both show that the bubble moves in a stick-slip manner while the laser translates continuously. The interferometry confirms the front contact line extension by the laser-NP heating, the de-pinning process of trailing TPCL followed by the slip of the surface bubble. Evaluating the driving force at the trailing TPCL due to the increased contact angle confirm that the thermal Marangoni effect has an insignificant role in the laser-directed surface bubble movement. Not only do the results of this work help elucidate the fundamental physics of laser-directed surface bubble movement in a NP suspension, but also, they demonstrate the capability for controlled contact line deposition and precise control of bubble movement without pre-deposited optically resistive thin-films. There can be useful implications for a wide range of microfluidics and directed-assembly applications.^{127,128}

CHAPTER 7:

PLASMONIC SUPERCAVITATION ENABLES NANOPARTICLE PHOTO-EJECTION ACROSS AIR/WATER INTERFACE

The ability to separate miniscule solid particles (e.g., nanoparticles) from liquid is important to a wide range of applications, such as water purification, material deposition, and biomedical engineering. Such separation is usually achieved by displacing liquid via filtration or distillation. However, directly moving small particles out of liquid is difficult, especially when their sizes approach the nanometer scale, as the capillary force on the nanoparticle at the liquid interface is too large for common body forces (e.g., optical or magnetic force) to overcome. Here, we demonstrate the ability to eject metallic nanoparticles out of liquid with a laser excitation at their surface plasmon resonance wavelength. The laser applies an optical force on the nanoparticles to drive them toward the liquid surface. In the meantime, the laser can also intensely heat the nanoparticle to form a nanobubble encapsulating the nanoparticle (i.e., supercavitation), which achieves the liquid-nanoparticle separation and thus eliminates the capillary force on the nanoparticle at the liquid free interface. We show that such a mechanism can expel nanoparticles out of liquid as observed using a transient scattering experiment, which is further confirmed by molecular dynamics simulations. We also demonstrate depositing the nanoparticles on a solid surface not in contact with the liquid. This study reveals an interesting mechanism to separate nanoparticles from liquid and could potentially benefit separation, nanomaterials and biomedical applications.

7.1 Introduction

The ability to separate miniscule solid particles from liquid is essential to a wide range of applications that need particle separation,^{129–133} concentration^{4,6–9,134} and deposition.^{16,76,77,79,135–140} For example, to study the toxicological effects of engineered nanoparticle (NP) aerosols on the human respiratory system,^{141–144} direct deposition of solid NPs onto human cells would be ideal for in-vitro experiments, but current technologies^{145,146} mostly rely on using aerosols to carry such NPs.^{147,148} Existing methods for separating solid particles from the hosting liquids, such as filtration and distillation, usually achieve solid-liquid separation by displacing liquids, *i.e.*, passing liquids through a membrane or evaporating it into vapor. However, directly moving small particles out of liquid is more challenging, especially when their sizes approach the nanometer scale. These tiny particles can be stranded at the liquid/air interface because of the capillary force, which has led to applications such as self-assembly.^{149–152} But such forces are so strong, scaling with the inverse of particle radius, that common body forces are too weak to drive small particles out of the liquid. For example, for an NP with a diameter of 120 nm, the capillary force^{153,154} on it would be $\sim 10^{-8}$ N at the water/air interface. However, body forces like optical scattering forces and magnetic forces commonly used to drive suspended NPs are many orders of magnitude smaller than the capillary force. For example, the dispersive optical scattering force on a 120-nm-diameter gold/silica core-shell NP is ~10⁻¹² N even with a relatively high optical fluence of $9 \sim 15 \text{ mJ/cm}^{2,1,31,36,37}$ and the magnetic force on a 10-nm-diameter colloidal iron oxide NP in magnetic fields with strengths of 5~15 Tesla is only $\sim 10^{-18}$ N.¹⁵⁵ However, if there is a way to separate surrounding liquid from the solid

NP surface prior to reaching the liquid interface, there will be a chance that the NP can escape from the liquid without being stranded by the capillary force. It has been demonstrated that optically excited localized plasmonic heating can lead to nanoscale vapor bubbles to encapsulate the NPs, *i.e.*, supercavitating NPs, if the optical fluence is above a certain threshold,^{34,49,51,52,81} which may help realize the desired liquid-NP separation. These supercavitating NPs can also be driven by optical scattering forces toward the liquid interface guided by the light.^{1,2,36}

In this work, we demonstrate the ability to eject metallic NPs out of liquid with a laser excitation at the surface plasmon resonance (SPR) wavelength of the NPs. The laser is shown to function as both a supercavitation exciter and an optical force provider, that creates the aforementioned liquid-NP separation and in the meantime drives the supercavitating NPs toward the liquid interface. We show that the optically driven supercavitating NPs can move out of liquid as observed using a transient scattering experiment, which is also verified by molecular dynamics (MD) simulations. We also demonstrate the NP expulsion by depositing them onto a glass surface not in contact with the liquid. Our temperature field analysis using finite element thermofluidic simulations confirm that the observed ejection of NPs from liquid does not originate from boiling or evaporation. Our study reveals a novel mechanism to enable NP-liquid separation and could potentially benefit separation, nanomaterials and biomedical applications.

7.2 Results and Discussions

We first show experimentally that Au NPs in a suspension can be driven toward the air/liquid interface and expelled from liquid under the illumination of a laser at the SPR peak wavelength. The optical system is shown in Figure 32a, in which a droplet of Au NP suspension with a concentration of $\sim 1 \times 10^{15}$ particles/m³ is held by a thin glass substrate. The Au NP consists of a silica core (100 nm in diameter) and a thin Au shell (10 nm in thickness), supporting the SPR peak at ~800 nm in water. An 800 nm femtosecond pulsed laser is focused by a $20 \times$ objective lens onto the air/liquid interface at the tip of the droplet, which is the source laser used to excite the NPs. Since the laser wavelength matches the SPR of the core-shell Au NPs in the suspension, it can intensely heat up the NPs and generate nanobubbles to encapsulate the NPs to achieve supercavitation.^{2,36,52} The side view of the droplet is monitored by a high-speed camera with a $10 \times$ objective lens. We use the dark-field scattering method^{1,56} with an additional HeNe probe laser (2 mW, at the wavelength of 632.8 nm) illuminating the air side of the air/liquid interface around the focal point of the source laser to monitor the dynamics of the ejected NPs (see schematic in Figure 32a). We note that the intensity of the probe laser (0.64 W/cm^2) is very low and thus its weak optical force should not influence the dynamics of NPs. It is also noted that we use an optical filter to block the source laser light to reach the image sensor of the camera in the dark-field scattering measurement.

As shown in Figure 32b (left), the source laser is focused on the air/liquid interface, and the air region monitored by the camera field of view is illustrated by a dashed black square. In the right panel of Figure 32b, where we used the source laser with an optical fluence of 22.8 mJ/cm² at the focal point, we can observe many red glowing dots in the dark field. These glowing dots represent the Au NPs ejected out of the suspension into air as they scatter the probe laser light in the diffraction limit.^{1,2,36,56} As shown later in Figure 3, these glowing dots collected by a receiving substrate are proven to be individual Au NPs. We note that these glowing dots are unlikely due to any pure water droplets, since pure water is transparent to the 800-nm source laser or the 632.8-nm probe laser, and there are no water interfaces to enable any optical force on the liquid itself to eject pure water droplets out of the bulk. It is also unlikely that some water droplets can come out of the bulk liquid together with photo-ejected NPs. The Au NP surface is not functionalized by any chemical groups leading to relatively weak interfacial interactions between NP and the surrounding water molecules. Moreover, the generated nanobubble can separate the NP from its surrounding water while it is still in water.¹



Figure 7.1: Experimental system for monitoring the photo-ejected Au NPs across the air/liquid interface. (a) Schematic of the experimental setup to observe the photo-ejected Au NPs into the air by a source laser at the SPR wavelength. Gravity is in the downwards direction. (b) Left: bright field optical image with an LED illumination backlight showing the suspension droplet and the source laser beam focused on the air/liquid interface.
Right: dark-field optical image of the air side of air/liquid interface, which captures the photo-ejected Au NPs. Each red glowing dot corresponds to the diffraction-limited scattered light of the probe laser from a single Au NP.^{1,2}

When the NP suspension is irradiated by the source laser, the optical scattering force can push the NPs toward the liquid interface.^{1,2} This force originates from the scattering of the incident photons on the NP surface, which gives a mechanical momentum to the NP in the light propagation direction.^{156–158} The amplitude of this force is around 1.1×10^{-11} N
with the highest optical fluence at the focal point of 22.8 mJ/cm² used in our experiment.¹ However, such a force is about three orders of magnitude smaller than the capillary force ($\sim 10^{-8}$ N), which can strand the NP at the liquid/air interface (Figure 33a).

For the core-shell Au NP studied in this work, when the source laser has an optical fluence above a certain threshold (~7 mJ/cm²),⁵² a nanobubble can be generated surrounding the intensely heated plasmonic NP and encapsulate it in vapor (i.e., supercavitation). Our femto-second pulsed laser has a fluence of 22.8 mJ/cm² which is well above this threshold, and thus supercavitation can occur.^{1,2,51,52,56} Furthermore, our previous transient scattering pump-probe experiments have confirmed the formation of nanobubbles using the same laser setup and parameters as in this work.^{1,159} While the optical dispersive force from the source laser can drive the NP toward the liquid/air interface, supercavitation separates the solid NP from the liquid via a thermally induced phase change process^{34,160–162} before the NP reaches the liquid/air interface, which in turn eliminates the need to overcome the capillary force at the liquid/air interface (Figure 33b). We note that the size of the nanobubble, which is estimated to be in the order of O(100)nm in radius,^{1,52} or the nature of the nanobubble (vapor vs. gas)^{32,34} does not influence the photo-ejection mechanism as long as the supercavitation serves the purpose of separating the NP from the surrounding liquid.



Figure 7.2: Microscopic mechanism of supercavitating NP moving out of liquid interface. Schematics showing (a) the NP stranded at the liquid/air interface due to the capillary force, but (b) with a supercavitation which separates NP from liquid within the liquid, the NP can pass through the interface without experiencing the capillary force at the liquid/air interface. Lower panel: The schematic of supercavitating NPs ejected out of liquid by laser. MD simulation snapshots of (c) a non-supercavitating NP moving toward and stranded at the interface, and (d) an intensely heated NP with supercavitation moving out of liquid.

To confirm this hypothesis, we perform a series of MD simulations of a solid NP immersed in liquid moving toward the liquid interface without and with thermally induced supercavitation. We simulate an Au NP with a radius of 1 nm immersed in liquid argon, which has a free surface (Figures 33c and d). In one case, both the NP and the liquid are kept at 90 K, and thus no supercavitation is present. In the second case, the NP is heated to and maintained at 1000 K to excite a nanobubble encapsulating the NP.⁸⁰ We note that as long as the supercavitation can be generated, the exact heating temperature of the NP will not influence the conclusion of the simulations. As shown in Figure 33c, the NP is stranded by the liquid interface due to the capillary force. However, when a supercavitation is

generated to encapsulate the NP, the NP can move across the liquid interface without any impedance (Figure 33d). In this case, the NP-liquid separation is achieved when the nanobubble is generated, and when the NP approaches the liquid interface, there is no longer a capillary force holding back the NP from moving out of the liquid. We note that while these simulations are on a simplified model system of NP-in-liquid-argon, the observation should be generally applicable to verify our hypothesis. There are many ways real systems can be more complicated than the model simulated here. For example, strong hydrogen bonds may exist between NP and liquid molecules depending on the NP surface functionalization. We can mimic such stronger interfacial interactions by tuning up the energy constant of the interaction between the NP and the liquid in our simulations. However, after increasing the energy constant of the L-J potential by 10 times, the observation stays the same, i.e., the NP with supercavitation can still escape from the liquid and move into the air. Therefore, it confirms that the thermally excited supercavitation enables the light to separate the NP from liquid and eject it across the air/liquid interface into the air.

To further confirm that the observed laser-driven photo-ejection of Au NPs is due to the supercavitation, we need to exclude the effect of evaporation or boiling of the NP suspension due to the laser-induced volumetric heating,³⁷ which may also spread NPs into air from the suspension droplet (Figure 32). We perform thermofluidic simulations using the finite element method to calculate the steady-state temperature profile of a liquid droplet subject to laser heating due to the light absorption of the suspended plasmonic NPs. The simulation model is shown in Figure 34a, in which a water hemisphere with a radius of 1 mm is used to simulate the suspension droplet in the experiment. The plasmonic volumetric heating following a Gaussian distribution is the heating source in the system with the highest intensity located at the tip of the hemisphere, which mimics the focused laser beam (Gaussian beam) in our experiment.^{2,36,37} The heating power of the system is determined by the laser optical fluence and NP concentration in the suspension. Since the highest temperature should occur at the laser focal spot, *i.e.*, the tip of the droplet, we plot the steady-state surface temperature profile of the hemisphere along the red line indicated in the model shown in Figure 34a to investigate the potential evaporation or boiling effect.



Figure 7.3: Confirmation of supercavitation as the mechanism for the laser-driven photo-ejection of NPs out of the liquid. (a) The geometrical configuration of the model for thermofluidic simulations to calculate the surface temperature profile of an Au NP suspension droplet under the plasmonic volumetric heating effect. The region highlighted in red indicates the region where the plasmonic volumetric heating occurs due to the illumination from a Gaussian beam. The red solid line depicts the arc line along which the surface temperature is visualized. (b) The steady-state surface temperature profiles of the droplet along the arc line in four cases with different optical fluences and NP concentrations to realize different plasmonic heating powers. Different cases are labeled by Roman numbers I-IV. I: 22.8 mJ/cm² and 2.2×10¹⁵ particles/m³, III: 22.8 mJ/cm² and 3.0×10¹⁵ particles/m³, and IV: 5.4 mJ/cm² and 2.5×10¹⁵ particles/m³. The water boiling temperature of 373 K is indicated by a green dashed line. The back-scattered scanning electron microscope (SEM) images for cases (c) II, (d) III, and (e) IV are shown. The insert in (c) highlights an individual Au NP (~120 nm diameter).

Four cases with different heating powers are studied by changing the optical fluence and NP concentration. The temperature profiles of the four cases are plotted in Figure 34b. As expected, all the four cases have a symmetric surface temperature profile with the maxima located in the middle corresponding to the laser focal point. In case I (red dash line in Figure 34b), where the optical fluence and NP concentration are respectively 22.8 mJ/cm² and 2.2×10^{15} particles/m³, the maximum temperature is ~373 K, which is the threshold of water boiling. Case II (black solid line in Figure 34b) uses the same peak optical fluence (22.8 mJ/cm²) but a lower NP concentration of 1.0×10^{15} particles/m³. These parameters are the same as we used in the experiment to visualize the NPs ejection in Figure 32. Because of the lower heating power in case II, the maximum temperature is only \sim 50 $^{\circ}$ C – well below the water boiling threshold. This means the observed Au NPs in air we previously imaged in Figure 32b (right) are not the results of bulk liquid boiling that might spit out small suspension droplets. To further investigate the Au NP photo-ejection mechanism, we placed a thin glass slide at a distance of 0.5 mm away from the tip of the suspension droplet (see Figure 32a), so that the NPs expelled out of the liquid by the laser can be deposited on the slide and then can be visualized using SEM. As the back-scattered SEM image shown in Figure 34c, a large number of individual Au NPs are deposited on the glass slide. The insert in Figure 34c highlights a zoomed view of an individual NP, whose diameter is ~120 nm, and elemental composition confirms that these are Au NPs from the suspension droplet.

As a comparison to case II, which has a maximum surface temperature below the boiling point, we study another case, case III, where the optical fluence is kept at 22.8 mJ/cm², but the NP concentration is increased to 3.0×10^{15} particles/m³. The resulted higher heating power leads to a maximum temperature of ~160 °C, well above the boiling threshold (orange line in Figure 34b). In the experiment with the parameters corresponding to this case, we can also observe NPs deposited on the glass slide, but different from the scattered-distributed individual NPs in case II, we find many small clusters of NPs

deposited on glass slide in case III. The back-scattered SEM image in Figure 34d shows an example of such clusters containing around ~100 NPs. As shown in our previous work,^{1,2} supercavitating Au NPs moving in liquid do not tend to aggregate or form clusters at this concentration. Therefore, when they are ejected out of the liquid interface, they should be deposited individually as we see in case II (Figure 34c). However, when the heating power is sufficiently high to cause the droplet to boil as in case III, there can be tiny droplets splashing out of the suspension droplet. These tiny droplets can contain many NPs, and when they reach the glass slide and dry out, they can leave small clusters of NPs on the glass slide through a contact line deposition mechanism.^{16,163}

While the maximum temperature in case II (~50 °C) is not sufficient for boiling, the elevated temperature can increase evaporation. To ensure such enhanced evaporation cannot cause NPs to escape from the liquid droplet, we study another comparison case IV, where the peak optical fluence is reduced to 5.4 mJ/cm² but the NP concentration is increased to 2.5×10^{15} particles/m³, to still achieve the similar surface temperature as case II (blue solid line Figure 34b). We note that the peak optical fluence of 5.4 mJ/cm² is lower than the supercavitation threshold, 7 mJ/cm², as reported previously.⁵² In this case IV, there is no NP deposited on the glass slide that can be observed in the back-scattered SEM (Figure 34e). This further confirms that supercavitation is the pre-requisite for the laser to expel the NPs out of liquid.

A potential application of this technique using photo-ejected NPs out of liquid is writing NP patterns on the surfaces which are sensitive to liquids. Although different NP deposition methods exist,^{24,36,79} most of them are based on wet processes, which require immersing the surfaces in liquids that contain the target NPs. However, this requirement can induce problems for sensitive materials or devices, such as metals or electronics that cannot be immersed in liquid solvents due to the concerns like corrosion or short-circuiting. Here, we use this photo-ejection enabled NP deposition technique to demonstrate the writing of a ~2 mm-long line of individual Au NPs on a glass substrate by translating the bottom substrate linearly while performing the deposition (see the schematic of setup in Figure 35a and SEM image in Figure 35b). The distance between the bottom glass substrate and the tip of the droplet is ~200 μ m. Under this distance and NP concentration of 1.0×10¹⁵ particles/m³, the deposition rate is around a few hundreds of NPs per minute. It is interesting to see that the deposited NPs are spread out across the width of the written line with a range of ~330 µm as can be seen in Figure 35b. The density of deposited NP increases closer to the center of the written line. We believe the spread of NP is because the NPs are leaving the liquid interface over a range of angles and locations with respect to the laser beam axis. Using the dimensions shown in Figure 35a, we can estimate that the spread angle of the NP deposition is $\sim 39.5^{\circ}$, which is similar to the estimated angle (35.8°) from the dark-field microscopy which tracks the locations of the NPs ejected out of the liquid (Figure 35c).

The $1/e^2$ diameter of the Gaussian source laser beam at the focal point, which is at the tip of the droplet, is ~12 µm, and the spread of the laser beam envelop after exiting the liquid interface is much smaller than the observed spread of the trajectories of NPs coming out of the liquid (Figure 35c). Thus, the cause of the spread in the NP exiting angle is unlikely to be the divergence of the laser beam.



Figure 7.4: NP pattern writing and ejection angle analysis. (a) Schematic of the NPs-line deposition experiment. (b) The back-scattered SEM image of the line of deposited Au NPs on the substrate by the laser with a fluence of 22.8 mJ/cm² and an NP concentration of 1.0×10^{15} particles/m³ in the droplet. The red dashed lines draw the approximated boundaries of the deposited line to guide the eyes. (c) The dark-field microscopy spatial distribution of the NPs photo-ejected into the air region (greyscale). The bright spots (circled in yellow) represent the locations of NPs ejected into air. The calculated 1/e² intensity profile of the Gaussian source laser beam is overlapped in the image. (d) The 3D MD-simulated trajectories of 18 different supercavitating NPs moving from liquid into air (the interface is located at 160 Å).

We believe the spread angle is due to the stochastic nature of the nanobubble formation and the relative position of NP inside the nanobubble. It is known that the nanobubble formation is stochastic as the nucleation of the vapor bubble depends on the local temperature profile and the defects of the NP surface.^{34,164} This can lead to the randomness in the fluidic forces on the NP, which can in turn change its moving direction.^{80,165–167} Moreover, the relative position of NP inside the nanobubble is also stochastic, undergoing ballistic Brownian motion within the bubble,⁸⁰ and the randomness of the NP-bubble position can lead to different optical configurations and thus re-direct the dispersive optical scattering force direction on the NP.^{1,56} Supercavitating NPs can indeed move with some randomness in their directions, although in the long spatial range they still stay within the laser envelope, which is understandable as their movements are driven by the laser. When they approach the liquid interface, the fluctuations in the NP momentum cause deviation from the laser beam focusing axis as they come out of the liquid (see the schematic in Figure 33b). The same phenomena can also be observed in MD simulations where we launch 18 supercavitating NPs one-by-one toward the liquid interface from a distance (~4 nm) away from the interface (Figure 35d). We find that each of the NPs comes out of the liquid interface at a different angle and a different, similar to that observed in our experiments. While NP deposition is demonstrated as an example, there can be other applications using the photo-ejection mechanism of NPs, such as directing NPs across the interfaces between immersible liquids, and selectively ejecting different plasmonic NPs using lasers with wavelengths matching their specific SPR peaks.

7.3 Summary

In conclusion, we have demonstrated laser-driven photo-ejection of plasmonic NPs from liquid, which would not have been possible using conventional body forces. The laser with a wavelength at the SPR peak of the NPs can induce an intense heating effect and form supercavitations. This process achieves the liquid-NP separation via a thermally induced phase change mechanism, and thus when the NPs are driven to the liquid free interface by the optical scattering force, they can move out of liquid without being stranded by the capillary force on the NP surface. Using finite element thermofluidic simulations, we prove that the observed NPs ejected out of liquid do not originate from any boiling or evaporation effect, confirming the supercavitation as the key. The NPs expelled out of liquid by the laser can be deposited on a substrate. By visualizing the deposited NPs, we observed a spreading angle larger than the divergence of the Gaussian laser beam, and this is attributed to the stochastic nature of nanobubble formation and the relative position of NP inside the nanobubble which result in fluctuations in the NP moving direction. This study reveals an interesting mechanism to separate NPs from a suspending liquid environment and could potentially lead to applications that utilize or need NP dry deposition and separation.

CHAPTER 8:

FUTURE WORKS

8.1 Plasmonic Suspended Bubble in NP Suspension

As we introduced in Chapter 1, there are two major types of plasmonic bubbles have been investigated in this work. However, in recent experiments, we observed another type of plasmonic bubble, which is a microbubble with a diameter of tens of micrometers that can be trapped on the upper side of incident laser beam in the bulk liquid of NP suspension. Moreover, the motion of this suspended bubble can be directed by laser at a speed up to ~1 mm/s. Based on our primary study, we believe the trapping and motion of suspended bubble should be attributed to the Marangoni flow around the bubble that induced by the plasmonic heating effect by laser. Therefore, we plan to employ some finite element simulations to reveal the flow filed around the bubble and explain the mechanism behind this phenomenon.

8.2 Molecular Bridge Reduces the Optical Fluence Threshold of Plasmonic Nanobubble Generation

As discussed in previous chapters, supercavitating vapor nanobubbles generated surrounding the plasmonic NPs can benefit a large range of opto-thermal applications, like optically control of NPs motions, surface bubble generation on transparent surface and NP pattern writing. In order to generate supercavitations, a large amount of optical energy is usually used in experiments. For instance, the optical fluence threshold to generate supercavitation on our CS NP is about 7 mJ/cm²,⁵² which corresponds to hundreds of mW laser power. However, according to our calculations, the temperature of the NP under such high laser power is about 1000 K higher than the critical temperature to generate supercavitations.⁵⁷ This means the interfacial heat transfer efficiency between NP and surrounding water layer is not very high. Borrowed the idea in ref.¹⁶⁸, we plan to functionalize the CS NP with molecular functional chemical ligands, i.e., molecular bridges. These molecular bridges can be used to increase the interfacial heat dissipation efficiency, and very likely to reduce the optical energy threshold of supercavitation generation.

8.3 Bubble Nucleation and Growth on Microstructure Surfaces under Microgravity

Understanding the nucleation and growth dynamics of the surface bubbles generated on a heated surface can benefit a wide range of modern technologies, such as the cooling systems of electronics, refrigeration cycles, nuclear reactors and metal industries, etc. Usually, these studies are conducted in the terrestrial environment. As space exploration and economy expanding at an unprecedented pace, the aforementioned applications potentially deployable in space call for the understanding of thermal bubble phenomena in a micro-gravity setting. In this work, we investigate the nucleation and growth of surface bubbles in space, where the gravity effect is negligible compared to ground. We observe much faster bubble nucleation, and the growth rate can be ~30 times

higher than those on ground. Our finite element thermofluidic simulations show that the thermal convective flow due to gravity around the nucleation site is the key that effectively dissipates the heat from heating substrate to the bulk liquid and slows down the bubble nucleation and growth processes. Due to the micro-gravity field in space, the thermal convective flow is negligible compared to terrestrial environment, leading to the localization of heating around the nucleation site and thus enable faster bubble nucleation and growth in space. We also find that bubble nucleation can be influenced by the characteristic length of the nanostructures on the heating surface. The nanostructures behave as fins to enhance the cooling of the surface. With finer nanostructures enabling better surface to liquid heat transfer, the bubble nucleation takes longer.

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