
Plasmon assisted optothermal control and manipulation of colloids and fluids

A thesis

*submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy*

by

Vandana Sharma

(Reg ID: 20163494)



INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH,
PUNE

CERTIFICATE

Certified that the work incorporated in the thesis entitled ("Plasmon assisted optothermal control and manipulation of colloids and fluids") submitted by ***Vandana Sharma*** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

Date: 09th January 2023



(G V Pavan Kumar)
Supervisor

Declaration

I declare that this written submission represents my research work in my own words and where others' ideas or works have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Abstract

Plasmo-fluidics is an emerging field which integrates plasmonics and microfluidics at nano/microscale. Using plasmons, we can confine light to regions beyond the diffraction limit of light. This helps to create strong electric fields in small volumes and also generate heat in the metallic nanostructures because of Joule heating. A fluidic environment on the other hand provides flexibility in designing reconfigurable devices which can be difficult to create in a solid state device.

Herein, we will discuss how light-matter interaction and heat generation in a fluidic environment can be utilized to manipulate and control other dielectric/metallic nanostructures. It can give rise to several thermodynamic processes in the fluid such as thermophoresis, convection, bubble formation and Marangoni flows.

Firstly, we will discuss surface plasmon polaritons assisted assembly of colloids. Typically, colloids undergo diffusive Brownian motion in a fluid. Herein, we modulate the dynamics of the colloids by locally heating metallic nanostructures, such as gold microplate and silver nanowire. The excitation of surface plasmons generates heat in these structures which is subsequently released into the fluid. The resulting temperature gradient created in the system drives the colloids from a random Brownian motion to a directed motion towards the metallic structure. This motion is attributed to thermophoretic migration of colloids. Using this process, we create a long range assembly of colloids whose dimension can be controlled by modulating several parameters such as polarization of the incoming beam, size of the colloids as well as the surface/volume ratio of the heating structure. We also show directional pulling and transport of a single colloid from one location to another by exciting surface plasmon polaritons which are confined quasi-one dimensionally. Next, we focus our attention towards microbubble formation and consequent manipulation of nanostructures. While the above discussed methods work on the basis of thermophoresis, the microbubble based manipulation relies on temperature gradient dependence of the surface tension on the surface of the bubble. The generation of a microbubble creates strong marangoni flows which helps to move the particles at high speeds, which is usually not possible if we rely only on the convection currents induced by heating a nanostructure alone. Finally we will conclude by discussing some challenges in the field and future direction of the work.

List of Publications

Included in thesis:

- **Vandana Sharma**, Sunny Tiwari, Diptabrata Paul, Ratimanasee Sahu, Vijayakumar Chiakkadi and G.V. Pavan Kumar, Superdiffusive pulling, trapping, and assembly of colloids using nanowire plasmons, *Soft Matter* 17(48),10903-10909 (2021)
- **Vandana Sharma**, Diptabrata Paul, Shailendra K. Chaubey, Sunny Tiwari, and G.V. Pavan Kumar, Large-scale optothermal assembly of colloids mediated by a gold microplate, *Journal of Physics: Condensed Matter*, 32(32), 324002 (2020)

Not included in thesis:

- Sunny Tiwari, Utkarsh Khandelwal, **Vandana Sharma**, and G V Pavan Kumar, Single Molecule SERS dynamics in a single nanoparticle driven thermoplasmonic tweezer, *The Journal of Physical Chemistry Letters*, 12(49),11910-11918 (2021)
- Sunny Tiwari, Chetna Taneja, **Vandana Sharma**, Adarsh B. Vasista, Diptabrata Paul, and G V Pavan Kumar, Dielectric microsphere coupled to a plasmonic nanowire: a self-assembled hybrid optical antenna, *Advanced Optical Materials*, 8 (11), 1901672 (2020)

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Dedicated to my parents

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Chapter 1

Introduction

Optical manipulation arises from light-matter interaction wherein light-driven forces are utilized for non-invasive manipulation of matter. Optical manipulation of colloids is an active research area with implications in light-matter interaction studies, including optical trapping [1][2], optical binding [3][4][5], sub-topics of soft-matter physics such as light-driven assembly [6], swarming[7] and locomotion of biological matter in a fluidic environment [8][9].

Conventionally, optical tweezers have been utilized to trap colloidal particles, and biological cells with sizes ranging from nanometre to micrometre scale [10][11]. Optical tweezers can trap objects by using focused laser beams to create a deep potential well through an interplay between scattering and gradient forces [3][4]. Also, it is difficult to trap metallic nanostructures due to their strong absorption and, scattering [12][13]. These methods are generally limited by the number of particles that can be trapped simultaneously. To create large-scale assemblies, we have to look beyond the conventional trapping methods and employ additional forces.

Optothermal manipulation is one such technique which relies on establishing a temperature gradient in the system. Generally, the generation of heat is considered counter-intuitive to the process of trapping, but it can be harnessed for our advantage. Recently, thermoplasmonically driven studies have been conducted to establish temperature gradients in the systems [14][15][16]]. This is achieved by the excitation of a plasmonic structure, which can absorb part of the light and generate heat due to photon–phonon conversion [17][18]. It can give rise to several thermodynamic processes in the fluid, such as thermophoresis, convection [19], bubble formation [20][21][22] and Marangoni flows[23][24]. However, designing a general platform for optothermal manipulation still remains challenging.

Through this introductory chapter, we will try to take the reader through a broad overview of the important topics required to understand the rest of the thesis. Firstly, we will go through the basics of plasmonics and the associated heat that can be generated in such a system. Next, we will touch upon conventional as well as plasmon-assisted

optical trapping. The final step is to merge both the heating effects of plasmonics and optical trapping to realize optothermal control and trapping of colloids.

1.1 Interaction of light with metallic nanostructures

1.1.1 Surface plasmons

When an electromagnetic wave interacts with a metallic nanostructure, the free electrons of the metal start oscillating at the frequency of the input light. This collective oscillation of free electrons in a metal is termed as plasmons[25][26]. The light-matter interaction can be tailored by modifying the geometry of the structure for targeting specific applications. We can broadly classify plasmons into two categories: Localized surface plasmons (LSPs) and Surface plasmon polaritons (SPPs).

Localized Surface Plasmons: When a nanostructure whose size is less than or comparable to the wavelength of the input light is illuminated, the conduction electrons oscillate with the frequency of the incoming electromagnetic wave. When the frequency of the incoming light is close to the natural frequency of the plasmons, it results in a localized plasmon resonance[27][28] (figure 1.1). A high density of optical states near the plasmonic structure leads to the enhancement of the electric field, higher absorption and emission of light and heat dissipation due to joule heating.

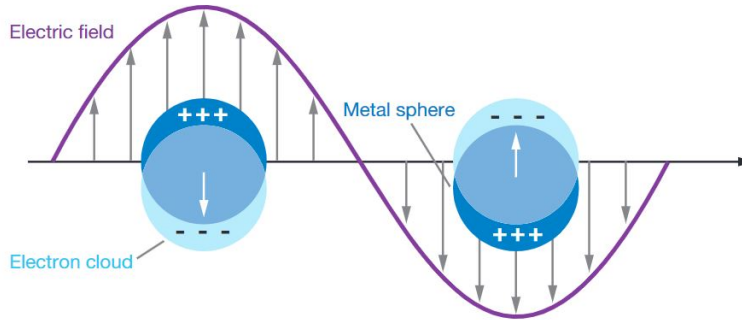


FIGURE 1.1: Schematic showing the localized surface plasmons in a metallic nanoparticle. Figure adapted from [27] with permission.

Surface plasmon polaritons: are collective oscillations of free electrons and photons at a metal-dielectric interface[25][29][26]. One component of the SPPs is evanescently confined in the perpendicular direction. One dimension of the nanostructure has to be greater than the wavelength of the input light. One of the main advantages of SPPs is their ability to confine light beyond the diffraction limit, allowing for sub-wavelength manipulation. There are several methods for generating SPPs, including

prism coupling, grating coupling, and focusing highly collimated optical beams onto the nanostructure. These configurations have been detailed in[29]. Figure 1.2 (a) shows the surface plasmon propagation at the interface of a metallic and a dielectric surface. The SPPs suffer losses while propagating and gradually attenuate after a certain distance known as its propagation length δ_{SPP} , which depends on the dielectric permittivity of the metal defined as[26]:

$$\delta_{SPP} = \frac{1}{2k''_{SPP}} = \frac{c}{\omega} \left(\frac{\epsilon'_m + \epsilon_d}{\epsilon'_m \epsilon_d} \right)^{\frac{3}{2}} \frac{(\epsilon'_m)^2}{\epsilon''_m} \quad (1.1)$$

where, k''_{SPP} is the imaginary part of the complex wavevector of the SPP. ϵ'_m and ϵ''_m are the real and imaginary part of the complex dielectric function of the metal. ϵ_d is the permittivity of the dielectric material.

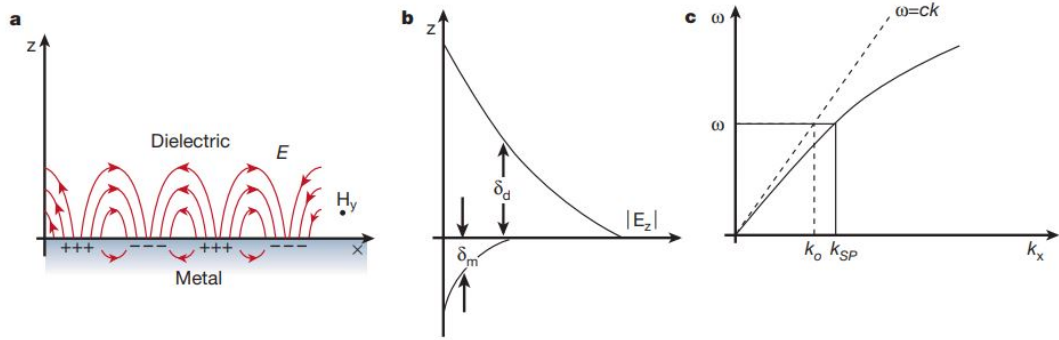


FIGURE 1.2: Surface plasmon polaritons at the interface of a metal and a dielectric medium (a) The field component perpendicular to the surface is enhanced and decays exponentially with distance. (b) The decay of the evanescent field in the metal and dielectric medium. (c) Momentum mismatch problem when coupling light to the metallic structure. Figure is reproduced from [30] with permission.

The fields also decay perpendicular to the surface into the metallic as well as dielectric media. Figure 1.2 (b) shows these evanescent decaying components. δ_d and δ_m are the decay lengths in the dielectric and metallic media, respectively. δ_d is of the order of half the wavelength of light, and δ_m is determined by the skin depth of the metal. Figure 1.2 (c) shows the dispersion curve of the SPPs. The problem of momentum mismatch and how to overcome it will be detailed in the next chapter.

1.1.2 Heat generation in a metallic nanostructure

For several decades, plasmonics has primarily focused on specific areas such as optical antenna[31], modulation of molecular fluorescence[32][33], surface-enhanced Raman scattering[34], non-linear optics[35] to name a few. However, some part of optical energy also gets dissipated as heat which can be undesirable for above mentioned applications. Plasmonic losses can either be enhanced or reduced depending on the application that is targeted. Thermoplasmonics deals with utilizing the heat dissipation in plasmonic nanostructures to our advantage by remotely controlling the thermally induced phenomena at nanoscale[36]. Before going into details about its applications, first, let us look at the physics of plasmonic heating.

Let us consider a metallic nanoparticle with complex permittivity $\varepsilon(\omega)$ illuminated with an electromagnetic wave with frequency ω . Upon illumination, the free charges of the nanoparticle start oscillating at the input frequency. This electronic oscillation generates heat via Joule heating. The heat power density can thus be defined as:

$$q(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) \quad (1.2)$$

where $\mathbf{J}$ is charge per unit area per unit time and $\mathbf{E}$ is the electric field inside the nanoparticle. Since, $\mathbf{J} = -i\omega\mathbf{P}$ and $\mathbf{P} = \varepsilon_0(\varepsilon - 1)\mathbf{E}$, the heat power density can be described as:

$$q(\mathbf{r}) = \frac{\omega}{2}\varepsilon_0 \text{Im}(\varepsilon)|\mathbf{E}(\mathbf{r})|^2 \quad (1.3)$$

The heat generated thus depends on the square of the electric field inside the structure, which depends on the size and shape of the nanoparticle. The total heat delivered by the nanoparticle can be derived by integrating over its volume:

$$Q = \frac{\omega}{2}\varepsilon_0 \text{Im}(\varepsilon_\omega) \int_V |\mathbf{E}_\omega|^2 d\mathbf{r} \quad (1.4)$$

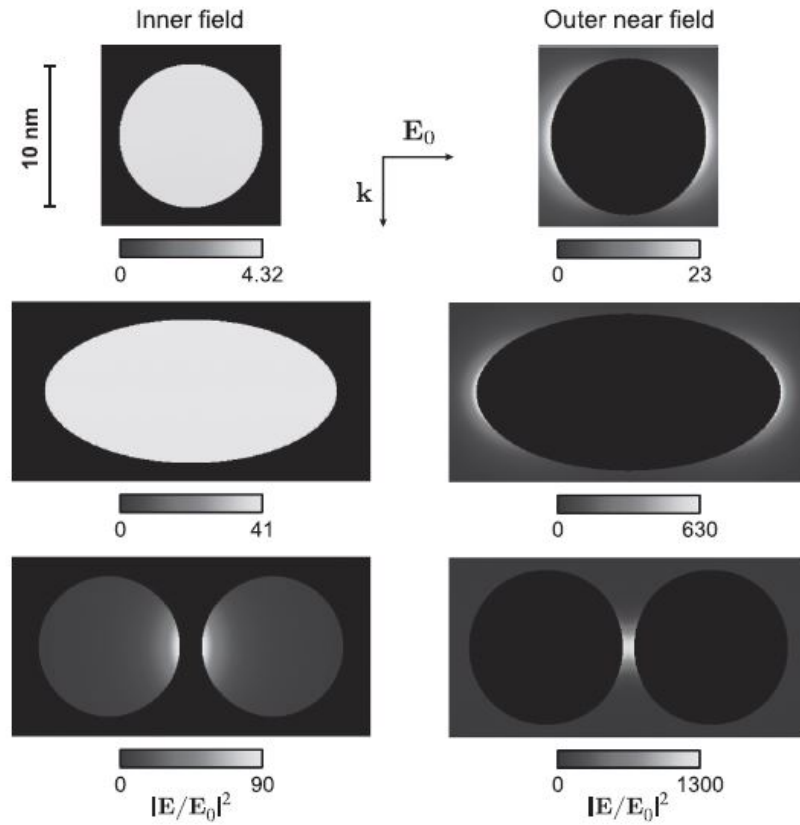


FIGURE 1.3: Normalized near field electric field for a 10 nm gold nanoparticle, a 10 nm wide and 20 nm long ellipsoid and a dimer. The figure is adapted from [17] with permission.

The distribution of the electric fields can be very different inside and outside the nanoparticle. When we talk about the enhancement of the electric field in the context of thermoplasmonics, we intend to enhance the electric field inside the nanostructure. Figure 1.3 shows the electric field near field intensities for different configurations of gold nanostructures. In the case of a dimer, the electric field is more intense between the gap. We know that the heat is generated due to electric field intensity inside the nanostructure where charges can flow freely. For this very reason, another important point to be noted is that optical hotspots do not always coincide with the thermal hotspots[37]. If we have a dimer where an optical hotspot is generated between the two nanoparticles, it would not necessarily translate to a thermal hotspot [37].

1.1.3 Heat transfer to the surrounding area

Once the heat is generated in a nanoparticle, it will be dissipated into the surrounding environment. This dissipation can happen through three channels, namely, *diffusion*,

radiation and convection. The primary source of heat transfer in plasmonics is diffusion and we will be discussing that in greater detail.

Diffusion

The heat generation inside the nanoparticle is much faster ($\approx$ ps) compared to its dissipation to the surroundings ($\approx$ ns– μ s) depending on the characteristic size of the system. The differential heat diffusion equation is given by:

$$\rho(\mathbf{r})c_p(\mathbf{r})\partial_t T(\mathbf{r}, t) - \nabla \cdot (\kappa(\mathbf{r})\nabla T(\mathbf{r}, t)) = q(\mathbf{r}, t) \quad (1.5)$$

where, ρ is the density, κ is the thermal conductivity of the medium, c_p is the specific heat at constant pressure. When the medium is uniform, κ is constant and the resulting equation becomes:

$$\rho c_p \partial_t T - \kappa \nabla^2 T = q \quad (1.6)$$

In thermoplasmonics, the nanostructure is usually immersed in a fluidic environment such as water. In this context, the heat diffusion equation can be solved in two parts. First, we solve the heat diffusion equation for the nanostructure.

When considering a continuous wave illumination, a *steady state* is established, and the above equation can again be simplified by removing the dependence of temperature on time.

The resulting equation becomes:

$$-\kappa \nabla^2 T = q \quad (1.7)$$

For a spherical nanoparticle, the heat diffusion equation becomes:

$$-\kappa \frac{1}{r^2} \partial_r (r^2 \partial_r T) = q \quad (1.8)$$

The above equation can be solved for temperature yielding:

$$T(r) = \frac{Q}{4\pi\kappa_s a} + T_\infty \quad (1.9)$$

where, Q is the total heat delivered by the nanoparticle, κ_s is the thermal conductivity of the surrounding medium, a is the radius of the nanoparticle and T_∞ is the ambient temperature. So, while the heat distribution inside the nanoparticle can vary significantly at different locations, the temperature essentially remains constant due to the high thermal conductivity of the metal.

Since there is no heat source outside the nanoparticle, the heat diffusion equation becomes:

$$\partial_r (r^2 \partial_r T) = 0 \quad (1.10)$$

By solving for temperature, we get the temperature at a distance r as:

$$T(r) = \frac{Q}{4\pi\kappa_s r} + T_\infty \quad (1.11)$$

So, the temperature inside the nanoparticle remains constant and then falls as $1/r$ outside of it.

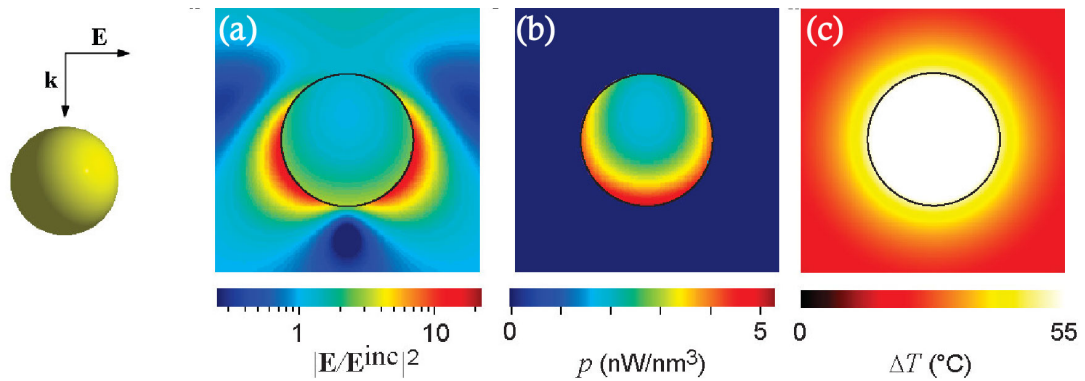


FIGURE 1.4: Heating of a 100 nm gold sphere immersed in water incident with the light of wavelength 530 nm at intensity $1 \text{ mW}/\mu\text{m}^2$. (a) Electric field near field intensity. (b) heat generation density (c) Increment in the temperature at equilibrium. The figure is adapted from [38] with permission.

As shown in figure 1.4(a), a 100 nm gold sphere is illuminated with a light of wavelength of maximum absorption at 530 nm. The electric field near field distribution, power density and increase in the temperature are shown. We can see that even though the distribution of the electric field and power density is non-uniform, the temperature of the gold sphere is uniform due to the high thermal conductivity of the gold. For complicated geometries, analytical solutions are not possible and numerical simulations involving finite element method, finite difference time domain methods, to name a few, can be solved.

Convection

Convection refers to heat transport via fluid flow. A bulk movement of the fluid is involved in the heat transfer mechanism. When convection is the driving mechanism for heat transfer, although the initial heat transfer is characterized by conduction from the

heat source to the surrounding fluid, the bulk transfer of heat happens through the mass transport of the fluid. It can be broadly classified into two categories, namely natural convection and forced convection.

Natural convection: When a fluid is heated from below, its temperature increases which leads to its thermal expansion. Upon thermal expansion, the hotter layer of the fluid becomes less dense, as a consequence it rises up due to buoyant forces and its place is taken by the heavier, colder layer of fluid from the top. The whole process repeats again when the lower layer again gets heated up and the fluid is continuously circulated in the system. Though less common, it can also be induced by surface tension.

Forced convection: When an external source (such as fan, pump etc.) is used to induce convection in a system, it is called forced convection.

At the macroscopic scale, convection is usually the dominant mechanism of heat transfer. However, at microscopic length scales such as the ones we are dealing with in thermoplasmonics, this is no longer the case. Rayleigh number (Ra) can be used to determine whether heat diffusion or convection effects will dominate. If $Ra \ll 1$, heat diffusion is the dominant mode of heat transfer and if $Ra \gg 1$, convection is the main source. Usually, we are dealing with nanostructures embedded in water as the fluid medium. Due to low Rayleigh number of water at microscopic scales, i.e. $Ra \ll 1$, convection can be mostly ignored and diffusion is the main driving force for heat transport[15].

Radiation

Thermal radiation constitutes the emission of electromagnetic waves from a body that has a temperature above an absolute temperature of 0 K. Since matter is composed of atoms and molecules, which are further constituted by charged particles like electrons and protons, the interaction between these particles leads to charge acceleration which generates electromagnetic waves, i.e. photons away from the body. Radiative heat transfer does not need the presence of a medium and can transmit through vacuum as well. The radiation does not consist of a single frequency, but rather a broad range of frequencies comprising a characteristic spectrum. The frequency distribution is governed by Planck's law. The thermal radiation power u_ν per unit surface area, per unit of solid angle and per unit frequency ν at absolute temperature T is given by:

$$u_\nu(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/(k_B T)} - 1} \quad (1.12)$$

where h is the Planck constant, k_b is the Boltzmann constant, c is the speed of light in the medium.

Integrating the above equation over ν , the total power emitted by the body is given by

the Stefan-Boltzmann law:

$$P = \sigma AT^4 \quad (1.13)$$

where σ is the Stefan-Boltzmann constant and A is the surface area of the radiating body.

In thermoplasmonics, where the metallic nanostructure is immersed in liquid, the transfer of thermal energy through radiation is negligible and can be ignored for all practical purposes.

1.2 Optical trapping

Due to the invention of lasers in the 1960s, the trapping of microscopic objects was made feasible by Ashkin et al.[2][8]. Since then, optical trapping methods have opened up many exciting avenues for scientists, like trapping objects from sub-nanometre to micrometre scale[39][40], cooling and trapping of neutral atoms[41][42][43] dynamics of biological systems[44][45][46] and many more. This significant feat was achieved by utilizing optical forces exerted by light on particles of interest through the conservation of electromagnetic and mechanical momentum.

Essentially, an optical tweezer consists of a tightly focused laser beam which can hold tiny objects in three dimensions[47]. In laboratories, it is achieved by focusing the laser to a diffraction limited spot using a high numerical aperture objective lens. The fluidic sample is enclosed in a spacer held on a microscope stage. The stage can be motorized for precise handling and displacement of tweezed particles. Usually, a Gaussian beam (TEM_{00}) is used in trapping experiments, although nowadays higher order beams are also used quite extensively[48]. The focused laser provides gradient force towards the laser focus and a scattering force in the direction of laser propagation. This creates an attractive potential well, so when a particle is slightly pushed away from the trap, it experiences an attractive force towards the centre. The microscopic objects are also under constant Brownian motion, so the depth of the optical potential should be a few k_bT , where T is the room temperature.

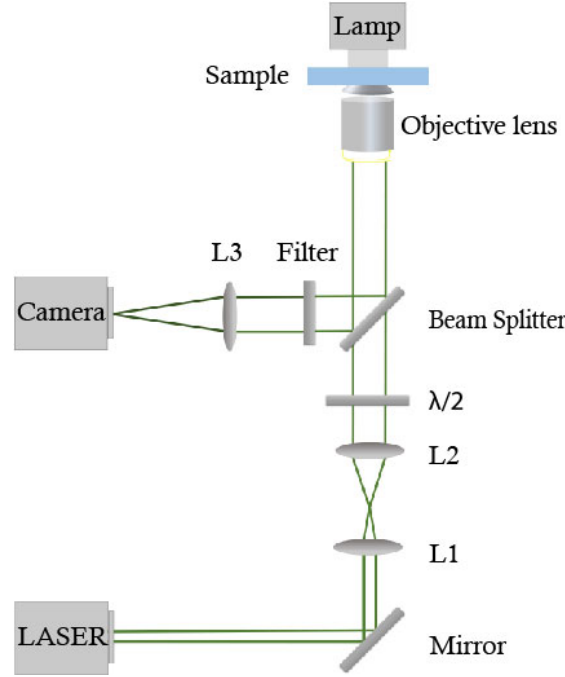


FIGURE 1.5: Schematic of a typical optical tweezer setup.

A schematic of a typical optical tweezer that can be utilized to trap particles is shown in figure 1.5. It commonly consists of a focused laser beam of suitable wavelength and a microscope equipped with a camera to observe and record the motion of the particles. The laser beam is focused onto the sample using a high numerical aperture objective lens. In this figure, an inverted microscope is shown. An inverted microscope is a type of microscope where the objective lenses are below the stage and the light source is above the stage. In this configuration, the specimen is mounted on the stage above the objective lenses and is viewed from below. Inverted microscopes are commonly used in research for observing samples in fluids.

To understand optical forces on nanostructure, the size of the object relative to the wavelength of the particle has to be considered[47]. Accordingly, different trapping regimes can be defined. When the size of the particle $d \ll \lambda$, a Rayleigh or dipole approximation can be applied. When $d \gg \lambda$ the optical forces can be described through ray or geometrical optics. But when the dimension of the particle is comparable i.e. $d \approx \lambda$, the particle can not be approximated by a dipole and a full electromagnetic scattering theory is required.

Let us consider these cases one by one.

1.2.1 Geometrical optics $d \gg \lambda$

When the size of the structure is much larger than the wavelength of the light, the trapping of the particle can be explained by considering the ray optics. Let us assume

that a particle with a refractive index n_p is immersed in a medium with the refractive index n_m . The laser light is decomposed into a set of rays as shown in figure 1.6, which impinges on a dielectric bead. The ray gets reflected as well as refracted upon hitting the dielectric bead. The ray gets refracted from the first surface and then upon exit from the second surface of the structure. This results in a change in the momentum of the light, and as a result of Newton's third law of motion, the particle experiences a momentum change in the opposite direction. However, it is to be noted that a particle can not be trapped by a single ray alone as it will continually push the particle in the direction of the incoming beam. To resolve this, a counter-propagating beam of light may be used. A counter to this method is to use a highly focused light beam using a high-NA objective lens, the light that originates from the opposite ends of the lens converges the light to a tight spot. Most often, a Gaussian beam is used in the trapping experiments, which has a maximum intensity at the centre of the beam. The intensity profile of a Gaussian beam is given by[49]:

$$I(r, z) = I_0 \left(\frac{w_0}{w(z)} \right)^2 \exp \left(\frac{-2r^2}{w(z)^2} \right) \quad (1.14)$$

where r is the radial distance from the centre of the beam, z is the axial distance from the waist or focus of the beam, w_0 is the radius of the waist, and w_z is the radius at which the intensity falls to $1/e^2$ of its axial value. Figure 1.6 shows the force acting on a dielectric particle when it is placed in a homogeneous field, a Gaussian beam and a focused Gaussian beam.

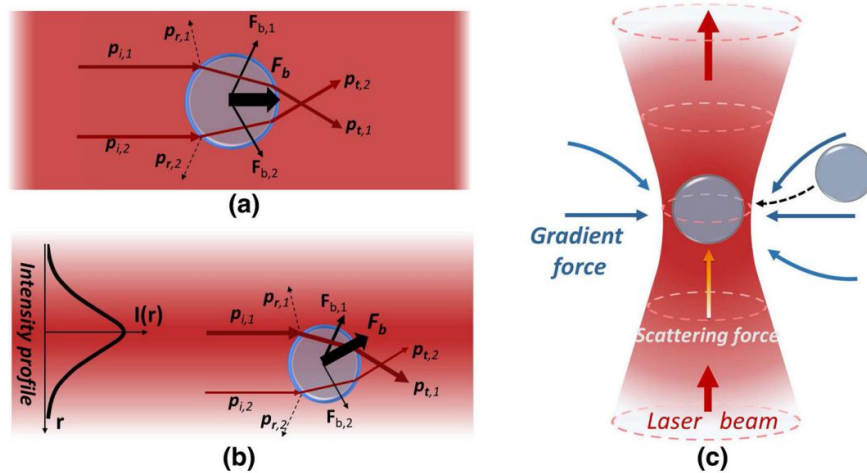


FIGURE 1.6: Schematic of the optical forces acting on a spherical particle in ray optics approximation when it is placed in a (a) homogeneous field. (b) Gaussian beam (c) focused Gaussian beam. The figure is adapted from [50] with permission.

The resulting trap becomes a three-dimensional potential well. Whenever the particle displaces slightly away from the centre of the beam, the refracted beams create a restoring force proportional to the displacement towards the centre of the beam:

$$F \approx -k_{x_i}(x_i - x_{ieq}) \quad (1.15)$$

where x_i can be x, y or z respectively and k_i is the corresponding trap stiffness. In order for a trap to stay stable, the gradient force should overcome the scattering force, which results from the reflection of photons.

It is also important to calibrate the optical trap carefully to accurately determine the trap stiffness, which is a measure of the trap's ability to hold onto a particle. There are several methods that have been developed for calibrating optical traps. One common method is the equipartition method which as the name suggests involves the equipartition theorem. In order to properly utilize the equipartition method for calibrating an optical trap, it is necessary to first measure the position variance of the trapped bead. This can be done by tracking the particle's position within the trap using a high speed camera or other imaging system. The position variance can then be used to calculate the trap stiffness along the x and y-axis. It is important to note that the equipartition method is only valid for small oscillations and may not provide accurate results for larger amplitudes. Another methods such as power spectrum analysis, autocorrelation analysis, mean squared displacement analysis can also be applied to confirm the measurement and ensure the quality of the data. [51] [52].

1.2.2 Dipole approximation: $d \ll \lambda$

When the size of the structure is much smaller than the wavelength of the trapping beam, the particle can be essentially considered as a point dipole and its interaction with the electromagnetic field intensity can be used to understand the optical force acting on the particle. We start by considering the Lorentz force acting on the dipole in an electromagnetic field given by:

$$\begin{aligned} \vec{F} &= (\vec{p} \cdot \nabla) \vec{E} + \frac{d\vec{p}}{dt} \times \vec{B} \\ &= \alpha \left[(\vec{E} \cdot \nabla) \vec{E} + \frac{d\vec{E}}{dt} \times \vec{B} \right] \end{aligned} \quad (1.16)$$

where $\vec{p}$ is the dipole moment of the particle, $\vec{E}$ and $\vec{B}$ are the electric and magnetic fields respectively, also it is assumed that the particle is in the linear response regime, i.e. $\vec{p} = \alpha \vec{E}$.

By using:

$$(\vec{E} \cdot \nabla)\vec{E} = \nabla \left(\frac{1}{2}E^2 \right) - \vec{E} \times (\nabla \times \vec{E}) \quad (1.17)$$

and Faraday's law:

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (1.18)$$

The resultant equation can be written as:

$$\vec{F} = \alpha \left[\frac{1}{2} \nabla E^2 + \frac{d}{dt}(\vec{E} \times \vec{B}) \right] \quad (1.19)$$

Now, we take a temporal average over the electromagnetic field oscillation period. The second term in the above equation is some constant of the Poynting vector and since the field oscillates too rapidly, this term turns out to be zero and the time-averaged optical force can be written as:

$$\vec{F}_{gradient} = \frac{1}{2} \alpha \nabla |E|^2 \quad (1.20)$$

Rewriting in terms of intensity:

$$\vec{F}_{gradient} = \frac{1}{2} \frac{\alpha}{c\epsilon_0} \nabla I \quad (1.21)$$

This equation shows that when a particle has a positive polarizability, i.e. when a particle has a higher refractive index than the surrounding medium it is attracted towards the regions of highest light intensity and when the particle has a lower refractive index than that of the surrounding medium it is expelled from high-intensity regions.

To a first approximation, equation 1.14 can be written as:

$$I(\rho) = I_0 \exp \frac{-2\rho^2}{w_0^2} \quad (1.22)$$

where ρ is the radial coordinate, I_0 is the maximum intensity of the beam and w_0 is the waist of the beam.

When a particle displaces by a small amount:

$$I(\rho) \approx I_0 \left(1 - \frac{2\rho^2}{w_0^2} \right) \quad (1.23)$$

Now the gradient force can be rewritten as:

$$\vec{F}_{gradient} = -k_\rho \rho \quad (1.24)$$

where

$$k_\rho = 2 \frac{\alpha}{c\epsilon_0} \frac{I_0}{w_0^2} \quad (1.25)$$

The trap stiffness is proportional to the light intensity and to the real part of the polarizability. Also, it is inversely proportional to the beam area, indicating that a small beam area or a tighter focusing will give rise to a stronger trap.

In addition to the gradient force, a scattering force also acts on the dielectric particle. Again, under Rayleigh approximation, the scattering force acting on the particle can be written as:

$$\vec{F}_{\text{scat}}(\mathbf{r}) = \frac{k^4 \alpha^2}{6\pi c n_0^3 \epsilon_0^2} I(\vec{r}) \hat{z} \quad (1.26)$$

This scattering force acts in the direction of beam propagation.

1.2.3 When $d \approx \lambda$

When the size of the particle is comparable to the wavelength of the trapping beam, neither ray optics nor dipole approximation can be applied. In such a scenario, Maxwell equations with appropriate boundary conditions have to be solved.

1.3 Plasmon-assisted trapping

Surface plasmon engineering based optical traps have turned out to be very promising in trapping particles which can not be usually trapped through conventional means. Surface plasmons offer advantages in two contexts:

- (i) they are confined close to the surface of the metallic structure, and
- (ii) the wavelength of the surface plasmons is less than that of the free space wavelength.

These characteristics enable intense localization of the electromagnetic field into subwavelength regime which can enhance the lateral confinement of the potential. While dielectric particles are easier to trap because of negligible scattering forces, metallic particles are more challenging to trap owing to their strong absorption and scattering.

The plasmon resonances of these metallic nanostructures have been employed to trap them efficiently. Additionally, patterned plasmonic structures on dielectric materials such as gold nanopads[53][54], thin films[55][56], nanoapertures[57][58][59], nanoantennas[60][61][62] have also been utilized. Figure 1.7 shows some of the plasmonic based optical trapping platforms.

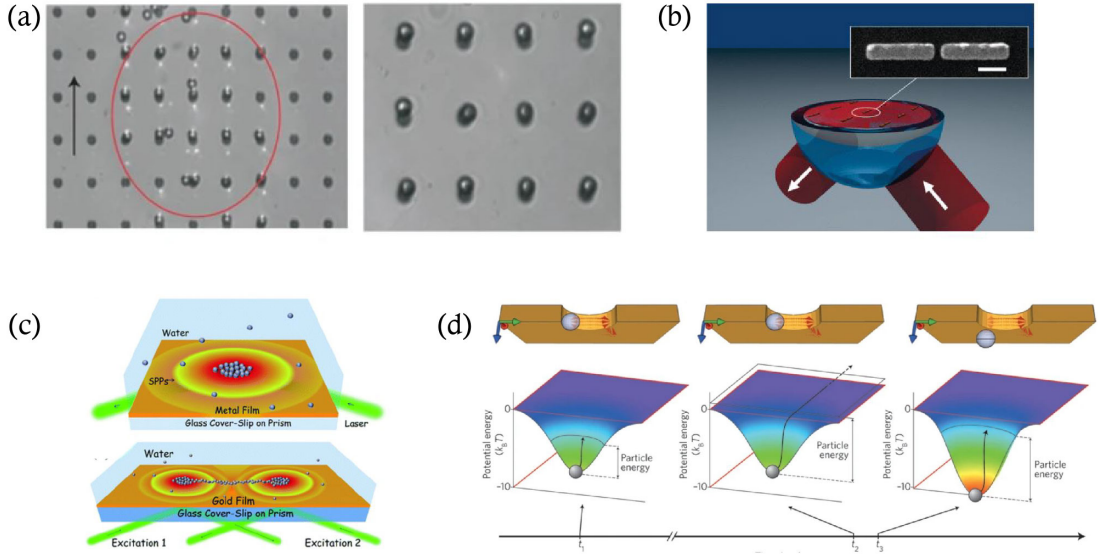


FIGURE 1.7: Plasmon-assisted traps based on (a) nanopads (b) nanoantenna (c) thin film (d) nanoaperture. The figure is adapted from (a) [53] (b) [60] (c) [56] (d) [63] with permission.

While plasmonic based platforms have advanced significantly, there is a cost to pay in terms of heat that is generated by these nano/microstructures. As the nanostructure gets heated, the trap becomes more unstable and higher laser powers might be required to trap these objects. While the heating effect is generally considered detrimental in surface plasmons based trapping and wave-guiding experiments, researchers have been working to utilize these to one's advantage. This has given rise to a new subset of studies collectively termed as thermoplasmonics[17]. The temperature related effects have been applied to certain applications such as photothermal imaging and therapy[64], cancer therapy[65] and so on. A variety of photothermal effects can be realized during thermoplasmonic heating and we will be reviewing them in some detail in the next section.

1.4 Photothermal effects and trapping

Now that we have covered the background for surface plasmons and associated optical as well as plasmon assisted trapping we can combine the two and look at secondary effects generated by heating in plasmonic structures and how they can be utilized to trap nano/ microstructures. Some of the commonly observed phenomena are thermophoresis, thermoelectricity, thermoosmosis, marangoni convection, depletion, and

photophoresis.

1.4.1 Thermophoresis

Thermophoresis is an interfacial phenomenon wherein particles show preferential motion under a temperature gradient[66][67]. These temperature gradients can be setup in a system through plasmonic heating. As we know, particles in a fluid are under constant Brownian motion, thermophoresis imposes an additional drift on the motion of these particles as a result of which the particles can go either from hot to cold or cold to hot region depending on its Soret coefficient. Thermophoresis has been used as one of the particle manipulation technique[14][9][68].

For such a system, the mass flux is given by[69]:

$$J = -D\nabla c - cD_T\nabla T \quad (1.27)$$

where J is the mass flux, D is the Brownian diffusion coefficient, c is the concentration gradient of the particles, D_T is the thermal diffusion coefficient or more rightly can be called as thermophoretic mobility. The associated thermophoretic velocity is described as:

$$v_T = -D_T\nabla T \quad (1.28)$$

Under steady-state profile when the net flow of mass is zero J :

$$\frac{-\nabla c}{c} = \frac{D_T}{D}\nabla T \quad (1.29)$$

$\frac{D_T}{D}$ is defined as the Soret coefficient S_T . Soret coefficient compares the strength of thermophoresis to normal diffusion defined by the Einstein coefficient D . This gives:

$$\frac{-\nabla c}{c} = S_T\nabla T \quad (1.30)$$

If $S_T > 0$, the particles move from hot to cold region and if $S_T < 0$, particles migrate from colder to hotter region. Thermophoresis has been studied experimentally in liquids using DNA strands[70], colloids[71] and molecules[67][72]. The sign of the Soret coefficient can depend on several factors such as particle size, ph of the solution, size of the particle, salinity, and particle concentration. A number of techniques such as Laser beam deflection, thermal diffusion forced Rayleigh scattering, fluorescence microscopy, and thermal lensing have been employed to the study the Soret effect. Some of the

proposed mechanisms to explain the intricate physical and chemical processes involved in thermophoresis are:

- Thermoosmosis
- Thermoelectric effect
- Dispersion forces

One or more of these processes can contribute to thermophoresis. Let us look at a brief overview of these mechanisms.

1.4.2 Thermoosmosis

When a colloidal particle is dispersed in a fluid, charges (positive or negative) are likely to appear on its surface. As a result, there is an accumulation of counterions in the vicinity of the colloid's surface, whose concentration gradually decreases as we go away from the surface[69][73]. These two layers of positive and negative charges surrounding the colloid is known as electrical double layer. The potential difference between these two layers is called zeta potential, ζ . The densities of the positive and negative ions differ from the bulk value. As shown in figure 1.8, suppose the surface of the colloid is negatively charged. As the first layer of ions is thin and the second layer of counterions is much thicker, the total charge of the ions near the colloid $n_+ + n_-$ is positive and an additional pressure $P = (n_+ + n_-)k_bT$ develops which is positive. The distribution of these ions in local equilibrium is given according to the Poisson-Boltzmann expression:

$$n_{\pm} = n_0 \left(e^{\mp e\psi/k_B T} - 1 \right) \quad (1.31)$$

where n_0 is the bulk density of the ions, ψ is the electrostatic potential.

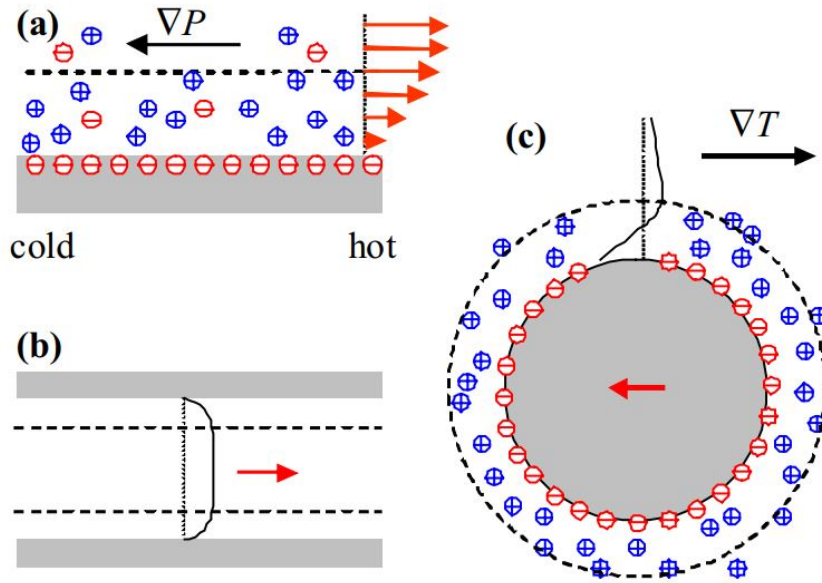


FIGURE 1.8: Thermosmotic flow in the electric double layer driving the colloid from hot to cold regions. (a) Thermally-induced flow in the electric double layer near a negatively charged surface is known as thermosmotic flow. The pressure within the boundary layer is slightly higher at the cold side and drives the charged liquid towards the warm side. The velocity profile of this flow reaches its maximum value beyond the screening length, which is indicated by the dashed line. (b) The solid line indicates the velocity profile of thermophoresis along the charged walls, which drives the fluid towards the hot end of the microchannel. (c) The movement of a charged particle in a temperature gradient is shown by the solid line in the figure. The particle moves towards the left and the flow direction changes within the boundary layer. The velocity of the fluid reaches its maximum beyond the screening length and then decreases as the distance increases. Figure is reproduced from [69] with permission.

Under a temperature gradient ∇T , the pressure varies along the boundary of the colloid. The pressure is higher towards the cold surface. Due to a gradient in the osmotic pressure, there is a flow of fluid from lower to higher temperature and consequently the colloidal particle is dragged in the opposite direction i.e. towards the lower temperatures with a velocity:

$$\mathbf{u} = -\frac{\varepsilon \zeta^2}{3\eta} \frac{\nabla T}{T} \quad (1.32)$$

where, ε and η are the permittivity and the viscosity of the fluid. The quadratic dependence of the zeta potential, ζ was first established by Ruckenstein[74].

1.4.3 Thermoelectric effect

According to Ruckenstein's model, all colloidal particles should move from hotter to colder regions. We know experimentally that under a temperature gradient, colloids also move from cold to hot regions which can not be accounted for by the above model. Hence, other mechanisms are needed. Additionally, we consider the thermoelectric response of the dissolved ions in the solution. Under a temperature gradient, these ions can move with different strengths and sometimes in the opposite directions. The different Soret coefficient of the positive and negative ions, results in charge separation which in turn generates an electric field within the system[69]. In steady state, thermoelectric field is given by:

$$E_T = \frac{k_B T \nabla T}{e} \frac{\sum_i Z_i n_i S_{Ti}}{\sum_i Z_i^2 n_i} \quad (1.33)$$

where, e is the charge, i are the ionic species, Z_i is the charge number, n_i is the concentration of ions and S_{Ti} is the Soret coefficient of different species. This is also known as electrolyte Seebeck effect in analogy with solid state physics. The thermoelectric velocity in this case is given by:

$$\mathbf{u} = -\frac{\varepsilon \zeta \psi_0}{\eta} \frac{\nabla T}{T} \quad (1.34)$$

The sign of the velocity depends on the zeta potential, the thermopotential parameter ψ_0 which may take either positive or negative sign. If, thermoelectric velocity is more than Ruckenstein velocity, the particle may drive towards hotter regions.

1.4.4 Dispersion forces

The London dispersion forces are the Van der Waals forces that arise due to instantaneous dipole – induced dipole interaction. Upon heating, the density profile of the fluid becomes inhomogeneous due to thermal expansion of the fluid[17][69].

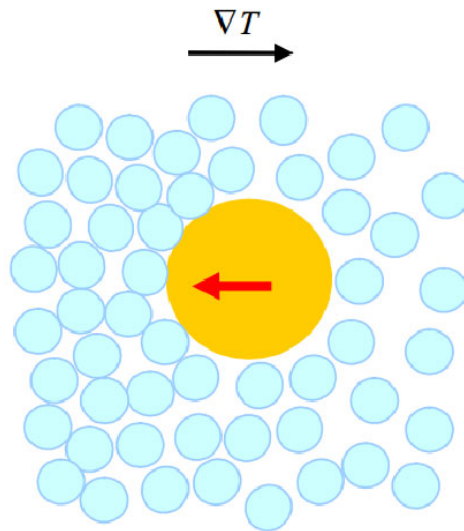


FIGURE 1.9: Due to the non-uniform density of the fluid, the dispersion forces attract the colloid towards the colder side. Figure is adapted from [69] with permission.

The fluid is strongly bound to the colloidal particle at the colder side due to stronger Van der Waals interaction. As a result, the fluid moves along the colloid's surface to the hotter side. This in turn causes the colloid to move in the opposite direction.

The velocity is given by:

$$\mathbf{u} = -\frac{2\beta H}{9\pi\eta d_0} \nabla T \quad (1.35)$$

where β is the thermal expansivity of the fluid, H is the Hamaker constant of the colloid-fluid interaction and d_0 is the molecular length scale.

1.4.5 Marangoni convection

Marangoni convection results from surface tension gradients in the system[75][23][76][77]. The surface tension gradients can be generated either by the gradients in chemical composition of the solvent, concentration of species, or temperature distribution at the interface between two phases, usually liquid-air. When the surface tension varies with the temperature, the effect is usually termed as thermocapillary effect. The heat generation in plasmonics can lead to microbubble formation. These microbubbles can be produced either through continuous wave illumination or pulsed illumination. Figure 1.10 shows some examples of bubble formation. Under a temperature gradient along the liquid-air interface, consequent surface tension gradient also changes which gives rise to the Marangoni flows in the system.

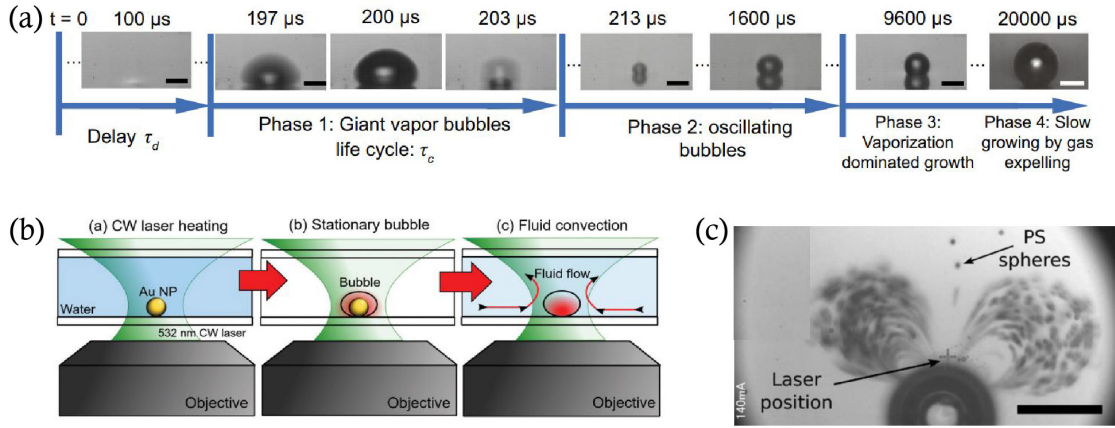


FIGURE 1.10: Bubble dynamics (a) Evolution of a plasmonic bubble under continuous wave illumination at 83 mW input power. (b) Schematic of the Marangoni flow around a microbubble generated over a Au nanoparticle coverslip. (c) Marangoni flow around a microbubble generated over a local plasmon resonator. Figures are adapted from (a)[78] (b) [77] and c[23] with permission.

1.5 Outline of the thesis

This thesis focuses on combining plasmonics and trapping methods to realize optothermal control and trapping of colloidal matter in a fluid environment. Surface plasmons are excited on an extended two dimensional gold microstructure and one dimensional silver nanowire. This leads to both absorption of incident light as well as photon-phonon conversion which sets up a temperature gradient in the system. As explained in the previous section, a number of complex photothermal effects are associated with the heating of a plasmonic system. In this work, we particularly utilize thermophoresis and Marangoni convection for colloidal manipulation. The thesis is divided into following sections:

Chapter 2: Surface plasmon excitation, numerical calculations and particle tracking methodologies

In this chapter, we establish the techniques and methodologies utilized in the rest of the work. The various platforms for surface plasmon excitation are discussed. We also discuss some of the methods employed to study the dynamics of colloidal matter such as particle tracking and Voronoi analysis. Finally, we conclude by discussing the finite element method based numerical simulations to calculate near-field electric field, temperature distribution and convective flows in the system.

Chapter 3: Large-scale optothermal assembly of colloids mediated by a gold microplate

In this chapter, we show large scale assembly of silica colloids by using their thermophoretic property. Heat is generated in the system by exciting a two-dimensional gold microplate through evanescent excitation. The assembly of colloids is dependent on various parameters like surface to volume ratio of the gold microplate, polarization, particle size and composition of the colloidal material.

Chapter 4: Optothermal pulling, trapping, and assembly of colloids using nanowire plasmons

In this chapter, we confine propagating plasmons in one direction using a silver nanowire. The silver nanowire is excited using a high numerical aperture objective lens. This leads to the control and manipulation of a single colloid along the silver nanowire. By increasing the number density of the colloids, multiparticle assembly of colloids around the nanowire can be achieved.

Chapter 5: Marangoni flow driven trapping and manipulation of nano/microstructures

In this chapter, we show the generation of microbubble on a thin plasmonic film using an evanescent excitation. Marangoni flows are generated in the system, which drives the colloids to move in two vortices on the microbubble.

Conclusion and future directions This chapter details the limitation of our work and the prospective future direction and challenges in the field.

Chapter 2

Surface plasmon excitation, numerical calculations and particle tracking methodologies

To study plasmon assisted optothermal processes, we have to equip ourselves with essential tools which will be required to study such systems. The first step is to excite surface plasmons. There are a lot of available systems and configurations in which SPPs can be excited, like extended 2- dimensional metallic films[\[55\]](#), gold plates[\[68\]](#), quasi 1-D metallic nanowires and so on. We choose the appropriate plasmonic platform according to the question at hand. We will also discuss finite element method based numerical calculations, which have been employed in the thesis to calculate the near-field electric field around the metallic structure and the resulting temperature distribution in the system. Numerical methods to study the flow profile of the fluid are also discussed. Since we are dealing with colloids, we also employ various particle tracking techniques. By analyzing the trajectories of the colloids, one can study the dynamics of the colloids, their interaction with external fields as well as other colloids, phase transitions and so on. A suitable particle tracking algorithm has to be employed while tracking colloids, as particle tracking programs depend on the kind of illumination of the colloid. Sometimes, the distribution of light on the colloid's surface is Gaussian in nature, perhaps a dark ring around a bright centre; in dark field illumination, it has a dark centre with a bright ring. Hence, one has to employ a suitable tracking mechanism in order to be able to track the colloids.

In this chapter, we will discuss about:

- Techniques for surface plasmon polariton excitation
- Particle tracking and Voronoi decomposition
- Numerical simulation details

2.1 Techniques for surface plasmon polariton excitation

The excitation of surface plasmon polaritons can be facilitated through various means, like prism coupling, grating coupling, and highly focused beams through high numerical aperture objective lenses. To achieve surface plasmon excitation, we have to satisfy certain momentum-matching conditions.

The dispersion relation for SPP excited at a flat metal-dielectric interface is given by:

$$k_{\text{SPP}} = k_0 \sqrt{\varepsilon_d \varepsilon_m / (\varepsilon_d + \varepsilon_m)} \quad (2.1)$$

where, k_{SPP} is the SPP wavevector, k_0 is free space wavevector, ε_d and ε_m are the permittivities of the dielectric material and the metal. The dispersion relationship curves for light in free space, light in a dielectric medium and surface plasmon polaritons are plotted in figure 2.1 (a)[26]. Since the SPP dispersion curve lies to the right of the photon's dispersion curve, light can not couple to the metal through conventional means from free space and an extra momentum has to be provided to excite polaritons. In order to achieve this, we have to employ specific experimental techniques to increase the wavevector of the light. This can be done by passing it through a medium of high refractive index so that the dispersion curve of the light in the dielectric medium can cross the dispersion curve of plasmons so that the wavevector can be matched for plasmon excitation[79].

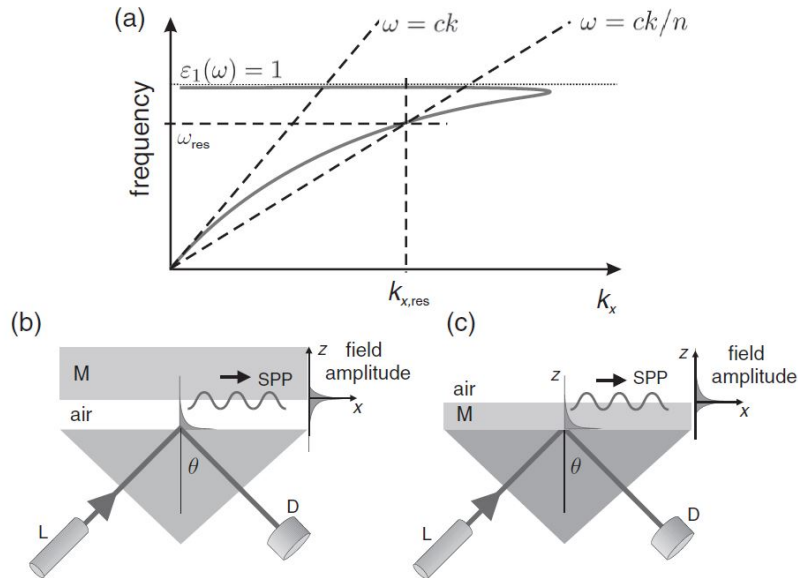


FIGURE 2.1: (a) Dispersion curve of light in free space, in dielectric medium and of surface plasmon polaritons is shown. Excitation of plasmons in (b) Otto configuration (c) Kretschman configuration. The figure is reproduced from [79] with permission.

2.1.1 Total Internal Reflection based coupling

Prism-based coupling is one way to match the momentum of the photons to the SPPs wavevectors through photon tunneling. Mainly two configurations like Kretschman[80] or Otto[81] are employed. In both configurations, light is directed at the prism at such an angle that it gets totally internally reflected. In the Kretschman configuration, as shown in figure 2.1 (c), the light gets totally internally reflected at the prism-metal interface. At such an angle, the in-plane component of the incoming light matches with the SPP wavevector at the metal-air interface. The thickness of the film should be thin enough so that the photons can tunnel through it. Such a condition is satisfied when:

$$k_{\text{SPP}} = k_0 \sqrt{\epsilon_d} \sin \theta \quad (2.2)$$

When the metal film is thick, and the photons can not tunnel through the metal film, an alternate geometry like the Otto configuration can be used. This is depicted in figure 2.1 (b). In this case, a small gap between the prism and the metal film exists so that evanescent component from the prism/air side can couple to air/metal surface. However, maintaining a small gap between the prism and the metal can be challenging.

We use the Kretschman configuration in prism-based coupling. Instead of directly depositing a thin film on the prism, gold film on a coverslip is prepared through Thermal vapor deposition. Silicon oil is placed on top of the film to match the refractive index of the coverslip with the prism, which is then placed on top of the prism.

2.1.2 High Numerical aperture based optical excitation

An alternative to prism coupling is using highly focused optical beams[26][79]. For this purpose, an objective lens with a high numerical aperture is used to excite the surface plasmons. This configuration can be used to excite SPPs on a metallic surface as well as metallic nanowires. The focused excitation beam has a large angular spread, so that we can have certain angles $\theta > \theta_c$, the critical angle required for TIR so that wavevector matching condition is satisfied for angle:

$$\theta_{\text{SPP}} = \arcsin(\beta/nk_0) > \theta_c \quad (2.3)$$

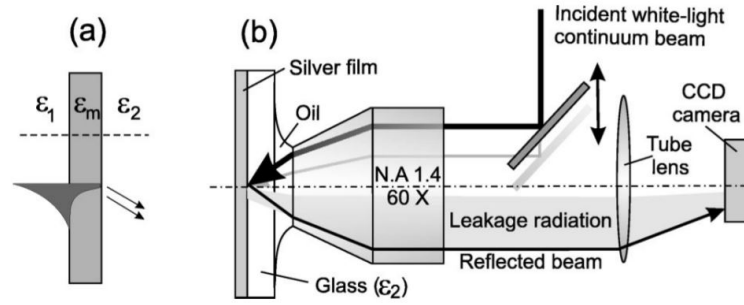


FIGURE 2.2: Schematic of the excitation of surface plasmon using a high numerical aperture objective lens. The figure is adapted from [79] with permission.

This excitation scheme is shown in figure 2.2.

We use a highly focused beam to excite plasmons on silver nanowire[82]. For plasmon excitation, the polarization of the incoming beam is kept parallel to the long axis of the nanowire. The beam is focused at one end of the nanowire, SPPs are excited, which out-couple from the distal end of the nanowire. Figure 2.3 shows the excitation of SPPs on a silver nanowire. The surface plasmons shown in figure 2.3 (c) are imaged through near field technique called Scanning near-field optical microscopy (SNOM)[83].

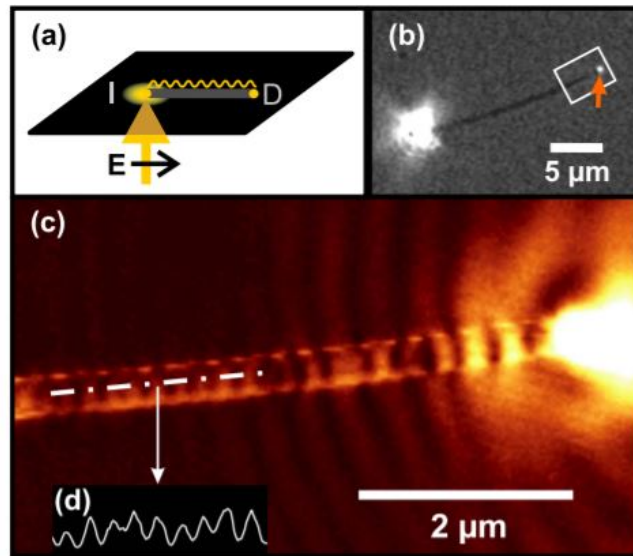


FIGURE 2.3: Surface plasmon propagation (a) Schematic of the excitation in a silver nanowire (b) Scanning electron microscopy image of the nanowire (c) Scanning near field optical microscopy image of the nanowire boxed in (b) (d) Cross-cut along the white dotted line in (c).

The figure is adapted from [84] with permission.

2.2 Particle tracking techniques

Tracking colloids and mapping out their trajectories at high spatial and temporal resolution is imperative for characterizing the system under study[85]. The positions of a number of colloids can be tracked using digital video microscopy[86]. In optical trapping experiments, such tracking methods can be used to calibrate the trap and obtain information about the trap stiffness. Our set-up is equipped with a CCD camera which operates at 20 fps to capture the video of the colloids dispersed in the fluid. Once a video is recorded, further analysis is done through various particle tracking techniques. Figure 2.4 shows an example of two kinds of illumination that can be found for a particle.

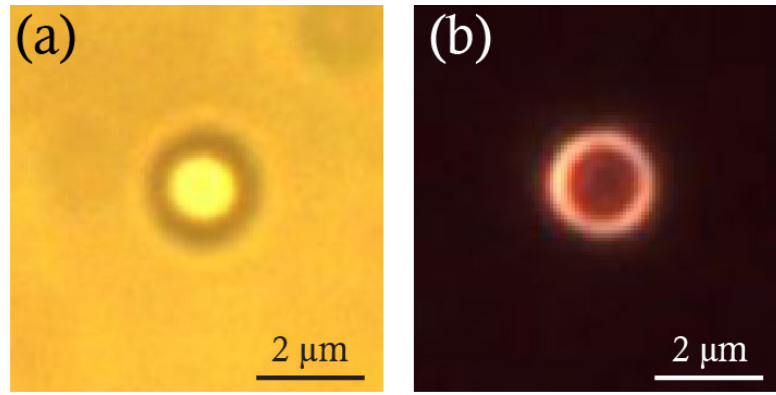


FIGURE 2.4: Illumination of a dielectric bead (a) Bright field (b) Dark field.

Figure 2.4 (a) has a silica particle under bright field illumination with a dark ring around it. For such an illumination, the intensity profile is usually Gaussian and is given by:

$$I(x, y, \{x_0, y_0; \sigma\}) = I_0 \exp \left(-\frac{(x - x_0)^2 + (y - y_0)^2}{2\sigma^2} \right) \quad (2.4)$$

The dielectric particle in figure 2.4 (b) is under dark field illumination, it is dark in the centre with a bright ring around it. For such a particle, the intensity distribution can be written as:

$$I(x, y, \{x_0, y_0; \sigma, R\}) = I_0 \exp \left(-\frac{\left(\sqrt{(x - x_0)^2 + (y - y_0)^2} - R \right)^2}{2\sigma^2} \right) \quad (2.5)$$

Generally, the algorithm for tracking both of these particles would be different. Many tracking algorithms work on feature point detection methods. It assumes that the

intensity distribution of the particles is Gaussian to the first order[47]. There are several steps involved in the detection procedure, which can be broadly divided into:

- *Enhance the image:* A digital image can suffer from several distortions which could have been inadvertently introduced due to optics, non-uniform illumination of the colloids, non-uniform sensitivity of the pixels of the camera etc. If the colloids are well separated, the image is convolved with a Gaussian Kernel.
- *Locate the particles:* The next step is to locate the position of the particle. A local intensity maxima above a certain threshold is defined, which acts as the preliminary position of the tracked particle.
- *Refine the position of the particles:* Assuming that the position obtained through the above step is close to the actual centroid of the particle, further refinement by calculating offsets is applied, and the true centre of the particle is calculated. The above step is applied to particles in all the frames to obtain the spatial coordinates of all the desired particles in all the frames.
- *Link the trajectories of the particles:* Once we have the value of each coordinate associated with each particle, the next and final step remains to connect or link these coordinates in successive frames. Each particle in one frame has to be uniquely identified with another particle in the next frame. This is done by defining a characteristic distance that a particle would have covered between successive frames. This parameter can be set in manually by the user. For a Brownian particle, this distance can be defined as $\sqrt{4D\Delta t}$, where Δt is the time difference between two frames.

Some commonly used packages used in this thesis are Trackmate (ImageJ) [86] and Trackpy(Python)[87]. Both of these packages are user-friendly.

2.2.1 Voronoi decomposition

Where is the nearest hospital in case of emergency or the nearest cafe on a hot summer day? People make these kinds of spatial relationship choices every day. These kind of spatial relationships can be easily solved by proximity diagrams like Voronoi[88][89]. In simpler terms, if we have a region with two points (hospitals, cafes etc.), as shown in figure 2.5 (a), Voronoi divides this area into two regions such that all the points in region 1 will be closer to point A and all the points in region 2 will be closer to point B as shown in figure 2.5(c).

Mathematically, if we have set S consisting of n points in a plane, our goal is to associate with each point ' k ' a region which consists of all points which are closer to the point ' k ' than any other point ' k' ' in the set S :

$$\text{Vor}(K) = \{p : \text{distance}(k, p) \leq \text{distance}(k', p), \forall k' \in S\} \quad (2.6)$$

Starting with a simple case of 2 points A and B, a Voronoi is constructed by:

- Join the two points A and B by a line.
- Draw a perpendicular bisector to this line.
- This perpendicular bisector divides the plane into two Voronoi regions.

A similar strategy is followed for constructing a Voronoi with three sites, as shown in figure 2.5 (b) and 2.5 (d).

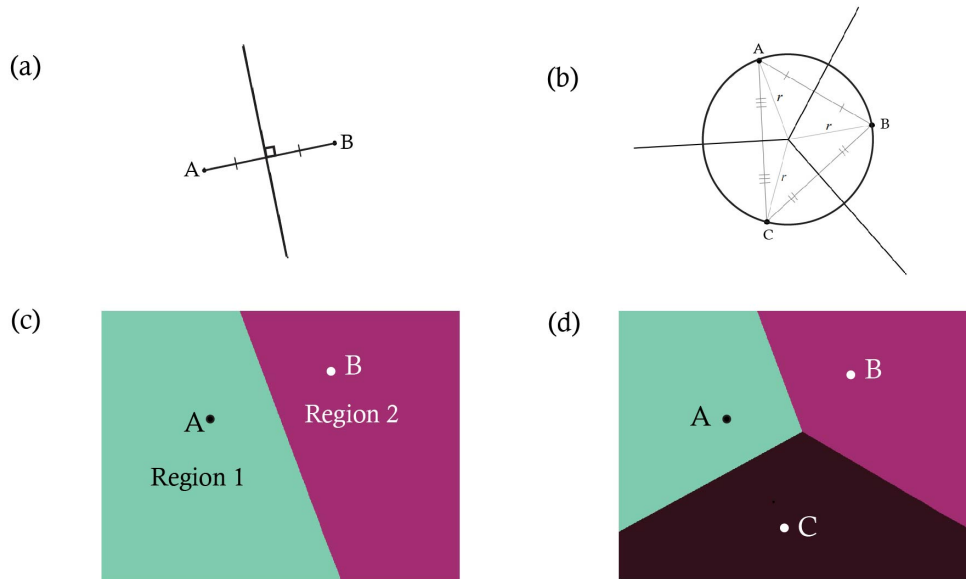


FIGURE 2.5: Voronoi diagram (a) and (c) Construction of a Voronoi for two sites. (b) and (d) Construction of a Voronoi for three sites.

The division of a plane into these regions is useful in domains of biology, metallurgy, epidemiology, finite element analysis to generate finite element meshes to avoid small angles and so on. Voronoi tessellation has been extensively used in colloidal systems to characterize their morphology[85], defects, dislocations, and phase transitions, to name a few. Suppose we have a perfect periodic arrangement of colloids in a hexagon; for such a system, we will obtain a honeycomb type of structure in its Voronoi diagram, square cells for a square arrangement of colloids, i.e. the number of sides of a Voronoi cell represents the local arrangement of the colloids. Experimentally, the arrangements of colloids are usually not in perfect order and the deviation from an ideal arrangement can be studied by constructing these Voronoi diagrams.

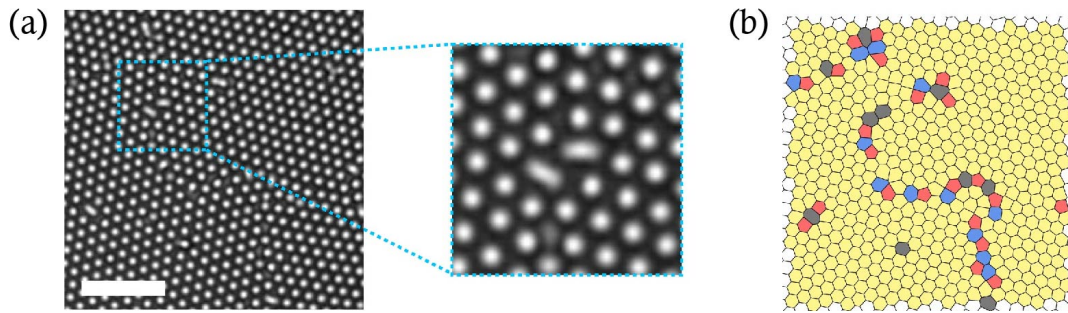


FIGURE 2.6: Colloidal crystal (a) Optical image of the colloidal crystal. The zoomed-in image shows the impurities present in the crystal. (b) Voronoi diagram for the crystal color coded according to the coordination number. Figure is adapted from [85] with permission.

The structural arrangement of colloids is closely related to their physical properties. Thus, mapping out the Voronoi tessellation provides important information about the colloidal crystal. Figure 2.6 (a) shows a colloidal crystal. The zoomed-in image shows the aspherical impurity in the system. Figure 2.6 (b) shows the corresponding Voronoi diagram, where regions are color-coded according to their coordination number.

2.3 Numerical Modeling

To understand a wide variety of physical phenomena like electromagnetic wave propagation, heat transfer, and fluid flows, certain differential equations have to be solved. If the system under study is simple, the equations can be solved by hand. More than often, the systems that we are dealing with are quite complex, and a direct quantitative evaluation of these physical quantities is not possible. Hence, specific numerical techniques have to be employed, which come handy in the understanding of these physical phenomena. Many such numerical analysis tools are available to solve these equations numerically, like Finite element method (FEM), Finite difference time Domain method and so on. In our case, numerical modeling of nanostructures is an indispensable tool required to gain further insights into light-matter interactions in plasmonics. In this thesis FEM based numerical computation in COMSOL is applied to compute:

- Near-field electric field
- Temperature profile
- Convective and Marangoni flows

The finite element method (FEM) is a numerical method for solving differential equations widely used in engineering and scientific fields to analyze and design complex systems. It involves discretizing a continuous domain into a set of smaller, interconnected elements, which allows the differential equations to be approximated and solved numerically. The FEM has several advanced features that make it a powerful tool for solving a wide range of problems, including the ability to handle complex geometries, variable material properties, and time-dependent or nonlinear behaviors. Some of the advanced features of the FEM include:

1. Adaptive meshing: This allows the FEM to automatically refine or coarsen the mesh in areas where the solution is changing rapidly or where it is expected to be less accurate.
2. Higher-order elements: These allow for more accurate solutions by using higher-order polynomials to approximate the solution within each element.
3. Multiphysics modeling: This allows the FEM to simulate multiple physical phenomena simultaneously, such as heat transfer, fluid flow, and structural mechanics.
4. Parallel computing: This allows the FEM to take advantage of multiple processors or computers to solve larger or more complex problems in a shorter amount of time.

The accuracy of the solution obtained using the FEM depends on the quality of the mesh used to discretize the problem, as well as the accuracy of the numerical method used to

solve the resulting equations. In the following sections, we will discuss the computation of the physical quantities mentioned above.

2.3.1 Near-field electric field

Calculation of near-field electric field distribution is of paramount importance when dealing with plasmonics and its associated effects. Electric field enhancement is essential in constructing optical antennas, bio-sensing, signal enhancement in surface-enhanced Raman scattering and so on. A lot of these processes utilize the enhancement of scattering cross-sections, however, absorption cross-section is also enhanced, which leads to the heating of the plasmonic material. Hence, to understand thermoplasmonically driven processes, the first step is to calculate the near-field electric field of the structure.

A direct measurement of near-field electric field is not possible through conventional microscopes, and specialized techniques like (SNOM)[90] have to be employed.

To calculate the electric field distribution in a nano/microstructure illuminated with a laser in COMSOL, the following steps can be followed:

1. Open COMSOL and start a new model by selecting the "Electromagnetics" physics interface.
2. Import the 3D geometry of the structure into COMSOL. One can do this by either creating the geometry from scratch using the built-in modeling tools, or by importing a 3D CAD model.
3. Define the material properties of the structure and the surrounding medium. This includes the permittivity and conductivity of each material.
4. Set up the laser excitation by defining the laser wavelength, polarization, and incident angle.
5. Use the "Frequency Domain Electromagnetic" or "Time Dependent Electromagnetic" analysis to solve for the electric field distribution in the structure.
6. Visualize the electric field distribution by creating a contour plot or 3D plot of the electric field magnitude or electric field vectors.
7. If desired, one can also calculate other quantities, such as the electric potential, power density, or absorption.

It is also important to mesh the geometry properly. In COMSOL, meshing refers to the process of dividing a model into smaller elements or cells, called mesh cells, in order to accurately solve the differential equations that describe the physical phenomena in the model. The mesh cells are used to approximate the solution at discrete points within the model domain, and the solution is then interpolated between these points to obtain

a continuous solution. The quality and resolution of the mesh can have a significant impact on the accuracy and convergence of the solution, so it is important to choose an appropriate mesh size and type for the model. There are several different mesh types available in COMSOL, including structured, unstructured, and hybrid meshes, and the appropriate choice depends on the specific features and geometry of the model. Further details can be accessed at [91].

We numerically calculate the electric fields of complex nanostructures by solving Maxwell's equations with suitable initial and boundary conditions by employing Electromagnetic waves, and frequency domain module in COMSOL. We solve this by using frequency domain study node, which solves for the time-harmonic wave equation for the electric field. Let us start with a simple example of the interaction of light with a gold sphere. Figure 2.7(a) plots the near-field electric field calculation for a 100 nm gold nanoparticle illuminated with a Gaussian beam of 633 nm. The polarization of the incoming is along the x-axis. The electric field is strongly concentrated around the nanostructure and gradually decays as we move further away from the gold nanoparticle.

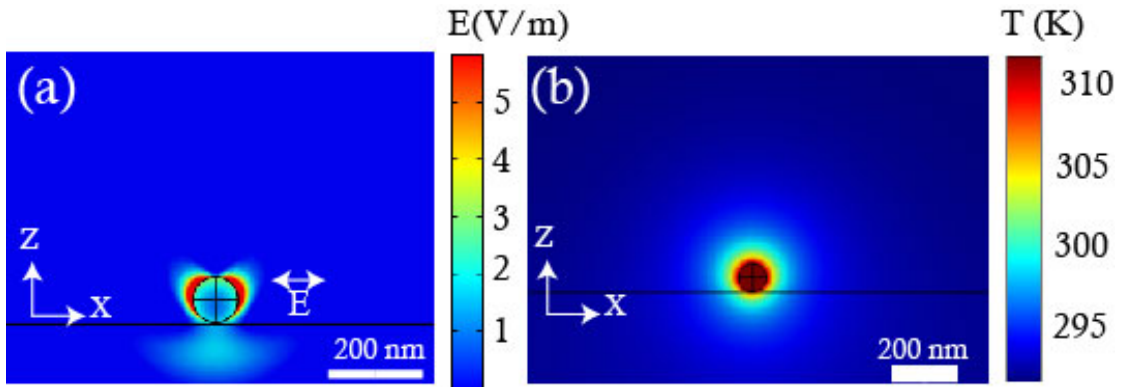


FIGURE 2.7: (a) Near field electric field (b) temperature distribution profile for a 100 nm gold nanoparticle illuminated with a 633 nm Gaussian beam.

2.3.2 Temperature profile calculation

Once the electric field is calculated, we can move to the next step of solving the heat diffusion equation to calculate the temperature inside as well as outside the nanostructure. For this, we add an additional module of Heat transfer in solids and fluids, which solves for conduction, convection and radiation and couple this to the Electromagnetic waves module by using multiphysics electromagnetic heating. The following heat diffusion

equation is solved to get the temperature profile of the system:

$$\rho c_p \partial_t T - \kappa \nabla^2 T = q \quad (2.7)$$

where ρ is the density of the material, c_p is the specific heat at constant pressure, κ is the thermal conductivity of the material and q is the heat source. Figure 2.7(b) plots the temperature profile for the 100 nm gold nanoparticle. The temperature distribution remains constant over the nanoparticle (due to the large thermal conductivity of gold) and then decays exponentially as we go away from the nanostructure.

2.3.3 Flow profile

As the temperature increases in the surrounding medium of the gold nanoparticle, the surrounding fluid gets heated up. This can lead to convection currents in the system. For this Laminar flow module is coupled to the existing two modules discussed above. Laminar flow module is only applicable as long as the Reynolds number remains below a certain critical number, above which the fluid may transition to a turbulent flow. To calculate the contribution of the convection, the Navier-Stokes equation is solved:

$$\partial_t \mathbf{v}(\mathbf{r}, t) + (\mathbf{v}(\mathbf{r}, t) \cdot \nabla) \mathbf{v}(\mathbf{r}, t) = \nu \nabla^2 \mathbf{v}(\mathbf{r}, t) + \mathbf{f}_{th}(T(\mathbf{r}, t)) \quad (2.8)$$

where $\mathbf{v}(\mathbf{r}, t)$ is the velocity of the fluid, $\mathbf{f}_{th}$ is the force per unit mass due to temperature non-uniformity, ν is the viscosity of the fluid. In addition, Boussinesq approximation is also applied[92]. Figure 2.8 shows the flow profile around a 100 nm gold nanoparticle. The maximum speed of the flow for a temperature of $15 \times 10^{-12} m s^{-1}$ which is negligible. This shows that for a small nanostructure, the convective flow is not prominent and can be neglected for all practical purposes. However, large convective currents may be produced if we have an ensemble of a large number of particles where we might get a much large temperature increase over a wider surface area.

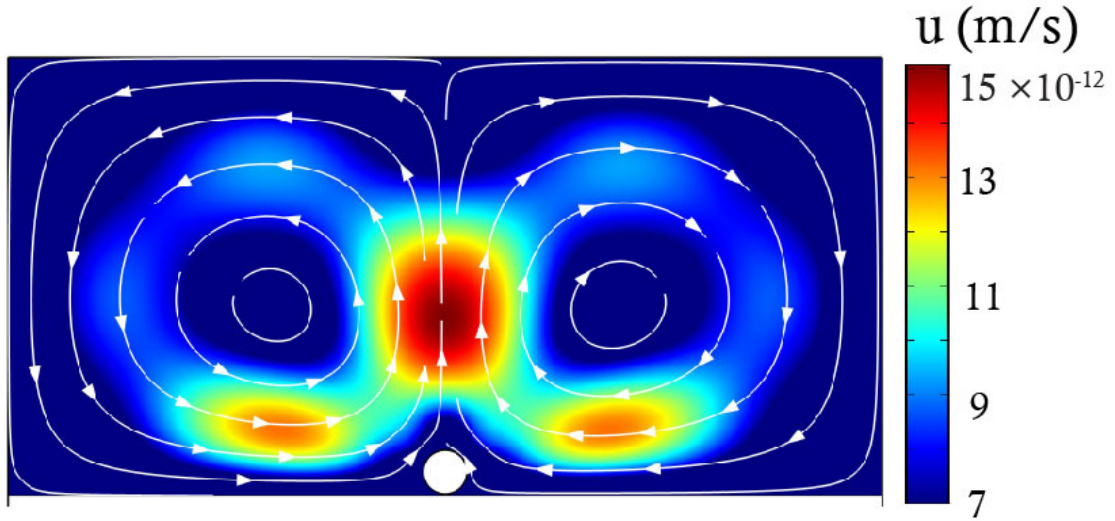


FIGURE 2.8: Convective flow profile for a 100 nm gold particle. The velocity of the fluid is negligible.

Besides convective flow, one can also have Marangoni convection in the system. We will talk about it in the context of a bubble where we have a two-phase system. One is air (inside the bubble) and the other is outside the bubble (water). In this case, an additional boundary condition has to be applied at the interface of air/water. It will be discussed in more detail in chapter 5.

Chapter 3

Large-scale optothermal assembly of colloids mediated by a gold microplate

In this chapter, we will discuss the formation of large scale assemblies and different parameters used to control and manipulate it. The chapter is an adaptation of the research article "Journal of Physics: Condensed Matter 32(32),324002 (2020)".

3.1 Introduction

Light-activated colloidal assembly and swarming can act as model systems to explore non-equilibrium state of matter. In this context, creating new experimental platforms to facilitate and control two-dimensional assembly of colloidal crystals are of contemporary interest. Study of colloidal particles on large scale provides the opportunity to study poly-crystals[93], glass transition [94][95] [96], jamming [97], packing structures [98][85] and two-dimensional melting [99]. To this end, various approaches have been utilized such as using plasmonic thin films [55][56], modulated light fields [100], Lorentz force between plasmons [101], light scattering of trapping laser by nanoparticles [7][102] and many more. One of the methods to assemble colloids is to utilize their temperature gradient dependent motility. In this context, thermophoresis has been used in variety of studies to trap colloidal objects [9][14]. Recently, thermoplasmonically driven studies have been conducted to establish temperature gradient in the systems [15][16]. In this context, thermophoresis has been utilized to manipulate multiple particles down to the level of a single particle [103][104][105].

Herein, we report large scale assembly of colloidal particles by utilizing opto-thermal effects of a single gold microplate. These microplates are prepared chemically as well as lithographically. Additionally, the choice of gold microplate is advantageous, as a flat structure is more efficient in generating heat compared to another structure of the same volume due to more accessibility to the volume of the structure [106]. We utilize an evanescent configuration to excite a single gold microplate. We show reverse

thermophoresis of silica particles which migrate from a colder to a hotter region and compare it with the response of polystyrene particles (PS). A single gold structure can assemble silica particles in a region spatially much larger than its own size, up to 10 times its own dimension. We quantify the temperature distribution through numerical simulations. The assembly is polycrystalline in nature and is quantified through coordination number and hexagonal order parameter. We further investigate the effect of changing the surface to volume ratio (S/V) and particle size on the assembly. The scale of assembly varies as we switch our polarization from in plane (p) to perpendicular (s) to the plane of incidence. We emphasize that the assembly process is thermal gradient driven and can be potentially harnessed for composition-specific assembly and sorting of colloids in optical fields.

3.2 Design of the system

The schematic of the experimental design is shown in figure 3.1. The gold microplates dispersed in ethanol were dropcasted on a clean coverslip and left to dry. A small volume (30-50 μL) of fluid containing colloids was dropcasted on the coverslip. A 532 nm continuous-wave laser (300 mW) was used to excite the gold plate. A half wave plate was used to control the input polarization. The laser was loosely focused using a 100 mm lens and was totally internally reflected at the water-glass interface using a dove prism. The size of the evanescent spot is approximately 200 μm . The gold microplate was placed in the excitation region. A white light source was coupled through the bottom of the sample for better visibility. A 60x, 1.20 NA water immersion objective lens was used to capture the scattered light. The scattered excitation laser was rejected using a 532 nm edge filter and the data was captured with a CCD camera.

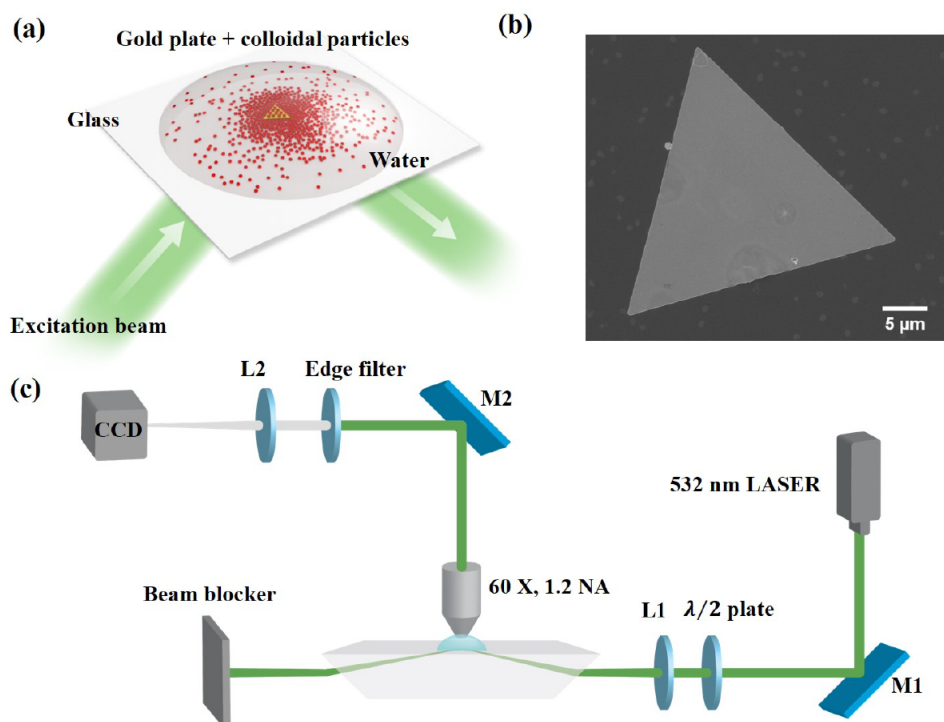


FIGURE 3.1: (a) Schematic illustration of the assembly of colloidal particles on the surface and around the gold microplate. The microplate is shown as a yellow triangular plate and the colloidal particles are indicated by red spheres, which were initially dispersed throughout the solution. The arrows indicate the direction of excitation. (b) Field emission scanning electron microscopy (FESEM) image of a representative gold microplate used in the experiments. (c) Schematic of the experimental setup: 532 nm laser excitation is incident on the gold microplates. The laser is weakly focused through a 100 mm lens (L1) and undergoes total internal reflection through the dove prism. The video is recorded by a CCD after rejecting the direct excitation using a 532 nm edge filter. Figure is reproduced from [68] with permission.

3.2.1 Sample preparation

Gold microplates were prepared using a method as described in [107]. 6 mL of ethylene glycol was heated at 150° C. The temperature was constantly monitored using a thermometer. Once the temperature equilibrated, 1 mL of 0.2 M Chloroauric acid (HAuCl_4) was added. After 5 minutes, 3 mL ethylene glycol solution of Polyvinylpyrrolidone (PVP) was injected into the solution. The molar ratio of PVP/Au was kept at 30. The solution was continuously and vigorously stirred for 30 minutes. After a few minutes, the appearance of shiny, metallic gold in the solution indicated the formation of gold microplates. The solution was brought to room temperature and washed with ethanol and acetone several times. Finally, the solution was rinsed with milli-Q water and dispersed in ethanol for storage. The typical length and width of the gold microplates

prepared chemically is shown in figure 3.1 (b).

Gold microplates with different S/V ratio were prepared using photolithography. Firstly, positive photoresist was spin-coated on glass coverslips followed by baking at 110 °C for 1 min. The pattern of the structures was transferred to the substrate by photomask using 405 nm laser followed by immersion in developer solution and cleansing. A 3 nm Chromium was coated as an adhesive layer and gold of desired thickness was coated by thermal vapor deposition.

Colloids ranging from 0.97 μm - 3 μm were used in the experiments. Silica beads (500 nm, 1 μm , 2 μm , 3 μm) were purchased from microsphere-nanosphere. Polystyrene particles (0.97 μm) were purchased from Sigma-Aldrich. All the colloidal particles were diluted and dispersed in milli-Q water.

3.2.2 Numerical simulation details

Temperature distribution and temperature gradient distributions were obtained by solving electromagnetic wave and heat transfer in solids and fluids modules in 3D. The velocity profile of the fluid was obtained by solving for laminar flow in 2D. To get an estimate of the temperature and velocity profiles that could be generated in a micron sized gold triangle, we performed finite element method (FEM) based numerical simulations. Since simulating the exact size of the structure used in the experiments is computationally expensive, we considered a box of dimensions 10 μm x 7 μm x 7 μm . An equilateral gold triangle with side of 2 μm , thickness 50 nm was simulated. All the domains were meshed through user defined values. The structure was illuminated through total internal reflection at 532 nm laser excitation.

3.3 Results and Discussion

3.3.1 Optothermal assembly of silica particles

We first demonstrate the long-range assembly of 3 μm SiO_2 (silica) particles around a triangular gold microplate with each side being $\approx 24 \mu\text{m}$. The concentration of the particles was 450 particles/ μL . This assembly is facilitated by an opto-thermal potential well created by an evanescent excitation of the gold microplate. As the laser excitation was turned on, we observed a change in the particle dynamics from Brownian motion to a directional movement towards the gold microplate as shown in figure 3.2. Within the first 30 seconds, the particles get accumulated on the surface of the gold microplate with uniform spacing as shown in the inset of figure 3.2. It is to be noted that although the particles accumulate on the gold microplate frequently, they do not always assemble

in a similar way. As time progresses, more particles started to accumulate around the microplate. The formation of multilayers of the particles can also be observed in the snapshot taken at 80 min within a region close to the microplate, making distinction between the individual particles difficult. A large scale assembly extending up to $292\ \mu\text{m}$ was formed at 80 min. Thus, a single gold microplate under evanescent excitation is able to accumulate particles up to a distance which is approximately 10 times its own dimension. It is to be noted that since the electric field from the edge of the gold plate decays exponentially, extending up to few hundreds of nm, compared to the particles' assembly size of hundred of microns, the assembly of the particles cannot be facilitated by optical forces alone and is a result of the heat generated due to the structure. We attribute this long-range assembly mainly to thermophoretic migration of silica particles.

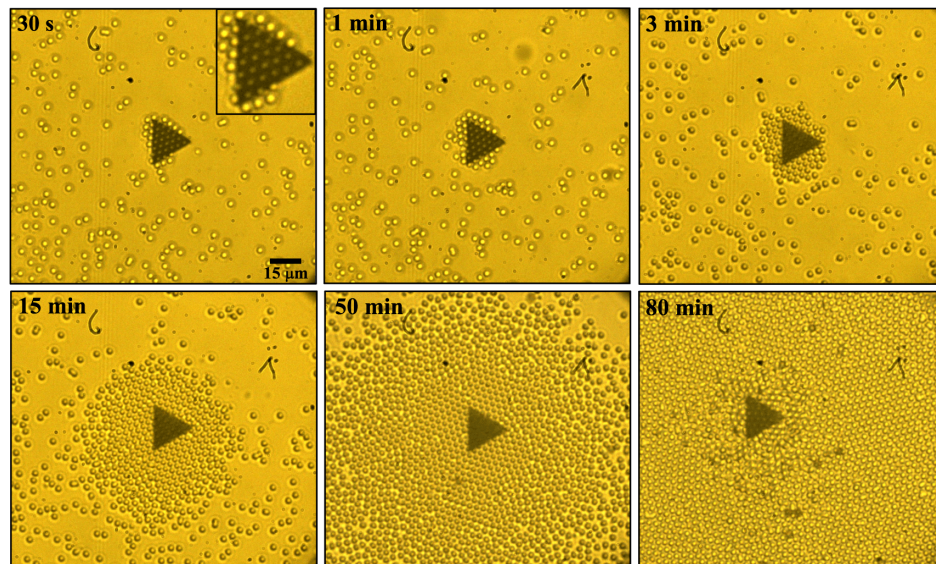


FIGURE 3.2: Time series images of the gradual accumulation of the $3\ \mu\text{m}$ silica particles around the gold microplate. The figure shows the snapshots of the assembly at different times ranging from 30 seconds to 80 minutes. The inset at 30s shows a zoomed-in image of the gold microplate. The accumulation of the particles on top of the microplate can be clearly seen. The accumulation increases gradually and starts to saturate around 80 minutes. Figure is reproduced from [68] with permission.

In order to explain this assembly process, we can decompose the forces acting on the silica particles, as (a) thermophoretic force and (b) convective force. Thermophoretic force acting on a particle can be either positive or negative depending on the particle-solvent interaction. Convection current on the other hand has a toroidal nature inside the water droplet, and can bring the particles close to the microplate and then transport them away from the plate [19]. An interplay between these two forces is crucial in

either assembling the particles close to the microplate or diffusing them back into the solution. In the absence of the gold microplate, the only force acting on the particles is the evanescent field of the laser excitation. We did not observe any assembly of the particles in this case, implying that the optical force due to evanescent field of the laser alone does not have any role in the assembly of the particles. When the gold plate is introduced in the same electromagnetic field, there is a redistribution of electronic charges and an induced field is set up inside the structure. The electronic current generated by oscillating electrons dissipates energy via the Joule effect and the heat power density $q(\mathbf{r})$, at any location $\mathbf{r}$ is given by [17]:

$$q(\mathbf{r}) = \frac{\omega}{2} \varepsilon_0 \text{Im}(\varepsilon) |\mathbf{E}(\mathbf{r})|^2 \quad (3.1)$$

where, ε_0 and ε are the electric permittivity of the free space and the material respectively, ω is the frequency of illumination and $\mathbf{E}$ is the electric field at location $\mathbf{r}$ inside the structure.

Since the gold plate is immersed in water, the heat generated is conducted to the nearby regions. We found the maximum temperature increase to be 7.81 K at the upper surface of the gold microplate. The temperature profiles in x-y plane and x-z plane are shown in figure 3.3(a), (b) respectively. Figure 3.3(c),(d) show the temperature distribution along the dotted lines in figure 3(a),(b) respectively.

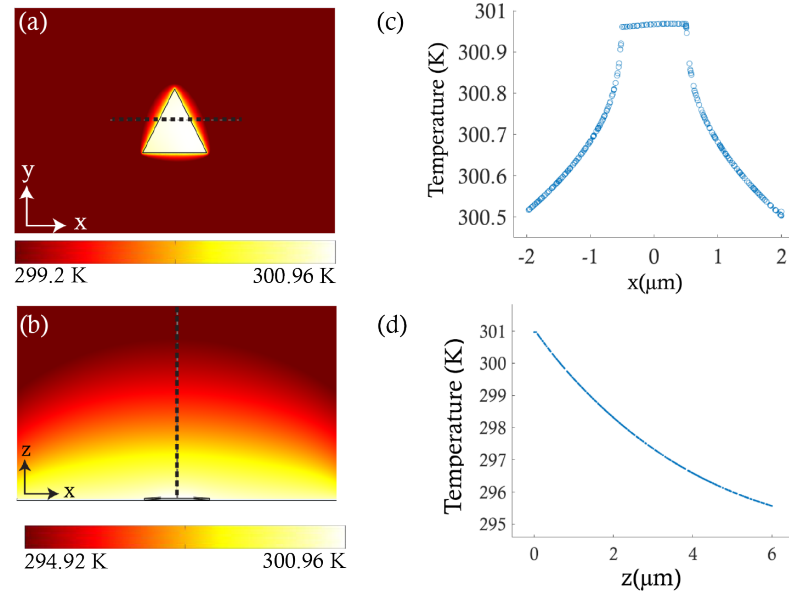


FIGURE 3.3: Finite element method simulations (a) Temperature profile distribution in x-y plane on the upper surface of the gold plate. (b) Temperature profile distribution in the x-z plane. (c) Temperature distribution along the dotted line in (a). (d) Temperature distribution along the dotted line in (b). Figure is reproduced from [68] with permission.

Figure 3.4(a)-(c) show the temperature gradients set up in the region surrounding the gold microplate in the x, y and z directions. By running a time dependent study of the system, we calculated the evolution of the temperature of the water at a point $1 \mu\text{m}$ above the surface of the gold microplate. Figure 3.4(d) shows that it reaches a steady state profile within few milliseconds.

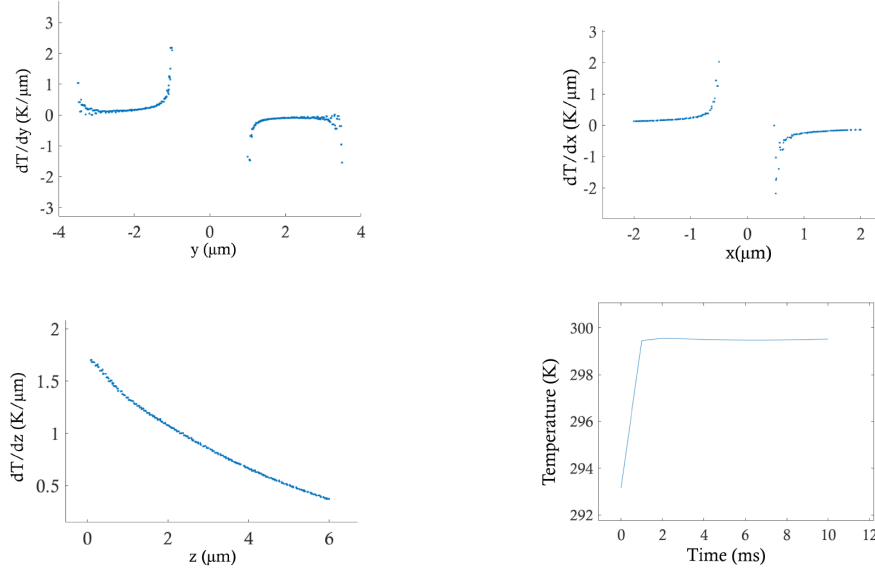


FIGURE 3.4: (a)-(c) Temperature gradients along x, y and z-directions are plotted. (d) Temperature of the water as a function of time at a distance 1 μm above the gold microplate. Figure is reproduced from [68] with permission.

The maximum convective velocity of the fluid obtained is $3.40 \times 10^{-16} \text{ m s}^{-1}$ as shown in figure 3.5. We also calculated the velocity of few incoming particles through video analysis as they approach the gold microplate within the first 30 s. The average velocity of the particles calculated was $1.18 \pm 0.44 \mu\text{m s}^{-1}$. Thus we can conclude that the convection in the fluid is negligible and the dynamics is governed by thermophoresis rather than convection. This is consistent with the study reported previously [15].

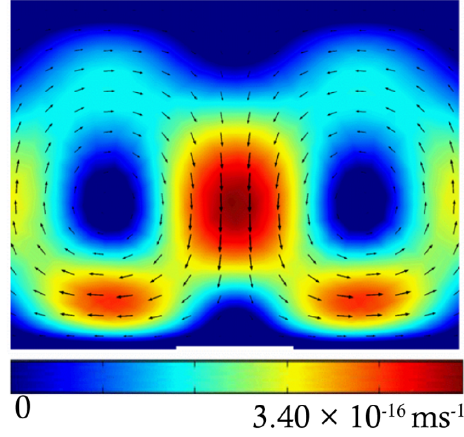


FIGURE 3.5: Convective velocity of the water above the surface of the gold microplate. Figure is reproduced from [68] with permission.

3.3.2 Analysis of the assembly

As shown in figure 3.2, with increasing time, the scale of the assembly grows and reaches a saturation point, where the number of particles accumulated within a given area do not increase significantly over time. We take a snapshot of the assembly after an approximate saturation point (≈ 80 min after laser is turned on) and characterize it. Characterization of the assembly is imperative to the study since it helps us recover information such as local ordering. One of the ways to measure local ordering of the assembly is to calculate network of nearest neighbour of a particle for a given set of particle coordinates. Although there are many ways to calculate such networks [108], Voronoi decomposition [109][110] is one of the unique method and its ease of application makes it particularly useful for our analysis. Voronoi decomposition pictorially maps out the extended 2D array of particles in the region of interest into a number of polygons. Each polygon is a Wigner-Seitz cell for a particle, where the number of side represents the number of nearest neighbours adjacent to the particle. Counting the number of edges of each polygon also gives us a hint towards the symmetry of the assembled 2D array of particles. This is subjected to an accurate measurement of the particle coordinates, since a slight displacement from a preferred lattice position may lead to a large change in the coordination around the neighbourhood of a particular particle.

Upon close assessment of the assembly formation in figure 3.6(a), two distinct regions can be identified. Region I, close to the gold microplate (marked by a white dotted

circle of diameter $\approx 47.8 \mu\text{m}$) where each particle cannot be individually identified due to multilayer formation; and region II outside the dotted circle, far away from the plate where apart from few defects, the assembly can be seen to be more uniform. We reject region I and analyze the assembly formed in region II. Particles in region II were mapped by trackmate [86]. The region of interest contains approximately 1900 particles. The mapped particle coordinates were then fed into a modified Voronoi analysis program. The orange hexagonal cells in figure 3.6(b) represent regions with particles having co-ordination number 6, whereas the blue cells show regions with co-ordination number other than 6. In our analysis, we have rejected the cells forming around the boundaries by using a modified Voronoi analysis [111] algorithm. It can be seen from the figure 3.6(b) that away from the boundaries, the hexagonal orange cells show more regular pattern compared to the peripheral cells. We plot the probability of a particle having coordination number from 3 to 8 in figure 3.6(c). It is evident that the majority of the assembly consists of particles with 6 nearest neighbours around them (marked with orange colored bin). Although particles may have six nearest neighbours around them, it does not necessarily assure hexagonal ordered packing. Hence, we further quantified hexagonal order parameter given by [5][85]:

$$\psi_6^j = \frac{1}{z_j} \sum_{m=1}^{z_j} \exp(i6\theta_m^j) \quad (3.2)$$

where, z_j defines the number of nearest neighbour to the j^{th} particle, m denotes the neighbours and θ_m^j is the angle between a reference axis and the line joining j^{th} and m^{th} particle.

We also calculated the mean size and polydispersity of the colloids. The mean size of the colloids was estimated by tracking the colloids in Image J. Once we got values of estimated diameter, mean size of the colloids was calculated as $2.72 \mu\text{m}$. Next, we calculated the polydispersity index (PDI) of the colloids. The PDI is a measure of the size distribution of colloids in a sample. It is calculated by dividing the square of the standard deviation of the size distribution by the mean size of the colloids. A sample is considered monodisperse when the PDI value is less than 0.1. The PDI value for our sample was found to be 0.05, indicating that the sample was fairly monodisperse. However, as there is still some polydispersity in the sample, it can lead to a deviation from a perfect hexagonal lattice arrangement of the colloids due to the introduction of several defects in the system.

In addition to our main experiments, we also conducted supplementary experiments in which we utilized microstructures of different shapes that were fabricated via lithography. These microstructures were disk-shaped. Although the colloids initially assembled

in a circular manner for several microns, the overall assembly did not demonstrate a clear trend and resembled an assembly similar to the triangular structure. However, our decision to utilize a triangular structure was primarily based on its ability to generate more heat compared to other shapes. The efficiency of generation of heat by nanostructures of different shapes has been documented in a previous study [106].

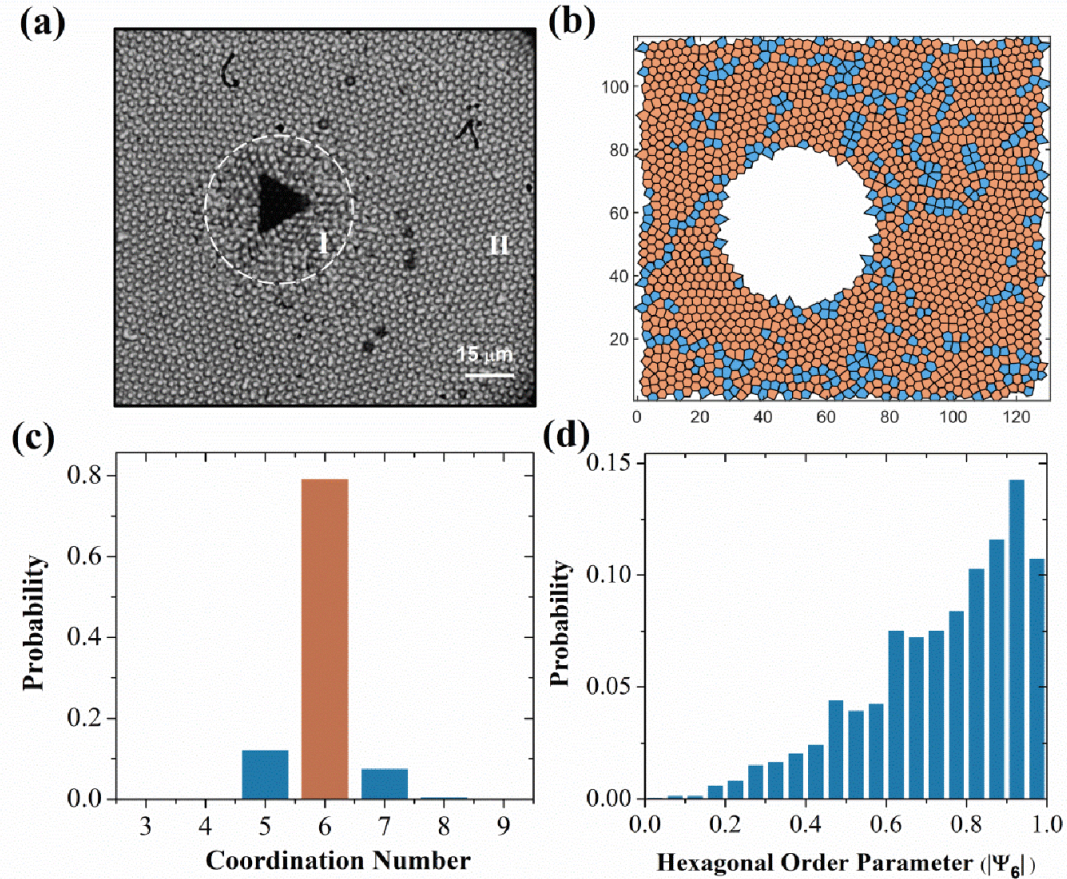


FIGURE 3.6: (a) Greyscale image of the assembly of dielectric particles (at 80 min), the region marked I marked by white dotted circle (diameter $\approx 47.8 \mu\text{m}$) has been removed since the particles cannot be identified individually. Particles positions in the region II was tracked and fed into Voronoi analysis program. The Voronoi tessellation is shown in (b) where the hexagonal cells depicting Wigner-Seitz cells of particles having 6 nearest neighbours are colored in orange and the assembly regions with particles having nearest neighbour other than 6 is shown with blue cells. The normalized distribution of the coordination number of the particles is shown in (c). (d) Hexagonal order parameter of the assembled particles. The distribution peaking around 0.95 depicts the closed hexagonal packing of the assembly. Figure is reproduced from [68] with permission.

As shown in figure 3.6(d), the histogram data peaks around 0.95, which indicates

close hexagonal ordering of the assembled particles. The broad distribution of the histogram data can be attributed to the large area under consideration which includes the particles having nearest neighbours other than 6.

Characterization of the assembly before the formation of second layer around 45 minute is shown in figure 3.7.

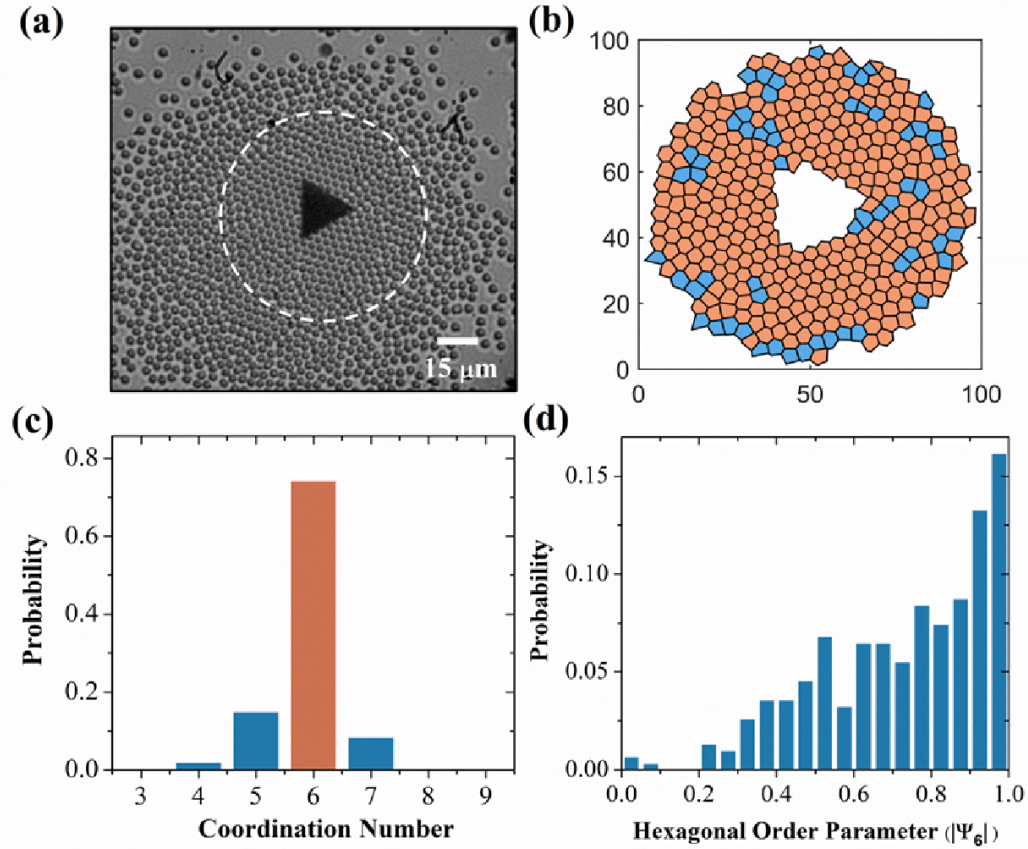


FIGURE 3.7: (a) Greyscale image of the assembly of dielectric particles (around 45 min). The region inside the dotted white circle was analysed. The positions of the particles were tracked and fed into voronoi analysis program. The Voronoi tessellation is shown in (b) where the hexagonal cells depicting Wigner-Seitz cells of particles having 6 nearest neighbours are colored in orange and the assembly regions with particles having nearest neighbour other than 6 is shown with blue cells. The normalized distribution of the coordination number of the particles is shown in (c). (d) Hexagonal order parameter of the assembled particles. The distribution peaking around 1 depicts the closed hexagonal packing of the assembly. Figure is reproduced from [68] with permission.

3.3.3 Effect of excitation polarization on the assembly

Since, the heat generated by a metallic structure essentially depends on the electric field distribution inside the structure, we performed a polarization dependence study keeping the excitation power constant at 300 mW. We observed that the particles assembled for both s and p polarized light, but the extent of the assembly is different in both the cases. First, we kept the polarization of the excitation as s i.e. perpendicular to the plane of incidence. The snapshot is taken at 25 min as shown in figure 3.8(a). Then, we switched off the laser and allowed the particles to re-disperse into the solution. Now, we switched the polarization from s to p, i.e. parallel to the plane of incidence. When the polarization is kept at p, we observed that the particles experience a greater force of attraction towards the microplate. The particles assemble faster and also cover larger area in the same time period as can be seen by comparing figure 3.8(a) and figure 3.8(b). It can be explained on the basis of the difference in the amount of heat generated in both the cases. In order to generate heat in a structure, it is essential to excite the bulk of the volume. Compared to a p polarized light where the electric field can excite the bulk of the volume, s-polarized light is less efficient in generating heat. Thus, the polarization plays an important role in controlling the extent of the assembly and can be tuned according to the structure at hand.

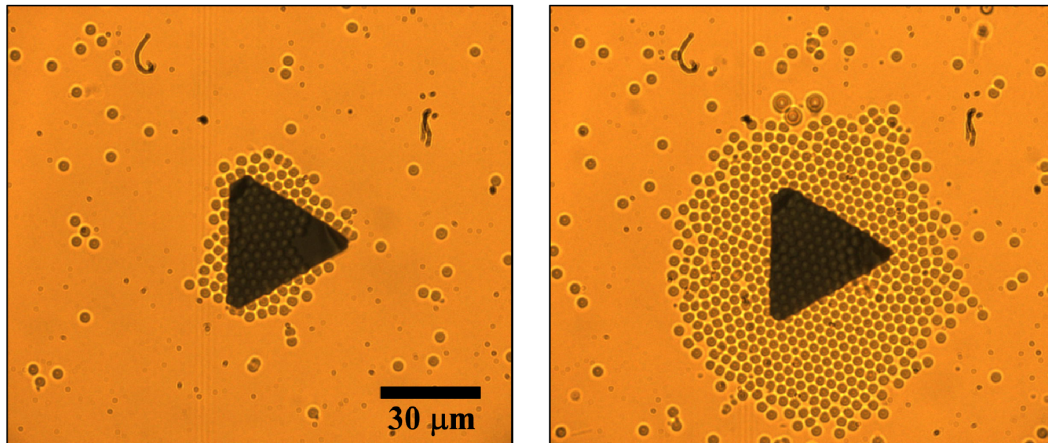


FIGURE 3.8: Polarization dependence of the microplate on the accumulation of the particles: (a) Accumulation of the particles at 25 min when the input excitation is s-polarized. (b) Assembly extends up to tens of microns at 25 min when the excitation is p-polarized. Figure is reproduced from [68] with permission.

3.3.4 Effect of surface to volume ratio of the microplate

Since, surface to volume ratio of a structure plays a crucial role in power dissipation and in turn efficient generation of heat, the size of the assembly can be tuned accordingly. Since efficient excitation of the volume of the structure is essential, to do a comparative study we kept the volume of all the structures same and varied the surface area. We lithographically prepared structures of sizes $10\ \mu\text{m}$ ($S/V: 14.28\ \mu\text{m}^{-1}$), $15\ \mu\text{m}$ ($S/V: 32.10\ \mu\text{m}^{-1}$) and $20\ \mu\text{m}$ ($57.14\ \mu\text{m}^{-1}$). The experiments were performed with $3\ \mu\text{m}$ silica particles and the size of the plate was varied. The snapshot of the assembly at 15 min for every size of the gold microplate is shown in figure 3.9(a). It can be seen from the snapshot that the efficiency of the assembly increases as we increase the surface area of the structure. For a $10\ \mu\text{m}$ plate, the particles are loosely bound to the structure and display fluid like state. Very few particles near the structure can be seen forming the second layer. As we switch to $15\ \mu\text{m}$ structure, the particles are more tightly bound to the structure and the second layer formation becomes prominent. Finally, when the S/V ratio is largest for $20\ \mu\text{m}$ structure, the extent of the assembly is substantially larger. The particles are tightly bound to each other even at longer distances and the second layer formation extends up to $82\ \mu\text{m}$. Thus, the nature of assembly can be tuned to be either loosely or tightly bound, single or multilayer by tuning the surface to volume ratio of the structure.

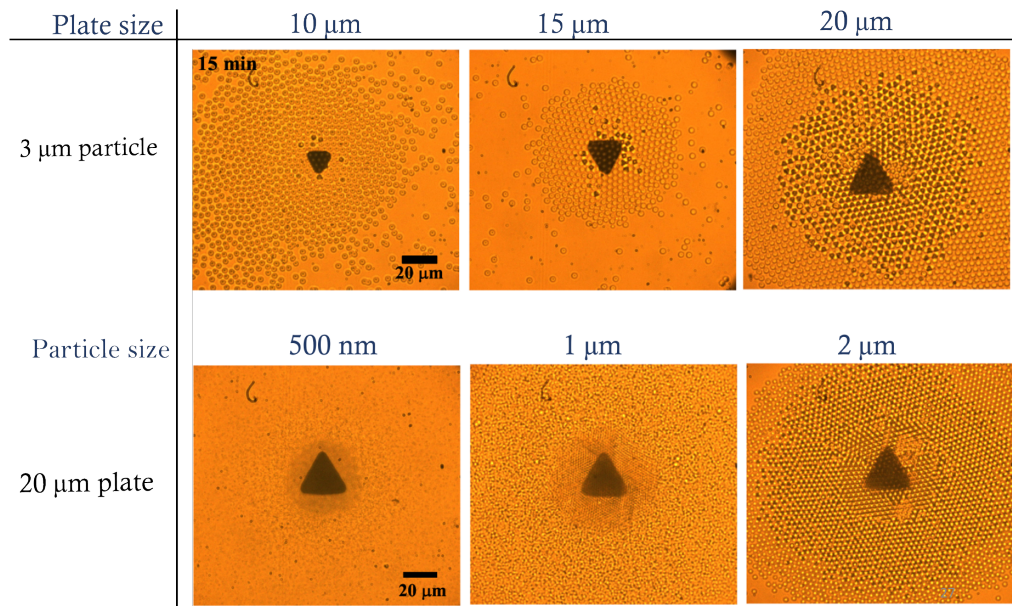


FIGURE 3.9: (a) For a fixed particle size of 3 μm , the surface to volume ratio of the gold microplate is increased by keeping its volume fixed (upper panel). As the surface area of the microplates increases from 10 μm to 20 μm , particles are more tightly bound to the plate and start accumulating at the second layer. (b) Keeping the size of the microplate constant, the size of the colloidal particles is varied from 500 nm to 3 μm (lower panel). The number of particles which are tightly bound to the gold microplate increases as the size of the particles is increased. All the snapshots are taken at 15 min. Figure is reproduced from [68] with permission.

3.3.5 Effect of particle size variation

Next, we kept the size of the structure constant and varied the particle size. The gold plate with largest surface to volume ratio (20 μm) was chosen as it is the most efficient for assembly process. Colloidal particles of sizes 500 nm, 1 μm , 2 μm and 3 μm were chosen for study. Upon laser excitation, there is a competitive behaviour between Brownian motion and thermophoresis. Figure 3.9(b) shows the snapshot of the assembly for different particle radii at 15 min. Particles of smallest size (500 nm) were tightly bound to the structure up to a distance of 34 μm .

Rest of the particles were loosely bound to the gold microplate. For 1 μm particles, the area which is tightly bound to the heat source increases and extends up 46 μm . As we further increased the size of the particles, diffusion decreased and more stable assembly was formed. 2 μm particles showed multi-stacking of the particles. We can observe multiple layer formation up to 4 layers. Figure 3.10 indicates the number of layers formed. 4th layer formation can be seen in some regions in the vicinity of the gold

microplate. 3rd and 2nd layers extend up to $45\ \mu\text{m}$ and $112\ \mu\text{m}$ respectively. Similar kind of assembly was also observed for $3\ \mu\text{m}$ particles as shown in last column of figure 3.9(a). This gives us an important insight regarding the optimization of the assembly by controlling the microstructure as well as particle size. Through the interplay of structure's surface to volume ratio and particle size, we can design the assembly process to achieve either single layer or multilayer assemblies.

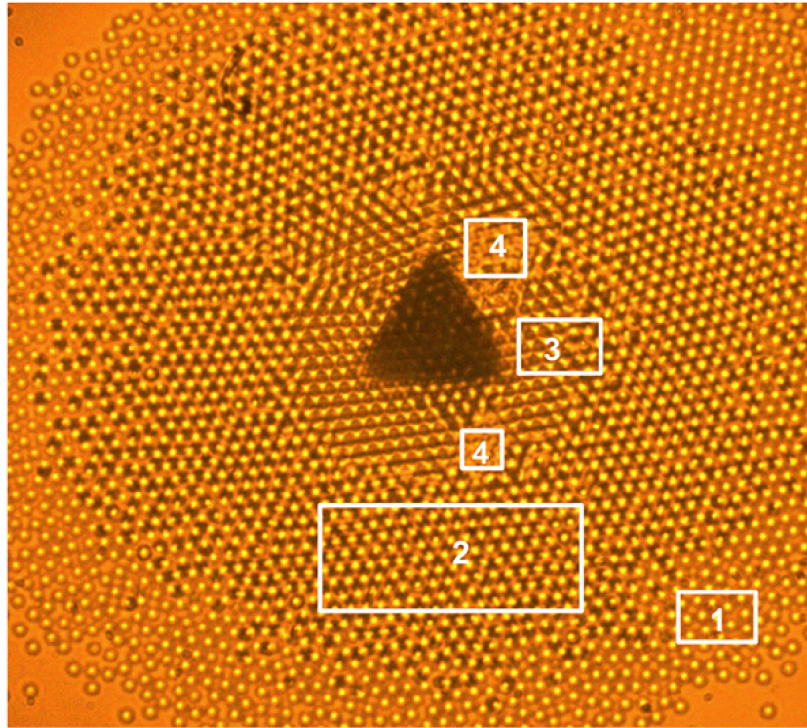


FIGURE 3.10: $2\ \mu\text{m}$ particles show multilayer formation for a $20\ \mu\text{m}$ plate. The number in the box indicates the number of the layer that has formed. Figure is reproduced from [68] with permission.

3.3.6 Effect of composition on the assembly: Silica vs Polystyrene particles

Since, thermophoresis is sensitive to the composition of the colloids [66], we investigated the accumulation with a particle of another material namely PS microspheres. A gold microplate was excited using $532\ \text{nm}$ laser, and a solution containing $0.97\ \mu\text{m}$ PS particles was injected on top of the microplate. We observed that few PS particles moved towards the gold microplate initially. There was no permanent accumulation of the particles near the gold microplate even after 30 min as shown in figure 3.11(a). Hence, we conclude that PS particles do not exhibit affinity towards the heat gradient as

compared to silica particles. To compare the assembly process of PS and silica particles under the same heat gradient, solution containing $1\ \mu\text{m}$ silica particles was injected into the sample. We observed that the silica particles assembled around the same microplate at the same input power as can be seen in figure 3.11(b). Although the PS particle has been shown to migrate away from the heat [19][103], we did not observe such movement of the PS particles. This might be attributed to different particle-solvent interactions in our system. Thus, we conclude that thermophoretic force can play an important role in the assembly process.

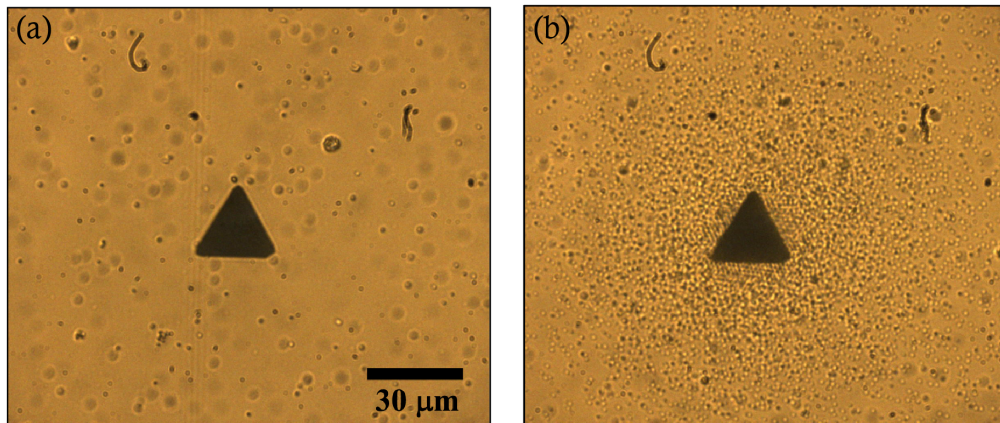


FIGURE 3.11: Comparison with polystyrene: (a) shows no accumulation of $0.97\ \mu\text{m}$ polystyrene particles after 30 min. (b) $1\ \mu\text{m}$ silica particles were added to the same solution. The accumulation of the particles starts after few seconds. The snapshot is taken after 30 min and shows the assembly of the silica particles. Figure is reproduced from [68] with permission.

The assembly of PS particles can be facilitated by excitation of an annealed gold thin film as reported in [112]. We excited a gold film of thickness $\approx 12\ \text{nm}$ evanescently, and observed accumulation of both silica and PS particles. We attribute this assembly to the generation of thermoplasmonic field. A thin gold film aids the generation of surface plasmon polaritons [6][113], facilitating the efficient assembly of PS particles. We can conclude that in our experiments, the PS particles do not exhibit affinity towards heat gradient and cannot be trapped by thermophoretic forces alone, but an additional plasmonic field can assist in trapping PS particles.

3.4 Conclusion

We have experimentally studied the assembly of silica microparticles under the influence of an optothermal field of evanescently excited gold triangular microplate. Our study shows that the silica particles show reverse thermophoresis and can create colloidal assembly up to hundreds of microns. The packing order has been quantified in terms of co-ordination number and hexagonal order parameter which peaks around 0.95. We conclude that it is important to excite the volume of the structure for efficient generation of heat by varying surface to volume ratio as well as directing the polarization perpendicular to the structure. Whereas, silica particles show a favoured accumulation towards heat, we did not observe similar trend in the case of $0.97\text{ }\mu\text{m}$ polystyrene particles. This material selective assembly may have implications in colloidal sorting. Our system is advantageous over traditional optical tweezers as it is capable of creating large-scale assemblies and may complement the existing thermoplasmonic platforms. By using an optically-excited heat source, we can possibly utilize the thermal gradient around a metal microstructure which can be harnessed in opto-thermofluidic devices. A more elaborate study of the nature of the interacting forces that drive the colloids will lead to better understanding of light activated colloidal matter.

Chapter 4

Optothermal pulling, trapping, and assembly of colloids using nanowire plasmons

In this chapter, we will discuss thermophoretic migration of a single colloid by using surface plasmons of the silver nanowire. The chapter is an adaptation of the research article "Soft Matter 17.48,10903-10909 (2021).".

4.1 Introduction

How do colloids[114][115][116][117] behave in the vicinity of an optical and/or optothermal potential? How can colloidal dynamics and assembly be controlled by harnessing optical excitation? These are relevant questions in driving soft matter out of equilibrium, where the driving force is provided by an optical excitation. In this study, we present directional pulling of dielectric colloids in the vicinity of an optically-excited metal nanowire. This movement further leads to spatio-temporal trapping of the same colloids. Upon increasing the concentration of the colloids, a two dimensional assembly emerges. This emergent process is found to be sensitive to the excitation polarization of the light illuminating the nanowire.

In this context, understanding the dynamics of colloids under such optical excitation schemes is relevant[118][119][120] [100][121]. Recently, colloidal manipulation using optical pulling forces has also gained significant interest[122][123][124][125]. Typically, colloids undergo diffusive Brownian motion[126]. Brownian motion is relevant to the understanding of the dynamics of soft matter and biological systems [127] as well as fabricated structures designed to mimic naturally occurring systems[115][128][129]. The study of the physics of systems out of equilibrium [130][131] is especially of pertinent interest as most of the living matter is far from equilibrium. In this context, colloids have been extensively studied to explore the dynamics of such systems[132][133][134]

[135]. The colloids have the advantage of easy manipulation under external fields[136][137][138][139][140][22][141]. Conventionally, colloids are trapped using a focused laser beam[2][11]. Although powerful, the conventional optical schemes are constrained by the diffraction limit of light[142]. As a complement to this, surface plasmon polaritons (SPPs) in metallic nanostructures can facilitate radiative and non-radiative pathways below the diffraction limit of light[68][55][56][6]. SPPs are surface electromagnetic waves at metal-dielectric interface[30]. They decay into the dielectric medium through radiative and non-radiative channels. Radiative channels can be harnessed for optical trapping and assembly through SPPs momentum, and non-radiative channels of SPPs can be used for optothermal assembly via thermophoretic[66][143][144] interactions.

Of relevance to this study is SPPs propagation along the silver nanowire[145][146]. When illuminated with a focused laser beam, these single crystalline, chemically-prepared nanowires can propagate SPPs. Given the geometry of the nanowire, quasi-one dimensional confinement of plasmons can lead to interesting optical and optothermal effects at sub-wavelength scales. Although SPPs in the silver nanowire have been studied extensively in the context of nanophotonics[147][148][149][150][151], their interface with soft-matter systems such as colloids is yet to be explored in detail[152][5]. SPPs have been utilized in the past to assemble particles on a large scale. But such studies have mainly relied on extended 2D plasmonic platforms such as metallic films[55][6].

Motivated by this, herein we report the directed pulling and trapping of a single silica colloid as well as assembly formation of colloids by utilizing a single, silver nanowire to create a non-equilibrium environment in the system. A laser beam (532 nm) is focused at the end of a silver nanowire, which leads to the excitation of SPPs. In this study, we explore the transport and trapping of single colloids (figure 4.1a), and multiparticle assembly (figure 4.1b) due to the optical excitation of the plasmonic silver nanowire. A representative optical image of SPPs propagating in a silver nanowire at 532 nm is shown in figure 4.1c(i). The excitation polarization of the focused laser beam is aligned along the nanowire axis. This leads to SPPs propagation which out-couples at the distal end of the nanowire (dotted circle in figure 4.1c(i)). The SPPs supported by the nanowire generate heat[17][153][154] which is subsequently released into the surrounding environment creating a temperature gradient in the system. The subsequent dynamics of the particles is studied by looking into the mean square displacement (MSD) of the particles. The MSD at time τ is defined as the ensemble average:

$$MSD(\tau) = \langle \Delta r(\tau)^2 \rangle = \langle [r(t + \tau) - r(t)]^2 \rangle . \quad (4.1)$$

where, $r(t)$ is the position of the particle at time t , τ is the time lag between two positions of the particle whose displacement is $\Delta r(\tau)$, $\langle \rangle$ is the average over time t , and/or

an ensemble-average over several trajectories.

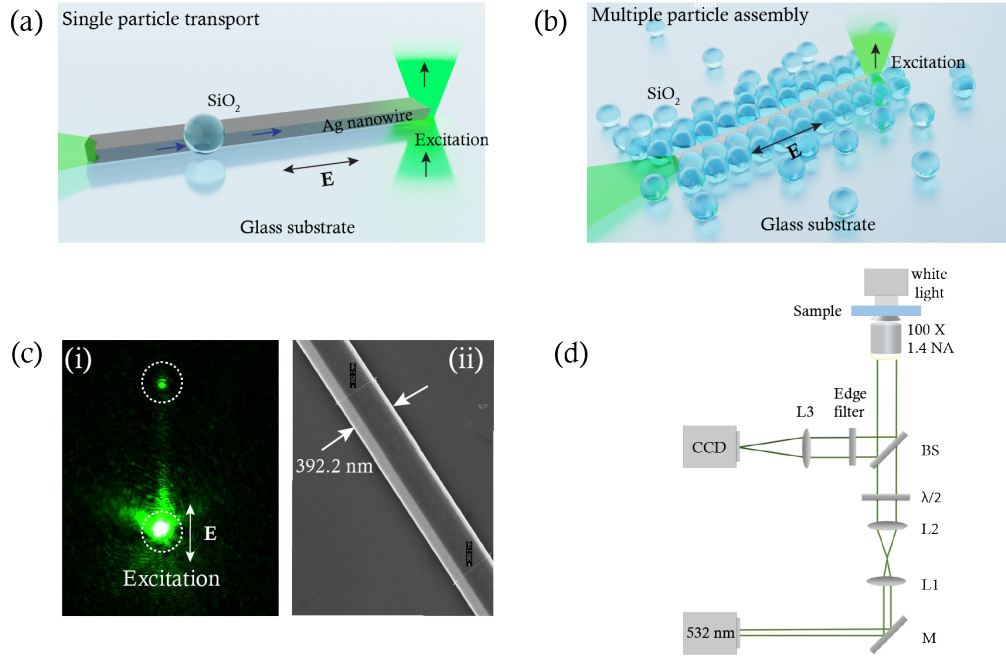


FIGURE 4.1: Schematic illustration of the experimental configuration. Silver nanowires are dropcasted on the glass substrate. One end of the Ag nanowire is excited using a 532 nm laser to excite the SPPs. The light out-couples from the distal end of the wire. Silica colloids dispersed in milli-Q water are dropcast on the glass substrate. The whole system is enclosed in a 120 μm chamber. (a) Schematic illustration of the single silica particle transport along the silver nanowire. (b) Schematic illustration of the multiple particle assembly along the silver nanowire. (c) (i) Excitation of SPPs along the silver nanowire when the polarization of the input laser is along the length of the nanowire. There are two white dotted circles in the figure. The first dotted circle represents the region of excitation, with excitation labelled next to it. The second dotted circle represents the outcoupled light at the distal end. (c)(ii) SEM image of a representative silver nanowire used in the experiments. (d) Schematic representation of the experimental setup. The silver nanowire is excited using a high numerical aperture 100 X, 1.4 NA objective lens. M is the mirror. The laser beam is expanded using a combination of lenses, L1 and L2. The polarization of the input laser is controlled using a half wave plate. The sample is illuminated from the top using a white light. The video is recorded by CCD after rejecting the elastically scattered light using a 532 nm edge filter. Figure is reproduced from [82] with permission.

4.2 Methods

4.2.1 Sample preparation and experimental design

Our experimental design constitutes a simple geometry wherein a silver nanowire is dropcasted on a glass substrate and left to dry. The silver nanowires are chemically synthesized using the polyol process[155]. The typical size of the silver nanowire used in the experiments is $\approx 300\text{-}400$ nm in diameter and $\approx 12\text{ }\mu\text{m}$ in length. The nanowire is characterized using scanning electron microscopy as shown in figure 4.1(c)(ii). The colloids consist of $2\text{ }\mu\text{m}$ silica beads (purchased from Microspheres-Nanospheres) and $2.2\text{ }\mu\text{m}$ polystyrene beads (purchased from micro particles GmbH). The colloids dispersed in milli-Q water are dropcasted on the glass substrate. The whole system is enclosed in a $120\text{ }\mu\text{m}$ spacer. Figure 4.1 (d) shows the schematic of the inverted experimental setup. A 532 nm laser is expanded using a combination of two lenses L1 and L2. A half wave plate is used to control the input polarization of the beam. One end of the silver nanowire is excited by tightly focusing the laser using a 100 X, 1.4 NA objective lens. The power at the sample plane is measured to be 5 mW. The polarization of the incoming laser is kept along the nanowire unless specified otherwise, for efficient excitation of the SPPs. The videos are recorded by the CCD at 20 fps after rejecting the elastically scattered light by a 532 nm edge filter.

4.2.2 Numerical simulations

The temperature distribution of the system is calculated using Finite element method based numerical simulations (COMSOL Multiphysics) by solving electromagnetic wave and heat transfer in solids and fluids modules in 3D. An $8\text{ }\mu\text{m}$ long silver nanowire with a diameter of 350 nm is excited using focused 532 nm gaussian beam. The whole geometry is simulated using free tetrahedral user defined mesh.

4.3 Results and Discussion

4.3.1 Single particle transport

A single nanowire dropcasted on a glass substrate can act as a guiding medium for the directed motion of the colloid from its captured location to the excitation point. The nanowire initially traps the particle at one of the locations of the wire depending on the initial position of the particle with respect to the wire.

Here, we demonstrate the trapping of the silica colloid from the distal end of the nanowire. If the particle is closer to any other location of the wire when it is in its

vicinity, it will get trapped there first, and then move towards the excitation point. One end of the silver nanowire is excited through a 100 X, 1.4 NA objective lens. The white dotted circle represents the excitation point. Figure 4.2(a) shows the time series images of a silica colloid transport along the nanowire. At $t = 0$ s, the colloid is freely diffusing in the water. As it comes closer to the wire, it gets trapped at the distal end at 13 s and starts to move along the nanowire. Within 65 s, the particle is trapped at the excitation point. To analyse the dynamics of the colloidal particle, it is essential to map out the trajectory and the associated MSD of the particle.

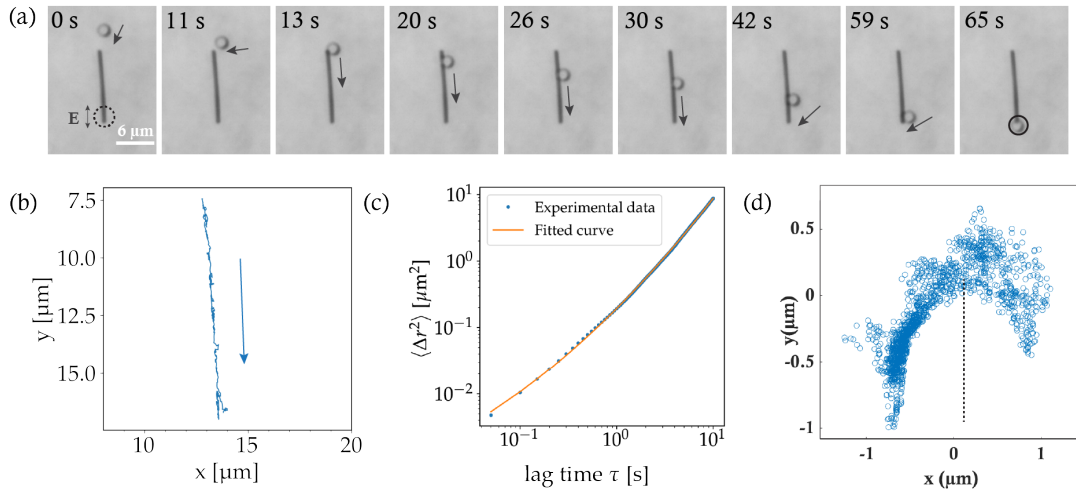


FIGURE 4.2: Single particle transport. (a) Time series images of the directed motion of the silica colloid along the silver nanowire from the distal end towards the excitation point of the laser. The polarization of the input laser is kept along the length of the silver nanowire for efficient excitation of SPPs. Black arrows indicate the direction of movement of the particle. The particle gets transported from one end of the nanowire to the other end within a minute. (b) The trajectory of the colloid is plotted. The blue arrow indicates the direction of particle transport. (c) Mean square displacement of the colloid. The blue dotted curve is the experimental data and orange curve is the fit. (d) Trajectory of the particle once it is confined at the excitation point. The dotted line represents the orientation of the nanowire with respect to the particle trajectory. Figure is reproduced from [82] with permission.

Since the particle continuously changes its micro-environment from diffusive to moving along the nanowire to permanent trapping at the excitation point, it is crucial to analyze the sections separately and not mix the resulting dynamics. Consequently, the particle is tracked from the moment it makes contact with the wire till it is transported to the other end before it gets trapped at the excitation location using Trackpy[87]. The associated trajectory of the particle is plotted in figure 4.2(b). The trajectory plot shows that the motion of the particle is highly directional. The blue arrow indicates the direction of the movement of the particle. To further investigate the nature of the colloidal transport, we plot the MSD of the colloid on a log-log scale for the same time interval, as shown in figure 4.2(c). The experimentally obtained data is plotted in dotted blue. The motion of the colloid on the nanowire can be considered as a combination of 1D Brownian motion and ballistic motion. The MSD for such a system can be described as[156]:

$$MSD(\tau) = \langle \Delta r(\tau)^2 \rangle = v^2 \tau^2 + 2D\tau. \quad (4.2)$$

where, v is the terminal velocity of the colloid due to the external force which pulls it towards the nanowire and D is the diffusion coefficient. Figure 4.3 shows the analysis of the velocity of silica colloid while it is being transported on nanowire over time. The displacement of the silica colloid was calculated for different frame differences (df) namely, 10,20,30 and 40 and corresponding velocity was calculated. The velocity of the colloid fluctuates roughly around a constant value.

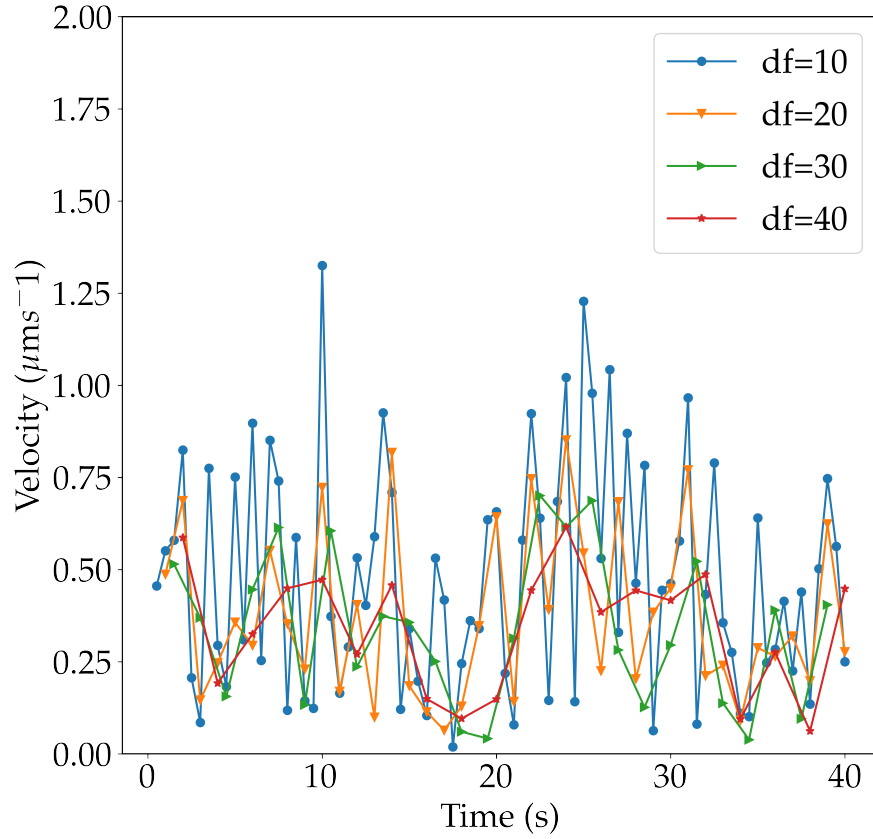


FIGURE 4.3: Displacements are calculated for frame differences (df) of 10, 20, 30, and 40 frames and corresponding velocities are plotted. The figure is reproduced from [82] with permission.

This shows that a single average velocity for the colloid can be extracted by fitting equation 2 to the experimentally observed data in figure 4.2(c), and we get v as $0.27 \mu\text{ms}^{-1}$ and a diffusion coefficient of $0.07 \mu\text{m}^2\text{s}^{-1}$. A comparative study for the Brownian motion of the ensemble of colloids which are under no laser excitation is given in figure 4.4.

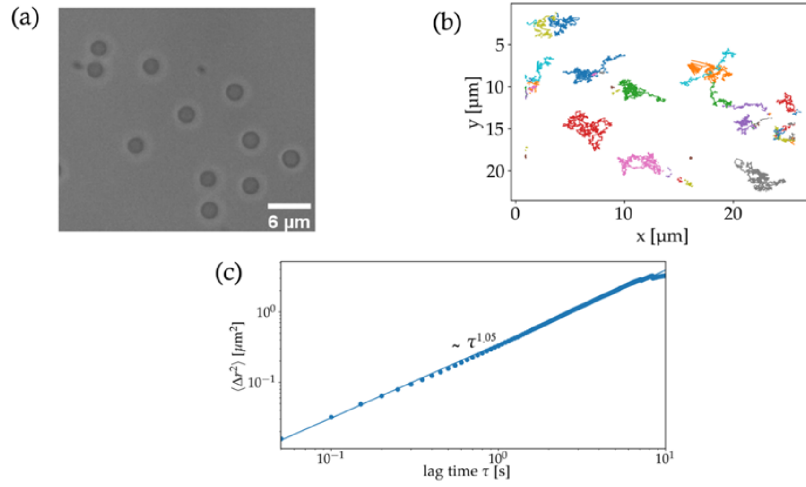


FIGURE 4.4: (a) Snapshot of particles undergoing Brownian motion. (b) Trajectories of the particles over a period of 50 s. (c) Ensemble MSD of all the particles. The diffusion exponent is 1.05. The Brownian motion of the particles is characterized when the particles are under thermal equilibrium i.e. there is no temperature gradient. The laser is switched off and the motion of the particles is recorded for 50 s. The trajectories of the particles are shown in figure 4.4(b). MSD of all the particles is averaged and plotted against lag time on a log-log scale as shown in figure 4.4(c). A diffusion exponent of 1.05 shows that the particles are undergoing Brownian motion. Figure is reproduced from [82] with permission.

Since, the colloid can be captured at any location of the nanowire, other examples of particle-wire transport system are given in figure 4.5.

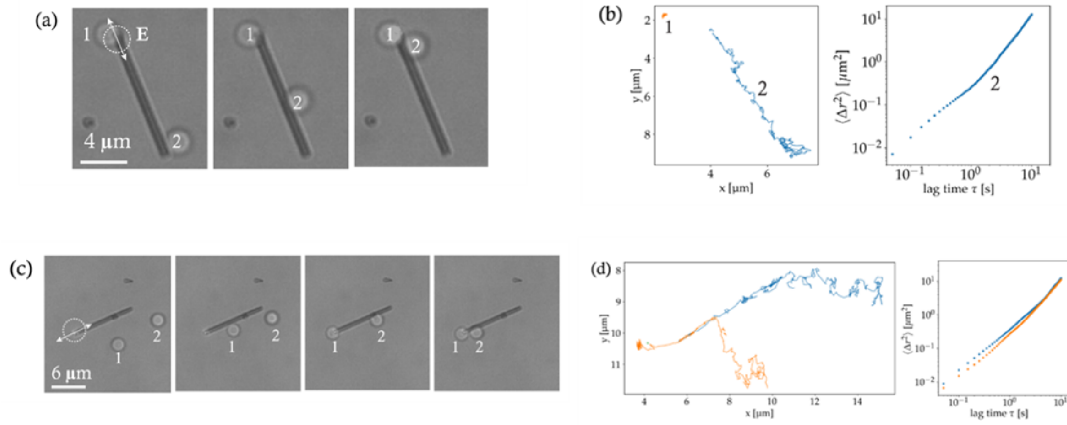


FIGURE 4.5: (a) Transport of a 2 μm silica colloid along the nanowire. The two particles are marked 1 and 2 for clear distinction between them. Particle 1 is already trapped at the excitation point. The corresponding trajectories of the two particles are plotted in (b). As particle 1 is trapped at the excitation point, its trajectory is localized and is represented by orange color. The trajectory of particle 2 is shown by blue color. The corresponding MSD of the particle 2 is also shown. Taking another case, two particles reaching the nanowire at different locations is also considered. (c) shows the series of images of two particles. Particle 1 is trapped by the wire near its middle point after which it starts to move towards the excitation point, whereas particle 2 is captured at the distal end. The trajectories of both the particles are shown in (d) marked by orange (particle 1) and blue (particle 2) color. The corresponding MSD of both the particles when they are trapped by the wire is shown in the next panel of figure 4.5(d). Figure is reproduced from [82] with permission.

A previous study reported the transport of a much smaller TiO_2 particle along the nanowire, but it is not permanently trapped and is pushed away from the excitation point into the solution[152]. In our case, once the silica colloid reaches the excitation point, it is permanently trapped there as long as the excitation laser is on. The trajectory of the trapped particle is shown in figure 4.2(d). By turning off the laser, the particle can again be released into the solution.

The efficient excitation of SPPs is crucial for the transport of the colloid. When a metallic structure is irradiated by an electromagnetic field, there is an associated heat generated in the system due to Joule heating[17]. After plasmons are launched along the nanowire, heat is generated at the excitation point as well as along the length of the wire due to plasmon dissipation. Consequently, the temperature of the nanowire increases and the heat is released to the environment. The temperature distribution details were obtained through COMSOL. The numerically calculated temperature distribution in the xy plane at $z=0$ is shown in figure 4.6 (a). The system attains a total temperature increment of ≈ 10 K at the excitation point. A plot of the temperature distribution at the

top of the wire at $z=317$ nm is plotted in figure 4.6 (b) which shows that the temperature is highest at the excitation point of the wire and gradually decreases along the length of the nanowire.

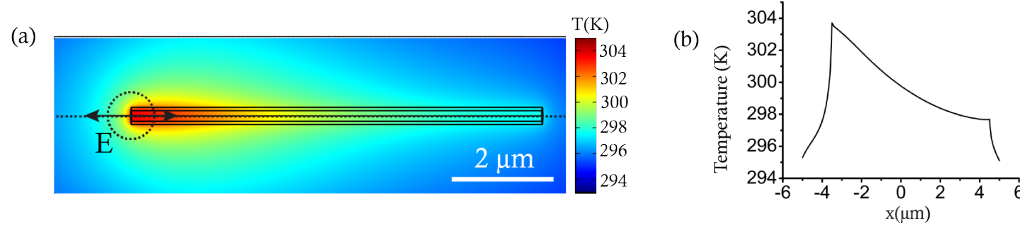


FIGURE 4.6: (a) Temperature distribution of the system in the x-y plane at $z=0$ i.e. at the base of the nanowire. (b) A crosscut along the top of the nanowire at $z=317$ nm shown in (a) as the black dotted line. The 0 in the graph corresponds to the centre of the nanowire. Figure is reproduced from [82] with permission.

As reported previously[68], silica colloids show thermophoretic migration from a lower temperature to a higher temperature. When the silver nanowire is excited, a temperature gradient is set up in the nanowire as well as its surroundings. Initially, the particle is moving freely in the water. When the colloid comes into the field of optothermal gradient of the system, it senses the temperature gradient and is pulled towards the excitation point having the highest temperature.

To compare with a particle of different composition, and to emphasize the role of thermophoretic interactions, experiments were also performed at the same laser power with the polystyrene (PS) beads of size $2.2 \mu\text{m}$. PS beads have been previously reported to move from a higher temperature to a lower temperature[19][103]. In our experiments, the PS particles initially come closer to the nanowire but as they come too close, they are repelled from the excitation point. The selective trapping of the particles shows that thermophoresis has a contributing factor in trapping the particle.

4.3.2 Confined dynamics of multiple colloids

A silver nanowire can not only trap and transport a single colloid but can also be used to assemble multiple particles along its length. A concentrated solution of silica colloids in milli-Q water was prepared so that multiple particles can come into the field of optothermal potential simultaneously. Figure 4.7(a) shows the time series images of the gradual assembly of the colloids along the length of the nanowire. At 0 s, two silica particles are trapped at the excitation point. Within 32 s, ten particles are aligned along the length of the nanowire.

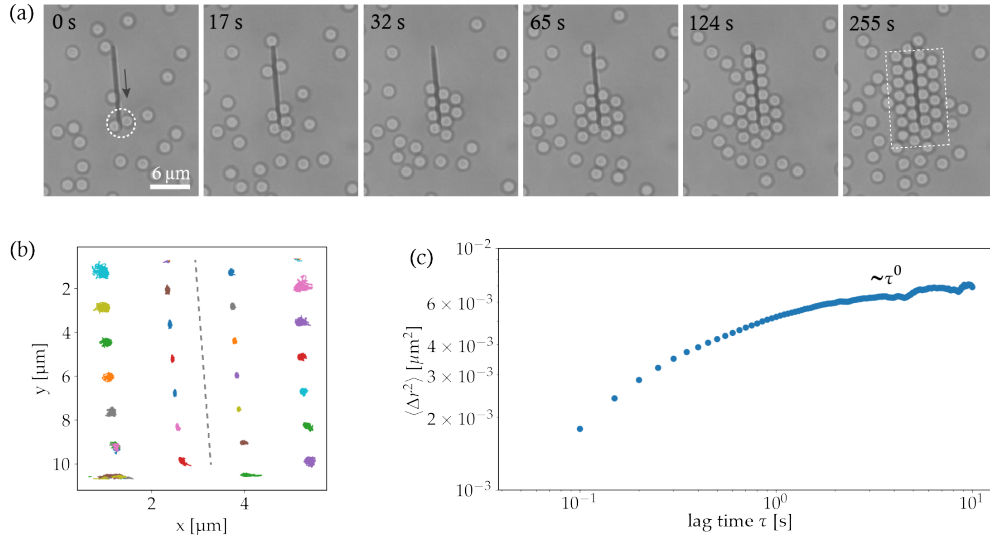


FIGURE 4.7: Confined motion of multiple particles. (a) Time series images of the gradual assembly of the colloids. Multiple layers of the colloids are formed along the length of the nanowire within 255 s. The dotted circle indicates the laser excitation point. The black arrow at 0 s indicates the direction of the motion of the colloids. The white dotted region indicates the region where colloids are tightly bound. (b) The trajectories of the particles in the white dotted rectangular region at 255 s are plotted over a time period of 150 s. (c) The averaged MSD of all the particles is plotted as a single curve. Figure is reproduced from [82] with permission.

As shown in figure 4.6(a), the temperature is higher towards the first half of the wire closer to the excitation point. Consequently, the particles first accumulate near the excitation end of the nanowire and start forming the second layer on both sides of the wire at 65 s. At 255 s, we observe a two layer formation of the colloids, which are stably trapped there as long as the laser excitation is on. The trajectories of the multiple particles shown in dotted white box in figure 4.7(a) over a period of 150 s are plotted in figure 4.7(b). The first layer closer to the wire exhibits stronger confinement to the nanowire as can be seen through the smaller spread of the trajectories of the individual colloids. Moreover, the trajectories are more confined perpendicular to the wire compared to along the wire. Since, the second layer of the colloids are not bounded by a third layer, they exhibit a larger spread in the trajectories perpendicular to the wire. The averaged MSD of all the particles is plotted in figure 4.7(c). The curve almost falls flat and saturates at large lag times with the diffusion exponent of ≈ 0 indicating the confined motion of the trapped particles. The movement of the particles is impeded and they can not freely diffuse away from the trapped location.

4.3.3 Polarization dependence of the assembly

The heat generated by the silver nanowire can be attributed to two factors. One is absorption by the wire, and the other is due to the generation of SPPs[157]. As mentioned previously, the SPPs play a crucial role in the generation of heat and consequently trapping the colloidal particles. Keeping the polarization of the beam along the silver nanowire leads to efficient excitation of SPPs as can be seen in figure 4.8 (a)(ii) and consequently, should lead to faster assembly process. Figure 4.8(a) and 4.8(b) compares the extent of the assembly for the two cases, one when the polarization of the incoming beam is along the length of the nanowire and second, when it is perpendicular to it.

First the polarization is kept along the nanowire and the snapshot of the assembly is taken at 7 minutes as shown in figure 4.8(a)(i). Once the assembly reaches the saturation point, the laser is switched off and the colloids are free to redisperse into the solution. Now, the polarization of the laser is switched to perpendicular to the wire. In this case the efficiency of excitation of propagating plasmons is drastically reduced and no outcoupling of the light from the distal end is observed as can be seen in figure 4.8(b)(ii). A snapshot of the assembly after the same time of 7 minutes is shown in figure 4.8(b)(i). A few particles near the excitation point and along the length of the wire can be seen but there is no significant assembly of the particles. The numerically calculated temperature distribution in the xy plane at $z=0$ is shown in figure 4.8(c). A comparative temperature distribution for the both the polarizations at the top of the wire is plotted in figure 4.8(d).

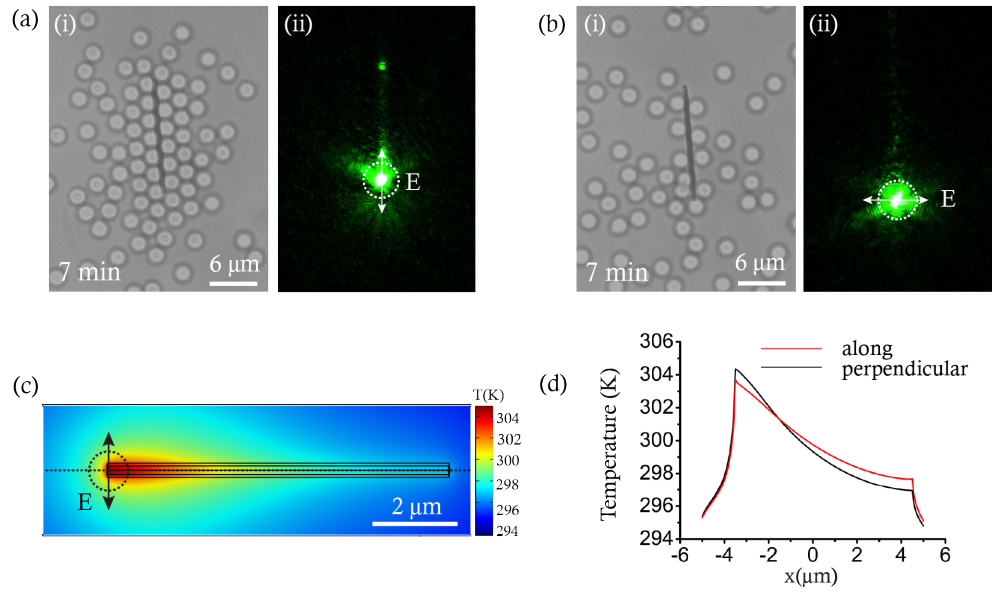


FIGURE 4.8: Polarization dependence of the assembly. (a) (i) Assembly of the colloids after 7 minutes when the polarization of the input laser is along the length of the silver nanowire. (ii) Excitation of silver nanowire. The light out-couples from the distal end of the wire. The dotted circle indicates the laser excitation point. (b)(i) There is no significant assembly of the colloids though few particles are trapped near the excitation point. (ii) Excitation of the wire when the polarization is perpendicular to the long axis of the wire. (c) Temperature distribution in the x-y plane at $z=0$, i.e. at the base of the silver nanowire. (d) A crosscut of the temperature distribution along the black dotted line at $z= 317$ nm, i.e. at the top of the nanowire is plotted for both the orientations of the polarization. The 0 in the graph corresponds to the centre of the nanowire. Figure is reproduced from [82] with permission.

A higher temperature increase at the excitation point is found in the case of perpendicular polarization. It can be attributed to the fact that at the excitation point the electric field is confined to a smaller region along the diameter of the wire leading to more localized plasmon excitation. The near-field electric field distribution for both the cases is shown in figure 4.9.

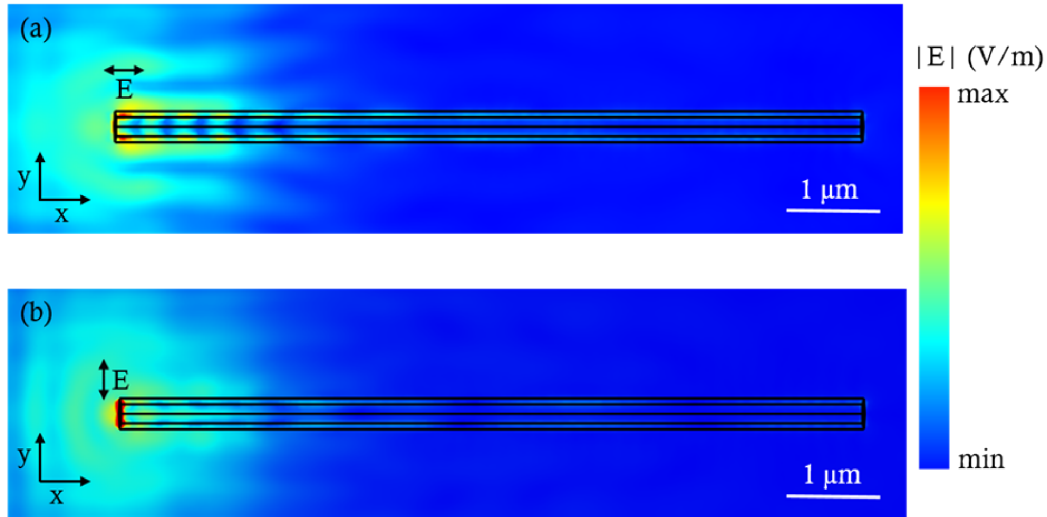


FIGURE 4.9: Calculated near-field electric field magnitude when one end of the nanowire is excited with polarization (a) along the nanowire and (b) perpendicular to the nanowire. Figure is reproduced from [82] with permission.

This enhances the temperature increment at this point, but the gradual fall in the temperature is more as there is less efficient excitation of plasmons along the nanowire and the resultant temperature increase due to plasmon dissipation is missing when there are no propagating plasmons.

4.4 Conclusion

We have experimentally studied the transport of the silica colloid by utilizing SPPs of a silver nanowire. Such a pulled colloid is spatio-temporally trapped at the nanowire excitation. Upon increasing the concentration of the colloids, we observed extended assemblies whose collective dynamics was studied and shown to be confined in nature. This assembly process is sensitive to the excitation polarization at nanowire input. This polarization-sensitivity was also corroborated in the simulated temperature distribution around the nanowire, thus indicating an intricate combination of optical and thermal effects facilitated by the nanowire SPPs. Given that the colloids are driven out of equilibrium by a quasi-one dimensional optothermal substrate, they may serve as interesting test-beds for active and driven matter at sub-micron scales. We envisage the utility of SPPs to create intriguing optothermal potentials to drive soft matter out of equilibrium, that can complement and improvise on conventional optical schemes.

Chapter 5

Marangoni flow driven trapping and manipulation of nano/micro-structures

5.1 Introduction

In the last two chapters, we demonstrated how plasmon assisted heating in metallic nanostructures can be utilized to induce thermophoretic motion of dielectric colloids. We also noted that the effect of convection in these phenomena was negligible. In this chapter, we will explore one more plasmon assisted phenomenon, namely Marangoni convection which directly influences the motion of the fluid allowing, us to manipulate an array of wide-ranging materials including, dielectric as well as metallic nano/microstructures [23][77]. This can be facilitated through the generation of microbubbles on plasmonic substrates.

Bubbles, in general play a crucial role ranging from nanometer to geophysical scales. Bubbles have been employed in ultrasound diagnostics[158], inkjet printing[159], drug and gene delivery[160], and many more. Bubbles can be perturbed both with sound and light. The acoustic dependence of bubbles has been utilized in a lot of areas[161]. We will focus on the interaction of light with the micron-sized bubbles.

In the last decade, bubbles have gained traction in the plasmonics community. Since metals are efficient converters of light to heat, using suitable laser wavelength and power, bubbles can be generated, ranging from nano to micro scales. An optothermal bubble is generated at a solid-liquid interface. The bubble is usually attached to the surface of the metal and maintains a truncated spherical shape. An optothermal bubble can be generated using either a pulsed laser or continuous wave (cw) illumination[17]. The dynamics of the bubble generation is quite different in both the cases. We will be talking about cw bubble generation and its applications.

Micro-bubbles have been utilized in developing new lithography techniques by

printing colloidal particles to substrates at desired locations[162], transport of particles to different locations[163], manipulation of biological structures[164] and many more. A very interesting application has been in its utilization as a plasmofluidic lens[165]. Plasmonics allows us to confine light beyond the diffraction limit at subwavelength scales through SPPs. It was shown that bubbles can act as tiny micro-lenses that can collimate, diverge, or focus these SPPs at micron length scales. The simplicity with which bubbles can be generated at any desired location on the substrate, and the fact that it can modify the light direction opens up a lot of interesting directions to look into. Another interesting aspect of the bubble that has been implemented to manipulate the micro-particles is to utilize the temperature gradient dependence of the surface tension on the surface of the bubble. It can generate strong Marangoni flows, which helps move the particles at very high speeds[166], which is usually not possible if we rely only on the convection currents induced by heating of a nanostructure[15].

The generally accepted methods of particle manipulation strongly depend on the dielectric contrast between the particle and the fluid it is embedded in. The experiments based on thermophoretic traps, as established in chapter 3 and chapter 4 can not be used to trap particles of all materials. Here, we overcome this disadvantage by introducing a microbubble based trap. We show that when a microbubble is generated, the colloids start tracing the flow of the fluid and start to rotate in the two counterclockwise vortices that are generated on the bubble surface. Unlike well established methods of particle rotation which usually utilize laser beam engineering like introducing angular momentum or spin in the beam to rotate the particles, here we can induce an orbital motion of the colloids with a relatively simpler experimental setup. This is achieved through surface tension gradients induced in the system, which we will explore in the following sections.

5.2 Physics of Microbubbles

5.2.1 Bubble formation under cw illumination

Bubbles can be generated by focusing a laser source on a metallic structure such as a single nanoparticle, an array of nanoparticles or an extended structure like a gold film. The temperature increase due to the heating of metallic structure gives rise to the formation of a bubble. In practice, air molecules are adsorbed on the surface of the substrate, and air molecules are also dissolved in the water. The formation of the microbubble was studied in [78], where the formation of microbubble was divided into four phases

which include a giant vapor bubble, oscillating bubbles, vaporization dominated growth and finally, slow expansion of the microbubble. This entire process is shown in figure 5.1.

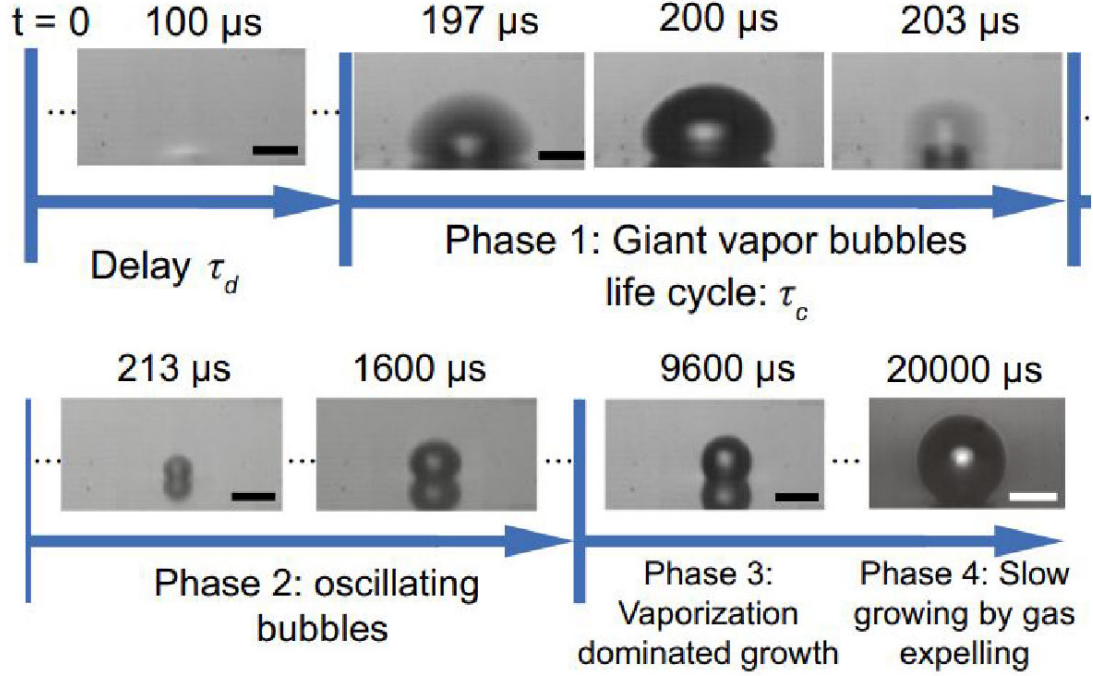


FIGURE 5.1: Time series images of the evolution of a plasmonic bubble.
Figure is reproduced from [78] with permission.

Once the bubble forms, the dissolved gases say, N_2 in the water diffuses into the bubble, and the bubble keeps on increasing in size until an equilibrium is reached between the chemical potential of the N_2 inside and outside the micro-bubble. If the microbubbles were made of only steam, they should disappear as soon as the laser is switched off. Such an air bubble shrinks slowly compared to bubbles generated in pulsed laser excitation and can remain stable for seconds, minutes, or even hours, even after the laser is switched off. The accepted temperature for the formation of a bubble in the literature under cw illumination is $\approx 230^\circ C$ [4]. The existence of a liquid above in a metastable state above its boiling temperature is called superheating. The pressure inside the microbubble is given by:

$$P_{MB} = P_\infty + \frac{2\gamma}{a} \quad (5.1)$$

where P_∞ is the ambient pressure, γ is the surface tension of the fluid, water in this case and a is the radius of the microbubble. For water, $\gamma \approx 0.059 Nm^{-1}$ at $100^\circ C$ at atmospheric pressure, which gives an internal pressure of 3.4 bar. For this pressure, the boiling point is larger than $100^\circ C$.

The differential equation governing the evolution of a microbubble is given by:

$$\dot{a} = -\frac{2\gamma DRT}{Ka^2 \left(P_\infty + \frac{4}{3}\frac{\gamma}{a}\right)} \quad (5.2)$$

where, D is the molecular diffusivity in the fluid, R is the gas constant, T is the temperature of the microbubble. For bubbles in the range of micrometers the term γ/a can be neglected. The above equation then becomes:

$$a(t)^3 = -\frac{6RTD\gamma}{P_\infty K}t + \text{const} \quad (5.3)$$

Now we can calculate the lifetime of the microbubble as:

$$\tau_{\text{MB}} = \frac{P_\infty K}{6RTD\gamma}a^3 \quad (5.4)$$

5.2.2 Marangoni convection in the bubble

Marangoni flows are generated whenever there are surface tension gradients in the system. The surface tension gradients can be generated either by the gradients in chemical composition or temperature at the interface of the bubble. The fluid must flow whenever there is a surface tension gradient in the system. A system can not remain stationary when there is an unbalanced force acting on it. Hence, a flow will be generated at the free surface of the bubble. Let us simulate the Marangoni flow for bubble and compare it with the convective flow using finite element based simulations in COMSOL.

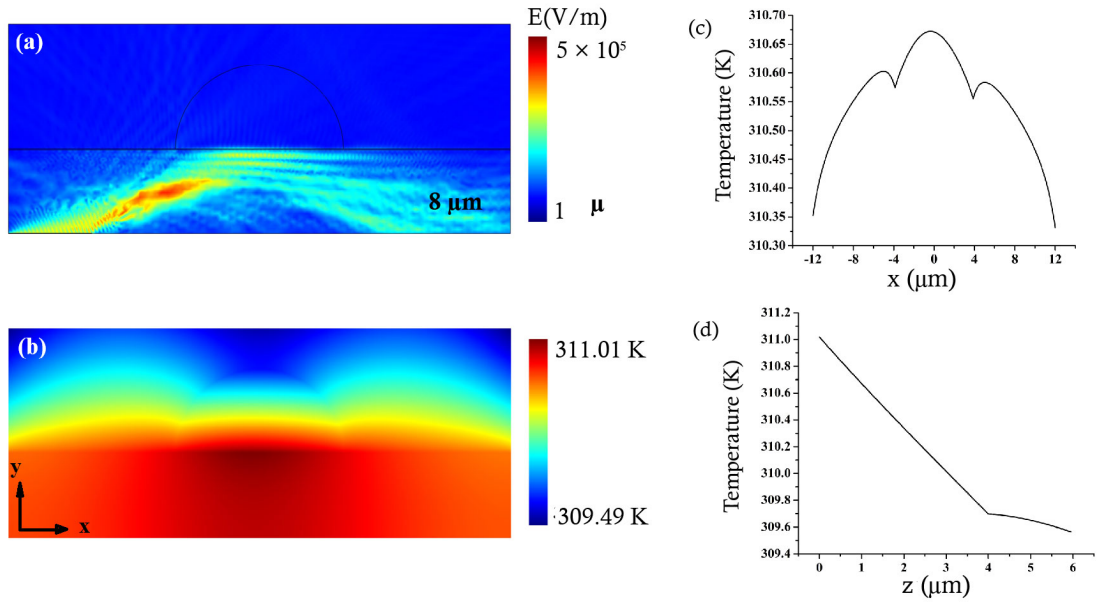


FIGURE 5.2: (a) Evanescent excitation of the bubble (b) Temperature profile distribution in the system. Temperature profile distribution (c) along x - direction at a distance $1 \mu\text{m}$ above the gold microplate. (d) along y -direction from the surface of the gold plate.

The electromagnetic wave module, heat transfer module in solids and liquids, and the laminar flow modules are solved simultaneously. The geometry of the box is $20 \mu\text{m} \times 10 \mu\text{m}$. A 50 nm thin gold layer is placed over the glass substrate. An $8 \mu\text{m}$ diameter bubble is placed over the gold film. The bubble is defined by considering a hemispherical geometry with the refractive index of air. The whole structure is illuminated through a 532 nm evanescent excitation as shown in Figure 5.2(a). The temperature field distribution is shown in Figure 5.2 (b). A crosscut is taken along x and y directions to get the variation of temperature along these directions. Figure 5.2(c) shows the temperature profile along x direction, at a distance $1 \mu\text{m}$ above the surface of the gold plate.

The temperature inside the bubble is greater than outside. Figure 5.2(d) shows the crosscut along y -direction from the surface of the gold plate to the top surface of the box. The temperature decrease in the y -direction is steeper than the x -direction.

The next step is to calculate the velocity field around the bubble. Two cases are studied. In the first case, the Marangoni effect was considered to play a role by introducing surface tension between the air/water interface of the bubble.

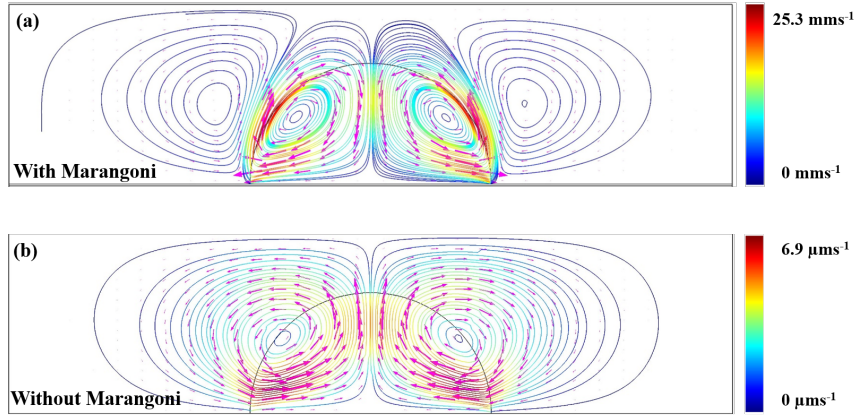


FIGURE 5.3: Velocity field profile around the bubble (a) when surface tension at the air/water interface of the bubble is taken into account. (b) without accounting surface tension effects. The streamlines are color coded with the magnitude of the velocity.

The resultant flow profile is shown in Figure 5.3(a). A maximum velocity of 25.3 mm s^{-1} is computed.

Next, the flow profile is simulated without considering the interfacial surface tension effects shown in Figure 5.3(b). Again, we observe two counter-rotating vortices, however the flow profile is different from Figure 5.3(a). This is expected to be the buoyancy driven convection current. The maximum velocity obtained in this case is $6.9 \text{ } \mu\text{m s}^{-1}$, which is less than that obtained in Marangoni convection driven flow.

5.3 Experimental Setup

A Gold film was prepared by thermal vapor deposition to act as a heating source. A 532 nm continuous wave (300 mW) laser was used to excite the gold film. The laser was loosely focused through a 100 mm lens and was totally internally reflected at the glass-gold interface using a dove prism. The polarization of the incoming light was perpendicular to the glass/gold interface (p-polarized) for efficient excitation of plasmons.

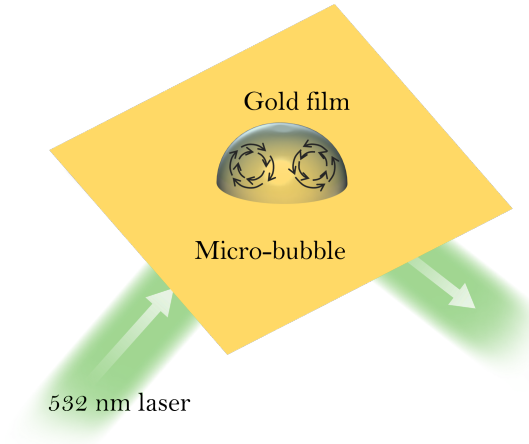


FIGURE 5.4: Schematic of the experimental setup

The size of the laser spot was approximately 200 micron. A droplet of milli-Q water approximately 30-50 μl was placed on top of the gold film. A 4x objective lens was used to capture the scattered light. The 532 nm edge filter was used to reject the elastically scattered light.

5.4 Results and Discussion

When the gold film is excited by a 532 nm laser, a microbubble with a diameter of 100 μm is formed. Initially, the bubble starts to grow and eventually reaches a steady state around 2.95 s. Figure 5.5 shows the time series of the snapshots taken at different times during the evolution of the bubble.

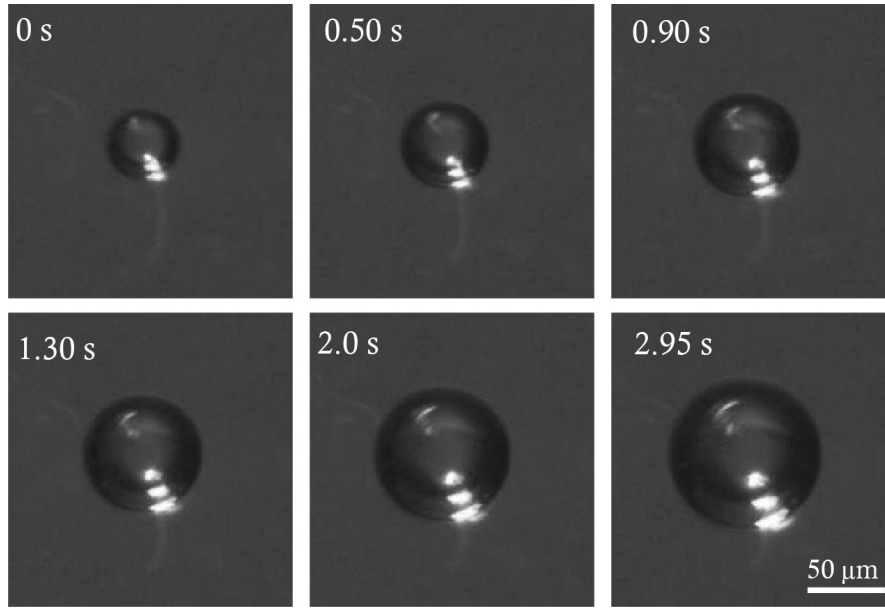


FIGURE 5.5: Time series images of the microbubble formation. The snapshots show the evolution of the microbubble from 0s to 2.95 s after which the microbubble reaches the maximum diameter.

Next, we demonstrate the trapping and manipulation of the movement of the colloids over the surface of the bubble. After the formation of the microbubble, the surface tension gradient induces two counter-rotating vortices on the surface of the bubble. The position of the laser spot is changed with respect to the bubble. The particles move away from the laser spot as the laser is scanned at various positions with respect to the bubble. Figure 5.6 shows the snapshots taken at different times.

To understand this, we have to look at the temperature gradients in the system. When the laser spot heats the gold plate, temperature gradients are induced in the system. The side of the bubble which is closest to the laser spot is expected to have the maximum temperature, and the temperature gradually reduces towards the other side. Since the surface tension is strongly dependent on the temperature, a surface tension gradient is also established in the system. Now, surface tension reduces with the temperature increase, and consequently, the surface tension reduces towards the warmer liquid (close to the laser) and is strongest at the cooler surface. Hence, surface tension is able to pull the liquid away from the laser spot. This generates two vortices, one of which is rotating clockwise and the other counter-clockwise as indicated in the Figure 5.6. With the formation of the vortices, the colloids are pulled towards the bubble due to the strong flow of water and start rotating along with the vortices.

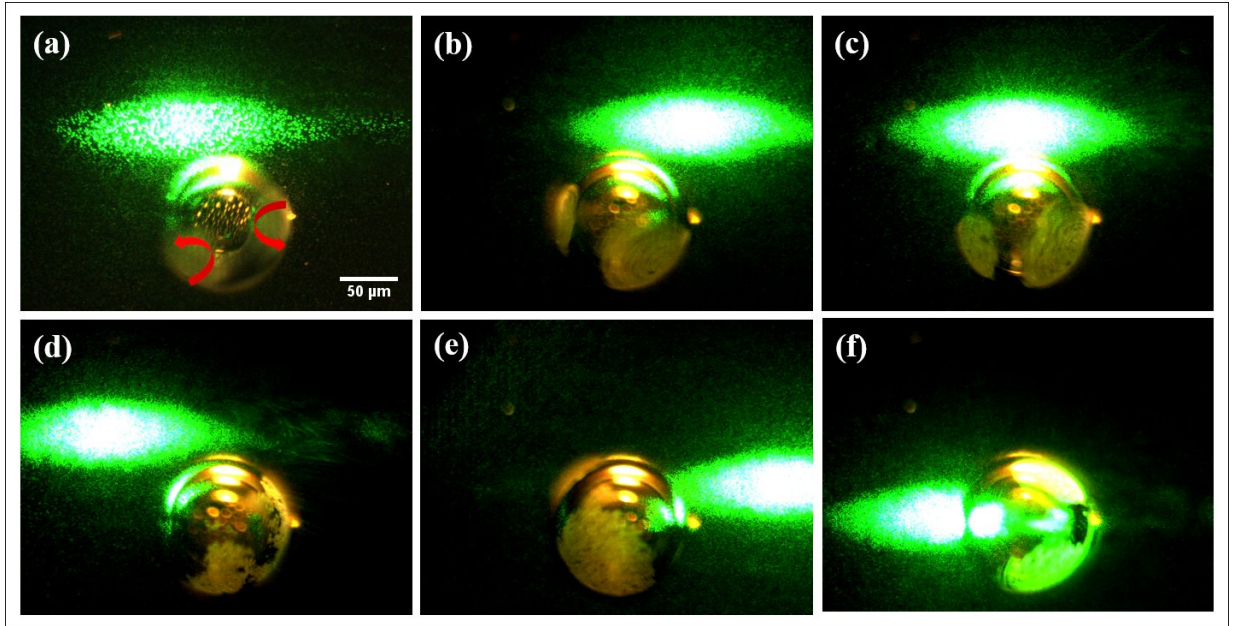


FIGURE 5.6: Series of images showing thermo-plasmonically generated Marangoni flows on the surface of the microbubble as a function of laser spot position. The direction of the movement of the vortices is indicated by red arrows in (a). The colloids are pulled along with the vortices due to strong flow of the water and start to rotate along two vortices.

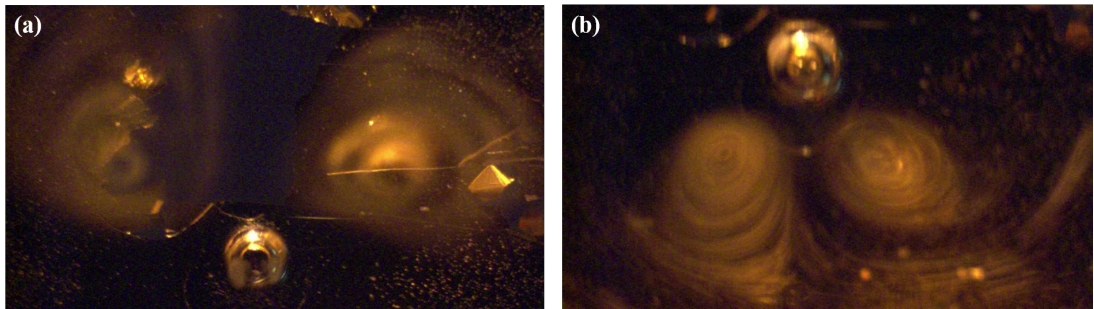


FIGURE 5.7: The thickness of the water layer gradually decreases and additional vortices can be seen in the horizontal plane of the bubble. (a) and (b) show the change in the position of all the 4 vortices as the position of the laser spot is changed.

As the time progresses, the water also evaporates and the thickness of the water layer keeps on decreasing. Eventually, we see the generation of vortices outside the bubble. Again the position of all four vortices can be changed by changing the laser spot as shown in Figure 5.7.

This offers the advantage of using the bubble to trap a wide variety of nano/micro-structures. We have been able to trap both metallic as well as dielectric particles. Also, we don't have to worry about the asymmetry in the structure. Silver nanowires, which are quasi 1-D nanostructures (length approximately $10\ \mu\text{m}$, diameter $350\ \text{nm}$) have

been trapped in the past by utilizing complex configurations [167], whereas multiple nanowires could be trapped using Marangoni flows.

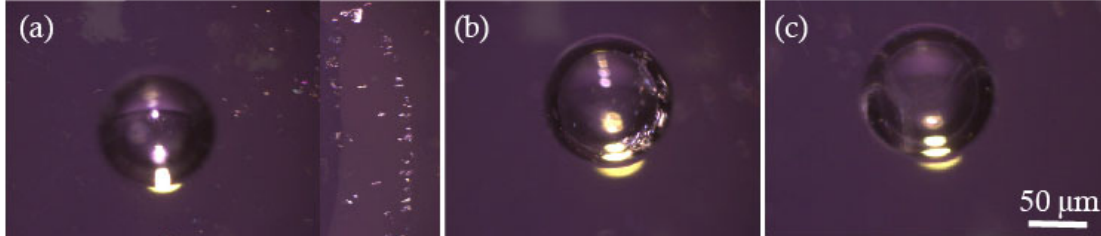


FIGURE 5.8: Schematic of a typical optical tweezer setup.

Figure 5.8 shows the trapping of silver nanowires by the microbubble. (a) shows the presence of silver nanowires in the sample that have stuck to the substrate. (b) shows the presence of the silver nanowires on the surface of the bubble. In this case, we can not visualize the individual wires clearly as we are using a low magnification objective lens. (c) shows the rotation of the wires along with the vortices. The possibility of trapping a single nanostructure using bubble still needs to be tested, however it is very efficient to trap a collection of particles.

5.5 Conclusion

We have experimentally studied the formation of the microbubble over a plasmonic platform by utilizing the photothermal property of the gold film. Such a bubble generates Marangoni flows around it leading to the formation of two counter-rotating vortices. We further show that the position of the particles over the bubble's surface can be manipulated by scanning the laser across the microbubble. Not only dielectric beads but plasmonic structures like silver nanowires could also be trapped. Our system provides an interesting platform for trapping and manipulation of the nano/microstructures and is independent of the dielectric constant of the object being trapped. We envisage that such a platform can be utilized to manipulate the nanostructures without using angular momentum or spin of the beam to rotate the particles.

Chapter 6

Conclusion and future direction

The work included in this thesis focused on realizing optothermal tweezers by integrating plasmonics with trapping methods. Plasmonic nanostructures not only confine light beyond the diffraction limit of light but also act as efficient heat sources due to light absorption and heat dissipation. The resultant temperature gradient in the system can give rise to rich set of thermodynamic processes such as thermophoresis, thermoosmosis, convection, phase transition such as bubble formation, and Marangoni convection to name a few. Among these thermal processes Chapter 3 and Chapter 4 detail particle assemblies due to thermophoretic migration of colloidal matter, whereas Chapter 5 exploits bubble formation and Marangoni convection. Herein, we will summarize whatever we have discussed so far and look at some of the limitations of the work as well some future directions:

Optothermal manipulation with thermophoresis

Chapter 3 and Chapter 4 utilize surface plasmon assisted thermophoretic migration of colloids. In Chapter 3, a gold microplate was excited using Kretschman configuration. Gold microplates can support plasmons in two dimensions and offer efficient generation of heat due to their planar structure. The excitation of surface plasmons generated heat in the system which was then released in to the surrounding environment. As a result, we observed large scale migration of colloids towards the microplate. The resultant colloidal crystal could be tuned by varying several parameters like surface/volume of the gold microplate, polarization of the incoming beam, and size and composition of the colloid.

In Chapter 4, surface plasmons were confined quasi one dimensionally along a silver nanowire to drive the directed pulling and transport of a single colloid. By increasing the concentration of the colloids, larger assemblies could be formed. The temperature profile and temperature gradients set up in the system were calculated using finite element based numerical method.

Limitations and future directions

The first challenge lies in predicting the Soret coefficient of the particles. As Soret coefficient is highly sensitive to the particle-solvent interactions, even a small change in the pH, salinity or electrolytic concentration can change the Soret coefficient of the colloids. Hence, it is imperative to engineer the colloid functionalization as well as solvent environment to gain better control over the migration of colloids. In our work, we could observe that thermophoretic migration was dependent on the composition of the colloid. Specifically, we could assemble silica colloids but polystyrene particles did not show any affinity towards the heating structure. This composition dependent movement of colloids can be possibly harnessed for selective trapping and sorting of colloids. Also, the temperature increment in the system were calculated numerically. It would be beneficial to measure the local temperature of the plasmonic nanostructures experimentally.

Optothermal manipulation with the microbubble

In Chapter 5, we generate microbubbles to trap and rotate colloidal matter at the surface of the microbubble. The temperature gradient in the system gives rise to a surface tension gradients which drives the fluid to flow from hotter to colder regions. Trapping colloids through fluid flow is advantageous as the trapping mechanism is independent of the dielectric properties of the colloids so that a wide array of plasmonic as well as dielectric particles can be manipulated.

Limitations and future direction

In the current work, we do not have a precise control over the size of the microbubble. A definitive control over the microbubble's size can help us to create controllable fluid flow. Furthermore, we could not translate the microbubble over the substrate by moving the laser position which limits its usability for the purpose of colloidal transport. Some advances have been made towards controlling the Marangoni flow speed by solvent modulation [76]. Thus, we can further benefit by optimizing the solvent environment to maximize the flow speeds. Such systems can potentially be utilized in microfluidic channels. As bubble dynamics involves an intricate play of optical, thermal and fluid physics, we need a multidisciplinary approach to gain better insights into the physical mechanisms involved.

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