PLASMONIC RESONANCE OF ACTIVE NANOPARTICLE DIMER SYSTEMS
IN THE PRESENCE OF OPTICAL BINDING FORCES

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ABSTRACT

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Optical properties of metal nanoparticles are related to the collective oscillations of loosely bound conduction electrons, popularly known as plasmonic resonance. Remarkably, such resonances are tunable with the composition and geometrical parameters of the nanoparticles. Multiple nanoparticles located in proximity show mutually influenced optical response that can be tuned by, along with many other means, varying the interparticle separations. In this thesis, a tunable surface comprised of a Silver dimer was designed where the interparticle separation is varied with the aid of optical binding forces. When such a tunable surface is subjected to a narrow band light incidence, it can shift the center frequency of the incident light. Such frequency shifts can be controlled with their separation distances. The repulsive binding forces shift the response towards the higher wavelengths (redshift). For attractive binding forces, the output response band widens with a similar redshift.
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CHAPTER 1
INTRODUCTION

Intense research effort has been dedicated to the investigation of the properties of metal spherical and core shell nanoparticles. These particles have wavelength dependent complex permittivities with negative real parts and show plasmon resonance. Remarkably, this resonance frequency can be fine tuned with the physical parameters (i.e. sizes, shapes, presence of the other nanoparticles in close proximity). In this research work, such tunability was exploited to theoretically construct an electromagnetically tunable surface comprised of a Silver nanoparticle dimer loosely attached to an optically inactive substrate. The interparticle separation of the dimer is modified with the aid of optical binding force.

1.1 Historical Review

1.1.1 Optical Binding

Electromagnetic waves, possessing momentum and energy can exert forces on material surfaces. James C. Maxwell first formulated the mathematical frameworks that predicted [1] the radiation pressure of light. These frameworks later evolved in to the electromagnetic wave theory. Maxwell’s prediction was verified by the observation of light pressure on reflectors in vacuum [2, 3]. Then the theory was quantitatively verified by Poynting’s detailed calculations [4] of the radiation pressure. After the invention of the laser and followed by the inaugural demonstrations of optical forces by Ashkin [5], optomechanical effects received tremendous research efforts over the past four decades. The ability to manipulate colloidal microparticles and nanoparticles with light has been at the core of such endeavors.
Arthur Ashkin first demonstrated the manipulation of colloidal particles [5], which was then called optical guiding. At first, using a single horizontally propagating laser beam, the micron sized particles were drawn to the axis of laser and accelerated toward the direction of propagation. Then the addition of a second counter propagating laser beam of similar power eventually led to the capture of the particles. Thus the experiment demonstrated optical trapping action. At the heart of optical trapping is the interplay of the scattering and gradient forces. The scattering force pushes the particle away from the optical source. On the other hand the gradient force pulls the particle in to the high intensity light beam focus. When a balance is achieved between the aforementioned two forces, the particles get trapped in light, hence the term optical trapping. In 1986, A. Ashkin et al demonstrated particle confinement using a single beam gradient trap [6], and the technique gained popularity as the optical tweezers. Today this is the most ubiquitous method for optical micromanipulation of colloidal particles [7], neutral atoms [8], and even living cells [9].

The curiosity towards multiple particle trapping [7] eventually led to the discovery of optical binding phenomenon. In contrast to scattering and gradient forces, optical binding involves optically modified inter-particle interactions. The optical binding may be defined as the stable spatial reconfiguration of micro and nanoparticles due to light illumination and a simultaneous redistribution of incident light by the particles involved [10]. Here, the term “reconfiguration” refers to the settling of the particles at well-defined inter-particle distances in the system.

The possibility of a coupling between optically induced dipoles based on an exclusive quantum electrodynamic analysis was first expressed by Thirunamachandran [11]. Burns et al [12] presented a semiclassical treatment of pair potential energy plot against particle center separation. These two particles were identical and spherically shaped and they have considered the case where the inter-particle separation vector ($\vec{R}$) and the Poynting vector ($\vec{S}$) are mutually orthogonal. The rolling potential landscape of their work immediately spurred the interest of the scientific community
for its vast applicability. Consequently, Z. J. Ng et al [13] rigorously proved the possibility of the three dimensional stability of “optically bound” cluster consisting of three or more particles. Michael M. Burns et al experimentally demonstrated [12] a series of bound states formation between two 1.43 \( \mu m \) diameter plastic spheres in water with Ar laser of 10W and vacuum wavelength of 541.5nm. The same research group in 1990 [14] showed the coupled electromagnetic fields to microscopic dielectric objects and created arrays of extended crystalline and noncrystalline structures. Both the polarizable particles and the presence of light were proved to be necessary for such bound structure formation.

In 2002, Tatarkova et al [15] experimentally demonstrated the formation of a one dimensional array of 3 \( \mu m \) diameter and 2.3 \( \mu m \) diameter spheres with two counter-propagating 25mW continuous wave Ti–sapphire laser beams. They have reported the 48 \( \mu m \) of interparticle spacing. In 2003, W. Singer et al [16] reported the array formation with counter propagating near-IR laser beams of 1.064 \( \mu m \). The beads that were significantly larger than the laser wavelength are pressed against each other in an axial line. In contrast, the smaller beads were found to spontaneously and equidistantly arrange themselves into regular chains. The separation of the particles increased with the increasing bead sizes. In these types of counter propagating beam systems the electrostatic interactions play an important role [10].

The theoretical frameworks for such experimental observations began to take shape soon afterwards. M. Mansuripur [17, 18] and B. Kemp et al [19] have derived the optical force from the Lorentz force acting on the currents due to polarization of the dielectric and bound charges at the boundaries. Tomasz M. Grzegorczyk et al [20, 21, 22] focused on the infinite cylindrical geometries and used the Foldy [23]–Lax [24] multiple scattering equations to formulate the exact interactions between the particles. Using the side scattering arrangements and plane wave illumination in the perpendicular direction of cylinder axis, they have demonstrated optical guiding, optical sorting and even optical confinement between two arrays of fixed cylinders.

Two broad classes of optical binding are most commonly discussed in the liter-
nature. First of them is the lateral optical binding \[12\] where the particle separation vector \(\vec{R}\), the incoming power-flux direction \(\vec{S}\) and the incident electric field \(\vec{E}_i\) are all mutually orthogonal. Dholakia et al \[10\] have defined the lateral binding based on the \(\vec{S}\) and \(\vec{R}\), where the electric field is parallel to the interparticle separation vector but perpendicular to the power flux. Another class of optical binding is the longitudinal binding where the particle separation vector is parallel to the direction of power flow \[15, 16\]. For the first type of optical binding the particles might be aligned in the direction of the electric field or magnetic field. However, in the case of electric field directed alignments, a \(\phi\) directed force also acts between the particles. This force tends to align the particles in the direction of the magnetic fields, in which case the \(\phi\) directed force becomes zero.

1.1.2 Plasmon Resonance in Metallic Nanoparticles

Plasmonics has been a leading research matter in nanophotonics and it describes how electromagnetic excitation can be confined over sub-wavelength dimensions. The conduction electron of the metal is loosely bound with the positive nucleus. As a consequence, in a given metal crystal all of the positive atomic centers forms the core and the conduction electrons become delocalized from the atomic center. These electrons collectively form the “electron cloud”. This electron cloud is not confined to any particular atom, rather they wander around the entire metal crystal freely. When a metallic entity, either a bulk metal or metal microparticles or metal nanoparticles, is subject to an external electromagnetic excitation, the conduction electrons start to oscillate along such external stimuli. In this process, the electrons themselves radiate electromagnetic waves that couple with the incoming radiation. This phenomenon is defined as the plasmonic resonance. The plasmonic resonance, in general, results in an enhanced optical force in metallic nanoparticles \[25\]. Two classes of plasmon resonance exist in nature. The first one is surface plasmon polariton and the other one is localized surface plasmon resonance. *Surface plasmon polaritons* (or *SPP* in short) can be defined as the electromagnetic excitations that are propagating in an
evanescent fashion at the interface between a dielectric and a conductor (i.e. metal). The surface plasmon polaritons can be thought of electromagnetic surface waves resulting from the coupling between the fields and the oscillating electron plasma of the conductor. The SPP is characterized by their dispersion, propagation length, and the amount of field confinement. Its counterpart, the localized surface plasmons, or surface plasmons in short, are non-propagating excitation of the metals' conduction electron plasma. These arise from the scattering of electromagnetic waves from the sub-wavelength sized particles. The shapes of the particles offer a restoring force on the displaced electrons and therefore a resonance occurs. Such resonances result in a field enhancement both inside and outside the particle. This resonance is called localized surface plasmon resonance or sometimes localized plasmon resonance in short.

Plasmonic resonance has a plethora of extremely useful applications in Raman scattering [26], plasmonic resonance based sensing [27], cancer detection [28] and treatment [29], modeling of living tissue [30], plasmonic photovoltaics [31] and so on. Inspired by the fundamental question of how atomic and molecular physical behavior develop with varying sizes of the particles, the search for new material has been intensified. Due mainly to this reason, the colloidal solutions of metallic (especially Ag and Au) nanoparticles have long fascinated the scientific community.

The term nanoparticle is a generalized term that encompasses small clusters (fewer than 100 atoms) or giant molecules (1 nm) or larger particles with tens to hundreds of atoms (diameters of 10 nm to 100 nm) [32]. The larger nanoparticles are known among the scientific community as "colloids". The nanoparticles are comprised of metals in their neutral valence state or as their oxides, sulphides, selenoids etc. Recently, semiconductor nanoparticles have also attracted much attention due to the presence of their bandgaps and the means to control those bandgaps to give rise to the transitions between different regimes of the electromagnetic spectra [33, 34, 35]. These metal nanoparticles are prepared by metal vapor synthesis [36], reduction of metal salts with the reducing agents such as Sodium Citrate, phosphor,
Sodium borhydride or Hydrogen [37]. Turkevich and collaborators have reported the successful synthesis of gold nanoparticles with average diameter of 20nm [37, 38, 39].

The recorded evidence of colloidal gold as a coloring agent dates back as early as the fourth century as shown in Figure 1.1. The Lycurgus cup look green when illuminated with an ambient light. However, the same cup looks bright red when illuminated with a transmitted light (i.e. the light source located inside the cup). Only recently, the reason for such “anomalous” characteristic has been attributed to the presence of gold and silver microparticles and nanoparticles present in the cup. In the 19th century, Michael Faraday pointed out the ruby red color of the colloidal gold originates from the presence of “aggregates” of gold atoms [40]. However, analyzing the aggregates any further was not possible during his time due to the lack of modern analytic tools such as the transmission electron microscopy (TEM). For isolated, nanoscale metal particles with the diameter comparable to the penetration depth of an electromagnetic waves into that metal, the clear distinction between the surface plasmon and bulk plasmon vanishes [41]. An external electromagnetic excitation can

Figure 1.1: The Lycurgus cup. Late Roman Ampire 4th Century AD. (British Museum, London, UK)
penetrate the nanoparticles, unlike the their bulk counterparts. Such a penetration can shift the quasi-free ground state electrons with respect to the particles’ metal ion lattice as shown in the Figure 1.2. The resulting surface charges are of opposite in charge on the opposite surfaces of the metal. This produces a local restoring force within the particle itself. Such a restoring force is proportional to the shift of the electron cloud. The coherently shifted electron cloud of the metal nanoparticles can thus be modeled as an oscillator with the resonance frequency being dependent on various physical parameters. If a metal nanoparticle is excited resonantly, the amplitude of the induced electromagnetic surface plasmon can exceed the exciting fields in the orders of $10^{14}$. This phenomenon is called the optical near field enhancement.

![Figure 1.2: Illustration the of plasmonic oscillation for a sphere](image)

1.2 Optical Binding Forces in Metallic Nanoparticles

The optical binding force in metallic nanoparticles very often manifests itself into a number of interesting properties. These have been well studied in the literature. The presence of substrates has negligible effects on optical binding forces in dielectric particles [42]. The presence of substrates, on the other hand, has profound impact on metallic nanoparticles. In case of plasmonic spherical homodimers placed on a Gold substrate, the optical binding force was found to be boosted due to the supply of additional charges from the substrate in to the nanoparticles [43]. When a
symmetry-breaking method is introduced by an adjacent semi-infinite dielectric substrate to a nanocube, an interaction between bright dipolar and dark quadrupolar modes occurs in the cubes. This consequentially results in bonding and antibonding hybridized modes [44]. The resultant Fano resonance occurring from the overlapping of such modes dominates the scattering spectrum [45]. Recently, the Fano resonance [46] based reversal of near field optical binding force reversal has also been reported [47] in the plasmonic cube homodimer systems on a plasmonic substrate with the whole simulation set up submerged in water. In the spherical homodimer systems, however, such reversal of near field optical binding force is found to be absent for both without substrate [48, 49, 50] and with the presence of a substrate [43, 51].

The absence of Fano resonance based near field optical binding force reversal in spherical homodimer systems has spurred the investigations of such properties in the heterodimer systems. In [52] based on Lorentz-force dynamics, the authors have illuminated the light from a specific side of the simulation setup and forcefully broke the symmetry of spherical heterodimer-configurations. The lateral and longitudinal near-field binding force reversal was demonstrated without the presence of Fano (interacting resonance modes) resonances. Thus the longitudinal and lateral binding forces’ reversal mechanisms follow completely different methods.

1.3 Thesis Work

In this thesis work, the theoretical design of a tunable surface with two metallic nanoparticles where the interparticle separation is varied with the aid of optical binding forces has been attempted. At first, the optical binding force in nanoparticles is investigated starting from the simple analytical expression presented in [10]. This formulation is then cross-checked with the Maxwell stress tensor based approach with full field solution in the Rayleigh regime. When a good agreement between the two methods are reached, the stress tensor method has been expanded to a narrowband light illumination. Next, the simplest case of a surface consisting of a
dielectric dimer is investigated. Due to the lack of wavelength dependent properties of dielectric particles, the tunable surface was redesigned with silver dimers. Since these particles are slightly above the Rayleigh limit (particle radius $\ll \lambda/20$), the discrete dipole approximation is employed during the investigation process. When such a tunable surface is subjected to a narrow band light incidence, it can shift the central frequency of the incident light. The amount of such shifts can be controlled with their separation distances which has been varied with optical binding force.
The optical binding phenomenon involves more than one particle. It may be defined as the stable spatial reconfiguration of nanoparticles due to light illumination and a simultaneous redistribution of incident light by the particles. The optical binding force between two radiating dipoles has a closed form solution derived exclusively by Dholakia et al [10]. Starting from that equation, the aim of this chapter is to evaluate the applicability of that equation to the metallic and active Rayleigh particles.

2.1 Closed form expression

Dholakia et al [10] assumes two identical radiating dipoles to model the optical binding force between them. When light or any other electromagnetic excitation hits a small object, the object behaves like a small radiating (Hertzian) dipole and develops a dipole moment. This dipole moment is given by \( p = \alpha E_0 \). For a linear, homogenous and isotropic medium, this dipole moment is parallel to the incident electric field \( E_0 \). This dipole moment is also called polarization and the term \( \alpha \) is called \textit{polarizability}. Polarizability is, in general, a complex number. It plays a crucial role in force computation. In the mathematical formulations, however, it is often convenient to work with the effective polarizability \( \alpha_{eff} \) that incorporates the
Figure 2.1: Coordinate system for optical binding force

radiation reaction terms [53, 54]

\[
\alpha_{\text{eff}} = \frac{\alpha_0}{1 - \frac{ik_0}{6\pi\epsilon_0\epsilon_b}} = \alpha' + i\alpha'', \tag{2.1}
\]

with

\[
\alpha_0 = 4\pi\epsilon_0\epsilon_b a^3 \frac{\epsilon_p - \epsilon_b}{\epsilon_p + 2\epsilon_b}, \tag{2.2}
\]

where, \(\epsilon_p\) and \(\epsilon_b\) are the relative permittivity of the particle and background medium, respectively. \(\alpha'\) and \(\alpha''\) are the real and imaginary parts of the effective polarizability. We consider two particles A and B, with A at the center of a coordinate system defined by fig 1. Let \(\vec{R}\) denotes the interparticle separation vector, with \(\vec{R} = \hat{y}R\sin(\phi) + \hat{z}R\cos(\phi)\).

A linearly polarized incident plane wave propagating along the x axis with wave vector, \(\vec{k} = \hat{x}k_0\) and incident electric field \(\vec{E}^iA = \vec{E}^iA = \hat{z}E_0 e^{ik_0x}\). For a unit amplitude plane wave \(E_0 = 1\). In this condition, the particle B will experience both \(\hat{r}\) and
\( \hat{\phi} \) directed forces, which are given as [10]

\[
F_{r}^{B} = \frac{|\alpha_{\text{eff}}|^{2}|E_0|^{2}}{8\pi\epsilon_0\epsilon_b R^4} \left\{ [2k_0^2 R^2(2\cos^2(\phi)) - 1] + 3(1 - \cos^2(\phi))]\cos(k_0R) \\
+ [k_0^3 R^3(2\cos^2(\phi)) - 1] + 3k_0 R(1 - \cos^2(\phi))]\sin(k_0R) \right\},
\]

(2.3)

and

\[
F_{\phi}^{B} = \frac{|\alpha_{\text{eff}}|^{2}|E_0|^{2}}{8\pi\epsilon_0\epsilon_b R^4} \left\{ [(k_0^2 R^2 - 3)\cos(k_0R) - 3k_0 R\sin(k_0R)] \right\}.
\]

(2.4)

If we place the particles along the incoming electric field (\( \hat{x} \)) or incoming magnetic field (\( \hat{y} \)) direction, the \( \phi = 0 \) and we can only consider \( F_{r}^{B} \). For an identical sphere pair, the force on the particles will be exactly equal and opposite [10]. Therefore the total optical binding force will be,

\[
F_{\text{bind}} = F_{r}^{B} - F_{r}^{A}.
\]

(2.5)

To obtain a graph of optical binding force, a similar situation as [10] is considered. A unit amplitude plane wave with wavelength \( \lambda = 1024 \text{nm} \) is incident on two identical nanoparticles with radii, \( r = \lambda/25 \) and \( \epsilon_p = 16.0 \) located in vacuum. The electromagnetic wave is propagating in the \( x- \) direction with \( z- \) polarized electric field as shown in Figure 2.1. The particle centers are located along the \( z \) axis (i.e. \( \phi = 0 \)). Under such a scenario, the optical binding force between the particles is shown in Figure 2.2. In this figure, the force computed with the particles aligned with the electric field direction(\( \hat{z} \)). The graph also points out the stable and unstable optical binding force locations. The zero crossing points where the force transition is negative to positive values are the stable optical positions or optical binding locations.
Figure 2.2: The optical binding force (computed from closed form expressions by Dholakia et al [10]) between two identical nanospheres with radii $\lambda/25$ is subjected to a unit amplitude plane wave irradiation. The background is considered to be vacuum ($\epsilon_b = 1.0$).

2.2 Maxwell Stress Tensor [MST] Approach

The expression presented in [10] is to be validated based on a stress tensor based approach. Although the close form solution is fine to work with, such equations were derived assuming two single radiating dipoles. This may not be able to capture the binding force involving two metallic particles. Moreover, the expressions presented in [10] is extremely limited to homodimer systems where the particles are located along the y-axis or z-axis or yz plane, only. Thus, the optical binding force calculation using some simplified formulations might lead to serious errors in interacting particles [55]. In addition, these simplified expressions are incompatible with the DDA approach. Under these circumstances, we have employed a rigorous scheme of computing the optical binding force in the metallic nanoparticle dimer systems based on [19] with complex $\epsilon_p$ for metallic spherical particles.

The stress tensor based force calculation involves the following two processes [19]

- Calculation of the electric and magnetic fields using a suitable method.
2.2.1 Field Solution

The MST approach requires the total fields in the vicinity of the nanoparticles. The appendix A explains the computation of the total electric fields for a single nanoparticle. Here, we extend that formulations to the multiple particle case. As a generalized version, we derived the system of equations for core-shell nanoparticles shown in Fig 2.3. If the particle is very small compared to the wavelength such that \(ka \ll 1\), the scatterer can be thought as a point source, and we can assume the small particle is radiating like a Hertzian dipole. Assuming that the spherical particle-center is located at the origin the incident field is

\[
\vec{E}_{inc} = \hat{z} e^{i k x},
\]

where \(k = \omega \sqrt{\mu_0 \varepsilon_0}\) is the wavenumber. The field solution takes the following form [56]

\[
\vec{E}_{scat} = \frac{-i \omega \mu_0 \Pi}{4 \pi r} e^{i k r} \left\{ \hat{r} \left[ \left( \frac{i}{k r} \right)^2 + \frac{i}{k r} \right] 2 \cos \theta + \hat{\theta} \left[ \left( \frac{i}{k r} \right)^2 + \frac{i}{k r} + 1 \right] \sin \theta \right\} \quad (2.7a)
\]

\[
\vec{H}_{scat} = \frac{-i k \Pi}{4 \pi r} e^{i k r} \left[ \frac{i}{k r} + 1 \right] \sin \theta. \quad (2.7b)
\]
A core-shell nanoparticle is formed when a homogeneous particle with radius is surrounded by a spherical shell with radius \( b \), as shown in Figure 2.3. The solution of the Laplace equation for this system gives an approximately constant field close to the origin in the case of static limit \((kr << 1)\). The corresponding potentials in the core, shell, and background regions, which satisfy boundary conditions, can be written as [57, 58, 59],

\[
\begin{align*}
\phi_c &= -E_0 \frac{9\epsilon_s}{(\epsilon_s + 2\epsilon_b)(\epsilon_c + 2\epsilon_s) + (a/b)^3(\epsilon_s - \epsilon_b)(2\epsilon_c - 2\epsilon_s)} r \cos \theta, \\
\phi_s &= -E_0 \frac{3(\epsilon_c + 2\epsilon_s) - 3(2\epsilon_c - 2\epsilon_s)(a/r)^3}{(\epsilon_s + 2\epsilon_b)(\epsilon_c + 2\epsilon_s) + (a/b)^3(\epsilon_s - \epsilon_b)(2\epsilon_c - 2\epsilon_s)} r \cos \theta, \\
\phi_b &= -E_0 r \cos \theta + E_0 \frac{(\epsilon_s - \epsilon_b)(\epsilon_c + 2\epsilon_s) + (a/b)^3(\epsilon_c - \epsilon_s)(\epsilon_b + 2\epsilon_s)}{(\epsilon_s + 2\epsilon_b)(\epsilon_c + 2\epsilon_p) + (a/b)^3(\epsilon_c - \epsilon_p)(2\epsilon_p - 2\epsilon_b)} \frac{b^3}{r^2} \cos \theta.
\end{align*}
\]

(2.8a) (2.8b) (2.8c)

Here, \( c, s, \) and \( b \) denotes the core region, shell region and the background medium, respectively. All of these potentials satisfy boundary conditions. The polarizability of these particles can be computed directly as a proportionality constant from the amplitude of the dipole component in the external domain. In other words, the polarizability of a core-shell nanoparticle in the Rayleigh limit is the proportionality factor of a dipole moment given by [59, 60, 61],

\[
\alpha = 4\pi\epsilon_0 b^3 \frac{(\epsilon_p - \epsilon_b)(\epsilon_c + 2\epsilon_p) + (a/b)^3(\epsilon_c - \epsilon_p)(\epsilon_b + 2\epsilon_p)}{(\epsilon_p + 2\epsilon_b)(\epsilon_c + 2\epsilon_p) + (a/b)^3(\epsilon_c - \epsilon_p)(2\epsilon_p - 2\epsilon_b)},
\]

(2.9)

where \( \epsilon_c \) and \( \epsilon_b \) are the dielectric constants of the core and background medium, \( \epsilon_p \) is the frequency dependent complex dielectric function of shell material, and \( a \) and \( b \) are the radii of core and shell, respectively. The polarizability of a single homogeneous spherical particle can be also derived from this equation if \( \epsilon_c = \epsilon_p \) and \( a = b \).

The magnitude of the dipole moment \( II \) can be obtained from
\[ I_l = -i \frac{4\pi ka^3}{\eta_b} \left( \epsilon_p - \epsilon_b \right) \left( \epsilon_c + 2\epsilon_p \right) + (a/b)^3 \left( \epsilon_c - \epsilon_p \right) \left( \epsilon_b + 2\epsilon_p \right) E_0. \] (2.10)

Scattered fields of the spherical core-shell nanoparticle can be determined from Eq. 2.7 by using the dipole moment given by Eq. 2.10.

**Solution for multiple particles**

The field solution of single core-shell nanoparticle can be expanded for any number of core-shell nanoparticles by using the multiple scattering theory. If we consider two particles \( j \) and \( k \), the excitation fields \( \vec{E}^{(j)}_{\text{exc}} \) and \( \vec{E}^{(k)}_{\text{exc}} \) can be determined by the Foldy [23] and Lax [24] self-consistent formula, which was previously applied to arbitrary cylindrical particles for trapping and binding. Foldy–Lax multiple-scattering equations for the excitation fields \( \vec{E}^{(j)}_{\text{exc}} \) and \( \vec{E}^{(k)}_{\text{exc}} \) at particles \( j \) and \( k \) can be written as:

\[
\vec{E}^{(j)}_{\text{exc}} = \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(jk)} \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(kj)} \vec{G}^{(k)} \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(jk)} \vec{G}^{(j)} \vec{E}^{(k)}_{\text{inc}} + \ldots 
\] (2.11a)

\[
\vec{E}^{(k)}_{\text{exc}} = \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(kj)} \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(k)} \vec{G}^{(j)} \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(kj)} \vec{G}^{(k)} \vec{E}^{(j)}_{\text{inc}} + \ldots 
\] (2.11b)

where,

\[
\tilde{G}^{(jk)} = -\alpha_k \left[ \frac{k_b^3}{4\pi\epsilon_b} \frac{e^{ik_b r_{jk}}}{k_b r_{jk}} \left( \hat{r}_{jk} \hat{r}_{jk} 3(\Gamma(r_{jk}) + 1) - \tilde{I}(\Gamma(r_{jk}) + 1) \right) \right]. 
\] (2.12)

Here, the position of particle \( k \) referenced to particle \( j \) is defined as the vector \( \vec{r}_{jk} \equiv \vec{r}_k - \vec{r}_j \). So, \( r_{jk} = |\vec{r}_{jk}| \) and \( \hat{r}_{jk} = \vec{r}_{jk}/r_{jk} \). The scattering equation can be rewrite as

\[
\vec{E}^{(j)}_{\text{exc}} = \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(jk)} \left[ \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(kj)} \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(jk)} \vec{G}^{(k)} \vec{E}^{(j)}_{\text{inc}} + \ldots \right], \] (2.13a)

\[
\vec{E}^{(k)}_{\text{exc}} = \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(kj)} \left[ \vec{E}^{(j)}_{\text{inc}} + \tilde{G}^{(jk)} \vec{E}^{(k)}_{\text{inc}} + \tilde{G}^{(jk)} \vec{G}^{(j)} \vec{E}^{(k)}_{\text{inc}} + \ldots \right]. \] (2.13b)
The terms inside the brackets are, respectively, $\vec{E}_{exc}^{(j)}$ and $\vec{E}_{exc}^{(k)}$. So, the Eqs. 2.13 can be re-written as

$$\vec{E}_{exc}^{(j)} = \vec{E}_{inc}^{(j)} + \bar{G}^{(jk)} \vec{E}_{exc}^{(k)},$$  \hspace{1cm} (2.14a)  

$$\vec{E}_{exc}^{(k)} = \vec{E}_{inc}^{(k)} + \bar{G}^{(kj)} \vec{E}_{exc}^{(j)}.\hspace{1cm} (2.14b)$$

For any number of particles, the multi-scattering solution can be extended. The solution for the $j^{th}$ particle can be written as a linear system

$$\vec{E}_{exc}^{(j)} = \vec{E}_{inc}^{(j)} + \sum_{k \neq j} \bar{G}^{(jk)} \vec{E}_{exc}^{(k)}. \hspace{1cm} (2.15)$$

The system can be expressed as a linear system, $[\bar{I} - \bar{G}] \vec{E}_{exc} = \vec{E}_{inc}$, where $\bar{I}$ is identity matrix, and $\bar{G}$ can be written as a matrix in terms of $G^{(jk)}$ is defined by Eq. 2.12 and $G^{(jk)} = 0$ if $j = k$.

$$\vec{E}_{exc} = \begin{bmatrix} \vec{E}_{exc}^{(1)} \\ \vec{E}_{exc}^{(2)} \\ \vdots \\ \vec{E}_{exc}^{(J)} \end{bmatrix}, \quad \bar{G} = \begin{bmatrix} \bar{G}^{11} & \bar{G}^{12} & \cdots & \bar{G}^{1J} \\ \bar{G}^{21} & \bar{G}^{22} & \cdots & \bar{G}^{2J} \\ \vdots & \vdots & \ddots & \vdots \\ \bar{G}^{J1} & \bar{G}^{J2} & \cdots & \bar{G}^{JJ} \end{bmatrix}.$$  

Once the excitation fields are known, the scattered electric field is determined by applying the generic scattering matrix $\bar{G}$ to arbitrary observation points.

**Validation of the fields**

As a bench-marking of the scattered fields, a linear, isotropic, homogeneous nanosphere with dielectric constant $\epsilon_p = 4.0$ was considered. The radius of the sphere was 51.5nm and subjected to a unit amplitude plane wave of wavelength $\lambda_0 = 1024nm$. Then, the total (scattered + incident) electric field was computed by using the Rayleigh approximation as well as the Mie theory. Figure 2.4 shows the xz pattern of the
total fields computed by both of the methods. Here, the good agreement between
the patterns validates the calculation procedure of the electric field computation.

In order to validate the scattered magnetic field, two different types of waves
were considered. The first one is \( +z \) directed wave with the incident electric field
polarized in the \( +x \) direction. The total magnetic field pattern is shown in Figure
2.5(a). Next, we rotate the unit amplitude plane wave incidence. This time the
electric field is propagating in the \( +x \) direction. The magnetic field pattern for this
case is presented in Figure 2.5(b). The rotation of the overall pattern as well as the
constant value of the maximum magnetic field provides the necessary bench-mark of
the magnetic field computation.

2.2.2 Force calculation using MST

Field and material contributions are combined by using the time and space dependent
field vectors \( \vec{E}(\vec{r}, t) \), \( \vec{H}(\vec{r}, t) \), \( \vec{D}(\vec{r}, t) \) and \( \vec{B}(\vec{r}, t) \) in the Maxwell – Minkowski equations as

\[
\nabla \times \vec{H}(\vec{r}, t) - \frac{\partial}{\partial t} \vec{D}(\vec{r}, t) = \vec{J}(\vec{r}, t) \quad (2.16a)
\]
\[
\nabla \times \vec{E}(\vec{r}, t) + \frac{\partial}{\partial t} \vec{B}(\vec{r}, t) = 0 \quad (2.16b)
\]
\[
\nabla \cdot \vec{D}(\vec{r}, t) = \rho(\vec{r}, t) \quad (2.16c)
\]
\[
\nabla \cdot \vec{B}(\vec{r}, t) = 0. \quad (2.16d)
\]

Here, \( \vec{J}(\vec{r}, t) \) is the free current density, and \( \rho(\vec{r}, t) \) is the free charge density and \( \mu \) and \( \epsilon \) are the permeability and permittivity of the background medium, respectively.

The electromagnetic wave equation described in terms of the Electric field is given by,

\[
\nabla^2 \vec{E}(\vec{r}, t) - \mu \epsilon \frac{\partial^2}{\partial t^2} \vec{E}(\vec{r}, t) = 0 \quad (2.17)
\]
Figure 2.4: The validation of the scattered electric fields. Figure (a) shows the xz pattern of total electric field (scattered + incident) computed from the Rayleigh Approximation. Figure (b) shows same pattern computed using the Mie theory.
Figure 2.5: The validation of the scattered magnetic fields. Figure (a) shows the xz pattern of total magnetic field (scattered + incident) for the $+z$ directed and $+x$ polarized plane wave. Figure (b) depicts the same pattern for a $+x$ directed and $+z$ polarized plane wave. The rotation of the field pattern and constant value of the $|H_{\text{max}}|^2$ validates the magnetic field computation.
From which the electric field vector $\vec{E}(\vec{r}, t)$ is computed as:

$$\vec{E}(\vec{r}, t) = \hat{\epsilon} E e^{i(\vec{k}.\vec{r} - \omega t)}$$  \hspace{1cm} (2.18)

Where, $\hat{\epsilon}$ is the arbitrary polarization of the electric field. $\vec{k}$ is the wave vector $[m^{-1}]$ that signifies the direction of propagation and for a linear isotropic background medium and its value is given by, $k = \omega \sqrt{\mu \epsilon}$.

The complex Minkowski stress tensor [62, 63, 19] is computed from the fields outside the particles by,

$$\bar{T} = \frac{1}{2} (\bar{D} \cdot \bar{E}^* + \bar{B}^* \cdot \bar{H}) \bar{I} - \bar{D} \bar{E}^* - \bar{B}^* \bar{H}.$$  \hspace{1cm} (2.19)

Finally, the total force $\bar{F}$ is calculated by integrating the stress tensor just outside the particle surface over a volume $V$ and enclosed by a closed surface area $A$ in a homogeneous medium [62, 19],

$$\bar{F} = -\frac{1}{2} \Re \left\{ \int_A d\vec{a} \cdot \bar{T}(\vec{r}) \right\},$$  \hspace{1cm} (2.20)

where $d\vec{a}$ is the area element and $A$ represents the closed integration path. Once the force in three dimensions is computed, $\bar{F} = \hat{x} F_x + \hat{y} F_y + \hat{z} F_z$, the particle orientation is examined to decide which component of the force is to be considered for binding force computation. For instance, if the particle centers are oriented along the x axis, then the force component $F_x$ is contributing to the optical binding phenomenon.

The alternate force expression of optical force is given by Zemánek et al [64],

$$\bar{F} = -\frac{1}{2} \epsilon_b \Re \left\{ ik \alpha_{eff} E_0^2 \right\}.$$  \hspace{1cm} (2.21)

Thus, the force crucially depends on the effective polarizability, $\alpha_{eff}$. In the MST based calculations, the effective polarizability derived in [65] is used

$$\alpha_{eff} = \frac{\alpha_0}{1 - \frac{2}{3} i k^3 \alpha_0},$$  \hspace{1cm} (2.22)
Where the $\alpha_0$ is computed from Eq. 2.9 for a sphical particle with $a = b$ and $\epsilon_c = \epsilon_p$. Now, the force on particle A exerted by the particle B is given by,

$$\vec{F}_A = \hat{\psi} \vec{F}_\psi.$$ \hfill (2.23)

Here, $\psi$ denotes the appropriate axis under consideration (x, y or z). Due to the symmetry of the system, $\vec{F}_A$ is equal in magnitude of $\vec{F}_B$, but opposite in sign. Therefore, the optical binding force is given by

$$\vec{F}_{\text{bind}} = \vec{F}_B - \vec{F}_A.$$ \hfill (2.24)

2.3 Optical Binding Force Comparison

unit amplitude plane wave with wavelength $\lambda = 1024\, nm$ is incident on two identical nanoparticles with radii, $r = \lambda/25$ and $\epsilon_p = 16.0$ located in vacuum. The electromagnetic wave is propagating in the $\hat{z}$ direction with $\hat{x}$ polarized electric field. The particle centers are located along the $x$ axis. Under such a scenario, the optical binding force calculated based on the MST approach, is shown in Figure. 2.7. A scattering force in the direction of propagation ($\hat{z}$) will also act on both of the particles. At this moment, this scattering force is ignored. Figure 2.8 shows the comparison between the forces calculated by the two aforementioned methods. The figure shows a slight phase shift is present between the forces computed by the two different methods. This is attributed to the different computation schemes. Between
Figure 2.7: The optical binding force (computed from MST approach) between two identical nanospheres with radii $\lambda/25$ is subjected to a unit amplitude plane wave irradiation. The background is considered to be vacuum ($\epsilon_b = 1.0$).

the two, the MST approach is more acceptable because it gives a very good insight into the physical picture of the system.

2.4 Narrow-band Light

At this point of the discussion, the MST based approach for a unit amplitude plane wave will be extended to the case of a narrowband light incidence. For theoretical purposes, the unit amplitude plane wave is the mostly used light source. A unit amplitude plane wave is a theoretical entity that possesses a infinitely stretched wavefront. This requires infinite energy, which is physically not possible. Therefore, in practice, such a source of light is impossible to construct. All though the light received by an observer at very large distance from an infinitesimally small light source could be considered a plane wave. In reality all of the light sources possess a band of different frequencies (or, wavelengths). In this theoretical work, a narrow-band light is modeled to be comprised of infinitely many plane waves with different
wavelengths and amplitudes. The narrow-band light constructed in this way for this thesis is depicted in the Figure 2.9.

2.5 $F_{\text{bind}}$ for narrow-band light

The optical binding force between two nanoparticles is computed by summing over the contributions of optical binding force of all of the components of a band-wide light, using the stress tensor method.

A narrow band electromagnetic wave with varying bandwidths are incident on two identical metallic nanoparticles with radii, $r = \lambda/25$ and $\epsilon_p = -0.6 + 1.28i$ located in water $\epsilon_b = 1.33$. The electromagnetic waves is propagating in the $\hat{z}$ direction with $\hat{x}$ polarized electric fields. The particle centers are located along the x axis. Under such a scenario, a plot of $F_{\text{bind}}$ versus $R$ for different bandwidth is given in Figure 2.11. As expected, with a gradual increase of the bandwidths, the total optical binding force increases. However, for linear homogeneous spheres placed in a
Figure 2.9: Decomposition of a narrowband light into a number of plane waves with different wavelengths (frequencies).

linear homogeneous medium, the zero optical force locations remain the same.
Figure 2.10: Narrow-band electromagnetic waves with different $\lambda$ ($\omega$)
Figure 2.11: The optical binding force between two metallic nanoparticles ($\epsilon_p = -0.6 + 1.28i$) placed under water ($\epsilon_b = 1.333$) computed using the MST approach.
CHAPTER 3
TUNABLE SURFACE DESIGN

The tunable surface is constructed with a dimer of Silver nanoparticles. In this chapter, the step by step construction of a tunable surface is presented. At the end of the chapter, the tunability is shown with respect to a narrowband light incidence.

3.1 The tunable surface

The (tunable) surface that was constructed is comprised of two identical nanospheres, A and B, forming a homodimer. The axis of the homodimer is located along the \( x \) axis as shown in the Figure 3.4. Each of the particle has a radius of 100\( nm \). The centers of the particles A and B are located respectively at \((-d/2, 0, 0)\) and \((d/2, 0, 0)\). Here, \( d \) denotes the center to center distance at the equilibrium (i.e., no external electromagnetic field). In the simulation process, a surface to surface \( s_1 \) was defined. Then \( d \) was computed simply by adding \( 2 \times \text{radius} \) of the nanosphere with \( s_1 \), i.e., \( d = s_1 + 2 \times r \), where \( r \) is the radius of each of the nanospheres. In this simulation, \( d \) was selected to be 250\( nm \).

The dimer is attached with a substrate (S). That substrate is considered to be electromagnetically transparent, for the sake of simplicity. The only function of the transparent substrate is to loosely contain the dimer in such a way that when an attractive binding force acts, the center to center distance very slightly changes from \( d \) to \( d - \delta \). For the opposite case of repulsive binding force, the center to center difference becomes \( d + \delta \). Due to the dimer’s attachment to the substrate, both of the nanospheres cannot go beyond this distance range \((d \pm \delta)\) in either of the cases.
In the simulation process, $\delta$ was set to be $25\text{nm}$ and to demonstrate the tunability, both the attractive and repulsive forces were considered. Finally, the entire system is placed in vacuum ($\epsilon_b = 1.0$).

3.2 Analysis Procedure

The simplified Rayleigh scattering limit requires the radius of the particle should be less than or equal to $1/20$ of the incident electromagnetic wavelength. Whenever the size of the nanoparticle goes beyond this limit or there is a presence of other nanoparticles in the vicinity of the given nanoparticle, the Rayleigh scattering limit is no longer applicable. In this analysis process, the Discrete Dipole Approximation was applied to study the tunability of the surface.

The Discrete Dipole Approximation or DDA [66] is a popular method for solving electromagnetic wave scattering problems that involve particles of arbitrary shapes and sizes. It is an integral equation technique where electromagnetic wave scatter-
Figure 3.2: The DDA representation of a sphere whose outline is shown in green.

Polarizable particles are approximated by a number of dipoles. Each of such dipoles is a polarizable point and is related to the local value of the polarization vector. These polarizable particles are located in a lattice with lattice spacing $d$ that is determined by the number of particles used ($N$) and the total volume ($V$) of the original particle that is to be modeled given by the simple relation $V = N d^3$. The DDA representation of a sphere is shown in Figure 3.2. The “staircase” structure of the original particle affects the accuracy of the model. Therefore, a large number of dipole particles are needed to be considered. However, increasing the number of particles results in severely big computation time. Based on these two trade-offs, this thesis work utilized the total number of particles as $N = 33$.

3.2.1 Input and Output

A narrowband light with electric field polarized in the $\hat{x}$ direction and propagating in the $\hat{z}$ direction was considered. This input electromagnetic wave spanned from 200 nm to 800 nm with the peak located at 490 nm wavelength. The bandwidth of the input light was 100 nm.
To compute the output response, at first a computation domain was selected which contained the near field region of the particle A. It spans from $x = -d/2 - r, z = -r$ to $x = -d/2 + r, z = +r$. Radially, from the center of the particle A, the computation domain spans from $r$ to $1.001 \times r$. However, for accurate computation of the output electric field, all of the dipoles $(33 + 33 = 66)$ in both of the particles (A and B) were included in the calculation process. Figure 3.3 shows the output total electric field (scattered + incident) pattern in the vicinity of the particle A for a wavelength of $440\,nm$ and plane wave amplitude of 0.6 within the narrowband light. Due to the symmetry of the system, the exact scattering electric field pattern will appear for particle B, which was omitted from output computation considering lengthy computation times. Once the total electric field pattern was obtained near particle A, the maximum of such electric field value was noted against the corresponding wavelength. A complete algorithm for the computation of the tunable surface is presented in the Appendix D.

3.2.2 Error Minimization

The staircase computation scheme of the DDA approach always involves some error. To obtain an accuracy of 96.97%, the total number of DDA elements have to be 29,647. This takes a long time to finish computation. The way this was bypassed was normalizing the output. Starting from just 2 DDA elements, it was found that the $output/\max(output)$ peaks at relatively same location in the wavelength axis as the number of DDA particles increase to 33. Since the primary focus of the study is to demonstrate a shift of input narrow band central frequency, the exact value of the electric and magnetic fields are of little importance at this phase of the investigation.
Figure 3.3: The electric field pattern of one of the particles in the computation domain.
3.3 Tunability of the Surface

With the surface constructed and the analysis procedure fixed, different types of particles were used and the tunability was tested. At the very beginning, two dielectric particles were used for both the vacuum and an inverted medium. After that, two silver nanoparticles were considered as the dimer component.

Dielectric Dimer

Dielectric particles are linear in nature and usually show no wavelength dependent scattering properties. In this work, we used two dielectric particles of radii 100nm, where the dielectric constant of each of the particle is $\epsilon_p = 4.0$, and both of them were placed in vacuum ($\epsilon_b = 1.0$). The dielectric constant of each of the particles is $\epsilon_p = 4.0$ and both of them were placed in vacuum ($\epsilon_b = 1.0$). In this case, no shift in the input narrowband central wavelength was observed.

Next, the whole dielectric system was placed in an inverted medium (i.e. $\epsilon_p < \epsilon_b$). In this case, however, a red shift of 10nm of the central wavelength (frequency) was observed.
Single Metallic Nanoparticle

At this stage, it was evident that to achieve a tunable surface, metallic nanoparticles must be involved. Metallic nanoparticles show excellent properties of wavelength (or frequency) dependent dielectric constants. In [67], the authors have noted optical constants $n$ and $\kappa$ of some noble metals (copper, silver, and gold) based on reflection and transmission measurements on vacuum-evaporated thin films at room temperature. They had selected the spectral range to be from $0.5\,eV$ to $6.5\,eV$ along with a film-thickness range $185 - 500\,\AA$. These data are readily available at www.refractiveindex.info. Once the wavelength dependent $n$ and $\kappa$ are known, the real and imaginary parts of the dielectric constant of the metals are calculated as

$$\epsilon_{re} = n^2 - \kappa^2,$$

and

$$\epsilon_{im} = 2n\kappa.$$

Here, the subscripts re and im respectively denote the real and imaginary part of the dielectric constant of the metal nanosphere. Once the real and the imaginary parts are known, the dielectric constant of the metal is simply

$$\epsilon(\lambda) = \epsilon_{re} + i\epsilon_{im}.$$  \hspace{1cm} (3.1)

Figure 3.5 shows the wavelength dependency of the dielectric constant of the Silver. The Figure 3.6 shows the response of a single Silver nanoparticle. The shift of the central wavelength (frequency) is evident, although the two distinct peaks are quite notable.
Figure 3.5: The wavelength dependent permittivity of Silver. Plotted from Johnson and Christae data [67] collected from www.refractiveindex.info

Figure 3.6: The response of a single Silver nanoparticles with respect to a narrowband light incidence.
Figure 3.7: The response of a single Silver nanoparticles with respect to a narrowband light incidence.

Silver dimer

The response of our tunable surface is shown in Figure 3.7. Both the narrow band input electric field and the normalized total output electric fields are plotted against the wavelength. For demonstration purposes, we have considered both the attractive and repulsive binding forces. When an attractive force is acted between the particles, they come closer. This intensifies the confined energy in the system, thereby broadening the spectrum. However, for repulsive force, the band gets narrower. In both case, a prominent 120 nm is observed in the peak response.
Optical binding forces represent a special type of light matter interactions, involving multiple particles. Unlike simpler interactions, such as the scattering and gradient forces, optical binding force has far reaching implications. This thesis work demonstrates the two major approaches of modeling the optical binding phenomenon in three dimensions based on classical electrodynamics. One of them is the closed form solution. However, this approach has some inherent limitations and serious drawbacks. The oversimplified approach to derive such an expression leads to error for dissimilar particles. The expression also becomes useless for larger particles where the electrostatic limit is no longer applicable. It is this setback that led to the Stress-Tensor based approach for the optical binding force. Unlike the former one, this gives a more detailed picture of the physical system in hand, demonstrating in detail all of the the key factors such as the electric and magnetic fields, the wave vectors and so on. Moreover, all of these quantities have been validated using other techniques, such as COMSOL Multiphysics, Mie theory, or by intuitively using incidence rotations. This ensures that each of these methods demonstrated in comparison to the MST approach validates the MST as more accurate, and true to the dynamics of the system. Although the closed form solution is applicable only for the unit amplitude plane waves, the MST based approach is extendable to any type of incidence. In this thesis, we extend the MST to the a narrowband light. In this thesis, we extend the MST to the narrowband light and the Maxwell Stress Tensor based formulation. The optical binding force was accomplished and extended to the case of narrowband light incidence. After the narrowband light incidence for
optical binding had been utilized, a tunable surface based on optical binding forces was devised with a Silver nanoparticle dimer systems. In this concluding chapter, we revisit some of the theoretical interpretations of the results obtained in this work.

4.1 Interpretations of the theoretical works

The conceptual conclusions inferred from the theoretical works presented in this thesis are briefly summarized here. This illustrates a better fundamental overview of electrodynamics accompanies optical binding and narrowband light shifting properties.

- **Secondary peak in single Ag response:** The response of the single silver nanoparticle show two peaks. The shorter one is called the secondary peak, which corresponds to the plasmonic resonance condition where the real part of the silver dielectric function crosses zero line and also the imaginary part reaches maximum. This secondary peak is absent in the dimer response. This is because the plasmonic response of the active particles are influenced by the surrounding environment and the presence of other plasmonic entities in close proximity. When a dimer is excited with a narrowband light, their mutual influence suppresses the secondary peak. In other words, the presence of the second nanoparticle alters the dielectric function and the resonance frequency.

- **Band Widening with attractive binding force:** Arrays of nanoparticles are excellent for energy confinement in nanoscale. This confinement increases with decreasing inter particle separation. When an attractive force acts among the nanoparticles, they come closer to each other reducing the interparticle separation. This enhances their energy confinement. This increased energy manifests as wider band in the output response.
4.2 Future developments

The theoretical modeling of optical binding forces using Maxwell-Minkowski stress tensor has been demonstrated in this thesis. However, as with any thesis endeavors, there will always be some stones left unturned. The theoretical and experimental modeling of optical binding force based tunable surfaces could be implemented in numerous ways with innovative and improved outcomes.

- **Extension of the MST Method:** The Minkowski stress tensor based modeling of the optical binding forces is far more robust than any other approach. In the future, this can be extended to consider any number of particles placed in any type of background (i.e. anisotropic, bianisotropic etc). The MST approach can also be extended to heterodimer systems, where, the particles involved are dissimilar to one another in terms of sizes, shapes, and compositions.

- **Different types of incidence:** The simulation model presented in this work is based on either unit amplitude plane wave or the decomposition of narrow band light based on the plane waves. It will be worth investigating the tunable surfaces with other types of light incidence, such as, Gaussian beams, laser beams, Bessel beams or the interferences between them.

- **Tunable surface with higher number of particles:** The tunable surface that was designed in this thesis is based on a dimer only. This can be extended to higher number of particles such as trimers or quadromers of even higher.

- **The effect of substrate:** In order to keep matters simple, I have considered a substrate that is optically inactive. However, in the future, different types of substrates and their effects will be interesting to investigate.

- **Mie solutions:** To simulate the tunable surfaces, the discrete dipole approximation [DDA] was applied. Although the DDA can handle particles with
arbitrary sizes and shapes, for the spherical particle systems it will be worth developing Mie solutions which provides the exact solution. The development of such a program might be challenging. However, the reward will be the enormous relief from running 36 hour long DDA based subroutines for spherical particle systems.
APPENDICES

A: kDB SYSTEM

To determine the kDB [56] system first, we take the curl of the Eq. 2.16c in source free homogeneous isotropic media, $\vec{J} = 0$ and $\rho = 0$:

$$\nabla \times \left( \nabla \times \bar{E} \right) = -\nabla \times \frac{\partial}{\partial t} \bar{B} = -\mu \frac{\partial}{\partial t} (\nabla \times \bar{H}) = -\mu \varepsilon \frac{\partial}{\partial t} \left( \frac{\partial}{\partial t} \bar{E} \right) = -\mu \varepsilon \frac{\partial^2}{\partial t^2} \bar{E}$$  (A.1)

By employing vector identities $\nabla \times (\nabla \times \bar{E}) = \nabla (\nabla \cdot \bar{E}) - \nabla^2 \bar{E}$ and $\nabla \cdot \bar{E} = 0$ we arrive at

$$\nabla^2 \bar{E} = \mu \varepsilon \frac{\partial^2}{\partial t^2} \bar{E} = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \bar{E}$$  (A.2)

This is known as the wave equation. By solving the wave equation for $\bar{E}(\bar{r}, t) = \hat{x} E_0 \cos(kz - \omega t)$ we get

$$-k^2 \bar{E} + \frac{\omega^2}{c^2} \bar{E} = 0$$

The trivial solution $\bar{E} = 0$ represents the case with no incident electromagnetic waves. Thus, from $-k^2 + \frac{\omega^2}{c^2} = 0$ and replacing for $c^2$, we arrive at the dispersion relation

$$k = \omega \sqrt{\mu \varepsilon}$$  (A.3)

where $\vec{k} = \hat{x} k_x + \hat{y} k_y + \hat{z} k_z$. The time harmonic versions of Eqs. 2.16 can be written as following using identity $\frac{\partial}{\partial t} \equiv -i \omega$ in source free region
\[ \nabla \times \vec{H}(\vec{r},t) = -i\omega \vec{D}(\vec{r},t) \quad (A.4) \]
\[ \nabla \times \vec{E}(\vec{r},t) = i\omega \vec{D}(\vec{r},t) \quad (A.5) \]
\[ \nabla \cdot \vec{D}(\vec{r},t) = 0 \quad (A.6) \]
\[ \nabla \cdot \vec{B}(\vec{r},t) = 0 \quad (A.7) \]

At last, substituting \( \nabla = i\vec{k} \) is Eqs. A.8a gives the Maxwell – Minkowski equations in a source free region in KDB system

\[ \vec{k} \times \vec{H}(\vec{r},t) = -\omega \vec{D}(\vec{r},t) \quad (A.8a) \]
\[ \vec{k} \times \vec{E}(\vec{r},t) = \omega \vec{B}(\vec{r},t) \quad (A.8b) \]
\[ \vec{k} \cdot \vec{D}(\vec{r},t) = 0 \quad (A.8c) \]
\[ \vec{k} \cdot \vec{B}(\vec{r},t) = 0. \quad (A.8d) \]
B: RAYLEIGH SCATTERING FROM A SPHERE

When light or electromagnetic waves hit a particle, a part of the incident energy is absorbed by the particle and the rest of the energy in re-radiated by the particle. This re-radiation is known as the scattering. The exact solution for scattered electromagnetic fields have been derived by Gustav Mie [68]. However, if that particle is very small (radius < \(\lambda/20\)) in compared to the wavelength such that \(ka << 1\), the mathematics describing the scattering phenomenon becomes simplified. In this case, the particle can be thought as a point source. Therefore it is safe to assume that the small particle is radiating like a Hertzian dipole. This simplified formalism is known as the Rayleigh approximation and this type of scattering phenomenon is called Rayleigh scattering. The spherical particle is at the origin and the incident field is as [56]

\[ \hat{E}_{\text{inc}} = \hat{z}E_0 = E_0 e^{-ikx} \quad \text{(B.1)} \]

where \(k = \omega\sqrt{\mu_b\epsilon_b}\) is the wavenumber. The field solution takes the following form

\[ \hat{E}_{\text{scat}} = \frac{-i\omega\mu_b I\ell}{4\pi r} e^{ikr} \left\{ \hat{r} \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} \right] 2 \cos \theta + \hat{\theta} \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} + 1 \right] \sin \theta \right\} \quad \text{(B.2)} \]

\[ \hat{H}_{\text{scat}} = \hat{\phi} \frac{-ikI\ell}{4\pi r} e^{ikr} \left[ \frac{i}{kr} + 1 \right] \sin \theta \quad \text{(B.3)} \]

Magnitude of dipole moment \(I\ell\) can be determined by using the boundary conditions. The field is approximately constant in close to the origin for static limit, \(kr << 1\).

\[ \hat{E}_{\text{inc}} \approx \hat{z}E_0 = E_0 (\hat{r} \cos \theta - \hat{\theta} \sin \theta) \quad \text{(B.4)} \]

\[ \hat{E}_{\text{int}} \approx \hat{z}E_i = E_i (\hat{r} \cos \theta - \hat{\theta} \sin \theta) \quad \text{(B.5)} \]

\[ \hat{E}_{\text{scat}} \approx E_s (\frac{a}{r})^3 (\hat{r} 2 \cos \theta + \hat{\theta} \sin \theta) \quad \text{(B.6)} \]
Now from the static limit, at the boundary limits the tangential component of $\vec{E}$ and the normal component of $\vec{D}$ is continuous. So, from the boundary conditions

\begin{align*}
-E_0 + E_s &= -E_i \quad \text{(B.7)} \\
\epsilon_b E_0 + 2\epsilon_b E_s &= \epsilon_p E_i \quad \text{(B.8)}
\end{align*}

Internal and scattered field can be solved from the equations B.5 and B.6

\begin{align*}
E_s &= \frac{\epsilon_p - \epsilon_b}{\epsilon_p + 2\epsilon_b} E_0 \quad \text{(B.9)} \\
E_i &= \frac{3\epsilon}{\epsilon_p + 2\epsilon_b} \quad \text{(B.10)}
\end{align*}

Dipole moment can be obtained from the following equation

\begin{align*}
Il &= -i \frac{4\pi ka^3}{\eta_b} \frac{\epsilon_p - \epsilon_b}{\epsilon_p + 2\epsilon_b} E_0 \quad \text{(B.11)}
\end{align*}

Scattered fields of the spherical particle can be stated as below

\begin{align*}
\vec{E}_{\text{scat}} &= - (ka)^3 \frac{\epsilon_p - \epsilon_b}{\epsilon_p + 2\epsilon_b} E_0 e^{ikr} \{ \hat{\mathbf{r}} \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} \right] 2 \cos \theta + \hat{\mathbf{\theta}} \left[ \left( \frac{i}{kr} \right)^2 + \frac{i}{kr} + 1 \right] \sin \theta \} \\
\vec{H}_{\text{scat}} &= - \frac{\phi}{\eta_b} (ka)^3 \frac{\epsilon_p - \epsilon_b}{\epsilon_p + 2\epsilon_b} E_0 e^{ikr} \left[ \frac{i}{kr} + 1 \right] \sin \theta \quad \text{(B.12)}
\end{align*}
C: SCATTERING BY A CYLINDER

The geometry of the problem consists of an electromagnetic wave incident upon an infinite cylinder of radius a aligned in the z direction. The cylinder is characterized by \((\mu_p, \epsilon_p)\) and the background by \((\mu_b, \epsilon_b)\). The incident wave is assumed to be a plane wave. Many other field distributions, such as a Gaussian beam, can be described by a sum of plane waves. Therefore, the total solution for such incident fields can be described as a superposition of solutions resulting from a plane-wave. The incident, scattered, and internal fields are expanded in cylindrical waves given by the coefficients \(\bar{N}_n, \bar{M}_n, R_g\bar{N}_n, and R_g\bar{M}_n\) and the solution is given by [69]. The incident electric field is polarized in the z direction and propagates in the plane \((kz=0)\). The magnetic fields are obtained from Faraday’s law

\[
i \omega \mu \bar{H}(\bar{\rho}) = \nabla \times \bar{E}(\bar{\rho}) \tag{C.1}\]

\[
\nabla \times \bar{M}_n = K \bar{N}_n \tag{C.2}\]

\[
\nabla \times \bar{N}_n = K \bar{M}_n \tag{C.3}\]

\[
\bar{E}_{inc}(\bar{\rho}) = \hat{z} E_0 e^{i k_i \bar{\rho}} = \sum_{n=-N}^{N} a_n R_g \bar{N}_n(K_b, \bar{\rho}) \tag{C.4}\]

\[
\bar{H}_{inc}(\bar{\rho}) = \frac{k_b}{i \omega \mu_b} \hat{z} E_0 e^{i k_i \bar{\rho}} = \sum_{n=-N}^{N} a_n R_g \bar{M}_n(K_b, \bar{\rho}) \tag{C.5}\]

where the wavenumber in the background medium is given by the dispersion relation \(k_b^2 = \omega^2 \mu \epsilon\). The scattered fields are

\[
\bar{E}_{scat}(\bar{\rho}) = \hat{z} E_0 e^{i k_s \bar{\rho}} = \sum_{n=-N}^{N} a_n^s \bar{N}_n(K_b, \bar{\rho}) \tag{C.6}\]

\[
\bar{H}_{scat}(\bar{\rho}) = \frac{k_b}{i \omega \mu_b} \hat{z} E_0 e^{i k_s \bar{\rho}} = \sum_{n=-N}^{N} a_n^s \bar{M}_n(K_b, \bar{\rho}) \tag{C.7}\]
The internal fields are also regular at the origin and can be computed from

\[ \vec{E}_{\text{int}}(\vec{\rho}) = \hat{z} E_0 e^{ik_z \hat{\rho}} = \sum_{n=-N}^{N} c_n \bar{R}_n(K \rho) \] (C.8)

\[ \vec{H}_{\text{int}}(\vec{\rho}) = \frac{k_p}{i \omega \mu_p} \hat{z} E_0 e^{ik_z \hat{\rho}} = \sum_{n=-N}^{N} c_n \bar{R}_n m_n(K \rho)\] (C.9)

\[ \bar{N}_n(K \rho) = \hat{Z} k \hat{H}_n^{(1)}(K \rho) e^{in\phi} \] (C.10)

\[ \bar{M}_n(K \rho) = \hat{Z} k \hat{J}_n^{(1)}(K \rho) e^{in\phi} \] (C.11)

Here, \( H_n^{(1)}(\cdot) \) and \( J_n(\cdot) \) is the Hankel function of the first kind and the Bessel function, respectively. The observation point coordinates \((\rho, \theta, \phi)\) represent the point for the evaluation of the fields. The angle \( \phi \) is used to represent the incident direction of the illuminating wave. For a general dielectric and magnetic medium, the boundary conditions give a system of equations that must be solved for the unknown coefficients

\[ a_n = i^n e^{in\phi} \frac{E_0}{K_b} \] (C.14)

\[ a_n^* = \frac{b_1 m_{22} - b_2 m_{12}}{m_{11} m_{22} - m_{21} m_{12}} \] (C.15)

\[ c_n = \frac{b_1 m_{21} - b_2 m_{11}}{m_{12} m_{21} - m_{22} m_{11}} \] (C.16)

The matrix elements and right-hand side for the linear system are

\[ m_{11} = -k_b \hat{H}_n^{(1)}(k_b a) \] (C.17)

\[ m_{12} = k_p \hat{J}_n(k_p a) \] (C.18)

\[ m_{21} = -k_b \hat{H}_{n+1}^{(1)}(k_b a) + \frac{n}{a} \hat{J}_n(k_b a) \] (C.19)
\[
m_{22} = \frac{\mu_b k_p}{\mu_p k_b} \left[ k_p \hat{j}_{n+1}(k_pa) - \frac{n}{a} \hat{j}_n(k_pa) \right]
\]

\[
b_1 = a_n k_b \hat{j}_n(k_ba)
\]

\[
b_2 = a_n \left[ k_b \hat{j}_{n+1}(k_a a) - \frac{n}{a} \hat{j}_n(k_p a) \right]
\]
The computation algorithm for the tunable surface response

1. Decompose the narrow band light into plane waves.
2. Decompose each particle into DDA entities.
3. Start: Plane wave light, compute $\varepsilon_{\text{metal}}(\omega)$.
4. Compute E field and the maxima of E field at the particle vicinity.
5. Check if complete? If NO, go back to step 4. If YES, proceed.
6. Error minimization by normalization: $E_{\text{norm}} = E_{\text{max}}/\max(E_{\text{max}})$.
7. Plot.

The computation algorithm for the tunable surface response
REFERENCES


