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Electrodynamics of Illuminated Nanojunctions

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Electrodynamics of Illuminated Nanojunctions

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Electrical Engineering and Computer Science

by

Faezeh Tork Ladani

Dissertation Committee:
Professor Eric Olaf Potma, Chair
Professor Vartkess Ara Apkarian
Professor Kumar Wickramasinghe

2017
DEDICATION

This piece of work,
To fellow researchers and potential collaborators
who want to build upon relevant topics.

The Joy of Completion,
To my extended lovely family,
particularly my parents, my siblings, and my adorable nieces and nephews
for whom this PhD means the world!
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ABSTRACT OF THE DISSERTATION

Electrodynamics of Illuminated Nanojunctions

By

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Doctor of Philosophy in Electrical Engineering and Computer Science

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A fundamental nano-structure is the gap formed when two materials are placed in close proximity to one another. If the junction thus produced is in the (sub)-nanometer range, the structure often exhibits unique optical properties when illuminated with light. Because it confines electromagnetic fields to nanoscopic dimensions, the nanojunction provides an exquisite platform for conducting studies on nano-objects and molecules placed in the junction. The response of such a molecule-nanojunction system is especially strong if it supports the accumulation of oscillating charge density along with concentration of the electromagnetic field upon illumination, as is the case when surface plasmon resonances are present. Characterizing the fields in these nanosystems is cumbersome because of the complex nature of near-fields in the junction, yet it is indispensable for the endeavor. In this dissertation we model two examples of illuminated nanojunctions that are extensively used in light-matter interaction experiments: (i) the nanojunction of a plasmonic nanoantenna made of a sphere dimer (nanodumbbell), which we will use to study optical chirality in surface-enhanced Raman scattering, and (ii) the nanojunction of a sharp atomic tip with a planar substrate, with relevance to photo-induced force microscopy. We develop analytical formalisms and perform full wave simulations to study the electrodynamics of the nanojunction based on various observables in the respective experiments.
We find that in the gold nanodumbbells, the nanojunction morphology dominates the near-field behavior and far-field scattering spectrum of the nanodumbbell, regardless of the overall shape of the nanoparticles. Moreover, the asymmetry in the nanojunction can lead to a significant chiroptical response. In the second example, we observe that different scattering mechanisms in the nanojunction affect the field gradient in the nanojunction, which can bring about photo-induced forces that are within the detectable range of a conventional scan probe instrument. We also observe that multiple-scattering mechanisms can lead to a sign reversal in the photo-induced force, a phenomenon that cannot be predicted by simpler models.
Chapter 1

Introduction

With advances in nanotechnology and the demand for analytical technologies with high spatial resolution, down to the molecular level, a broad range of structures that fall under the definition of “nanojunction” is of particular importance. A nanojunction is generally formed by two proximal nanostructures whose neighboring boundaries (nanojunction walls) are found at nm-scale distances, substantially smaller than the size of the nanostructures themselves. With this definition, a variety of morphologies can be recognized as nanojunctions [1], such as the troughs in gratings [2], planar metal-insulator-metal (MIM) structures [3], and the gaps formed in bowtie nanoantennae [4]. Of particular interest are nanojunctions which intrinsically support a high localization of charges under optical illumination. For this purpose, at least one of the walls is required to geometrically point towards the junction for accumulation of charges upon applying an electric field. We introduce two main categories of these junctions whose walls are defined by curved-curved (C-C) surfaces and curved-flat (C-F) surfaces.

C-C junctions are formed by placing two nanoparticles of comparable dimensions in
close proximity, i.e., bowtie nanoantenna, or dimers of nanoparticles such as Figure 1.1

a. C-F junctions are formed by placing an equivalent nanoparticle in close proximity
to a flat surface (i.e., planar substrates). By “equivalent” we include a broader range
of geometries (i.e., pointed micro-structures) whose behavior can be modeled with an
equivalent particle or effective volume in the physical phenomenon under study. For
example, an AFM tip under light illumination is optically modeled as a nanoparticle
of the dimension of the tip apex, as far as the near-field electrodynamics is concerned
[5]. In this category, while the flat surface may guide propagating surface waves, the
curved wall supports accumulation of charges in the nanojunction.

Such nanojunctions are broadly useful in applications that involve light-matter inter-
actions down to molecular lengths scales, provided that at least one of the structures
supports localized plasmon resonances. Because these resonances lead to hot spots
with enhanced electromagnetic field, they are capable of significantly (or nonlinearly)
enhancing light-matter interactions in their proximity. Examples include, but are not
limited to, tip-enhanced Raman Scattering (TERS), photo-induced force microscopy
(PiFM), surface enhanced Raman scattering (SERS) by individual or combinations of
a variety of nanoparticles such as spheres, nanorods, split rings, and bowtie structures.
[6, 7, 4, 8, 9, 10].

Figure 1.1: The morphology of a general nanojunction is depicted. (a) shows a general
Curved-Curved (C-C) junction and (b) shows a general Curved-Flat (C-F) junction.
In this dissertation, we investigate the electrodynamics of these two categories of nanojunctions under time-harmonic optical illumination. In particular, we focus on two specific examples with direct relevance to SERS spectroscopy and PiFM measurements. This study not only addresses some important questions that have been raised in recent experiments [11, 12], but also suggests new geometries for nanojunction engineering with exotic applications in imaging and spectroscopy, as well as realization of optical magnetism at sub-10-nm scales. Before introducing the fundamental questions under investigation for these nanojunctions, we point out the distinction between the detection scheme in the corresponding experiments, which leads to a different approach for analyzing these nanojunctions. We discuss this matter in more detail in the following.

Gold nanodumbbells as an example of the C-C nanojunction

Individual gold nano-dumbbells are extensively utilized in single molecule Raman scattering, where detection of the scattering field is performed in the far-field [13, 14]. Many theoretical studies have been carried out to explain the optical response of nanodumbbells, including analytical methods such as multipole methods and generalized Mie theory [15, 16, 17], plasmon hybridization [18, 19], transformation optics [20], full wave simulations, and experimental data [21, 22, 23]. Scattering and radiation properties have been modeled in analogy with RF dipole antennas [24, 25, 26, 27], and the enhancement of optical activity in the presence of chiral molecules has been investigated as well [28]. In spite of the extensive accumulated knowledge about this structure, current models are unable to fully address the optical activity of gold nanodumbbells (nominally achiral object), which was recently demonstrated experimentally in a SERS study [12]. The experimental observation of chirality in the nanodumbbell system urges more research studies of the electrodynamics of this
nanostructure. In particular, one of the aspects relevant to chirality is the fact that in practice the nanoparticles making the nanodumbbells are not perfect spherical objects. TEM images of real nanodumbbells used in experiments suggest that the structure may have asymmetries, either on the surface of the particles as facets and sharp edges, or through the relative orientation of the two nanoparticles with respect to each other [23, 12]. In addition, the nanojunction morphology (1nm), which cannot be easily explored by TEM images, may significantly influence the response of the nanodumbbell under different illuminations. Exploring the latter becomes even more essential, knowing that nanojunctions of such short gaps are subject to change due to different physical phenomena such as heating and/or electromagnetic and intermolecular forces [29, 30].

Chapter 2 is dedicated to address the impacts of the nanojunction morphology on the overall response of the nanodumbbell. This theoretical study is a combination of analytical modeling and full wave simulations. Numerical simulations give us freedom to consider a variety of asymmetries in the structure and to study the impacts in the near-field of the nanojunction, as well as the far-field scattering cross section (detection scheme). We then employ analytical modeling to provide insights into the physics responsible for the observed chiral behavior. In this context, we explain the behavior of the nanojunction analytically using a multipolar decomposition of the field. We further investigate how these multipoles, especially electric and magnetic dipoles, contribute to the optical chirality. Moreover, the study finds that the optical magnetization is of comparable magnitude as the electric response, suggesting several designs for non-magnetic nanomaterials that nonetheless display optical magnetism.
**PiFM setup as an example of C-F nanojunction**

In the C-F category, we consider a sharp tip that is placed closely to a planar surface, as sketched in Figure 1.1 b. This geometry is relevant to scan probe techniques in general, and PiFM in particular. Here we are interested in understanding the electrodynamics in the tip-sample nanojunction that enables PiFM measurements. In PiFM, electromagnetic coupling between the tip and the substrate provides a mechanism for detecting the photo-induced forces experienced by the tip in the presence of the sample. Because the photo-induced forces depend on the polarizability of the sample (nanoparticle), measuring the forces exerted on the tip provides a probe for the spectroscopic properties of the specimen. Experimental findings suggest that PiFM is promising for various nano-scale applications such as imaging and spectroscopy at the single molecule level [31, 32, 33].

Simple analytical models based on the image dipole and dipole-dipole interaction provide clear insights into the behavior of the photo-induced force exerted on the tip [34, 31, 35, 36, 37]. However, these models do not account for all the scattering pathways in the tip-substrate junction, and generally predict photo-induced forces that are below what is observed experimentally. To acquire a more complete picture of the origin of the detected force, more advanced models are needed.

In PiFM, the tip not only facilitates the near-field detection, but also comprises one of the walls of the nanojunction. The tip is known to provide high field enhancement due to excitation of localized surface plasmons at the tip apex [5, 38, 39, 40]. This means the probe itself significantly contributes to the light-matter interaction. Therefore, a detailed study of the near-field electrodynamics of the nanojunction including a tip, substrate and a nanoparticle (or single molecule) is essential for a better physical understanding of the relevant optical interactions, and interpretation of the
detected signal. In particular, different coupling mechanisms in the nanojunction can strongly influence the photo-induced forces, probed by the tip. Although numerical full wave simulations are useful, ultimately they are unable to provide the information that is required to distinguish the different mechanisms at play in the tip-sample junction. Therefore, an analytical modeling of the system that allows for segmenting the problem into fundamental physical mechanisms contributing to the overall observable force is indispensable. Such models can guide the design of photo-induced force microscopes based on the relevant mechanisms that constitute the force.

In chapter 3, we present an electrodynamic model of the PiFM system based on a dipolar model for the tip and the scattering Green’s function of a planar stratified substrate, so that different scattering mechanisms in the junction are studied separately and their contribution in the overall response is investigated as well. We find that for practical polarizabilities of molecule and tip, multiple scattering effects may not significantly affect the local field intensity at the tip, but they are essential in calculations of the field gradient. While neglecting higher order multipoles of the tip limits the quantitative accuracy of our model, it still provides clear evidence of the detectability of the force in the experimental setup and points to several force phenomena that are not captured in simpler models.
Chapter 2

Nanojunction morphology and chirality of nanodumbbells

In this chapter, we study the effects of asymmetry on near-field and far-field radiative properties of plasmonic nanoantennas consisting of a nanosphere dimer (nanodumbbells). By asymmetry, we refer to deviations of the structure from sphericity. In particular, we investigate how these types of asymmetry may lead to chiroptical response of a nanodumbbell, which is nominally an achiral structure. For this purpose, we first discuss the electromagnetic concepts that will be addressed throughout the chapter. Then, we present numerical calculations of a dimer formed from perfect spheres as a reference. We continue by introducing different levels of asymmetry and their impact on the behavior of the nanodumbbell, either in the field enhancement and absorption in the near-field, or the scattering cross section as the observable at the far-field detector. Moreover, we decompose the dimer response in terms of electric and magnetic multipolar equivalent sources, and discuss how the interaction of these sources may lead to chiral behavior. We show that although a perfectly symmetric spherical dumbbell is achiral on average, hot spots of local chirality can appear within...
an appreciable space, which may impact single molecule experiments based on the molecule location in the gap. Moreover, we show that the gap morphology dominates the response of the nanodumbbell, and any asymmetry in the plane of polarization strongly impacts the excitation of higher-order multipoles, as well as the chiral response. In fact, this asymmetry can provide volume-averaged optical chirality which is orientation dependent, i.e., the handedness changes upon 90 degree rotation of the nanodumbbell in the plane of polarization.

2.1 Electromagnetic concepts

The electromagnetic concepts that are explored in the context of nanodumbbells include extinction of light by small particles through scattering and absorption, expansion of the electric field in terms of vector spherical harmonics, and equivalent multipolar sources for a small scatterer, and finally the local density of optical chirality.

2.1.1 Scattering and absorption cross sections

Assume an electromagnetic beam is traveling in a nonabsorbing medium. If one or an ensemble of small arbitrary particles is placed in the beam of the electromagnetic wave, as shown in Figure 2.1, some of the energy of the incident beam is lost when measured at the detector. The loss of energy is due to the sum of absorption and scattering by the particles. This extinction of energy, or power, can be used as the characteristic response to study the behavior of arbitrarily-shaped particles to light illumination.
Figure 2.1: Some power of the incident beam is extinguished at the detector due to absorption and scattering by the particle. The absorbed and scattered powers can be calculated by the surface integral of the respective poynting vectors (of total fields and scattered fields respectively) on an enclosing surface $A$.

The absorbed power by the particle can be expressed by the surface integral of the total power flow, \[ \text{Re}\left\{ \left( E_0 + E_s \right) \times \left( H_0 + H_s \right) \right\} / 2 \] over a closed surface such as $A$ in Figure 2.1. In the expression of the scattered power, however, only the scattered field is considered, \[ \text{Re}\{ E_s \times H_s \} / 2. \] Note that the surface normal direction is opposite in the surface integrals related to the scattered and absorbed power. By this consideration,

\[ P_{\text{ext}} = P_{\text{sc}} + P_{\text{abs}}. \] (2.1)

Note the application of “loss” or “extinction” is broader and different than loss due to dissipation. In fact, ohmic losses can be only a small portion of the absorbed power. Extinction, scattering, and absorption cross sections are defined based on the ratio of the respective powers to the power density of the incident wave or irradiance, \[ |E_0|^2 / \eta \] where $E_0$ is the magnitude of the incident electric field and $\eta$ is the impedance of the medium. A detailed discussion of this concept can be found in [41]. For a dipolar scatterer with polarizability of $\alpha = \alpha' + i\alpha''$, the extinction, scattering, and absorption
cross sections read

\[ \sigma_{\text{ext}} = \frac{k}{\varepsilon} \alpha'' \]
\[ \sigma_{\text{sc}} = \frac{k^4}{6\pi\varepsilon^2} |\alpha|^2 \]  
\[ \sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{sc}} \] (2.2)

with \( \varepsilon \) being the absolute permittivity of the radiation space, with \( k \) as the wavenumber. For a spherical particle with radius \( r_p \) in this space, polarizability by Mie theory is given by [41, 42]:

\[ \alpha = \frac{6\pi\varepsilon i m \psi_1(mkr_p)\psi'_1(kr_p) - \psi'_1(mkr_p)\psi_1(kr_p)}{k^3 m \psi_1(mkr_p)\xi'_1(kr_p) - \psi'_1(mkr_p)\xi_1(kr_p)} \] (2.3)

where \( m = \sqrt{\varepsilon_m/\varepsilon} \) with \( \varepsilon_m \) referring to permittivity of the particle. Also, \( \psi_1(x) \) and \( \xi_1(x) \) are the Ricatti-Bessel functions of the first order [43]. For more complex structures, an effective polarizability can be associated with the structure, using numerically calculated cross sections and Eq. (2.2). However, the dipolar approximation is not valid for the whole spectrum of interest for our nanodumbbells. In fact, we are more interested to investigate excitation of higher-order multipoles in the nanojunction. Therefore, the next section provides a brief discussion on the extraction of multipoles, in particular magnetic dipole and electric quadrupole, using the numerically calculated fields.

\[ \text{2.1.2 ~ Equivalent multipole moments of complex nanostructures} \]

Electric polarizability and induced dipole moment is a sufficient model for very small and smooth particles whose local field does not significantly vary over the volume of
the particle (i.e., the particle is uniformly polarized). However, for bigger particles, or in nanojunctions, the electric field over the particle volume may exhibit strong gradients, and circulations. This can excite higher-order multipoles. For perfectly spherical particles, these multipoles can be calculated analytically through (generalized) Mie theory based on the expansion of the incident field in the spherical coordinates [41, 44, 15]. For more complex geometries, an analytical solution may not exist, but the same idea may be used to determine the effective or equivalent multipoles for the structure, if the scattered field by the complex geometry is known. Since the vector spherical harmonics form a complete orthonormal set, expansion of the numerically scattered field into this basis system results in unique coefficients proportional to the equivalent multipole moments located at the origin of the respective coordinate system [45, 46, 47].

Regarding the nanodumbbells, we are interested to investigate the excitation of the first three multipole moments (electric dipole, magnetic dipole, and electric quadrapole) in the nanojunction, and their impact on both the near-field response of the nanojunction as well as the far-field scattered spectrum. While generalized Mie theory provides an analytical solution for completely spherical particles, in the case of asymmetric structures, or structures with fine features such as a gap, it is necessary to carry out large order expansions to obtain convergent results for the local fields. Nevertheless, the far-field will be dominated by lower order multipoles.

We keep our geometry model general for exploring the effects of asymmetry in the nanojunction, as well as the structure. Therefore, we choose to study the latter through the evaluation of equivalent multipole moments. In this regard, we calculate the scattered electric field using COMSOL multiphysics, and use the numerically calculated field for projection onto vector spherical harmonics. Details of numerical calculations will come in the next section. The general solution to the scalar
Helmholtz equation in spherical coordinates, at location \( \mathbf{r} = (r, \theta, \phi) \), reads [45]

\[
\psi_{nm}(\mathbf{r}) = b_n(kr)P_n^m(\cos \theta)e^{im\phi} \tag{2.4}
\]

where \( b_n^{(1)}(kr) \) and \( P_n^m(\cos \theta) \) refer to the spherical Bessel functions, and the associated Legendre polynomials, respectively. \( k = n\omega/c \) is the intrinsic wavenumber in a medium with refractive index \( n \). The vector spherical harmonics \( \mathbf{M}_{nm} \) and \( \mathbf{N}_{nm} \) for expressing TE and TM waves can be defined by curl operation on the vector \( \psi_{nm} \mathbf{r} \) [44]. Therefore,

\[
\mathbf{M}_{nm}(\mathbf{r}) = \nabla \times (\psi_{nm} \mathbf{r}), \quad \mathbf{N}_{nm}(\mathbf{r}) = \frac{1}{k} \nabla \times \mathbf{M}_{nm}(\mathbf{r}) \tag{2.5}
\]

which read

\[
\mathbf{M}_{nm}(\mathbf{r}) = b_n(kr)e^{im\phi} \begin{bmatrix} 0 \\ i\pi_{nm}(\cos \theta) \\ -\tau_{nm}(\cos \theta) \end{bmatrix} \tag{2.6}
\]

and

\[
\mathbf{N}_{nm}(\mathbf{r}) = e^{im\phi} \frac{1}{kr} \begin{bmatrix} n(n+1)b_n(kr)P_n^m(\cos \theta) \\ \xi_n(kr)\tau_{nm}(\cos \theta) \\ i\xi_n(kr)\pi_{nm}(\cos \theta) \end{bmatrix} \tag{2.7}
\]

in which

\[
\xi_n(kr) = \frac{\partial}{\partial r} [rb_n(kr)] \\
\pi_{nm}(\cos \theta) = \frac{m}{\sin \theta} P_n^m(\cos \theta) \\
\tau_{nm}(\cos \theta) = \frac{\partial}{\partial \theta} P_n^m(\cos \theta), \tag{2.8}
\]
in which \( b_n(kr) \) refers to spherical Bessel functions, and specifically to spherical Hankel functions when propagating waves are concerned. For more details on the special functions, and the corresponding recurrent formulas see Refs [45, 43, 48]. Based on the notations in [45, 49], any electric field, in particular the scattered field of the nanodumbbell can be expanded as

\[
E_{sc}(r) = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} E_{nm} [a_{nm} N_{nm}(r) + b_{nm} M_{nm}(r)] \quad (2.9)
\]

where

\[
E_{nm} = |E_0|^2 \frac{(n+2m-1)!}{2(n-m)!} \sqrt{\frac{2n+1}{4\pi (n+m)!}} \quad (2.10)
\]

with \( |E_0| \) being the magnitude of the incident field. In Eq. (2.9) the radial dependence of \( N_{nm} \) and \( M_{nm} \) is expressed by spherical Hankel functions, \( h_n^{(1)}(kr) \), to represent outward traveling waves from the structure. Also, the prefactor \( E_{nm} \) is defined to compensate the asymmetric definition of the associated Legendre functions for \( \pm m \).

As a result, the calculation of the multipole moments in Cartesian coordinates includes a symmetric combination of the dimensionless scattering coefficients, \( a_{nm} \) and \( b_{nm} \). Now consider that the closed surface \( A \) in Figures 2.1 is a spherical coordinate surface, \( r = a \), for which we have the numerical value of the scattered field. By projection of the scattered field onto the vector spherical harmonics calculated on \( A \), we can compute the scattering coefficients as the following:

\[
E_{nm} a_{nm} = \frac{\int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi \, E_{sc} \cdot N_{nm}^*}{\int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi \, |N_{nm}|^2} \quad (2.11)
\]

\[
E_{nm} b_{nm} = \frac{\int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi \, E_{sc} \cdot M_{nm}^*}{\int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi \, |M_{nm}|^2}
\]

Note that analytically the results is not dependent on \( r = a \), as long as the surface
encloses the whole structure, but is dependent on the selection of the origin. The equivalent multipoles for a structure refers to the multipoles that are located at the origin of the coordinate system and produce the same scattered field as the structure. In principle, numerical evaluation of Eq. (2.11) should also be independent of the value \( r = a \). However, since the scattered field is calculated numerically, and the mesh quality is generally decreased by getting far from the structure, evaluation of the scattering coefficient may include an \( r \) dependent numerical tolerance thus we have chosen the minimum possible \( a \), for better accuracy.

Having the scattered coefficients, and comparison of their far-field radiation of the multipoles in Cartesian coordinates, we can write the multipole moments in Cartesian coordinates \[46\]

\[
\begin{bmatrix}
  p_x \\
  p_y \\
  p_z 
\end{bmatrix} = C_0 \begin{bmatrix}
  a_{11} - a_{1-1} \\
  i(a_{11} + a_{1-1}) \\
  -\sqrt{2}a_{10}
\end{bmatrix}
\]

with \( C_0 = \frac{\sqrt{6\pi} e^{i\phi}}{k^3} \). The dual Cartesian magnetic moment \( m/c \) is written the same in terms of \( b_{1m} \) coefficients. For the symmetric traceless representation of the electric quadrupole tensor, \( \bar{Q} \), the two vectors, \( \bar{Q} \cdot \mathbf{x} \), and \( \bar{Q} \cdot \mathbf{z} \) are as the following:

\[
\begin{bmatrix}
  Q_{xx} \\
  Q_{yx} \\
  Q_{zx}
\end{bmatrix} = D_0 \begin{bmatrix}
  i(a_{22} + a_{2-2}) - \frac{k\phi}{2}a_{20} \\
  a_{22} - a_{2-2} \\
  i(a_{2-1} - a_{21})
\end{bmatrix}
\]

(2.13)
and

\[
\begin{bmatrix}
Q_{xz} \\
Q_{yz} \\
Q_{zz}
\end{bmatrix} = D_0 \begin{bmatrix}
 i(a_{2-1} - a_{21}) \\
 a_{2-1} + a_{21} \\
 \sqrt[3]{6}a_{20}
\end{bmatrix}
\]  \hspace{1cm} (2.14)

with \( D_0 = \frac{\sqrt[3]{30}\varepsilon}{4k^4}. \)

### 2.1.3 Optical Chirality

Optical chirality is an electromagnetic wave property in exact analogy with geometrical chirality. A chiral object is distinguishable from its mirror image. The concept of local density of optical chirality (LDOC) was first shown purely mathematically by Likpin [50] in the context of a conservation law based on Maxwell’s equations, even though the name along with a physical meaning came later as presented in Ref [51]. We should mention that both geometrical chirality and chirality of an electromagnetic wave was known long before. However, LDOC as a local characteristic of the optical wave has been introduced very recently to be of direct relevance to optical activity of chiral molecules [51]. LDOC of a time harmonic field is expressed by [51, 52, 53]

\[
C = -\frac{\varepsilon\omega}{2} \text{Im}(\mathbf{E}^* \cdot \mathbf{B})
\]  \hspace{1cm} (2.15)

where \( \mathbf{E} \) and \( \mathbf{B} \) refers to the local electric field and magnetic flux density, respectively. LDOC is a pseudoscalar with the sign defining the handedness. It is usually normalized with respect to the chirality of right-handed or left-handed circularly polarized light (CPL),

\[
C^{\text{CPL}} = \pm \frac{\varepsilon\omega}{2c} |\mathbf{E}_0|^2
\]  \hspace{1cm} (2.16)
especially when enhancement of LDOC is concerned in the context of optical activity. Strong LDOC is not exclusive to interaction of light with obviously chiral geometries. It has been theoretically shown that a linearly polarized illumination of symmetric nanostructures, and asymmetric interference of incident and scattered field, can lead to a chiral field that exhibits even stronger chirality than that of CPL [52]. Similarly, Banik et al experimentally demonstrated giant optical activity in the Raman response of gold nanodumbbells, nominally an achiral object [12]. Note that in the Raman experiment, the signal is detected at a different frequency from the incident light. Therefore, no interference with incident field leads to the observed optical chirality. In this scenario, the asymmetry due to the retardation and the excitation of the magnetic dipole aligned with the electric dipole of the nanodumbbell have been suggested as being responsible for the chiroptical response of the nanodumbbells. In this context, it is beneficial to study the LDOC of the nanodumbbells in the nanojunction where hot spots of electric field intensity and SERS are expected. We want to study the LDOC and chiroptical response in correlation with the excitation of multipoles. For the first level of modeling, we only consider electric and magnetic dipoles, but with a general polarization. The quasi-static approximation of these sources can be written as:

\[
E_p = \frac{1}{4\pi\varepsilon r^3} f(p) \quad H_p = \frac{i\omega}{4\pi r^2} (\mathbf{n} \times \mathbf{p})
\] (2.17)

and

\[
E_m = -\frac{ik}{4\pi\varepsilon r^2} (\mathbf{n} \times \mathbf{m}/c) \quad H_m = \frac{c}{4\pi r^3} f(\mathbf{m}/c)
\] (2.18)

where the vector function \( f \) of a vector \( \mathbf{a} \) is \( f(\mathbf{a}) = 3\mathbf{n}(\mathbf{n} \cdot \mathbf{a}) - \mathbf{a} \), and \( \mathbf{n} \) is a unit vector pointing to the observation point. Note that we have written the fields for \( \mathbf{m}/c \) to be able to discuss the fields by sources in the same unit. LDOC due to the emitted
fields of these two sources is

$$C = -\frac{k}{2c} \text{Im}(I_{pp} + I_{pm} + I_{mp} + I_{mm}) \quad (2.19)$$

where $I_{kj} = E_k^* \cdot H_j$, $k,j = p,m$. Of the four terms on the right hand side of Eq. 2.19, $I_{pp}$ and $I_{mm}$ are real numbers and thus do not contribute to the LDOC in the near-field approximation. For example, for electric dipole source we have

$$I_{pp} = E_p^* \cdot H_p = -i\frac{\omega}{16\pi^2\varepsilon r^5} p^* \cdot (n \times p)$$

$$= \frac{\omega}{8\pi^2\varepsilon r^5} \text{Im}[n \cdot (p^* \times p)] \quad (2.20)$$

since $n \cdot (p^* \times p)$ is a purely imaginary number. Note that the final expression in Eq. (2.20) is also valid for the magnetic dipole source by only replacing $p$ with $m/c$. In addition, notice that even though the near-fields of these dipole sources are not chiral themselves, in the far-field two perpendicular components of the same dipole source can provide a chiral (elliptical polarized) propagating wave, if there is a proper phase shift between the components. In the near field, the interference of an electric and a magnetic type source can lead to non-zero LDOC, as shown in the following. $I_{pm}$ in Eq. (2.19) reads

$$I_{pm} = E_p^* \cdot H_m = \frac{c}{16\pi^2\varepsilon r^6} \left[3(n \cdot p^*)(n \cdot m/c) + p^* \cdot m/c\right]. \quad (2.21)$$

Also, $I_{mp}$ shows a similar orientation dependence on the dipole sources as

$$I_{mp} = E_m^* \cdot H_p = \frac{k^2\omega}{16\pi^2\varepsilon c r^4} \left[(n \cdot p)(n \cdot m^*/c) - (p \cdot m^*/c)\right]. \quad (2.22)$$
in which \((a \times b) \cdot (c \times d) = (a \cdot c)(b \cdot d) - (a \cdot d)(b \cdot c)\) is used. However, in the near field where \(kr \ll 1\), \(I_{mp}\) can be neglected in comparison with \(I_{pm}\). Therefore,

\[
C = -\frac{k}{32\pi^2\varepsilon r^6} \text{Im} \left[ 3(n \cdot p^*)(n \cdot m/c) + (p^* \cdot m/c) \right]
\]  

Eq. (2.23) shows the term \(p^* \cdot m/c\) contributes to the LDOC at any location in the near-field, and thus leads to a volume-averaged chirality of a certain handedness in the gap. Moreover, a location dependent projection of the sources, \((n \cdot p^*)(n \cdot m/c)\), may lead to hot spots of the LDOC. Therefore, even perpendicular electric and magnetic dipole components can cause LDOC with extrema happening along the direction where the two sources have the optimum projection. The location dependent term also suggests that symmetric location with respect to the location of the sources, will have the opposite handedness \((n' = -n)\). Therefore, this contribution on average is negligible in a volume symmetric with respect to the origin (location of the sources).

Note that the location dependent term in the LDOC may still be important in single molecule experiments if the chiral spots of one handedness cover an appreciable area in which a molecule may be located in the gap.

Before we turn to numerical results and analysis, we highlight that in the calculation of the LDOC in the nanodumbbells, we only use the equivalent multipoles of the nanodumbbell, obtained from the scattered field, and not the total field. With relevance to the dumbbell’s response in the Raman experiments, the total field is only the scattered field by the nanodumbbell.
2.2 Numerical calculations

Simulations of the gold nanodumbbells were done in COMSOL multiphysics 5.2, using the wave optics module, the frequency domain electromagnetic analysis. The structure of the ideal nanodumbbell consists of two spherical particles with 45 nm radius aligned along the $x$ axis with a 1 nm gap between the adjacent boundaries. In variations of asymmetric nanodumbbell, we try to keep the dimension of the asymmetric particle in the same range to reduce the impacts of size and volume on the plasmonic response of the particles, and to be able to investigate the impacts of shape (asymmetries) only. The two nanoparticles are covered in a spheroidal silica shell, with $150 \times 100 \times 100$ nm dimension. The nanodumbbell is located in spherical domain with PML and scattering boundary conditions to minimize reflections from the boundaries with free space. The dielectric function of gold is taken from Ref [54], and for silica is taken from Ref [55], which on average is constant, $n = 1.45$, in the spectral range of interest.

2.2.1 Ideal nanodumbbell spectra and surface charge

The geometry of the structure and the coordinate system is shown in Figure 2.2. Keep in mind that regardless of the polarization and propagation direction, we always show the geometry of the nanodumbbell in the $xz$ plane. In this arrangement the nanodumbbell is illuminated with a plane wave propagating along the $z$ axis. The polarization of the illumination can be either along $x$ or $y$, called the long and short axis of the dumbbell, respectively.
Figure 2.2: The nanodumbbell is illuminated with a plane wave propagating along the z axis, with linear polarization along x or y for excitation of the dumbbell along the long and short axis, respectively.

Figure 2.3 (a,b) shows the spectrum of the dumbbell, for excitation along the long (i.e., $\mathbf{E}_0 = E_0 \mathbf{x}$) and short (i.e., $\mathbf{E}_0 = E_0 \mathbf{y}$) axes. The field enhancement at the center of the gap, defined by $FE = |\mathbf{E}|/E_0$ is shown in blue, and the scattering and absorption spectrum is shown in red (solid and dashed, respectively). For the sake of comparison to a single nanopshere of the same radius, the Mie polarizability and cross sections for an individual sphere in silica were calculated by Eq. (2.2-2.3) and are shown in Figure 2.4. As is reported in the literature [56, 23, 57], for long axis excitation, in the strong coupling limit of the two particles, a hybrid plasmon mode with dipolar response (known as bright mode [7, 58]) is observed at 370 THz, red-shifted from the resonance of a single sphere by about 150 THz. This energy shift is associated with the binding energy of the dipolar plasmons on each sphere, hence the resonance is identified as the binding dipolar plasmon (BDP). The spectrum further consists of a resonance at 480 THz, (Figure 2.3 a), and another at approximately 540 THz (nominally dark modes [59, 60]) that can be distinguished in the scattering spectrum, although the latter is barely recognized in the absorption and field enhancement spectra. Before explaining more details on the spectrum of the dumbbell for long axis excitation, we make a comparison of this spectrum with the one obtained for
perpendicular polarization shown in Figure 2.3 (b). As expected, the two particles are not strongly coupled in this polarization and the spectrum is a simple sum of the spectra of the single nanospheres shown in Figure 2.4 (i.e., almost doubled in scattering and absorption amplitudes). Note that the field enhancement is degraded in the gap ($FE < 1$ in Figure 2.3 b) because of the destructive interference of the fields of the two dipoles. A slight dip is observed in the scattering spectrum of the dumbbell after the plasmon resonance, also recognized in the field enhancement spectrum, which is associated with excitation of higher-order multipoles.

![Figure 2.3](image)

Figure 2.3: Scattering, and absorption cross section (red), as well as the field enhancement (blue) spectrum of the symmetric nanodumbbell are shown versus frequency for (a) $E_0 = E_0x$ and (b) $E_0 = E_0y$. Corresponding wavelength range is shown on the top $x$ axis.
Figure 2.4: Spectra of (a) dispersive and dissipative polarizability (b) Scattering, and absorption cross sections for a single nanosphere, radius of 45 nm, in silica shell.

Studying the short axis polarization response has advantages. However, this polarization is not of interest for applications in which a hot spot is required in the nanojunction. Therefore, we focus our attention here on the long axis excitation of the dumbbell. In the excitation spectrum shown in Figure 2.3 (a), we note that the maximum scattering is red shifted relative to the absorption and field enhancement resonances. Using a Lorentzian model for this scattering resonance, the red shift can be understood as the result of energy lowering through the dipole-dipole interaction of collinearly coupled, in-phase dipoles with maximum scattering slightly red shifted from resonance. Also, this mode has the strongest scattering because the dipole plasmon couples effectively with the dipole antenna. The second resonance is associated with the magnetic resonance of plasmons due to retardation and the resulting asymmetry in the plasmon oscillations. Close to this resonance, quadrupole plasmons are excited that are weakly coupled to the nanoantenna.

By comparing the absorption, and field enhancement spectra (both obtained in the near-field), we observe distinct behavior of the two resonances at 370 and 480 THz. In particular, while the absorption level is almost identical, the field enhancement
of the second resonance is \( \approx 30\% \) lower than the one for the dipolar resonance. This lower field enhancement may translate to a \( \approx 75\% \) decrease in the Raman enhancement based on the forth power rule [61]. Therefore, it is valuable to have a clear understanding of the corresponding phenomena. Note that in the magnetic mode resonating at 480 THz, which is caused by asymmetric charge oscillation, we expect the hot spot to be slightly eccentric, and moved from the probing point (located at the center of the gap) in the evaluation of the field enhancement spectrum. This is more clear in the surface charge density plot shown in Figure 2.5. The maximum amplitude of the charge density for the two resonances are 61.1 and 56 \( C/m^2 \), respectively. This difference suggests only around 10\% difference in the field enhancement. However, the hot spot in the magnetic resonance is shifted from the center, in the direction of propagation. The 10\% difference may be associated with stronger ohmic losses at 480 THz. In other words, some of the absorbed energy is turned into heat and does not contribute to the electrodynamics of the nanojunction directly, even though it may contribute to changes in the junction’s morphology due to heat. The charge distribution at the quadrupole resonance is shown in the third column in Figure 2.5, which is featured by a loop of opposite charge around the central charge distribution. Note that although the distribution has a looped shape, the time dependence does not show a recognizable circulation of charge, but a convergent motion to the center of the gap. This charge distribution can be retrieved from \( l = 2, m = 0 \) in spherical harmonics (shown in the multipolar decomposition), but is displaced toward the gap.
Figure 2.5: Surface charge density distribution associated with the three resonances of the scattering spectrum, shows the excitation of electric dipole, magnetic dipole, and electric quadrupole plasmon modes in the gap. (a) Real and (b) imaginary parts of the surface charge density are plotted on the surface of a particle, with the center referring to the gap. The color bar (in $10^{-10} C/m^2$) shows the extrema of the respective plot.

In this section, we have seen that the asymmetry due to retardation gives rise to the excitation of the higher-order multipoles, especially the magnetic dipole which may impact chiroptical response of the nanodumbbells [12]. We will discuss this in more detail by presenting the equivalent multipolar sources in the coming sections. At the same time, asymmetry of the object is even more relevant when the different chiroptical response (left-handed, achiral, and right-handed) of different nanodumbbells is considered. In fact, we will show in the next section that the response of the nanodumbbells is highly sensitive to and dominated by the geometry of the nanojunction.
2.2.2 Asymmetry in the direction of wave propagation (retardation)

To investigate the effects of asymmetry on the dumbbell’s response in comparison to the perfect nanodumbbell standard, we introduce geometrical asymmetries at different levels either along the retardation direction, or in the plane of polarization. Also, we distinguish the appearance of the asymmetry in the gap region, from that is seen on the outer surface of the particles. This distinction is useful for evaluating the electron motion on the surface of the particles during the cycle. In other words, if the surface charge density of the dumbbell moves outside of the gap region, the asymmetric path on the outer surface of the particle leads to a different response.

In this section we discuss the effects of asymmetry in the direction of the wave propagation. We assume propagation in the $z$ direction, as in Figure 2.2, and incident polarization along the long axis, $x$. Figure 2.6 shows the structures under study. With first index referring to gap region, and the second index referring to the outer surface of the particle, we define four categories of structures as SS, SA, AS, and AA. For example, compared to the fully symmetric dumbbell (SS), the SA structure has a smooth symmetric gap similar to the SS dumbbell, but the outer region can deviate from a spherical surface by having facets and edges, or some asymmetry for the retarded wave traveling through the object. Meanwhile, we aim to keep the overall size, and volume of the particles to be in the range of 45 nm sphere to study only to the effect of geometrical asymmetries. In the definition of the A-gap structures, we keep the average gap distance to be 1 nm, the same as the original dumbbell. Based on our available CAD tools, the A-gap structures include a $15^\circ$ rotation of the axis. To make sure that this rotation does not influence the results beyond the asymmetry of the junction, a relevant simulation is done and reported in Appendix A. Also, note that in the A-gap structures the field enhancement probe is slightly shifted to a location
where the highest field is expected.

Figure 2.6: By introducing asymmetry in (i) the gap region and (ii) the outer surface of particles in the direction of propagation, we have four geometries under study, SS, SA, AS and AA. Dumbbells are shown with surrounding silica shell and the insets show the zoomed region around the gap for each dumbbell.

In Figure 2.7, we present the field enhancement, scattering and absorption spectra for these nanodumbbells. We see that the spectra of the S-gap dumbbells are almost identical. However, in the A-gap dumbbell spectrum, not only are the resonances shifted in comparison to the S-gap dumbbells, but also new resonances appear. In the A-gap dumbbells, the bright mode is slightly red shifted, otherwise they are identical in nature. The dark modes in A-gap structures are dramatically modified in both resonant frequency and amplitude. We can conclude that the behavior of the dumbbell is dominated by the gap morphology, and slight changes that are likely to happen in practice (even for individual structure during an experiment) can have
significant impact on the response of the dumbbell. This is because the majority of free electrons contributing to plasmon modes are confined to the gap region.

Figure 2.7: The near field and far field spectra of the dumbbells indicate that the gap morphology dominates the response of the dumbbell. The spectra of S-gap dumbbells are almost identical regardless of the gross shape. In contrast, A-gap dumbbells have a significantly different spectra.

To provide a deeper insight for the behavior of the modes in the gap, we present the calculated equivalent multipoles of the dumbbells based on Sec. 2.1.2. For this calculation, we have chosen the SS and AS structures, and plot the magnitude of all moments in Figure 2.8 in the same unit. The excitation spectra are shown for
each dumbbell, and the dominant components of each of the equivalent sources are tagged in the respective panel. In the case of SS dumbbell, we observe that the $|p_x|$ spectrum agrees well with the scattering spectrum. This pattern is expected since the dipole nanoantenna has $x$ polarization. Moreover, $|m_y|$ and $|Q_{xz}|$ become noticeable, with resonances corresponding to the same frequencies that were discussed in the scattering spectrum reported in the previous section.

An interesting feature which is not recognized in the scattering spectrum is a Fano type interference of $|m_y|$ and $|Q_{xz}|$ at 500 THz, where a dip in the $|m_y|$ spectrum coincides with a narrow resonance in $|Q_{xz}|$. To show this in more details, we plot the amplitude and relative phase of these two modes in Figure 2.9. A $\pi/2$ phase difference indicates the exchange of energy between the two modes. Such a feature is not observable in the scattering spectrum, but can be transferred to the far-field by a molecular reporter sensitive to the near-field magnetic dipole.
Figure 2.8: Asymmetry in the junction not only modifies the multipoles (that occurs even in the SS dumbbell because of the retardation and strong coupling) in magnitude and peak frequency, but also introduces excitation of new multipoles. Magnitude of all the multipole moments is plotted in $10^{-31} Cm$. 
Figure 2.9: (a) Magnitude and (b) relative phase of the significant electric quadrupole moment, $Q_{xz}$, and magnetic dipole moment, $m_y$, for SS nanodumbbells.

For the AS dumbbell, we observe similar features in the multipole spectra (slightly red shifted), in addition to new resonances that appear in the equivalent multipolar sources. First we note that the electric dipole source has a component in the direction of propagation, $p_z$, where the frequency of the maximum magnitude corresponds to that for the long axis electric dipole, $p_x$. $p_z$ is excited because the gap has an angle relative to the $z$ axis. Notice that the fields associated with the surface plasmons are normal to the surface, and thus the projection of the field on the surface of the particles induces charge oscillations in the $z$ direction. Moreover, to satisfy the plasmon oscillation boundary condition for both walls of the nanojunction, the location of the hot spot is moved to where the tangents to the nanojunction’s walls are par-
allel (Figure 2.10). Therefore, satisfaction of boundary conditions in the asymmetric nanojunction facilitates coupling and excitation of modes which otherwise could not be excited.

![Figure 2.10](image)

Figure 2.10: Norm of the electric field in the junction of the AS nanodumbbell is shown by the color map, and the direction of the electric field vector is indicated by arrows. The hot spot in the asymmetric junction happens where the two walls have the shortest gap (i.e., parallel tangents). Boundary condition imposes excitation of $p_z$ by $x$ polarized incident field.

The magnetic dipole moment is also impacted significantly by the asymmetry of the junction. In comparison to the magnetic dipole moment in the SS nanodumbbell, we see that existing features are more pronounced, and the moment is doubled in magnitude at the peak frequency. Moreover, a new and relatively strong resonance appears at the frequency of maximum $p_z$. In fact, the charge oscillation in the $z$ direction (due to junction asymmetry) and its image on the other wall of the nanojunction induces a net magnetic moment in the $y$ direction. This orientation of charge oscillation can destructively interfere with $Q_{xz}$ as seen in the spectrum. We also see that the presence of both $p_x$ and $p_z$ supports coupling to $Q_{xx}$, $Q_{zz}$ even in the lower frequency range,
which is not possible in the SS dumbbell. This example clearly demonstrates that the nanojunction asymmetry is directly relevant to the field, field gradient, and polarization that are required for substantial coupling to higher-order multipoles. However, we see that the major differences appear in the magnetic dipole moment. Because of this, in addition to circumventing the complexity of the analysis due to quadrupole components, we focus in the remainder of the Chapter on the electric and magnetic dipole moments.

We are now interested in comparing the normalized magnitude and relative phase of these components with respect to the dominant electric dipole moment, corresponding to the nanoantenna mode, $p_x$. Figure 2.11 shows the results for SS and AS nanodumbbells, respectively. First, note that the magnetic behavior of the dumbbell (represented by the magnetic dipole moment) can rise up to more than a third of the electric response in certain ranges of the spectrum. This amount of magnetic enhancement is substantial, given that the material is non-magnetic in this frequency range. In addition, the relative $\pi$ phase of $p_z$ and $m_y$ at $\approx 365$ THz for AS dumbbell, consistent with Ampere’s law, indicates that the first magnetic resonance is purely a geometrical effect due to the asymmetry of the junction. Thus this observation suggests new ways to engineer the junction for achieving magnetic features at sub-10-nm dimensions.
Figure 2.11: Normalized magnitude and relative phase of the significant electric and magnetic dipole moments with respect to $p_x$ are plotted for (a) SS, and (b) AS dumbbells.

Also, the relative phase spectra in Figure 2.11 show that the optimum phase shift, $\pm \pi/2$, between the perpendicular electric and magnetic dipoles occurs within some ranges of the spectrum, either for the $p_x-m_y$ pair (in both SS and AS), or the $p_z-m_y$ pair (only in AS dumbbell). Therefore, based on our description in Eq. (2.23) both structures support the presence of hot spots of LDOC in the gap region even for symmetric excitation ($E_0 = E_0\hat{x}$), as will be discussed in the subsequent sections. In the following section, we study the effects of junction asymmetry in the plane of polarization.
2.2.3 Asymmetry in the plane of polarization (wavefront)

We consider the case where the asymmetry appears in the plane of polarization, where both vectors of electric and magnetic fields experience the either the asymmetry of the entire structure or the asymmetry of the nanojunction alone. For this purpose, the AS dumbbell is illuminated by a plane wave with propagation along the $y$ axis, as shown in Figure 2.12.

![Figure 2.12: When asymmetry in the plane of polarization is concerned, we consider plane wave propagation along $y$ axis, so the wave fronts are parallel to $xz$ plane.](image)

We note that in this excitation scheme, the AS dumbbell introduces a new level of asymmetry because of a $15^\circ$ rotation of the top nanoparticle. Both the gross structure of the dumbbell and junction are asymmetric. However, we show in Figure 2.13, that such a rotation based asymmetry in the dimer, as well as the asymmetry (edges) in the outer surface of the particles (the bottom nanodumbbell) does not impact the response for the two symmetric excitation polarization (shown with red and blue colors), while a slight asymmetry in the gap of two *perfectly* spherical particles (top nanodumbbell) leads to significant linear dichroism. The gap morphology and the symmetric $\pm 45^\circ$ polarizations are shown in each inset in Figure 2.13. This example provides further evidence that confirm the dominance of the gap morphology in the response of the nanodumbbells. Therefore, the AS nanodumbbell in Figure 2.6 maintains the category of asymmetry, and any comparisons made between the results of
this section and the previous section relate to the effects of the junction asymmetry only.

Figure 2.13: Scattering (solid line) and absorption (dotted line) cross section spectra for the two incident polarizations (shown in the insets with red and blue arrows) shows the morphology of the nanojunction dominates the response of the dumbbells. Therefore, the asymmetric nanojunction in the top structure leads to a significant difference in the spectra of the two polarizations. On the other hand, the bottom structure has almost identical spectra for the two polarizations. Note that although the gross structure is asymmetric, the nanojunction is symmetric.

We now turn our attention to the AS nanodumbbell, using a new excitation scheme being referred to by \((\text{AS}, k_y)\), where the magnitude of the electric and magnetic dipole
components (in the same unit) for the three polarizations are shown in Figure 2.14. The geometry of the dumbbell (with the dumbbell’s long axis being aligned with x axis) and the incident polarization (in the xz plane), are shown in the insets. We first discuss excitation along the long axis, shown in the left graph. We compare the equivalent multipolar sources of this excitation, with relevant components in Figure 2.8 for the excitation along z axis, (AS,k_z). In other words, we compare the effects of asymmetry whether in the plane of polarization (Figure 2.14, the far left column) or in the direction of propagation (Figure 2.8, the right column). The electric dipole components are very similar in both cases. This is rational by noting that the asymmetry of the nanojunction experienced by E_0 is the same. However, the magnetic dipole components show a very different response in (AS,k_y) and (AS,k_z). First, notice that all three components of magnetic dipole show recognizable features in the spectrum for the (AS,k_y) case. This is due to the mix of retardation-based and geometry-based asymmetries which are now imposed in different directions and couple all the components to the electric dipolar plasmons. Note that H_0 = H_0z in (AS,k_y) excites features in m_z in analogy with H_0 = H_0y for (SS,k_z), except for a red shift. The gap asymmetry in the xz plane facilitates coupling of H_0 = H_0z to a minor yet interesting m_x feature in the (AS,k_y) case. The first resonant feature in m_y in the bright mode bandwidth, remains almost identical for both the (AS,k_y) and (AS,k_z) cases due to a pure geometry-based origin of induced charge density circulation. The multipolar decomposition, and comparison between the (AS,k_y), (AS,k_z) and (SS,k_z) cases provides detailed and very interesting information about the impacts of the retardation-based and geometry-based asymmetries on the coupling and interference of higher-order multipoles. Notice that much of the information is not easily recognized in Rayleigh scattering spectrum. Investigation of this data deserves further study.

The geometrical asymmetry in the plane of polarization provides a mechanism to
excite parallel components of electric and magnetic dipole moments, and thus contributes to a non-zero averaged LDLOC (Eq. (2.24)) in the gap, even within a symmetric volume around the center, and nominally symmetric excitation. To understand this mechanism better and study the handedness, we perform multipolar decomposition in a modeled linear dichroism experiment, (i.e. ±45° polarization), as shown in Figure 2.14 (middle and right columns).

![Electric and magnetic dipole moments](image)

**Figure 2.14:** Electric and magnetic dipole moments in the case of asymmetry in the plane of polarization. Magnitude of all the multipole moments is plotted in $10^{-31} Cm$.

Based on the equivalent sources shown, we see that the AS dumbbell response is stronger at $-45^\circ$ (right column) than at a $+45^\circ$ incident polarization. To understand why, recall Figure 2.10. The projection of $E_0$ onto the nanojunction walls at $-45^\circ$ leads to a stronger perpendicular component which can effectively drive the nanodumbbell. With this insight, we turn our attention to the chiroptical response of the nanodumbbells based on equivalent sources, in the next section.
2.2.4 Moments and Chiroptical response of the junction

Based on Eq. 2.23, and the multipolar decomposition discussed in the previous sections, we conclude that in the near-field, the SS dumbbell sustains hot spots of LDOC in the nanojunction, even though it is negligible on average when integrated over the entire gap volume. Similar results hold for the AS dumbbell, if the asymmetry is applied in the direction of propagation. It should be mentioned that asymmetry of the nanojunction imposes asymmetric averaging in the gap, and thus may lead to a non-zero LDOC even when considering the location dependent LDOC in Eq. 2.23. However, this may be negligible and may vary based on the geometry of the gap for individual nanodumbbells. On the other hand, non-zero projection of the dipole sources at the center is sufficient for a non-zero LDOC per unit volume in A-gap dumbbells, regardless of the volume of integration. In this section, we first discuss the location dependent LDOC and its impact on single molecule experiments in SS and AS dumbbells. Then we study the averaged LDOC of the AS dumbbells in relation to observations made in orientation-dependent handedness of gold nanodumbbells [12].

As shown in Figure 2.11 for the gold nanodumbbells, considerable electric and magnetic dipole moments, \( p_x, p_z \) and \( m_y \) are excited with a phase difference as large as \( \pi/2 \) at some frequencies. According to Eq. 2.23, the LDOC is proportional to

\[
C \propto (n_x n_y \text{Im}[p_x^* m_y] + n_z n_y \text{Im}[p_z^* m_y])
\]

To discuss the hot spots of LDOC, we consider the surface of the spherical particle in both SS and AS nanodumbbells in the gap region. On this surface, \( n_x \) is maximum at the center of the surface, and maintains its sign. Therefore, \( \text{Im}(p_x^* m_y) \) creates extrema of LDOC along the \( y \) axis, with opposite handedness for \( y < 0 \) and \( y > 0 \). The other pair, \( \text{Im}(p_z^* m_y) \), creates a four lobe pattern on the surface. In Figure
2.16 top row, we plot $\text{Im}(p_x^* m_y)$ and $\text{Im}(p_z^* m_y)$ as the relevant factor to hot spots of LDOC of the equivalent sources and corresponding handedness, for (a) SS and (b) AS dumbbells. The equivalent moments are taken from the previous section. This plot provides the first approximation for predicting the frequency of the “hottest” spots. Since the hot spots of LDOC occur in pairs of opposite handedness, the sign of $\text{Im}(p_x^* m_y)$ and $\text{Im}(p_z^* m_y)$ is not associated with a certain handedness (though some information regarding the relative handedness of certain spots may be deduced from the sign). Upon comparison with full wave simulated LDOC on this surface, we find that this simple model based on equivalent sources for the nanojunction predicts the frequencies of hot spots of LDOC very accurately. For these frequencies, the maps of the enhanced LDOC based on Eq. 2.15 and 2.16 are plotted in the second row along with the corresponding frequency and the peak values of each map. As expected, the AS dumbbell supports higher LDOC enhancement as a result of stronger magnetic dipole $m_y$ and the appearance of $p_z$. The color maps also indicate that the average location dependent LDOC is negligible on the surface because of odd parity with respect to $n_y$. However, note that the hot spots are quite strong, and happen over an appreciable area (middle circle has a radius of about 20 nm). In fact, in the AS dumbbell, LDOC have two orders of magnitude enhancement within areas of $\approx 4$ nm diameter. Therefore, the location dependent LDOC is capable of making significant impact on single molecules that may be located in the hot spot, given that the area overlaps with high field enhancement. The overlap of the hot spots of LDOC and field enhancement is expected in the gap region, and subject to further studies. Overall, investigating hot spots of LDOC for single molecule experiments is important, and indispensable where the optical activity is concerned.
Figure 2.15: Spectra of Im($p^*_x m_y$) (in magenta) and Im($p^*_z m_y$) (in black) provide qualitative measure of hot spots of LDOC in the gap for both (a) SS and (b) AS nanodumbbells. In the second row, full wave simulated LDOC is plotted on the lower particle surface, at frequencies associated with the extrema of the spectra. (a) 400 and 480 THz for SS, and (b) 365 and 445 THz for AS nanodumbbells. The ± value on each plot represents the enhancement of LDOC with respect to circularly polarized light, indicating strong swirling vortices in the gap, especially for the AS nanodumbbell.

We next focus on the case of asymmetry in the plane of polarization, where the nanodumbbell shows chiroptical response of a certain handedness. As discussed earlier in this section, the average LDOC based on equivalent sources is approximately proportional to Im [$p^* \cdot m / c$]. In Figure (Figure 2.17) the averaged LDOC in the gap calculated by COMSOL (a), and the corresponding LDOC factor based on equivalent sources (b) are plotted for the three polarizations shown with arrows in the gap geometry in the middle (black, blue and magenta for $-45^\circ$, $0^\circ$ and $+45^\circ$ respectively).
We reported the equivalent electric and magnetic sources in Figure 2.14. Comparison of Figure 2.17 (a) and (b), reveals that the current approximation is not sufficient for quantitative arguments. However, it provides a clear insight about the evolution of the handedness for different polarizations. In particular, notice that in both methods the 0° and +45° polarizations lead to the same handedness of LDOC and opposite to −45° polarization. It is expected that by including all contributions of these dual sources, and higher order multipoles such as electric quadrupole, the analytical model based on the equivalent sources should provide a better quantitative agreement with the full wave simulations.

![Graphs showing handedness over frequency](image)

Figure 2.16: (a) Full wave simulation of the averaged handedness over the volume of the nanojunction and (b) \(\text{Im}[\mathbf{p}^* \cdot \mathbf{m}/c]\) as a measure of handedness defined by equivalent sources. Similar handedness for 0° and +45° in both models demonstrate that the handedness of the chiroptical response of the nanodumbbell is defined based on the relative orientation of the polarization with respect to the gap normal.

This chiroptical response with a handedness defined based on the relative orientation of the incident polarization with respect to the gap normal (the normal to both walls in the nanojunction) suggests that the handedness is orientation dependent, as observed in [12]. Figure 2.17 provides further demonstration of changing handedness upon 90° rotation of an asymmetric nanojunction in the plane of polarization.
Figure 2.17: Handedness is changed by 90 degree rotation of the A-gap dumbbell in the plane of polarization

We showed that the junction morphology dictates the response of the nanodumbbells when the asymmetry is applied either in the direction of retardation or the plane of polarization. Based on the physical origin of this phenomenon (confinement of the free electrons in the gap region), we extend this conclusion to other types of asymmetry. Note that this conclusion is reliable as far as the object is still considered as a nanodumbbell. In other words, we exclude extreme cases of asymmetry for further investigation. Examples include significant modification in the volume and shape of the particles comprising the dimer, such that the isotropic response of the individual particles differs significantly. The multipolar decomposition of the fields provided deep insights into the chiroptical behavior of the nanojunction. The equivalent electric and magnetic dipole sources explain why the junction asymmetry in the plane of polarization is the origin of the orientation-dependent handedness in the nanodumbbells.

We remind the reader that LDOC in this chapter is discussed based the scattered field of the nanodumbbells and not based on the total field. Therefore, these results are applicable to nonlinear experiments in which the observable is at frequencies where
incident field interference is not relevant. Investigating the chiroptical response in Rayleigh scattering, is also a very interesting problem and valuable for future research endeavors. Although it is not the focus of this work, we mention that our preliminary investigations suggest that for the same relative polarization, the chiroptical response shows opposite handedness when interference with the incident field is considered in calculations of the LDOC. As the final remark of this chapter, the chiroptical response of the dumbbell may bring up a new tool for characterization of the nanojunctions as a complementary method to TEM imaging.
Chapter 3

Photo-induced forces in nanojunctions

In this chapter, we focus on another aspect of electromagnetic fields in nano-confined junctions: the forces induced by the applied optical fields. These photo-induced forces show a strong dependence on field gradients, which can be particularly large in nanojunctions, thus producing forces that are within the detectable range of an atomic force microscope (AFM). In photo-induced force microscopy (PiFM), these forces are used as a contrast parameter for imaging. Despite the promising qualities of PiFM, the characteristics of the forces in the tip-sample junction are complex, which complicates the analysis of PiFM images. Here we shed light on the properties of the photo-induced force exerted on the tip in various relevant geometries. First, using a simple analytical model, we calculate the detected force as the tip is moved into the evanescent field of a surface plasmon polariton on a flat gold film [36]. In this case, the tip maintains a sufficient distance from the substrate, and multiple scattering effects are not expected to play an important role. The situation is different when the tip is brought closer to the surface of the gold film. In the latter case, field confinement
between the tip and sample can be substantial, and multiple scattering effects can no longer be ignored. We address this problem by developing an analytical formalism for calculation of the electric field based on dyadic Green’s function (GF) for a multilayer planar substrate. We discuss the evaluation of the integral expression of the scattering GF in detail, and present a closed form solution which is accurate enough for most practical PiFM experiments. The GF approach is compared with the image dipole approximation, and we include a brief discussion of the effective polarizability. We then turn attention to the evaluation of the field gradient in the context of multiple scattering effects. We define the field enhancement factor, and a normalized gradient specific enhancement factor to distinguish the impact of the multiple scattering in the field and field gradient, and their overall influence on the photo-induced force. Before we study the behavior of the photo-induced force for our PiFM experimental setup, we discuss the photo-induced force on the tip in the presence of a dipolar particle in the nano-junction. Finally, we provide a brief discussion on the magnitude of photo-induced forces and the merits of the PiFM method for spectroscopic imaging.

3.1 Photo-induced Force Microscopy

In this Chapter, we will be concerned with the PiFM configuration as shown in Figure 3.1. In this configuration, the excitation field is a SPP mode supported by a gold film on top of a glass coverslip. In the Figure, the layered material consists of three planar media, labeled as 0, 1 and \( s \), where layer 1 constitutes the plasmonic material, here gold. The glass/gold interface is illuminated with light of wave vector \( k_s \) in the lower half space at an angle \( \theta_i \). At the SPP angle where the transverse wave vector matches the SPP wavenumber, SPP wave propagation is sustained along the lateral direction of illumination. A tip is located in the upper half space, close enough to interact
with the evanescent field in medium 0, but far enough to avoid strong perturbation of the fields. As we mentioned earlier, optical fields can exert mechanical forces on the objects with which they interact. Therefore, we expect that the photo-induced force exerted on the tip maps the SPP mode that extends into medium 0. As shown in Fig. 3.1, the system acquires PiFM \((f_{01}\text{ channel})\) and topography images \((f_{02}\text{ channel})\) simultaneously. For the flat gold films studied here, no significant features are expected in the topography image. Optical artifacts in the topography channel, due to light-induced changes in the tip-sample distance, are kept below the noise. In the PiFM channel, on the other hand, clear photo-induced forces with matching SPP features are observed upon illumination. In particular, the SPP angle, and SPP propagation length are measured according to what theory predicts. In the following section, we first present an analytical model for the calculation of the photo-induced force, followed by examples and comparison with experiments.

Figure 3.1: PiFM setup for mapping surface plasmon polariton propagation.
Mechanical forces induced by the electromagnetic field are fully described by the surface integral of the time-averaged Maxwell’s stress tensor (MST) [5]. Because modeling of the full three-dimensional problem near the tip-sample junction is costly, simplifications are required to retrieve the essential physics at play. Since the field distribution in the vicinity of a sharp tip is very similar to a dipole field distribution, a quite accurate analytical modeling is possible by considering the tip response with an effective dipole located at the center of the tip apex, i.e., higher order multipoles are assumed to be negligible [5]. Using this model, we can employ dyadic Green’s function (GF) for a multilayer planar substrate to investigate multiple scattering mechanisms in the nanojunction. The tip’s response to a time-harmonic field, using the \( e^{-i\omega t} \) convention, is described by the complex electronic polarizability \( \bar{\alpha} \), which gives rise to a dipole moment \( \mathbf{p} \) in the tip, where \( \mathbf{p} = \bar{\alpha} \cdot \mathbf{E} \). We will indicate tensor quantities in bold with an overhead bar. The net time-averaged force experienced by the dipole in a spatially inhomogeneous field, the enclosing surface integral of the time-averaged MST, can be expressed as: [5]

\[
\langle \mathbf{F}(t) \rangle = \frac{1}{2} \sum_l \text{Re} \left\{ \mathbf{p}^l \mathbf{\nabla} E^l \right\}
\]

where \( l = x, y, z \) labels the polarization components along each of the cartesian coordinates. In case the polarizability is isotropic, as defined by its diagonal elements \( (\alpha_{xx} = \alpha_{yy} = \alpha_{zz}) \) [62, 11], the force in Eq. (3.1) can be expanded as:

\[
\langle \mathbf{F}(t) \rangle = \frac{\alpha'}{2} \sum_l \text{Re} \left\{ E^l \mathbf{\nabla} E^l \right\} + \frac{\alpha''}{2} \sum_l \text{Im} \left\{ E^l \mathbf{\nabla} E^l \right\}
\]

where \( \alpha = \alpha' + i\alpha'' \), and \( E^l \) and \( \mathbf{\nabla} E^l \) are the local electric field and the gradient of the field for the different polarization components \( l \) of the field. In Eq. (3.2),
the first term is proportional to the real part of the polarizability. This term is called the gradient force since \( \frac{\alpha'}{2} \sum_l \text{Re} \{ E^l \star \nabla E^l \} = \frac{\alpha'}{2} \nabla |E|^2 \) has zero circulation, in other words, it is conservative. The second term, which is linearly dependent on the imaginary part of the polarizability, is often referred to as the scattering force. The scattering force cannot be represented as the gradient of a potential and so is non-conservative. The gradient force originates from field inhomogeneities and traps the particle at the location where the field intensity is maximum. The scattering force can be related to the momentum transfer from the radiation field, pushing the particle in the direction of the wave propagation, or more accurately along the Poynting vector of the propagating field. It should be mentioned that this physical interpretation is one of the possible ways in which the dipolar particle experiences the scattering force. Also, note that separating the photo-induced force into the gradient and scattering forces is possible when the particle of interest is isotropic with a scalar polarizability. For an anisotropic particle such as the tip, Eq. (3.2) is not generally valid, and we will use Eq. (3.1) to calculate the force instead.

In the following, we will denote the time averaged force, \( \langle F(t) \rangle \) as \( F \) without a time dependence and we note that all other parameters discussed here are expressed in the frequency domain.

### 3.2.1 Electrodynamics of the nanojunction

The nanojunction in PiFM is formed between the tip apex and the (multilayer) substrate. If PiFM is used for measuring properties of a nanoparticle or a molecule, the object is placed in the nanojunction. The relevant geometry is shown in Figure 3.2. The lower half space is illuminated with a plane wave of amplitude \( E_0 \) that is incident at the angle \( \theta_{in} \) relative to the surface normal. Eq. 3.2 shows that the optical
force on the tip is directly related to the local field and field gradient. The electric field above the substrate surface $z > 0$ in the absence of the tip is the transmitted plane wave with a wave vector and amplitude defined by the Fresnel equations for multilayer medium, which will be discussed in the next section. Using the dipolar model for the tip, we will apply dyadic Green’s function (GF) theory and establish the electrodynamic model for $p_t$ and $p_n$, the induced dipole moment in the tip and the NP, respectively, including all direct and indirect (through the substrate) interactions between $p_t$ and $p_n$.

![Figure 3.2: PiFM setup for probing photo-induced forces. An AFM tip and a nanoparticle (NP) are located above the substrate, and illuminated from below through the substrate.](image_url)

We will call the transmitted field the background field $E_b$. The subscripts $t$ and $n$ denote the location of the tip and NP, respectively, and will be used to indicate the region of interest for $E_b$. For the general configuration of the two scatterers in air for $z > 0$, as shown in Figure 3.2, the electric field at $r_t$ is the sum of (i) the background field at the location of the tip ($E_{b,t}$), (ii) the self interaction of $p_t$ through the substrate and (iii) the field scattered by $p_n$. Using dyadic Green’s functions (GF), we can write
the following:

\[ E_t = E_{bt} + \overline{G}_{sc,t,t} \cdot p_t + \overline{G}_{t,n} \cdot p_n \]  

(3.3)

where \( \overline{G}_{sc,t,t} = \overline{G}_{sc}(r_t, r_t) \) is the scattering GF which accounts for the self interaction of the tip via the substrate, and the total GF, \( \overline{G}_{t,n} = \overline{G}_{sc}(r_t, r_n) + \overline{G}_0(r_t, r_n) \), is the sum of the free space and the scattering GFs, which account for the direct and indirect (through the substrate) coupling of the tip and the NP. Assuming that both scatterers are above the planar multilayered medium \( z > 0 \), the scattering GF for an observer and source located at \( r \) and \( r' \), respectively, can be written as the integral of scattered plane waves in the angular spectrum representation [63]:

\[ \overline{G}(r, r') = \frac{i}{8\pi^2} \iint dk_x dk_y \frac{1}{k_{0z}} \times \left[ r^{TE} \hat{e}(k_{0z}) \hat{e}(-k_{0z}) + r^{TM} \hat{h}(k_{0z}) \hat{h}(-k_{0z}) \right] e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{K} \cdot \mathbf{r}'} \]  

(3.4)

Here, \( \hat{e}, \hat{h}, \hat{k} \) are the unit vectors for the electric field, the magnetic field and the wavevector, which form an orthonormal system for representing any TE/TM polarized wave. The wavevector \( \mathbf{k} \) describes propagation along \(+z\) and is written as \( \mathbf{k} = \hat{x} k_x + \hat{y} k_y + \hat{z} k_{0z} \). Similarly, \( \mathbf{K} \) is the wavevector for propagation along \(-z\) and is defined as \( \mathbf{K} = \hat{x} k_x + \hat{y} k_y - \hat{z} k_{0z} \), where the lateral components of the wave vector are indicated as \( k_x \) and \( k_y \), and the longitudinal component is written as \( k_{0z} = \sqrt{k_0^2 - k_x^2 - k_y^2} \) for \( z > 0 \). The intrinsic wavenumber \( k_0 \) is defined as \( \sqrt{\varepsilon \mu_0} (\omega / c) \). \( r^{TE} \) and \( r^{TM} \) are the transverse electric and transverse magnetic Fresnel coefficients, respectively. More details on the scattering GF will be given in the following sections.

Expanding the dipole moments \( p_j = \alpha_j \cdot E_j \) with \( j = t, n \) in Eq. (3.3), we arrive at
the following expression for the local electric field at the tip:

\[ E_t = [\bar{S}_{tt} - \bar{M}_{tn}\bar{S}_{nn}^{-1}\bar{M}_{nt}]^{-1}(E_{b,t} + \bar{M}_{tn}\bar{S}_{nn}^{-1} \cdot E_{b,n}) \] (3.5)

where \( \bar{S}_{jj} = \bar{I} - \bar{G}_{sc,\alpha} \cdot \bar{\alpha}_j \) is the self interaction matrix for scatterer \( j \) and \( \bar{M}_{jk} = \bar{G}_{jk} \cdot \bar{\alpha}_k \) is the mutual interaction matrix. In the expression of \( \bar{M}_{jk} \), the total Green’s function \( \bar{G}_{jk} \) tracks the influence of scatterer \( k \) on the fields at the location of scatterer \( j \). Note that the interaction matrices are unitless. Although Figure 3.2 shows a one layer substrate, this formulation is general for a multi-layered substrate with different permittivities in the \( (z < 0) \) region. In all cases, appropriate reflection and/or transmission coefficients should be used for calculating the scattering GF and \( E_b \). In the next section we discuss these matters in more detail.

### 3.2.2 Calculation of Fresnel coefficients for multilayer medium

The Fresnel equations for multilayer planar media has been well reported in the literature [64]. Here we briefly rewrite published expressions from Ref [64] for our setup. In the subsections (A) and in (B), we discuss the implementation of this formalism for calculating the scattering GF integrals.

**(A) Transmission coefficient in the \( E_b \) evaluation**

The substrate shown in Figure 3.2 can in general be represented as a stack of \( N + 1 \) layers (with indexes 1,...,\( N \) and \( s \)). Figure 3.3 generalizes this idea. Any polarization of the incoming plane wave can be decomposed into two independent polarizations, namely the Transverse Electric (TE or \( s \)) and Transverse Magnetic (TM or \( p \)) components, defined with respect to the plane of incidence and the wave vector. The
two polarizations are shown in Figure 3.3. Reflection (R) and transmission (T) coefficients which relate the amplitude of the reflected and transmitted field components to the corresponding incident amplitude, are calculated based on the continuity of the tangential field components at the boundaries.

Figure 3.3: Geometry definition of multilayer planar structure, boundaries perpendicular to z axis.

The polarization dependent parameters $U$, and $V$ denote the tangential field components, and $\gamma$ is the wave impedance (admittance) for TM (TE) plane waves in each layer. Table 3.1 shows the parameters for the two polarizations. Note that the sign of field amplitude is reserved for right hand side propagation.

Table 3.1: Polarization dependent parameters in evaluation of Fresnel coefficients

<table>
<thead>
<tr>
<th>polarization</th>
<th>$U$</th>
<th>$V$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE</td>
<td>$E_y$</td>
<td>$H_x$</td>
<td>$n \cos \theta_i/Z_0$</td>
</tr>
<tr>
<td>TM</td>
<td>$H_y$</td>
<td>$E_x$</td>
<td>$\cos \theta_s Z_0/n$</td>
</tr>
</tbody>
</table>

In analogy with the theory of transmission lines, both $U$ and $V$ can be written in
terms of positive and negative traveling waves according to $U = U^+ + U^-$ and $V = \frac{1}{\gamma}(U^+ - U^-)$. The transfer matrix, $T_n$ [64], is used to relate the total amplitude of the fields between the layers.

$$\begin{bmatrix} U_{n-1} \\ V_{n-1} \end{bmatrix} = T_n \begin{bmatrix} U_n \\ V_n \end{bmatrix}$$ (3.6)

In Eq. 3.6, $T_n$ is defined as:

$$T_n = \begin{bmatrix} \cos \Phi_n & -i \frac{1}{\gamma_n} \sin \Phi_n \\ -i \gamma_n \sin \Phi_n & \cos \Phi_n \end{bmatrix}$$ (3.7)

where $\Phi_n = k_{zn} d_n$, which denotes the longitudinal propagation phase in each medium. Note that $k_{zn}$ can in general be an imaginary number, in which case it represents an evanescent wave in the corresponding medium $n$. The transfer matrix for a stack of $N$ layers is the ordered multiplication of the $T_n$ contributions.

$$T = \prod_{n=1}^{N} T_n$$ (3.8)

The reflection coefficient is dependent on the geometry and illumination direction. Referring to Figure 3.3, the reflection coefficient is defined as $r = U^-_s / U^+_s$ and the transmission coefficient is written as $t = U^+_s / U^+_0$. Here the $+$ and $-$ symbols refer to the direction of propagation in $+z$ or $-z$ direction, respectively. With these
definitions, Eq. 3.6 can be rewritten as:

\[
\begin{bmatrix}
1 + r_{s0} \\
\gamma_s(1 - r_{s0})
\end{bmatrix}
= t_{s0} \hat{T}_n
\begin{bmatrix}
1 \\
\gamma_0
\end{bmatrix}
\]  

(3.9)

By solving Eq. 3.9 for \(r_{s0}\) and \(t_{s0}\) we obtain the following expressions:

\[
\begin{align*}
r_{s0} &= \frac{\gamma_s m_{11} + \gamma_0 \gamma_s m_{12} - m_{21} - \gamma_s m_{22}}{\gamma_s m_{11} + \gamma_0 \gamma_s m_{12} + m_{21} - \gamma_s m_{22}} \\
t_{s0} &= \frac{2\gamma_s}{\gamma_s m_{11} + \gamma_0 \gamma_s m_{12} + m_{21} - \gamma_s m_{22}}
\end{align*}
\]  

(3.10)

We use \(t_{s0}\) for the evaluation of \(E_n\) in Eq. 3.3.

(B) Reflection coefficient in the scattering GF integral

A similar treatment can be used to evaluate \(r^{TE}\) and \(r^{TM}\) in Eq. 3.4 for calculating the reflection of plane waves in the spectral domain. However, note that the layers indexes have to be reversed because the space of illumination is now effectively region 0 where the dipole is located. The reflection coefficients are functions of \(\theta = \sin^{-1}(k_\rho/k_0)\). For \(k_\rho > k_0\), \(\theta\) becomes a complex number, which includes evanescent waves. In the limit of \(k_\rho \to \infty\), these waves decay sharply and cannot penetrate into the layered medium. Therefore, in the limit \(k_\rho \to \infty\), \(r^{TE}\) and \(r^{TM}\) show asymptotic behavior for the reflection from the first boundary only.
3.2.3 The dyadic Green’s function for a planar layered media

Eq. (3.4) is usually rewritten into a Sommerfeld type integral in the angular-spectrum domain spanned by the lateral wavenumber defined as \( k_\rho = \sqrt{k_x^2 + k_y^2} \) [63, 65, 66]. In particular, if the source and observing point are both along the normal of the multilayer medium \((x = x', y = y')\), the dyadic GF reduces to the diagonal elements as follows [5]

\[
C_{sc}^{xx}(z, z') = C_{sc}^{yy}(z, z') = \frac{i}{8\pi k_0^2} \int_0^\infty dk_\rho \left\{ \frac{k_\rho k_0^2 r_{TE}}{k_{0z}} - k_\rho k_{0z} r_{TM} \right\} e^{ik_0 z D} \tag{3.11}
\]

\[
C_{sc}^{zz}(z, z') = \frac{i}{4\pi k_0^2} \int_0^\infty dk_\rho \frac{k_\rho^3 r_{TM}}{k_{0z}} e^{ik_0 z D} \tag{3.12}
\]

where \( D = z + z' \). Note that the integrands (GF representation in spectral domain) have poles associated with propagating waves, for \( k_{nz} = 0 \) in layer \( n \) of the medium in Figure 3.3. For lossless materials, i.e., region 0, for \( k_{0z} = \sqrt{k_0^2 - k_\rho^2} \), this pole appears on the real axis and thus contour deformation in the complex \( k_\rho \) domain is needed for calculation of the integrals. A detailed explanation of the numerical computation of the general Sommerfeld integral, in particular with regard to contour deformation, is available in [67]. Generally, numerical calculation of Sommerfeld integrals is a challenging task. Numerous studies have been reported to tackle this problem for different geometries, some of which use analytical approaches to approximate the integrals or reduce the numerical computational load by partial analytical solutions [68, 69, 70].

For our setup, \( x = x', y = y' \), we rewrite the integrals in Eq. 3.12 into two parts based on the limit set by the reflection coefficients. We show that the integrals can be partially calculated analytically. A residual integral is left for numerical calculation,
which in many cases can be neglected within a 5% tolerance range.

(A) Calculation of the scattering GF and closed form approximation

As mentioned earlier, \( r^{TE} \) and \( r^{TM} \) in Eq. 3.12 have a definite limit for \( k_{\rho} \to \infty \). For non-magnetic materials, \( r^{TE}_{01} = \lim_{k_{\rho} \to \infty} r^{TE} = 0 \), and \( r^{TM}_{01} = \lim_{k_{\rho} \to \infty} r^{TM} = \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0} \), which are the reflection coefficients from the top most layer for a TE/TM plane wave [68]. By summation and subtraction of this constant term in the integrals, we can split the integrals into two terms, one of which has a closed form solution. We explain the steps for calculation of \( G_{sc}^{xx}(z, z') \) in the following. Consider the integral of the TM modes in the \( G_{sc}^{xx}(z, z') \) as \( I_1 \)

\[
I_1(z, z') = \int_0^\infty dk_{\rho} k_{\rho} k_{0z} r^{TM} e^{ik_{0z}D} \tag{3.13}
\]

We write \( I_1 = I_{1,CF} + I_{1,\text{res}} \) where \( I_{1,CF} \) is

\[
I_{1,CF}(z, z') = \int_0^\infty dk_{\rho} k_{\rho} k_{0z} r^{TM}_{01} e^{ik_{0z}D} \tag{3.14}
\]

and has a closed form solution. We also define the residual integral \( I_{1,\text{res}} \), which is written as:

\[
I_{1,\text{res}}(z, z') = \int_0^\infty dk_{\rho} k_{\rho} k_{0z} (r^{TM} - r^{TM}_{01}) e^{ik_{0z}D} \tag{3.15}
\]

By a change of variables and rewriting \( I_{1,CF} \) in terms of \( k_{0z} \), Eq. (3.14) can be recast as

\[
I_{1,CF}(z, z') = -r^{TM}_{01} \int_{k_0}^{ik_{0}} dk_{0z} k_{0z}^2 e^{ik_{0z}D} \tag{3.16}
\]
where \( k_\rho \to \infty \). The closed form solution of Eq. 3.16 reads

\[
I_{1,CF}(z, z') = \frac{i r_{01}^{TM} k_0^2}{D} \left\{ 1 + \frac{i 2}{k_0 D} - \frac{2}{(k_0 D)^2} \right\} e^{ik_0 D} \tag{3.17}
\]

The computation of the residual integral is still handled numerically, but it is more attractive than computing the original integral in \( I_1 \) because the integrand of \( I_{1,\text{res}} \) decays much faster. The advantage comes from the fact that \((r^{TM} - r_{01}^{TM}) \to 0\) sharply with increasing \( k_\rho \). Note that for TE modes we cannot obtain a closed formula since \( r_{01}^{TE} = 0 \). However, our calculation shows that \( I_{1,\text{res}} \) constitutes is usually less than 5\% of the closed form solution for our applications. It should be mentioned that the error increases if \( D \) increases and also if \( r_{01}^{TM} \) has a resonance, meaning \( \epsilon_1 \approx -\epsilon_0 \).

Using the closed form solution, an approximate closed form for \( G_{zz}^{\text{sc}}(z, z') \) reads

\[
G_{zz}^{\text{sc}}(z, z') = \frac{r_{01}^{TM}}{8\pi D} \left\{ 1 + \frac{i 2}{k_0 D} - \frac{2}{(k_0 D)^2} \right\} e^{ik_0 D} \tag{3.18}
\]

In the same manner, we can solve the closed form for \( G_{zz}^{\text{sc}} \) as

\[
G_{zz}^{\text{sc}}(z, z') = -\frac{r_{01}^{TM}}{2\pi(k_0 D)^2} \left\{ i k_0 - \frac{1}{D} \right\} e^{ik_0 D} \tag{3.19}
\]

It is interesting to note that the closed form solution is very similar to the free space GF. We will compare the formulas and investigate the underlying physics, particularly in the context of the image dipole, in the next section.

**(B) Comparing \( \bar{G}_0 \) and \( \bar{G}_{\text{sc}} \) closed form, physical meaning image dipole**

The lateral and longitudinal components of the free space GF are

\[
G_{xx}^{\text{sc}}(z, z') = \frac{1}{8\pi d} \left\{ 1 + \frac{i 2}{k_0 d} - \frac{2}{(k_0 d)^2} \right\} e^{ik_0 d} + \frac{e^{ik_0 d}}{8\pi d} \tag{3.20}
\]
and

\[ G_0^{zz}(z, z') = -\frac{1}{2\pi (k_0 d)^2} \left\{ ik_0 - \frac{1}{d} \right\} e^{ik_0 d} \]  \hfill (3.21)

where \( d = z - z' \). We now compare the respective components of \( G_{sc}^{ll} \) and \( G_0^{ll} \). First note that Eq. (3.19) and (3.21) have a very similar format except for the presence of \( r_{01}^{TM} \) in Eq. (3.19), as well as a different radiating path \((D = z + z')\) compared to the direct path, \( d = z - z' \), in Eq. (3.21). In other words, \( G_{sc}^{ll} \) represents a dipole whose distance from the observer \( z \) is \( D \). The dipole is now radiating in free space and its weight \( r_{01}^{TM} \) includes the properties of the first layer. Note that regardless of the number of layers, only the top most layer contributes to the image dipole.

A similar analogy can be drawn between Eq. (3.18) and (3.20), except for the extra term \( \frac{e^{ik_0 d}}{8\pi d} \) in Eq. (3.20). We observe that TE waves do not contribute to the closed form evaluation of \( G_{sc}^{xx} \) in Eq. (3.12) because \( r_{01}^{TE} = 0 \). By comparing the additional term in \( G_{sc}^{xx} \) with the TM contribution, we may conclude that TE waves are negligible in the near-field. Eq. (3.18) and (3.19) provide a more accurate and complete form of the image dipole than the quasi-static image dipole approximation that is widely used such as in [71].

(C) Effective polarizability in proximity of a scattering boundary

The term “effective polarizability” is often used to address the properties of a dipolar scatterer in different scenarios. Here, as in [72, 73, 74, 71], we refer to it as the modification to the isolated (electrodynamic) polarizability of a dipolar scatterer because of the presence of a scattering object or boundary. In other words, the effective polarizability relates the total induced dipole moment to the background field (the
total field in the absence of the dipolar scatterer), as \( \mathbf{p} = \bar{\alpha}_{\text{eff}} \cdot \mathbf{E}_b \). The isolated polarizability, on the other hand, relates the total induced dipole moment to the local electric field, including the self interaction of the dipole through the scattering boundary, as \( \mathbf{p} = \bar{\alpha} \cdot \mathbf{E} \). This description, along with writing the local field as

\[
\mathbf{E}(\mathbf{r}) = \mathbf{E}_b(\mathbf{r}) + \bar{\mathbf{G}}_{sc}(\mathbf{r}, \mathbf{r}) \cdot \mathbf{p}(\mathbf{r}) \tag{3.22}
\]

leads to the most general definition of the effective polarizability as

\[
\bar{\alpha}_{\text{eff}} = \bar{\alpha} \cdot [\bar{\mathbf{I}} - \bar{\mathbf{G}}_{sc}(\mathbf{r}, \mathbf{r}) \cdot \bar{\alpha}]^{-1}. \tag{3.23}
\]

We will use this definition to simplify the formalism for the case where a nanoparticle is placed in the tip-substrate nanojunction. Self interaction of the nanoparticle will be expressed through its effective polarizability.

### 3.2.4 Notes on the field gradient

Another important parameter in the nano-junction, especially in the context of PiFM, is the field gradient. In this section, we investigate the effects of multiple scattering on the field gradient in the nano-junction. In particular, we define enhancement factors which compare the multiple scattering effects in the field and field gradient. We show the detailed formalism for the case when the nanojunction is empty (i.e., there is no particle between the tip and the substrate). We may thus set \( \bar{\alpha}_n = \mathbf{0} \) in Eq. (3.5). In this case, the expression for the electric field at the tip simplifies considerably. The components of the local electric field at the tip can then be written as:

\[
E_{lt}^l = \frac{E_{lt}^l}{S_{lt}} \quad l = x, y, z \tag{3.24}
\]
where \( S_{ll}^{\|} = 1 - \alpha_{l}^{\|} G_{sc,tt}^{ll} \), \( E_{ll}^{l} = E_{b0}^{l} e^{ik_{z}z_{t}} \) is the background field at the location of the tip, and \( k_{z} \) is the wavenumber along \( z \) for \( z > 0 \). Because we will consider an evanescent background field, we can use \( k_{z} = i\gamma \) to represent the field amplitude decay along \( z \) for \( z > 0 \). We assume that the polarizability of the tip is not dependent on the tip-surface distance, therefore using Eq. (3.24), the field gradient along the \( z \) direction is

\[
\frac{\partial}{\partial z} E_{l}^{l} = E_{l}^{l} \left[ -\gamma + \frac{\alpha_{l}^{ll} \partial G_{sc,tt}^{ll}}{S_{ll}^{ll} \partial z} \right].
\]  

(3.25)

Evaluation of \( \frac{\partial G_{sc,tt}^{ll}}{\partial z} \) in Eq. (3.25) is simply done by taking the \( z \) derivative of the integrand in Eq. (3.13). Note that this is equivalent to double the derivative of the closed form expression Eq. (3.17) with respect to \( D \) where \( D = 2z_{t} \), and evaluation of the new residual integral of

\[
\frac{\partial I_{1, res}(z_{t}, z_{t})}{\partial z_{t}} = 2i \int_{0}^{\infty} dk_{\rho} k_{\rho} k_{0}^{2} (r_{TM} - r_{01}^{TM}) e^{ik_{0}D}
\]  

(3.26)

The photo-induced force in the longitudinal direction can then be written as:

\[
F_{z} = \frac{1}{2} \sum_{l} \left| E_{l}^{l} \right|^{2} \left( -\gamma \alpha_{l}^{ll} + \left| \alpha_{l}^{ll} \right|^{2} \text{Re} \left\{ \frac{1}{S_{ll}^{ll}} \frac{\partial G_{sc,tt}^{ll}}{\partial z} \right\} \right)
\]  

(3.27)

The magnitude of the photo-induced force depends on two terms: one term that scales solely with the magnitude of the field components, and a second term that also shows a dependence on the field gradient. We will examine which quantity, the field or the field gradient, is the dominant factor in the typical PiFM scenario considered here. Both the field and its gradient depend on the self interaction term \( S_{ll}^{ll} = 1 - \alpha_{l}^{ll} G_{sc,tt}^{ll} \), which appears in the denominator in Eqs. (3.24) and (3.25). This self interaction term contains a resonance condition when \( \text{Re}\{\alpha_{l}^{ll} G_{sc,tt}^{ll}\} \approx 1 \) and \( \text{Im}\{\alpha_{l}^{ll} G_{sc,tt}^{ll}\} \approx 0 \), which
can be associated with a spatial resonance that gives rise to the local enhancement of the field. A detailed description of this phenomenon for a dipolar scatterer beside a plasmonic nanosphere is presented in [75].

To study how the field and the field gradient are affected by the process of multiple scattering, we define two quantities, namely the field enhancement factor $FE_{ll}$, which is normalized to the background field, and the normalized gradient specific enhancement factor $GSE_{ll}$, as

$$FE_{ll} = \frac{1}{|S_{ll}|}$$

$$GSE_{ll} = \left|\frac{\alpha_{ll}^{l2}}{-\gamma\alpha_{l}^{ll}\alpha_{ll}^{l2}}\right|^2 \Re \left\{ \frac{1}{S_{ll}} \frac{\partial G_{sc,tt}^{ll}}{\partial z_{t}} \right\}$$

The field scales with $FE_{ll}$, as determined by the spatial resonance described by $S_{ll}^{ll}$. The field gradient, on the other hand, has two contributions, one that scales as $FE_{ll}$ and the second that scales as $GSE_{ll}$. The latter term is the gradient specific term, which depends more strongly on the process of multiple scattering than the $FE_{ll}$ term. Hence, it can be expected that field gradient effects grow in importance when multiple scattering effects become more significant.

### 3.2.5 Different scattering paths in the presence of a nanoparticle in the nanojunction

Analyzing the isolated tip above a multilayer surface is useful for near-field probing of surface fields. In many PiFM applications, however, we are interested in imaging nanostructures on top of the substrate, such as sketched in Figure 3.2. We will first
explore the behavior of the confined fields in this configuration in the context of the scattering Green’s function. In particular, we aim to show the effects of indirect interactions through multiple scattering via the substrate (Figure 3.4 (a)) compared to direct scattering via the nanoparticle (Figure 3.4 (b)).

Figure 3.4: Schematic of the scattering pathways in the tip-nanoparticle interaction. (a) Pathways including scattering via the substrate, as described by $\bar{G}_{sc;tn}$. (b) Direct pathway, as described by $\bar{G}_0$.

To gain insight in the local field, Eq. (3.5) can be reduced to a set of scalar equations for the electric field at the tip in the limit of a diagonal polarizability tensor:

$$E'_l = \frac{E'_{bl} + \alpha'_{n,eff} G'_{tn} E'_{kn}}{1 - \alpha'_t \left\{ G'_{tt} + \alpha'_{n,eff} (G'_{tn})^2 \right\}} \quad (3.30)$$

where $\alpha'_{n,eff}$, the effective polarizability of the NP, is defined as:

$$\alpha'_{n,eff} = \frac{\alpha'_{n}}{1 - \alpha'_{n} G'_{sc;mn}} \quad (3.31)$$

Note that $\alpha'_{n,eff}$ includes the effects of the self interaction of the NP via the substrate. The numerator in Eq. (3.30) can be interpreted as a background field which induces the primary dipole moment in the tip, and the denominator $W'_{tt} = 1 - \alpha'_t \left\{ G'_{tt} + \alpha'_{n,eff} (G'_{tn})^2 \right\}$ accounts for all the multiple scatterings mechanisms that modify the
tip local field. We assume that the location of the NP is fixed, implying that \( \alpha_{n,\text{eff}}^{ll} \) and \( E_{b,n}^{l} \) are constant numbers in the calculation of the field gradient along \( z \). Under these conditions, we find the following expression for the field gradient along \( z \):

\[
\frac{\partial E_{t}^{l}}{\partial z} = -\gamma E_{b,t}^{l} + \alpha_{n,\text{eff}}^{ll} \frac{\partial G_{tn}^{ll}}{\partial z} E_{b,n}^{l} \frac{W_{tt}^{ll}}{} \\
+ E_{t}^{l} \alpha_{t}^{ll} \left\{ \frac{\partial G_{tn}^{ll}}{\partial z} + 2 \alpha_{n,\text{eff}}^{ll} \frac{\partial G_{tn}^{ll}}{\partial z} G_{tn}^{ll} \right\} \frac{W_{tt}^{ll}}{}
\]

(3.32)

We emphasize that Eqs. (3.30) and (3.32) include all scattering mechanisms shown in Figure 3.4(a), accounting for multiple scattering pathways to the tip via the substrate. Our aim is to understand to what extent scattering via the substrate contributes to the overall force experienced by the tip. Therefore, we also consider the dipole-dipole interaction model and define the field in the case of direct scattering between the tip and NP, ignoring the substrate contributions, as depicted in Figure 3.4(b). Under this condition, Eq. (3.30) reduces to

\[
E_{t}^{l} = \frac{E_{b,t}^{l} + \alpha_{n}^{ll} G_{0,tn}^{ll} E_{b,n}^{l}}{1 - \alpha_{t}^{ll} \alpha_{n}^{ll} (G_{0,tn}^{ll})^2}
\]

(3.33)

whose gradient along \( z \) can be obtained as:

\[
\frac{\partial E_{t}^{l}}{\partial z} = -\gamma E_{b,t}^{l} + \alpha_{n}^{ll} \frac{\partial G_{tn}^{ll}}{\partial z} E_{b,n}^{l} \frac{W_{tt}^{ll}}{} \\
+ E_{t}^{l} \alpha_{t}^{ll} \alpha_{n}^{ll} \frac{\partial G_{tn}^{ll}}{\partial z} G_{tn}^{ll} \frac{W_{tt}^{ll}}{}
\]

(3.34)

where the denominator now reads \( W_{tt}^{ll} = 1 - \alpha_{t}^{ll} \alpha_{n}^{ll} (G_{0,tn}^{ll})^2 \). Using the fields defined in Eqs. (3.30)–(3.32) or (3.33)–(3.34), we can compute the force for the two cases with the aid of Eq. (3.1). Before we turn to numerical evaluation of the force for different scenarios and examine the effect of multiple scattering through numerical computations, it is beneficial to look at the different scattering mechanisms separately,
through the analytical expressions of free space and scattering GFs. We mentioned that Eq. (3.18)–(3.19), which are very similar to those of the free space GF, are quite accurate for evaluation of the scattering GF in the near-field and closely related to the radiation predicted in the conventional image dipole model. Different scattering mechanisms which are shown in Figure 3.4 (a) are represented by $G_{sc,tt}^{ll}$, $G_{sc,nn}^{ll}$, $G_{sc,tn}^{ll}$, and $G_{0,tn}^{ll}$ in Eq. (3.30). The respective scattering paths are shown in orange, red, gray and black colors in Figure 3.4 (a). A preliminary comparison of the magnitude of these GFs can be achieved by considering the dominant term in the corresponding expressions which read

\begin{align*}
G_{0,tn}^{zz} &\approx \frac{e^{ik_0(z_t-z_n)}}{2\pi k_0^2 (z_t - z_n)^3} \\
G_{sc,tn}^{zz} &\approx \frac{r_{01}^{TM} e^{ik_0(z_t+z_n)}}{2\pi k_0^2 (z_t + z_n)^3} \\
G_{sc,tt}^{zz} &\approx \frac{r_{01}^{TM} e^{2ika_z}}{2\pi k_0^2 (2z_t)^3} \\
G_{sc,nn}^{zz} &\approx \frac{r_{01}^{TM} e^{2ika_z}}{2\pi k_0^2 (2z_n)^3}.
\end{align*}

From this simple approximation, we can conclude that in general $|G_{sc,nn}^{zz}| > |G_{0,tn}^{zz}| > |G_{sc,tn}^{zz}| > |G_{sc,tt}^{zz}|$ when the radius of the sample nanoparticle is considerably smaller than the radius of the tip apex. The same comparison is applicable to $xx$ components. Therefore, the image dipole of the nanoparticle in both the substrate and the tip is important, while previous reports based on dipole-dipole interaction only consider the image dipole of the nanoparticle in the tip. However, to be more accurate, we have to consider all these terms as expressed in Eq. (3.30) and (3.32). We will show that including all the scattering mechanisms through the substrate can make significant modifications to the dipole-dipole interaction model.
3.3 Behavior of the photo-induced force

In this Section, we present calculations of the photo-induced force for several typical experimental geometries that are relevant to PiFM imaging [76]. First, we will consider the photo-induced force exerted on the tip over a bare glass substrate. Second, we will highlight the photo-induced force when the tip is driven by a surface plasmon polariton on a thin gold film. Third, we will discuss the magnitude and behavior of the photo-induced force when the anisotropic polarizability of the tip is taken into account. Lastly, we will focus on the photo-induced forces between the tip and a polarizable nanoparticle on the substrate. Our goal is to show that the process of multiple scattering and tip anisotropy are important and can modify the magnitude and spectral dependence of the force considerably.

3.3.1 Computational details

For the isotropic model of the tip, we will assume that the tip behaves as a polarizable spherical particle with an effective dipolar response [77, 5, 78, 62]. In this case, the tip apex characterized by a $R = 30$ nm radius, similar to the experimental value reported in [36]. The tip is composed of gold and the template-stripped gold permittivity described in [54] is used in our calculations. The scalar polarizability of the tip is calculated with the aid of the Mie coefficients [41, 42] for a nanosphere of the apex dimension. For the anistropic tip, we will use the formalism described in Appendix C. The substrate is glass with a refractive index of 1.5. We will consider the forces in the vicinity of the bare glass surface as well as a glass surface covered with a 45 nm gold film, using the refractive index reported in [79]. The incident field is a $p$ polarized plane wave with $E_0 = 10^6$ V/m illuminated at $\theta_{in}$. In both cases, for the bare glass surface as well as the glass surface covered with gold, $\theta_{in}$ is set to $= 43.65^\circ$. 
to produce an evanescent background field for $z > 0$. Note that this angle is at the Kretschmann angle for the gold covered substrate, thus launching a surface plasmon polariton at the gold/air interface. Unless otherwise noted, we will focus on $F_z$, which is the photo-induced force directed along the $z$-axis.

To compute the force, the GF in Eq. (3.4) and its spatial derivatives are evaluated numerically. Once these functions are determined, the field and field gradient can be obtained analytically, which subsequently allow the calculation of the photo-induced force through Eq. (3.1). In the following Sections, we will provide explicit expressions for the fields and field gradients along $z$ that are relevant to the different sample geometries considered here.

### 3.3.2 Field versus field gradient

The distance dependence of $FE^{zz}$ and $GSE^{zz}$, defined in Eq. (3.28) and Eq. (3.29), respectively, are displayed in Figure 3.5. In panel 3.5(a), the enhancement factors are shown for the force measured in the vicinity of the bare glass surface. With reference to Figure 3.2, the surface-to-surface distance $d$ is defined as $z_t - R$. We see that $FE^{zz}$ shows only limited enhancement as a function of distance. A small enhancement is seen for shorter distances ($d < 10$ nm), due to the spatial confinement of the field in the tip-sample junction as described by $S_{tt}^{zz}$. The gradient specific enhancement factor, on the other hand, shows a much more prominent distance dependence. Since both quantities are normalized, we may compare the values of $FE^{zz}$ and $GSE^{zz}$ as the tip-sample distance is shortened. It is clear that the enhancement in the gradient specific contribution is significantly higher than the enhancement in the field, as expected for shorter distances when the effects of multiple scattering are becoming more relevant. Note that these results are relevant to the dipole approximation considered here,
Figure 3.5: Enhancement factor due to multiple scattering effect (MSE), comparing the distance dependence of the normalized field enhancement ($FE^{zz}$) factor and the normalized gradient specific enhancement ($GSE^{zz}$) factor using illumination at 450 THz. (a) Tip in the vicinity of a glass substrate. (b) Tip in the vicinity of a glass substrate covered with a 45 nm gold film.

which may underestimate the extend of field confinement effects. Even stronger field and field gradient effects are expected when multipoles are included [75].

In Figure 3.5(b) a similar comparison is shown between $FE^{zz}$ and $GSE^{zz}$ for the tip in the vicinity of the thin gold film. Due to stronger permittivity contrast at the gold/air interface compared to glass/air interface, the scattering GF for a gold/glass substrate has higher amplitude. Consequently, the field enhancement between the gold surface and the tip’s apex is more prominent. The field gradient specific enhancement is even more significant, especially for distances $d < 10$ nm. In this scenario, the behavior of the photo-induced force is largely dictated by the gradient field effects. The latter
observation is a direct consequence of the enhanced multiple scattering.

We observe that as the distance increases (as far as 30 nm), the effects of multiple scattering become negligible. This distance is where the tip no longer induces perturbations to the surface fields. Therefore, the PiFM imaging method can be used for probing surface fields, such as shown here for SPP modes. Under such conditions, the simple theory based on background field (B) is sufficient for the force calculation. This is confirmed in our experiment for imaging SPP on a flat gold surface of 30 nm thickness. The average tip location is 56 nm which translates to a 26 nm distance for a 30 nm tip. As shown in Figure 3.6, a simple analytical expression as given in Appendix B suffices for predicting the behavior of the force exerted on the tip by the SPP mode. As expected, a stronger force is observed under illumination with TM polarization, which launches the SPP mode, compared to incident light with TE polarization, in which case no SPP mode is excited. Note that the dominant contribution to the PiFM image is due to the amplitude of SPP field.
Figure 3.6: Force amplitude in as a function of the incident illumination angle. (a) PiFM images near the illumination spot for various incident angles for TM and TE modes. (b) Calculated force exerted on the tip based on Eq. (B.2) (c) Measured PiFM amplitude when the tip is placed in the tail of the propagating SPP mode

3.3.3 Photo-induced force over a glass substrate

We first examine the force when an isotropic tip is positioned over a bare glass substrate under evanescent illumination conditions. Figure 3.7 shows the frequency and distance dependence of the computed $F_z$ exerted by the evanescent background field on the tip in pN. Note that the minimum force sensitivity depends on the specifics of the AFM system used for force mapping and can vary from tens of fN to hundreds of
fN under ambient conditions [80, 81, 11]. For our system this value is about 0.1 pN [36]. In Fig. 3.7(a) the magnitude of the force is shown without the effect of multiple scattering, calculated as $F_z = \frac{\alpha'_t \gamma}{2} |E_{b,\text{eff}}|^2$ where $\alpha'_t$ is the dispersive part of the tip polarizability and $\gamma$ is the evanescent wavenumber of the background field (see Appendix A for details). In Fig. 3.7(b) the effect of multiple scattering effect is included. The spectral dependence of the dispersive and dissipative parts of the tip’s polarizability are indicated by the solid and dashed lines, respectively, in panel 3.7(c). In both cases, the photo-induced force $F_z$ is a negative (attractive) force, meaning that the tip is pulled toward the surface. In addition, the frequency dependence of the force closely traces the dispersive part of the polarizability, reaching its maximum value near the plasmonic resonance of the tip apex. However, there are also clear differences between Fig. 3.7(a) and (b). Without multiple-scattering, the distance dependence of the photo-induced force is shallow, largely dictated by the $z$-dependence of the evanescent background field. On the other hand, with multiple-scattering included, the force not only increases in magnitude by about 15-fold, but also becomes more localized. We see that the force is confined to shorter tip-substrate distances of up to 10 nm (Fig. 3.7(b)), displaying a much sharper distance dependence. This feature is a direct consequence of the coupling between the tip and the substrate, which grows nonlinearly as the tip approaches the substrate surface.
Figure 3.7: Time-averaged photo-induced force $F_z$ exerted on the gold tip as a function of frequency and tip-substrate distance $d$. (a) $F_z$ without including multiple-scattering. (b) $F_z$ calculated with multiple-scattering included. Force is given in picoNewton (pN). (c) Frequency dependence of the real (blue) and imaginary (red) parts of the tip’s polarizability.

The observed distance dependence of the force mimics the interaction between the tip dipole and its image in the substrate. The latter scenario in PiFM is usually referred to as the image dipole force, which, using a simple analytical model based on
dipole-dipole interaction, results in a \( \sim z^{-4} \) dependence for the gradient force when only the \( E_z \) component of the field is considered [76]. Our formalism includes all field components and generalizes the force for different illumination conditions. Figure 3.8 shows the distance dependence of the force for illumination at 450 THz using our GF model. We find that the photo-induced force is still highly confined, but does not follow exactly a \( z^{-4} \)-dependence over the entire range of frequencies and distances examined here. In Figure 3.8, for shorter distances up to \( \sim 9 \) nm, the GF-based calculation is in close agreement with a \( z^{-4} \)-dependence, while the results deviate for larger tip-sample distances. The difference largely reflects the effect of the different illumination conditions. Whereas the \( z^{-4} \) dependence is derived for propagating light, here we consider the force in an evanescent illumination field.

![Figure 3.8: Time-averaged photo-induced force \( F_z \) exerted on the tip as a function of tip position \( z_t \). Results from the scattering Green’s function analysis (blue solid line) are shown in addition to a \( z^{-4} \)-dependence (red dashed line). The agreement between the two models is good up to \( \sim 9 \) nm.](image-url)
3.3.4 Photo-induced force over a gold surface with surface plasmon polariton excitation

We next consider the photo-induced force for the case of a gold tip positioned over a glass substrate covered with a 45 nm gold thin film. As was clear from the discussion in Section 3.3.2, compared to the bare glass substrate, the field and its gradient under SPP excitation are more significant in the nano-junction formed by the tip and the gold surface. This translates into a higher magnitude of the force. In Fig. 3.9, the tip-sample distance dependence of $F_z$ is compared for the case of the bare glass surface and the thin gold film. As expected, the force in the case of the gold surface is stronger than what is measured over the glass surface. Under the conditions examined here, we find a force that is approaching 24 pN as the tip gets closer to the gold surface, more than two orders of magnitude stronger than the force experienced by the tip over the glass substrate.

Figure 3.9: Distance dependence of the photo-induced force exerted on the tip when exciting an SPP mode ($\theta_i = 43.65^\circ$) at the gold/air interface (blue line). The red dashed line corresponds to the same measurement on the bare glass substrate. Illumination is at 450 THz.
3.3.5 Photo-induced force at a tip with anisotropic polarizability

The spherical polarizability model is widely used to model an AFM tip. Yet, it is well known that an actual tip exhibits an anisotropic response, which gives rise to a stronger field enhancement in the longitudinal polarization direction of the excitation field [38, 39, 40, 5]. The stronger optical response along the axial dimension gives rise to photo-induced forces that are stronger than what is predicted in the spherical polarizability model. In this section, we investigate the possible effects of tip anisotropy on $F_z$ when adopting an anisotropic description of the tip’s polarizability. We use a polarizability model for a virtual prolate particle [82, 83], taking into account losses due to radiation [84]. The anisotropy factor, $AF$, is defined as the aspect ratio of the major to minor axis of the virtual prolate. It should be mentioned that the virtual prolate is an effective model meant to represent the stronger longitudinal polarizability of the tip rather than to describe the exact physical morphology of the apex. In this model, the location of the effective induced dipole moment of the tip is considered the same as the isotropic model, see Appendix C for details.

In Figure 3.10(a) we show the calculated frequency and distance dependence of the photo-induced force $F_z$ for $AF = 2$ when the tip is placed over the bare glass substrate. The spectral dependence of the longitudinal and transverse polarizabilities is plotted in Figure 3.10(b), clearly showing the enhanced response of the tip along the axial direction. The enhancement of the polarizability by about 5 times in the longitudinal direction that we consider here is within empirical ranges for a gold tip [40].

Compared to the isotropic tip, discussed in Fig. 3.7(a), Fig. 3.10(a) underlines that the photo-induced force can grow to substantial values when the tip’s anisotropy is included. We find that attractive forces up to 30 pN can be reached for $AF = 2$, an
increase of almost two orders of magnitude compared to the calculation in Fig. 3.7(a). The much stronger forces are a direct consequence of not only the enhanced local field but also of the steeper field gradient along $z$.

In addition to an enhancement of $F_z$, we see that the maximum force is now found at lower frequencies. This frequency shift is not only related to the shifted spectral resonance for $\alpha_{zz}$, but also to the spatial resonances that manifest themselves in the tip-sample junction. To illustrate the latter point, we show the magnitude of $F_z$ at 450 THz as a function of the anisotropy factor in Figure 3.11. As $AF$ is increased, the attractive photo-induced force grows to more than 50 pN before decreasing and turning into a repulsive force. This somewhat unexpected dependence can be explained through the concept of spatial resonance. The field enhancement is a function of the magnitude of the polarizability, producing a resonance when the scattered field amplitude matches the background field and interferes with it constructively. The (real) gradient of this spatial resonance in the field undergoes a sign change, resulting in a dispersive lineshape, and turning an attractive force into a repulsive force as the tip’s responsiveness continues to grow. The observed sign reversal of the force is remarkable, and emphasizes that, unlike most optical effects in the tip-sample junction, the force does not only scale with the field amplitude but also (very sensitively) with its gradient. A somewhat related effect has been observed for two polarizable particles placed in waveguide structures [85, 86]. In this scenario, geometric resonances also produce a sign reversal of the photo-induced force between the particles. We stress that the analysis provided here is derived under the dipole approximation. Inclusion of higher multipoles may affect the conditions under which spatial resonances become prominent.
Figure 3.10: Effect of anisotropic polarizability of the tip. (a) $F_z$ as a function of distance and frequency, using $AF = 2$. The tip is placed over a glass substrate, using $\theta_i = 43.65^\circ$. (b) Spectral dependence of the real (solid line) and imaginary (dotted line) parts of the tip’s polarizability tensors $\alpha_{zz}$ (red) and $\alpha_{xx}$ (blue) for $AF = 2$. 
3.3.6 Photo-induced force in the presence of a nanoparticle

To illustrate the basic features of the photo-induced force in the presence of a nanoparticle, we consider a generic nanoparticle of radius $R_n = 4$ nm that is placed on top of a glass substrate, right under the tip, and which exhibits a spectrally dependent polarizability as shown in Figure 3.12(a). The background field is evanescent as discussed before. Figure 3.12(b) shows the computed photo-induced force in the case of direct scattering (red dashed line) and multiple-scattering with the substrate effect included (blue solid line). It can be seen that the spectral signature of the NP is imprinted on the photo-induced force exerted on the (anisotropic) tip. The spectral dependence of the force follows the dispersive part of the polarizability. The latter is expected when the tip polarizability is dominated by $\alpha'_t$ [76], which is the case in this spectral range. This situation is relevant to actual experimental settings, as is reported in [33]. Figure 3.12(b) also makes clear that the influence of the substrate can be substantial.
In this particular example, the force is more than ten times stronger when multiple scattering via the substrate is properly accounted for. We find that the substrate effect can be significant, generally increasing the magnitude of the photo-induced force relative to the case of an isolated NP.

Figure 3.12: (a) Spectral dependence of the polarizability of a generic nanoparticle with radius $R_n = 4 \text{ nm}$ used in the computation of the photo-induced force. (b) $F_z$ exerted on the anisotropic gold tip (AF=2) calculated by including scattering pathways via the substrate (blue solid line) and by ignoring scattering pathways via the substrate (red dashed line). The surface to surface distance between the tip and the NP is 1 nm.
Chapter 4

Conclusions and Future Work

In this dissertation we have studied the electrodynamics of two realizations of a nanojunction: (i) the junction of a nanodumbbell used in surface enhanced Raman scattering (SERS) experiments, and (ii) the junction of an AFM tip and planar substrate used in photo-induced force microscopy (PiFM) setup. These two cases represent a broad range of nanojunctions which support localized charge oscillation. In these structures, if a surface in the excited nanojunction is plasmonically active then there will be a significant field enhancement resulting from the localized surface plasmons. This favorable field enhancement technique has become a popular choice for single molecule studies because of its ability to amplify the optical response of molecular compounds.

Despite their widespread utility and appeal, not every aspect of the junction’s response to optical radiation is fully understood. This incomplete understanding of junction electrodynamics limits our ability to interpret single molecule studies. Because of the molecule’s small dimensions, it samples the very details of the fields, field gradients and currents in the junction. In this dissertation, we have provided
a more detailed look at the illuminated junction for the two chosen geometries. Using theory and simulations, we have been able to clarify and quantitatively predict the nanojunction response in close agreement with experimental findings. Below we summarize our most important results.

**The nanojunctions in the nanodumbbells**

We showed that in the gold nanodumbbells, the junction morphology dominates the near-field behavior and far-field scattering spectrum of the nanodumbbell, regardless of the overall shape of the nanoparticles. More specifically, an asymmetry in the nanojunction not only shifts the bright mode, but also significantly impacts the resonant frequency and intensity of the dark modes (i.e., magnetic dipole and electric quadrapole). To further study these dark modes, we performed a multipolar decomposition of the scattered near-field by the nanodumbbells to analytically model the nanodumbbells with equivalent sources.

Multipolar decomposition reveals features such as Fano resonance between higher order multipoles in both symmetric and asymmetric dumbbells which cannot be detected in Rayleigh scattering, but may be investigated through nonlinear techniques. Moreover, it provides a clear understanding of how asymmetry of the junction leads to excitation of magnetic moments (i.e., circulation of electric charges), which are spatially confined within sub-10-nm range and have comparable magnitudes to the electric dipole at the corresponding frequency.

Furthermore, we investigated the effects of nanojunction morphology on the chiroptical response of the nanodumbbells. Based on this study, although nanojunction asymmetry in the direction of retardation may not have significant impact on optical activity, a slight asymmetry in the plane of polarization leads to chiral behavior of
the nanodumbbell, with a change in the handedness upon 90 degree rotation in this plane, as experimentally demonstrated in [12]. In the context of multipolar decomposition, we showed that in the case of a symmetric gap or asymmetry in the direction of retardation, equivalent electric and magnetic dipoles are created in physically orthogonal directions. We showed theoretically that such alignment of these sources creates hot spots of density of optical chirality in the nanojunction, with opposite handedness. Therefore, the average optical chirality in the nanojunction is negligible. On the other hand, asymmetry in the plane of polarization leads to equivalent sources with nonzero projection. We showed theoretically that such sources not only support hot spots of optical chirality, but also lead to an averaged chirality of one handedness. These equivalent sources define the handedness of the response upon different illuminations. However, for quantitative description of the optical chirality, we have to include higher order multipoles.

It should be mentioned again that all dumbbells, either with symmetric or asymmetric nanojunctions, support hot spots of density of chirality with opposite handedness on the walls of the nanojunctions. These hot spots usually appear over an appreciable area compared to molecule dimensions. Therefore, they may contribute to single molecule experiments in different manners based on the location of the molecule in the gap. Further studies are required to confirm this conclusion. Specially we suggest investigating the overlap of the hot spots of field intensity and hot spots of optical chirality.

As another suggestion for future work, we recall that the analyses of chirality in this dissertation have focused on the scattering response of the nanodumbbell in a nonlinear setup (optical chirality based on scattered waves only). It might be valuable to consider similar topics in a Rayleigh scattering scheme, knowing that the total field may behave differently based on the interference of scattering and incident
fields. To motivate this project, it should be mentioned that our preliminary studies on this suggest that the handedness of the chiral response is opposite when the optical chirality is calculated based on the total field. Studying and confirming this property of the nanodumbbell may open up new interesting capabilities of these structures in optical switching.

We also suggest that the experimental experts in the field consider investigating fabrication methods for a robust control and manipulation of the gap morphology, or even dynamic manipulation of the gap upon application of an actuator. This work, along with a systematic design of the asymmetric nanojunction for realizing optical magnetization at sub-10-nm scales, may open up a new field of endeavor for realizing optical “iron”, a material with huge magnetic response at optical frequencies.

**The nanojunctions in the PiFM**

For the case of nanojunction in the PiFM setup, we have developed an electrodynamic model to describe the optically induced forces in a tip-sample nanojunction based on dyadic Green’s functions for a planar multilayer substrate. Using this description, we have examined the magnitude and behavior of the photo-induced forces in different cases relevant to PiFM experiments. Our analysis has enabled a detailed look at the influence of field and field gradient effects in the dipolar limit, effects that cannot be easily examined independently when using finite element methods. In addition, our model has allowed us to study the ramifications of scattering pathways via the substrate and the effect of tip anisotropy, and how these mechanisms contribute to the observable force as measured in PiFM, in a physically intuitive and accessible manner.
In the calculation of the dyadic Green’s functions for our setup, we present a method for the efficient computation of the integrals in the evaluation of the scattering GF. For the relevant scenario where the source and observer are along the normal of the planar substrate, we provide closed form expressions of the dominant part of the integrands, where the remaining part decays much faster. In many cases, the modification due to the remaining integrand is less than 5% and the closed form expression is sufficiently accurate in the calculations. In addition, our formalism, which includes the propagation phase, provides a more accurate representation of the quasi-static image dipole. The propagation phase effect can be substantial in cases where the nanoparticle has a strong coupling with the substrate (e.g., spatial resonance). Based on this formalism, we also revisit the definition of the effective polarizability of the nano-particle, and investigate optical phenomena such as the photo-induced force, where not only the electric field, but also the field gradients are concerned.

The qualitative and quantitative observations made with this dyadic Green’s function approach go beyond what was learned from simpler models for the photo-induced force. Even though the dipolar approximation may lead to an underestimation of the local field amplitudes, the analysis presented here has allowed new and complementary insights to what finite element methods have revealed about photo-induced forces in PiFM type measurements.

Our analysis has brought forth the following points: 1) The magnitude of the photo-induced force in the tip-sample junction is a very sensitive function of the field gradient. Our analysis shows that multiple scattering effects via the substrate introduce steep gradients that give rise to a significant enhancement of the force. Neglecting multiple-scattering pathways via the substrate thus leads to an underestimation of the force. 2) For a tip with an isotropic polarizability, the photo-induced force
over a glass substrate is weak (less than a pN), but can be increased substantially when the substrate is covered with a thin gold film, raising the force into the tens of pN range. 3) The photo-induced force carries a spectral dependence that reflects the polarizability of a nanoparticle under the tip. Our scattering Green’s function analysis confirms that PiFM measurements can reveal spectroscopic signatures of particles probed by the tip. 4) Strong photo-induced forces are predicted when the tip anisotropy is included in the analysis. We also find a remarkable sign reversal upon increasing the tip’s polarizability, which we attribute to spatial resonance effects in the tip-sample junction. The sign reversal is a unique feature of the photo-induced force, which, unlike many optical signals, sensitively depends on the field gradients in the tip-sample nano-junction. Finally, by including the effects of multiple scattering and tip anisotropy, our model predicts photo-induced forces that approach the same order of magnitude as the forces reported in experimental PiFM studies. We note that by including higher-order multipoles of the tip, which have not been taken into consideration in the present analysis, further enhancement of the fields in the nano-junction can be expected, thus enabling an improved quantitative comparison with PiFM experiments.

For future work, incorporation of higher-order multipoles of the tip apex into the model is our next focus. Also, we plan to carry out theoretical and experimental research of force sign reversal, which is suggested by our model. Experimental observation of the force reversal would not only inspire confidence in the predictive qualities of our model, but also open new ways of controlling the magnitude and direction of photo-induced forces at the nanoscale.

As a final remark, while the excitation and detection schemes in the discussed experiments may differ significantly, the electrodynamics of the nanojunction is governed predominantly by its geometrical details, i.e., by the constitutive relations responsible
for satisfaction of the boundary conditions in Maxwell's equations. Therefore, contributions of this work may be extended to other nanojunctions of the C-C and C-F categories as well. We hope the work discussed in this dissertation provides useful insights and helps to propel the field of nano-scale spectroscopy and imaging.
Bibliography


Appendices

A Auxiliary example of asymmetry in the direction of retardation

Since the A-gap nanodumbbell geometry in Figure 2.6 includes a $15^\circ$ degree rotation of the top nanoparticle, it is rational to investigate the impact of this misalignment of the particles. With relevance to the results shown in Figure 2.7, we simulate the nanodumbbell in which the misplacement of the top nanoparticle is accomplished by a $15^\circ$ misalignment of the dumbbell as shown by the dashed line on the particle. Note that this misalignment is in the direction of propagation ($\mathbf{k} = k\mathbf{z}$). The spectra are reported in comparison with that of the SS dumbbell. We see that the scattering and absorption cross sections are identical. There is a slight amplitude difference in the local field enhancement. The reason is that the hot spot of the misaligned dumbbell is slightly moved from the center because of subtle and smooth asymmetry in the gap region as a result of moving the top nanosphere. We also make a distinction between this gap asymmetry and those reported in Figure 2.6, leading to significant changes in the spectra of the dumbbell.
Figure A.1: In comparison with Figure 2.13, the nanodumbbell response is very sensitive to asymmetry in the plane of polarization, but not as much sensitive if the asymmetry is applied in the direction of propagation.

We also point out that the gap asymmetry introduced here, though not important in this example ($k = k_z$), makes a significant difference when the near-field is considered in the plane of polarization (Figure 2.13).
B Background field and force without any scattering mechanisms

In the following, we assume the substrate/air interface illuminated by a plane wave from the substrate side. The resulting background field for \( z > 0 \) can be written as

\[
E_b(x, z) = E_{b0} e^{i(k_x x + k_z z)}
\]

where \( E_{b0} \), \( k_x \) and \( k_z \) are obtained from the Fresnel equations [5]. Using Eq. (3.1) the photo-induced force exerted by the background field on any isotropically polarizable particle can be expressed as:

\[
F = \frac{|E_b|^2}{2} \text{Re} \left\{ i\alpha^*(k_x \hat{x} + k_z \hat{z}) \right\}
\]  \hspace{1cm} (B.1)

Eq. (B.1) is valid for both \( s \) and \( p \) polarization states of the illumination field, with the exception that \( E_{b0} \) has to be calculated separately for each polarization state. In case the incident angle is beyond the critical angle, the transmitted field is evanescent, \( (k_z = i\gamma) \) and the force reads

\[
F = \frac{|E_{b0}|^2}{2} (\alpha'' k_x \hat{x} - \alpha' \gamma \hat{z}) e^{-2\gamma z}
\]  \hspace{1cm} (B.2)

We see that the \( z \)-directed force is an attractive force towards the substrate, which is exponentially decaying with \( e^{-2\gamma z} \) away from the interface. In addition, an \( x \)-directed scattering force is present due to propagation of the surface waves, which decays in the same manner as \( F_z \).
C Anisotropic polarizability

As discussed in 3.3.5, an AFM tip typically exhibits an anisotropic response, which gives rise to a stronger field enhancement in the longitudinal polarization direction of the excitation field. The anisotropy of the tip can be taken into consideration with an effective dipole model, in which the longitudinal component of the (diagonal) polarizability tensor is larger than the lateral components [38, 39, 40, 5]. Instead of using numerical models for the computation of the elements of the polarizability tensor, here we seek to describe the tip anisotropy analytically by modeling the apex as a virtual prolate. The advantage of the prolate model is that it includes the expected changes in the frequency response of the polarizability as the ratio of the longitudinal to lateral dimensions is varied. We assume a prolate with a major axis of length $a$ and a minor axis of length $b$. The static polarizability for such a prolate particle in SI units reads [82, 83],

$$\alpha_{ll} = V\varepsilon_0\varepsilon_h \frac{\varepsilon_l - \varepsilon_h}{L^l(\varepsilon_l - \varepsilon_h) + \varepsilon_h} \quad (C.3)$$

where $V = \frac{4\pi}{3}ab^2$ is the volume of the prolate, and $L^l$ is the depolarization factor:

$$L^z = \frac{1 - e^2}{e^2} \left(-1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right)$$

$$e^2 = 1 - \frac{1}{AF^2} \quad (C.4)$$

Here $AF = a/b$ is the anisotropy factor and

$$L^x = L^y = \frac{1 - L^z}{2} \quad (C.5)$$
We will also include the effect of dipole radiation damping by writing the anisotropic polarizability of the tip as: [84]

\[
\bar{\alpha}_t = \bar{\alpha} \left[ I - \frac{ik^3}{i6\pi\varepsilon_0\varepsilon_h} \bar{\alpha} \right]^{-1}
\]

This model for the polarizability captures the basic features of tip anisotropy, including reasonable estimates of the stronger longitudinal polarizability component and the associated red shift of the its longitudinal resonance frequency as \( AF \) is increased. Although the current model is not intended for definite quantitative predictions of the tip polarizability, we point out that for the small \( AF \) values considered in this paper, the predicted numerical values are within practical ranges. The enhancement of the longitudinal polarizability in this model compares well with the enhancement factor reported in the literature [39, 40, 5]. For instance, values reported in [40] based on numerical calculations of the enhancement factor for a 10 nm gold tip at \( \lambda = 830nm \) (far from the resonant frequency) is equivalent to a longitudinal polarizability enhancement, \(|\alpha^{zz}/\alpha^{xx}|\), of about 11. For \( AF = 3 \) in our treatment, the enhancement of the longitudinal polarizability is around 5 at the red side of the resonance, and is below 10 within the whole frequency range considered here.