HOT-CARRIERS AND LOSSES IN PLASMONIC NANOSTRUCTURES

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DECLARATION

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ABSTRACT

Despite the remarkable achievements that plasmonics has provided to the field of nanotechnology over the past few decades, we are now faced with the uncomfortable notion that losses associated with plasmonic excitations are limiting the field’s full theorised potential. This work addresses the source of these limitations and – rather than avoid – seeks to provide methods that utilise these losses.

Plasmonic decay leads to the production of hot charge carriers, that is, electrons and holes with energies notably greater than that of electrons at the Fermi level. Electron-electron scattering following production of such hot-carriers precedes temperature increases in the plasmon-supporting nanostructures. This thesis, in part, addresses this mechanism of heating in the context of plasmonic optical printing. Using computational simulations of both the temperature profile in and around an illuminated plasmonic nanoparticle and the resultant fluid velocity field in the surrounding media, we address the previously unresolved experimental issues surrounding inaccuracies in printing dense arrays of plasmonic nanoparticles.

This thesis also considers the extraction of these energetic hot-carriers, particularly in the context of plasmonic catalysis. A study into the use of hot-electrons following plasmonic decay in colloidal silver nanoparticles is presented, with a focus on their role in the oxidation of a non-fluorescent molecule into a fluorescent product. We then turn to consider the use of this plasmon-decay induced reaction in super-resolution experiments, with a view to unravelling the energetics and the spatial formation of hot-carriers following plasmon decay.
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I AN INTRODUCTION TO LIGHT-MATTER INTERACTIONS
1 AN INTRODUCTION TO PLASMONIC LOSSES

The past 15 years have seen a prominent rise in the interest in plasmonics. The ability to manipulate electromagnetic (EM) fields at the nanoscale – a scale well below that achievable with conventional optics – has encouraged and provided a huge research effort into the enhancement of optical processes, into the fabrication of precise nanoscale structures, and into such novel technologies as super-resolution imaging and optical cloaking.

Advancements, however, have been somewhat hampered by the suite of materials available to the average researcher. Silver and gold remain the most commonly seen metals within the field, chosen for their comparatively low rate of scattering of free-electrons and thus their high reflectivity in the optical regime [1]. Regrettably, these materials exhibit particularly high losses in the optical (and infrared) section of the EM spectrum, and consequently only a few practical plasmonic devices exist outside of research. Fluorescence sensors, for example, have seen marked improvements with the advent of plasmonics, but there are inherently inefficient devices [2]. It appears that only very inefficient devices may be improved; for devices where absolute efficiencies are high – such as solar cells and switches – the lossy material properties that plasmonics introduces gives rise to a decline in performance. Indeed, the efficiencies of all-plasmonic devices (that is, devices without any semiconductor material as a support) have yet to exceed 1% [3]. We must then face the uncomfortable notion that in its current state, losses are preventing plasmonics from reaching its theorised potential.

Many researchers are tackling this through turning to novel materials, other than silver and gold, that provide comparable field enhancements upon optical illumination with comparatively lower losses. Various oxides and nitrides have been explored for their plasmonic properties [4], as well as highly doped semiconductors [5] and innovative 2-dimensional materials [6]. All have exhibited promising properties – in particular CMOS compatibility, which noble metals lack [7] – but the ease of fabrication as seen with conventional plasmonic materials remains enviable.

Others have instead adopted the mindset that if absorption in the metals is unavoidable, why not put the losses to some productive use? Recent work has employed the products of plasmonic losses in such varied applications as photodetection devices [8] and nanoscale localised heat sources [9]. This thesis aims to further investigate the potential use and understanding of losses associated with plasmonics, in the context of thermal losses within the
fabrication of nanoscale geometries, and also in the practical use of hot-electrons – a by-product of plasmon decay.

1.1 OUTLINE OF THIS THESIS

This introductory chapter was aimed at introducing the scope of this thesis, namely the focus upon exploitation of losses (in various guises) from plasmonic nanostructures.

Chapter 2 formally introduces the field of plasmonics, taking an approach that sees the derivation of the most relevant concepts to our discussion directly from Maxwell's equations. Notably, we introduce the localised surface plasmon — the collective oscillation of charge in and around 3-dimensional nanostructures. We close this general discussion with a detailed look at both finite-difference time-domain and finite-element methods of computational electrodynamic simulation, which we go on to use throughout as tools of prediction and verification of the interaction of light with matter at the nanoscale.

Chapter 3 addresses the roots of plasmonic losses, with a focus on non-radiative losses and the decay of the plasmon into hot-carriers. A detailed review of the field follows, with an attempt at categorising examples of plasmonic hot-carrier exploitation into three camps: solid-state devices, plasmonic catalysis, and nanoscale heat sources.

The relevant theory underlining nanoscale heating is presented at the beginning of Chapter 4. The same chapter goes on to introduce the technique of optical printing: controlled binding of plasmonic nanoparticles to a functionalised substrate using solely optical means. Such a technique has only recently appeared in the literature and is limited in application by what appears to be a temperature-induced repulsion mechanism. Experimental and computational studies into the nanoscale heating of metallic printing particles are presented, with findings that allow us to overcome this repulsion and accurately, reliably, and quickly fabricate intricate arrays of plasmonic nanoparticles.

Chapter 5 turns to look at the role of plasmonic hot-carriers in super-resolution microscopy. There exists little work that explores the question of surface reactivity in the fabrication of plasmonic catalysts, despite the shared reliance of gold and silver as in industrial catalysis. Stochastic super-resolution methods are introduced, with a view to employ similar techniques in the study of hot-carrier transfer from plasmonic nanoparticles into other adsorbed molecules.

Chapter 6 continues the discussion from the preceding chapter, with a detailed experimental study of the transfer of hot-electrons from silver nanoparticles.
into an adsorbed model analyte resazurin. Efforts to study this at the ensemble level (just as to be expected in large scale industrial catalysis) are presented with findings that appear to be the first example of plasmonic catalysis on silver nanoparticles using solely decay-induced hot-electrons.

An attempt at the transfer of the ensemble methods detailed in chapter 6 to the single-molecule, super-resolution regime is the focus of Chapter 7, but this work is hindered by the presence of various, undesirable material issues. Much of this chapter is directed towards a discussion of the current system limitations and suggestions as how best to overcome these.

Chapter 8 serves as a brief conclusion to this thesis, where a perspective on future work is presented with a discussion of possible improvements to the experiments and of anticipated applications of hot-carrier production in plasmonic nanoparticles.
Electromagnetic (EM) radiation in the visible regime is of particular interest to us as it is here that the energies of the EM quanta typically match the energies required for many of the electronic transitions in matter. It is for this very reason that the human eye has adapted to accurately sense this optical region.

At the nano-scale, it is most appropriate to adopt the wave picture of the light quanta – the photon – as it allows us to address the interaction of matter with incident EM fields rigorously in a semi-classical framework. By restricting the discussion to metallic interaction with light, owing to the high density of the free carriers within the structure’s lattice, we may neglect a full quantum mechanical treatment even when considering structures just a few nanometres in size [10].

This chapter establishes the basic theory underpinning plasmonics, with a particular focus upon the concept of localised surface plasmon resonances. We adopt two complementary viewpoints to assist this: a macroscopic approach, which assumes the presence of a magnetic permeability and an electric permittivity, and a microscopic approach, which establishes the presence of these material dependent properties. The former is most useful when addressing the EM field’s behaviour upon interaction with matter, while the latter is particularly useful when, conversely, looking at the response of the medium upon interaction with the EM field.

2.1 MAXWELL’S EQUATIONS

Let us first adopt the macroscopic approach alluded to above. In SI units, the macroscopic Maxwell equations take the form:

\[
\nabla \cdot \mathbf{D}(r, t) = \rho(r, t) \tag{2.1a}
\]

\[
\nabla \times \mathbf{E}(r, t) = -\frac{\partial \mathbf{B}(r, t)}{\partial t} \tag{2.1b}
\]

\[
\nabla \cdot \mathbf{B}(r, t) = 0 \tag{2.1c}
\]

\[
\nabla \times \mathbf{H}(r, t) = \mathbf{j}(r, t) + \frac{\partial \mathbf{D}(r, t)}{\partial t} \tag{2.1d}
\]

Here, \( \mathbf{E} \) and \( \mathbf{H} \) refer to the electric and magnetic fields, respectively. \( \mathbf{D} \) and \( \mathbf{B} \) denote the electric displacement and the magnetic induction field. \( \mathbf{j} \) and \( \rho \) the current and charge densities. These quantities are observed across both spatial, \( r \), and temporal, \( t \), dimensions. We assume here that the current density is provided in the absence of any sources in the media.
It is relevant to note that the displacement may be linked to the electric field with the addition of the polarisation density, \( P \), which we shall address more rigorously in the next subsection:

\[
D = \varepsilon_0 E + P
\]  

(2.2)

For completeness, we should also note that the induction and magnetic fields may be related with the addition of a magnetization density term. We shall refrain from addressing magnetic media in this discussion, however.

Maxwell’s equations simply define the fields generated by charges and currents in a medium; we must introduce constitutive relations to assist us in describing how these are generated.

Generally, an electromagnetic field in a linear medium may be written as a superposition of monochromatic fields of the form

\[
E(\mathbf{r}, t) = E(\mathbf{k}, \omega)\cos(\mathbf{k} \cdot \mathbf{r} - \omega t)
\]  

(2.3)

where \( k \) and \( \omega \) are the wavevector and the angular frequency, respectively.

The induced displacement field may then be written as

\[
\mathbf{D}(\mathbf{k}, \omega) = \varepsilon_0 \varepsilon(\mathbf{k}, \omega)\mathbf{E}(\mathbf{k}, \omega)
\]  

(2.4)

Through an inverse Fourier transform, we can return to the time domain and obtain

\[
\mathbf{D}(\mathbf{r}, t) = \varepsilon_0 \int \varepsilon(\mathbf{r} - \mathbf{r}', t - t')\mathbf{E}(\mathbf{r}', t')d\mathbf{r}'dt'
\]  

(2.5)

The superscript notation \( \varepsilon \) here denotes the response in both space and time. The displacement is therefore both temporally and spatially dispersive. Spatially dispersive (or non-local) effects are prominent when the structure under consideration is of size on the order of the electron’s mean free path [11]. Otherwise the effect is weak and we may ignore it. We must fully consider, however, temporal dispersion.

The time dependence of the fields may be dropped as every spectral component of a general EM field can be treated separately as a monochromatic field. The time dependence of these harmonic components may then be separated from the spatial components, further simplifying the Maxwell equations under consideration [11].

By considering a linear, isotropic medium that can be described as spatially local and spatially dispersive, we can relate the fields via the material in question’s electric permittivity, \( \varepsilon(\mathbf{r}, t) \), and magnetic permeability, \( \mu(\mathbf{r}, t) \):

\[
\mathbf{D}(\mathbf{r}, t) = \varepsilon_0 \varepsilon(\mathbf{r}, t)\mathbf{E}(\mathbf{r}, t)
\]  

(2.6a)

\[
\mathbf{B}(\mathbf{r}, t) = \mu_0 \mu(\mathbf{r}, t)\mathbf{H}(\mathbf{r}, t)
\]  

(2.6b)
where $\varepsilon_0$ is the permittivity of free-space and $\mu_0$ is the permeability of free-space. Additionally, we note that the internal current density, $j$, may be related to the electric field via conductivity (Ohm’s law)

$$j(r, t) = \sigma E(r, t)$$

(2.7)

Expressing our fields as time-harmonic, along with the assistance of our constitutive equations, we can express Maxwell’s curl equations in terms of $E(r)$ and $H(r)$. In doing so, it is customary to replace the definition of permittivity with that of a complex dielectric constant, which implicitly contains information pertaining to the conductivity of the medium, i.e.:

$$\varepsilon(\omega) \rightarrow \varepsilon(\omega) + i \frac{\sigma(\omega)}{\omega \varepsilon_0}$$

(2.8)

Additionally, note that here we have dropped the spatial dependence – a simplification that remains valid as long as the dimensions in consideration are significantly shorter than the wavelength of study.

This complex, frequency dependent, dielectric constant is the main result of this subsection: it describes the optical properties of a metal in response to incident light.

### 2.2 Optical Properties of Metals

Before formally introducing the concept of a plasmon, we must first garner some understanding into the microscopic nature of materials. The complex dielectric function introduced above is determined mainly by the notion that conduction electrons inside a bulk material may move freely, and that incident photons are capable of exciting interband transitions if they are of energies exceeding the bandgap of the material in question. The presence of an electric field leads to the displacement $r$ of these conduction electrons. Such a displacement is associated to the dipole moment $\mu$ via $\mu = -er$, where $e$ is the charge of the electron. We can then introduce the macroscopic polarization density that describes the density of such electric dipole moments within the material

$$P = n\mu$$

(2.9)

where $n$ is the number density of electrons. Oscillating conduction electrons are subject to a damping effect via collisions occurring with a characteristic collision frequency $\gamma = 1/\tau$, where $\tau$ is the relaxation timescale associated with the free-electron gas – typically on the order of $10^{-14}$ s at room temperature. In the absence of any restorative forces, we may adopt the Drude-Sommerfeld model for the motion of the free-electron gas

$$m_e \frac{\partial^2 r}{\partial t^2} + m_e \gamma \frac{\partial r}{\partial t} = eE$$

(2.10)
where \( m_e \) denotes the mass of the (free) electron.

Taking the field to be harmonic in time (recall that the a broadband field may be decomposed into monochromatic harmonic components without loss of generality), and employing the particular solution of \( r(t) = r_0 e^{-i \omega t} \), where the complex amplitude \( r_0 \) incorporates phase shifts between driving field and response:

\[
r(t) = \frac{e}{m_e(\omega^2 + i\gamma \omega)} E
\]  

(2.11)

The macroscopic polarisation, \( P = -n e r \), is then given by

\[
P = -\frac{n e^2}{m_e(\omega^2 + i\gamma \omega)} E
\]  

(2.12)

and therefore, the electric displacement (via equation 2.2) yields

\[
D = \epsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} \right) E
\]  

(2.13)

where \( \omega_p^2 = \frac{n e^2}{\epsilon_0 m_e} \) is the plasma frequency of the free electron gas. We have therefore arrived at the dielectric function for this Drude free electron gas:

\[
\epsilon_{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}
\]  

(2.14)

### 2.2.1 Intercband Contributions

Application of this Drude-Sommerfeld theory to gold – a noble metal that will be employed throughout much of this discussion, which may be characterised using \( \omega_p = 13.5 \times 10^{15} \text{ s}^{-1} \) and \( \gamma = 115.36 \times 10^{12} \text{ s}^{-1} \) – while successful in the infrared regime, fails to accurately model the optical properties in much of the visible regime. Indeed, for wavelength shorter than around 500 nm, the measured imaginary dielectric function is much smaller than that predicted by the model. We can ascribe this to the ability of higher energy photons to promote electrons of lower-lying bands into the metal’s conduction band. Recall that up until now we have considered only the movement of free electrons; the incident field is also capable of driving oscillation of these bound electrons. By adopting the same approach as employed above in equation 2.10, albeit now with an additional restorative force with a spring-like potential that keeps the electrons bound to the crystal lattice, we arrive at the dielectric function of only these bound electrons undergoing interband transitions:

\[
\epsilon_{\text{interband}}(\omega) = 1 - \frac{\tilde{\omega}_p^2}{(\omega^2 - \omega_0^2) + i\Gamma \omega}
\]  

(2.15)

where \( \tilde{\omega}_p \), by analogy to the plasma frequency of the free electron model, is the effective plasma frequency of solely the bound electrons, \( \Gamma \) is the constant
describing the damping of these bound electrons (the spectral width of the Lorentz oscillator), and \( \omega_0 \) is the resonance frequency induced by the presence of the restorative force (the strength of the Lorentz oscillator).

The above Lorentzian dielectric function contribution due to interband transitions is only valid for transitions induced by illumination at the resonant frequency \( \omega_0 \). To further increase the accuracy of the model, we introduce a constant offset to the real part of the permittivity, \( \varepsilon_\infty \), that accounts for the integrated dispersive effect of all higher-energy interband transitions. The complete Drude-Lorentz model incorporating all of these contributions is then given as

\[
\varepsilon_{DL}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} - \frac{\omega_0^2}{(\omega^2 - \omega_0^2) + i\Gamma \omega}
\]

(2.15)

Figure 2.1 illustrates the dielectric function for gold, modelled through this summation of the constant offset (\( \varepsilon_\infty = 5.97 \)), an interband transition at 461 nm (2.69 eV), and the Drude-Sommerfeld theory for the free electrons. All material parameter values were obtained from the work of Vial and co-workers [12]. For reference, experimentally measured data from Johnson & Christy [13] is overlaid. Note that for much of the visible and near-infrared regimes, the model accurately reflects experimental observation. The use of just a single interband transition explains the deviation from observation at wavelengths shorter than around 500 nm – additional interband transitions at higher energies would correct this further.
By definition, surface plasmons are the quanta of surface-charge density oscillations. These propagating oscillations are naturally coupled to incident EM waves, and it is for this reason that they are often referred to as surface plasmon polaritons (SPPs). Let us then consider the simple planar interface of a metal, whose optical response may roughly be described by the complex dielectric function derived above $\varepsilon_1(\omega)$, and a dielectric material with a wholly real dielectric function $\varepsilon_2(\omega)$. We are looking for propagating homogenous solutions of Maxwell’s equations that decay exponentially with distance from the interface.

Figure 2.2  Geometry of the interface between two media, 1 and 2, with dielectric functions $\varepsilon_1$ and $\varepsilon_2$, respectively. The interface is defined by the $z = 0$ plane in a Cartesian coordinate system. In each half-space we consider only a single $p$-polarised wave as we are looking for homogenous solutions to Maxwell’s equations that decay exponentially with distance from the interface.

2.3 SURFACE PLASMONS

By definition, surface plasmons are the quanta of surface-charge density oscillations. These propagating oscillations are naturally coupled to incident EM waves, and it is for this reason that they are often referred to as surface plasmon polaritons (SPPs). Let us then consider the simple planar interface of a metal, whose optical response may roughly be described by the complex dielectric function derived above $\varepsilon_1(\omega)$, and a dielectric material with a wholly real dielectric function $\varepsilon_2(\omega)$. We are looking for propagating homogenous solutions of Maxwell’s equations that are bound to the interface.

We begin by combining Maxwell’s curl equations (2.1b, 2.1d) in the absence of external charge and current densities, and invoking the constitutive relations to yield the wave equation

$$\nabla \times \nabla \times E(r, \omega) - \frac{\omega^2}{c^2} \varepsilon(r, \omega) E(r, \omega) = 0$$

(2.16)

We shall consider a simple Cartesian geometry in which $z < 0$ refers to our metal, and $z > 0$ to our real dielectric function valued material (that is, the interface sits on the plane $z = 0$). Figure 2.2 illustrates such a geometry. In searching for solutions that are confined to the interface, it is justified to look for fields described by an exponential decay in $z$ in both subregions of our system, $j = [1, 2]$. Additionally, it is sufficient to consider only $p$-polarised waves as it can be shown that due to wavevector matching requirements, no solutions exist in the case of $s$-polarisation [11].
Such $p$-polarised plane waves in the half-spaces $j = [1,2]$ may be written as

$$E_j = \begin{pmatrix} E_{j,x} \\ 0 \\ E_{j,z} \end{pmatrix} e^{i(k_{j,x}x - \omega t)} e^{i k_{j,z}z} \quad j = 1,2 \quad (2.17)$$

where we have deconstructed the $E$ vector into its constituent components, considering only propagation in $x$ and $z$. The wavevector $k_x$ describes the propagation of the travelling, surface bound waves; we have ignored the corresponding $y$ component for symmetry reasons.

Through conservation of the wavevector parallel to the interface, the following relationship emerges

$$k_x^2 + k_{j,z}^2 = \varepsilon_j k^2 \quad j = 1,2 \quad (2.18)$$

where $k = 2\pi/\lambda$, with $\lambda$ denoting the wavelength in vacuum. Additionally, given that we have no sources within our system, that is $\nabla \cdot \mathbf{D} = 0$,

$$k_x E_{j,x} + k_{j,z} E_{j,z} = 0 \quad j = 1,2 \quad (2.19)$$

Alongside equations 2.18 and 2.19, which impose conditions on the fields within each respective sub-region of our system, continuity of parallel components of $E$ and the perpendicular components of $D$ lead to a set of continuity equations for the interface

$$E_{1,x} - E_{2,x} = 0 \quad (2.20a)$$
$$\varepsilon_1 E_{1,x} - \varepsilon_2 E_{2,x} = 0 \quad (2.20b)$$

A solution to the homogeneous system of equations described by 2.16, 2.17, and 2.18 then requires either $k_x = 0$, which fails to describe travelling excitations so is therefore not of interest here, or

$$\varepsilon_1 k_{2,x} - \varepsilon_2 k_{1,x} = 0 \quad (2.21)$$

The relationships between the angular frequency $\omega$ and the wavevector along the propagation direction and the perpendicular direction — the dispersion relations — are then given, respectively, as:

$$k_x^2 = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \frac{\omega^2}{c^2} \quad (2.22a)$$
$$k_{j,z}^2 = \frac{\varepsilon_j^2}{\varepsilon_1 + \varepsilon_2} \frac{\omega^2}{c^2} \quad j = 1,2 \quad (2.22b)$$

Given we have a mathematical description of these surface-bound waves, we now turn to discussion of the material requirements necessary for such modes to exist. A propagating wave at the interface requires a real $k_x$; this can be fulfilled if both the product and the sum of the dielectric are of the same sign. A surface-bound wave requires purely imaginary perpendicular components of the wavevector $k_{j,z}$, giving rise to exponentially decaying solutions. And
therefore, we may conclude that surface plasmon polaritons may exist only when the following conditions are upheld:

\[
\begin{align*}
\epsilon_1(\omega) \epsilon_2(\omega) &< 0 \\
\epsilon_1(\omega) + \epsilon_2(\omega) &> 0
\end{align*}
\]

indicating that one of the dielectric functions must be negative and have an absolute value greater than that of the other.

Recall figure 2.1, in which we have plotted the dielectric function of gold using both experimental data and the Drude-Sommerfeld model (with the inclusion of interband transitions). It is evident that gold (and indeed such other metals as silver and aluminium) has a small imaginary component and a large negative real component of the dielectric function. The interface between these metals and such dielectrics as glass and air \((\epsilon \sim 2.3 \text{ and } 1, \text{ respectively})\) is then capable of meeting the criteria set in equations 2.23 and sustaining propagating, exponentially decaying, surface plasmons.

### 2.3.1 Dispersion

Let us now study these properties of these SPPs in a little more detail. Take a general, complex dielectric function to describe the optical response of a metal

\[
\epsilon = \epsilon' + i\epsilon''
\]

where we have decomposed the function into its real and imaginary components, \(\epsilon'\) and \(\epsilon''\), respectively. Note also that we have dropped the explicit dependence on frequency for simplicity in notation. Additionally, let us take the other medium – the dielectric in half-space \(j = 2\) – to have a wholly real valued, positive dielectric function \(\epsilon_2\); this assumption reflects a good dielectric metal with negligible losses, such as air or water.

The previously derived dispersion relations (equations 2.22) then give complex wavevectors in both the parallel and perpendicular planes, \(k_x\) and \(k_{j,z}\), respectively. The imaginary part of \(k_x\), for example, describes the damping of the surface plasmon polaritons as it propagates along the interface, while the real part describes its wavelength. Using the same superscript notation as with the dielectric function, and taking the magnitude of the metal's imaginary dielectric function component to be much smaller than the real part, we can estimate the real and imaginary parts of \(k_x\), and therefore estimate values for both wavelength and the 1/\(e\) decay length of the surface plasmon polariton:

\[
\begin{align*}
\lambda_{\text{SPP}} &= \frac{2\pi}{k_x} \approx \lambda \frac{\epsilon_1' + \epsilon_2}{\epsilon_1'' \epsilon_2} \\
L_{1/e} &= \frac{2\pi}{k_x} \approx \lambda \frac{\epsilon_1' + \epsilon_2 + 2\epsilon_1' (\epsilon_1' + \epsilon_2)}{\epsilon_1'' \epsilon_2}
\end{align*}
\]

(2.25a)  (2.25b)
Using $\varepsilon_1 = -11.75 + 1.26i$ and $\varepsilon_2 = 1$ – the dielectric functions of gold and air at 633 nm, respectively [13] – we obtain a plasmon wavelength and decay length of approximately 606 nm and 123 $\mu$m, respectively.

Perpendicular to the plane, we can similarly determine $1/e$ decay lengths, both into the metal and into the dielectric material. Neglecting the small imaginary components of each wavevector above ($k_{j,z}$) and using the aforementioned
dielectric functions of water and gold, we can obtain perpendicular $1/e$ decay lengths of 176 nm into the metal and of 2.1 µm into the dielectric.

The above dispersion relations (equation 2.22) allow us now to address both energy and momentum requirements necessary to excite these surface plasmons. Figure 2.3a plots the dispersion relation for the interface of a gold-like metal described by the pure Drude-Sommerfeld dielectric function (equation 2.14) and air ($\varepsilon_2 = 1$). Here normalized to the bulk plasma frequency $\omega_p$, we note that due to the bound nature of the SPPs, excitations correspond to the region lying to the right of the light line within air. The high energy branch corresponds to $\omega > \omega_p$, a region in which the $z$ component of the wavevector within the metal is no longer purely imaginary. It is therefore not strictly bound to the surface, so we will not consider it any further. For much of the corresponding low energy branch, the SPP propagation resembles the light line. At higher energies, we reach an asymptotic surface-plasmon frequency

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_2}}$$  

(2.26)

which may be derived through inserting the Drude dielectric function directly into the dispersion relation in $x$. Crucially, note that for a given energy, the wavevector of the SPP is always higher than that of light travelling in the dielectric medium. This increased momentum arises from the strong coupling between surface charges and light: the light must effectively drag electrons at the metal surface. An SPP at an idealised planar interface may then not be simply excited by light in free space.

Figure 2.3b illustrates a more realistic metal, in which we have supplemented the Drude-Sommerfeld model with an interband transition at 450 nm (as discussed in section 2.2.1). There exists a continuous transition from the SPP dispersion into the previously forbidden upper band. Close to the surface-plasmon frequency, the mode is strongly localised within the metal and losses begin to increase significantly.

![Figure 2.4](image_url)  
Figure 2.4  Surface plasmon polariton excitation configurations. **a**, Otto configuration, in which the evanescent wave formed at the interface of the two dielectrics excites an SPP in the plasmonic metal across the gap. **b**, Kretschmann configuration, in which the evanescent wave passes through a thin film of plasmonic metal, exciting the opposite interface.
Excitation of the SPP requires an increase of the incident light's wavevector to above its value when travelling unimpeded. While simple far-field illumination does not allow this, near-field optics allow us to excite evanescent waves, capable of providing an additional momentum boost. Experimentally, perhaps the most common way to achieve this is through excitation of evanescent waves at the interface of an additional dielectric material with refractive index greater than that of the original dielectric; both Otto and Kretschmann configuration prism coupling, illustrated in figure 2.4, are reliant on this approach \[14,15\].

2.4 LOCALISED SURFACE PLASMONS

The discussion thus far has revealed that SPPs are propagating, dispersive EM waves coupled to the electron plasma at a two-dimensional metal/dielectric interface. Localised surface plasmons arise when we consider the electron plasma oscillation of three-dimensional nanostructures. By considering the scattering properties of such particles when illuminated with an oscillating EM field, we can investigate these non-propagating modes and highlight their resonant nature.

Let us begin by briefly considering the fields of a single dipole oscillating at frequency \(\omega\)

\[
E = \frac{1}{4\pi\varepsilon_0} \left[ k^2 (n \times \mu) \times n e^{i k r} + \left( 3n(n \cdot \mu) - \mu \right) \left( \frac{1}{r^3} - i \frac{k}{r^2} \right) e^{i k r} \right] e^{i \omega t} \tag{2.28a}
\]

\[
H = \frac{ck^2}{4\pi} \left( n \times \mu \right) e^{i k r} \left( 1 + i \frac{1}{kr} \right) e^{i \omega t} \tag{2.28b}
\]

Note that the magnetic field is transverse to the radial vector (of magnitude \(r\)), while the electric field has components both parallel and perpendicular to the unit vector \(n\). Recall that \(\mu\) denotes the electric dipole moment \[16\].

In the far field, that is \(kr \gg 1\), the fields approach

\[
E = \frac{1}{c\varepsilon_0} H \times n e^{i \omega t} \tag{2.29a}
\]

\[
H = \frac{ck^2}{4\pi} \left( n \times \mu \right) e^{i (kr + \omega t)} \tag{2.29b}
\]

Alternatively, in the near field \((kr \ll 1)\), these fields take on the form

\[
E = \frac{1}{4\pi\varepsilon_0} [3n(n \cdot \mu) - \mu] \frac{e^{i \omega t}}{r^3} \tag{2.30a}
\]

\[
H = \frac{i\omega}{4\pi} (n \times \mu) \frac{e^{i \omega t}}{r^3} \tag{2.30b}
\]

The electric field in this near field region is then a factor of \(1/c\varepsilon_0\) (approximately 375) larger than the magnetic counterpart and therefore our neglect of the
magnetic fields in the previous sections is justified. In the static limit \((k \to 0)\), the magnetic field vanishes entirely.

Given that the fields correspond to that of a static point dipole only oscillating in time, we shall adopt the quasi-static approximation, which neglects retardation effects and assumes that all electrons within the plasma surrounding a nanostructure respond simultaneously to an incident EM field. Note that our approximation holds only when the structure is significantly smaller than the wavelength of light – as is the case with many of the nanostructured systems that we shall consider. This approximation allows us to reduce the Helmholtz equation that describes the propagation of an EM wave to the analytically simpler Laplace equation

\[
\nabla^2 \Phi = 0 \tag{2.31}
\]

where \(\Phi\) is the potential.

In spherical coordinates, solutions of the Laplace equation take the form

\[
\Phi(r, \theta, \phi) = \sum_{l,m} \left[ A_{l,m} r^l + B_{l,m} r^{-l+1} \right] Y_{l,m}(\theta, \phi) \tag{2.32}
\]

where \(A_{l,m}\) and \(B_{l,m}\) are constant coefficients dependent on the relevant boundary conditions of the system, and \(Y_{l,m}\) are the spherical harmonic functions of order \(l\) and \(m\). We may simplify these solutions considerably by employing the azimuthal symmetry of the system.

2.4.1 PLASMON IN A SINGLE NANOPARTICLE

Let us address the problem of the illumination of a single spherical nanoparticle (NP) of radius \(a\). We can make the assumption that the incoming wave is homogenous and travelling along a single axis. This is illustrated schematically in figure 2.5. In the far-field, we then have the requirement that the incoming field has a potential of \(\Phi_0 = -E_0 r P_1^0(\cos \theta)\).

At the surface of the nanoparticle, it is necessary that the tangential electric fields are continuous and therefore we have the requirement that

\[
\left[ \frac{\partial \Phi_1}{\partial \theta} \right]_{r=a} = \left[ \frac{\partial \Phi_2}{\partial \theta} \right]_{r=a} \tag{2.33}
\]

where we have denoted the potential inside the sphere as \(\Phi_1\) and the potential outside the sphere as \(\Phi_2\). The potential outside is the superposition of the scattered potential and the incoming potential, that is \(\Phi_2 = \Phi_0 + \Phi_{scat}\).

Additionally, the displacement field must be continuous across the interface of the particle and its surrounding. Taking the nanoparticle and the surrounding medium to have general dielectric functions of \(\varepsilon_1\) and \(\varepsilon_2\), respectively, this yields the Dirichlet boundary requirement
\begin{equation}
\varepsilon_1 \left[ \frac{\partial \Phi_1}{\partial r} \right]_{r=a} = \varepsilon_2 \left[ \frac{\partial \Phi_2}{\partial r} \right]_{r=a} \tag{2.34}
\end{equation}

Evaluation of these boundary conditions leads to a potential in and outside of the nanoparticle of

\begin{align}
\Phi_1 &= -E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} r \cos \theta \tag{2.35a} \\
\Phi_2 &= -E_0 r \cos \theta + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 \cos \theta \frac{\varepsilon_1}{r^2} \tag{2.35b}
\end{align}

Calculating the fields via equation 2.31 then gives

\begin{align}
E_1 &= E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \left( \cos \theta \hat{r} - \sin \theta \hat{\theta} \right) \tag{2.36a} \\
E_2 &= E_0 \left( \cos \theta \hat{r} - \sin \theta \hat{\theta} \right) + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 \cos \theta \frac{\varepsilon_1}{r^2} \left( 2 \cos \theta \hat{r} + \sin \theta \hat{\theta} \right) \tag{2.36b}
\end{align}

Here \( \hat{r} \) and \( \hat{\theta} \) are the unit vectors in the radial and the polar directions, respectively.

Equation 2.36a reveals an important caveat to our derivation: the field is homogeneous \textit{inside} the nanoparticle, which is at odds with the notion that EM fields decay exponentially into metals. Recall that the quasi-static approximation only holds for small particles; indeed, it is only valid for structures smaller that the skin depth of the metal in use.

Notably, the potential and the field outside of the sphere can be seen simply the superposition of the incident field and that of a static dipole were it to be placed at the centre of the nanoparticle. This effective dipole, induced by the external field \( E_0 \), takes the value of

\begin{equation}
\mu = \varepsilon_2 \left[ 4\pi \varepsilon_0 a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \right] E_0 \tag{2.37}
\end{equation}

where the term inside the brackets is the \textit{polarisability} of the particle, \( \alpha(\omega) \). It is clear that this experiences a resonant enhancement when the denominator

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.5.png}
\caption{Schematic of homogenous sphere placed within an electrostatic field. The sphere of radius \( a \) can be described by the frequency dependent permittivity \( \varepsilon_1(\omega) \) and is immersed in medium of constant permittivity \( \varepsilon_2 \). \( s \) denotes the closed surface around the structure used to the powers removed and scattered by the nanoparticle.}
\end{figure}
approaches a minimum. Taking $\varepsilon_1$ to be a frequency dependent, complex quantity (recall our discussion of the optical properties of metals from section 2.2) and $\varepsilon_2$ to be wholly real, this Fröhlich condition is achieved when

$$\text{Re}[\varepsilon_1] = -2\varepsilon_2$$

Upon meeting this Fröhlich condition, we excite what is known as a localised surface plasmon resonance (LSPR).

### 2.4.2 PARTICLE CROSS-SECTIONS

Let us turn now to the question of the energy stored and power dissipated by this oscillating charge density at the nanoparticles surface. Recall that the fields around the structure are a superposition of the incident and scattered fields; the conservation of energy indicates that the total time-averaged Poynting vector, $\mathbf{S}_{\text{tot}}$, may be decomposed as

$$\mathbf{S}_{\text{tot}} = \mathbf{S}_{\text{inc}} + \mathbf{S}_{\text{scat}} + \mathbf{S}_{\text{ext}}$$

where $\mathbf{S}_{\text{inc}}$ and $\mathbf{S}_{\text{scat}}$ are the Poynting vectors of the incident and the scattered fields, and $\mathbf{S}_{\text{ext}}$ describes the EM power flow due to the interference of these incident and scattered fields.

Integrating over any closed surface $s$ containing the structure, we uncover the simple relations for the various energy channels at play in this system. No loss of generality ensues in taking the incident field to obey

$$P_{\text{inc}} = \int_{s} \mathbf{S}_{\text{inc}} \, ds = 0$$

Thus, the power scattered by the nanoparticle, the power removed from the incident beam, and the power extinct in the scattering process via interference are given as

$$P_{\text{scat}} = \int_{s} \mathbf{S}_{\text{scat}} \, ds$$

$$P_{\text{abs}} = -\int_{s} \mathbf{S}_{\text{abs}} \, ds$$

$$P_{\text{ext}} = -\int_{s} \mathbf{S}_{\text{ext}} \, ds$$

Note that the negative sign in the second arises due to the inwards orientation of the surface and leads to a positive value for the energy absorption. The physical meaning of the extinction may be understood via equation 2.39, leading to the energy relation

$$P_{\text{ext}} = P_{\text{abs}} + P_{\text{scat}}$$

That is, the extinction corresponds to the energy removed from the incident field via scattering and absorption. All the EM energy removed by the incoming
radiation in the scattering process is lost in the form of work performed by the incident electric field on the dipole moment induced in the nanoparticle. Again, this is illustrated schematically in figure 2.5

We now introduce the concept of the nanoparticle’s cross-section. Given that the absorption and scattering remove energy from incident fields upon interaction with the particle, we can associate an effective geometric cross section to each mechanism. The scattering cross-section is obtained by dividing the total radiated power by the intensity of the excitation plane wave. In the case of the sphere of radius $a$ acting as a radiating dipole, with an induced electric field as given by equation 2.36b, this results in a cross-section given as

$$\sigma_{\text{scat}} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha(\omega)|^2$$

(2.43)

Poynting’s theorem notes that the radiated power of any current distribution with a harmonic time dependence in a linear medium has to be identical to the rate of energy dissipation through energy sources or sinks [11]. In this case of the oscillating dipole, this is given by

$$P_{\text{abs}} = \frac{\omega}{2} Im[\mu^* \cdot E_0]$$

(2.44)

where the field is evaluated at the dipole’s origin. Recall that the dipole moment here relates to the particle’s polarisability via $\mu = \varepsilon_2 a E_0$. The absorption cross section then reads

$$\sigma_{\text{abs}} = \frac{k}{\varepsilon_0} Im[\alpha(\omega)]$$

(2.45)

Energy conservation allows us to define the extinction cross-section as the sum of the scattering and absorption cross-sections.

These cross-sections are notable as these are perhaps the most commonly used experimentally accessible quantities in nano-optical experiments, utilised at a metric of characterisation of the structure in question. In particular, the scattering-cross section is assessed via dark-field microscopy [17]. Remarkably, the cross-sections of a nanoparticle can become several times larger than the physical cross-section of the structure when illuminated at resonance. Figure 2.6a illustrates both the scattering and the absorption cross-sections for a spherical gold nanoparticle. In modifying the dielectric medium in which the structure is immersed we modify the polarisability of the dipole and therefore the particle’s cross-section magnitude and resonant position. This phenomenon is the basis of many sensing techniques that rely on the resonance shift [18-20].
Comparison of equations 2.43 and 2.45 indicate that the scattering and absorption cross-sections scale with $a^3$ and $a^6$, respectively. Therefore, scattering dominates for larger particles, while smaller particles absorb more efficiently. Interestingly, the transition between the two size regimes is characterised by a distinct colour change. Many coloured glasses employ this phenomenon to great visual effect: small gold nanoparticles embedded in the glass absorb blue and green light giving a red hue, while large particles scatter strongly in the green region of the spectrum, so appear green to the observer.

2.4.3 FIELD ENHANCEMENTS

Assessment of the fields in the vicinity of the nanostructure through equations 2.36 indicates that the resonant enhancement of the cross-sections is accompanied by a resonant enhancement of the electric fields in and around
the structure. Phenomenologically, we can describe this by noting that the electron gas inside our particle is moved backwards and forwards by a characteristic length, $L$, along the axis parallel to the incident field. This then begins to resemble a Fabry-Pérot cavity, whose resonance will be given as $\sin(k_{\text{eff}}L) = 0$, where $k_{\text{eff}} = 2\pi/\lambda_{\text{eff}}$ is the effective wavevector of the mode along the direction of polarization. This corresponds to the relation

$$L = \frac{n}{2} \lambda_{\text{eff}} \quad (2.46)$$

where $n$ is any integer. The lowest and most intense LSPR occurs for $n = 1$, where the nanostructure fulfils a half-wave resonance. The corresponding electric field is illustrated in figure 2.6b and has a maximum outside of the metal structure. Remarkably, LSPRs can give rise to field intensity enhancements of the order of 100 times [21].

This simplistic approach is reliant on our assumption that the nanoparticle is acting as an electric dipole; for larger structures this breaks down and we must adopt a more rigorous analysis of higher order modes (including those of quadrupole excitations). Gustav Mie developed a complete theory of the scattering and absorption of EM radiation by spherical structures through expansion of the internal and the scattered fields to a set of normal modes described by vector harmonics [22]. This formalism leads naturally to the discussion of dark modes and associated Fano resonances, arising through the presence and the interaction of multipole resonances that couple only very weakly to radiation. Both dark modes and Fano resonances are beyond the scope of this thesis, but I direct the reader to the work of Bohren and Huffman [23] and to a somewhat recent review by Luk’yanchuk et al. [24] for a more rigorous discussion.

### 2.4.4 Nanoantennas

In general, an antenna can be thought of as a device that is capable of channelling EM energy into the near-field region around itself when operating as a receiver, and capable of emission into the far-field region when acting as a transmitter. This efficient coupling between the near- and far-fields typically arises through impedance matching and is associated with high field enhancements in the antenna’s vicinity through the increase of energy density. Antenna theory typically addresses the microwave or the radio-frequency regions of the EM spectrum, but we have seen that metallic plasmonic nanostructures are good candidates for antennas in the optical regime: they couple into radiation in a surrounding zone larger than their geometric cross section, they offer spectrally narrow response, and they offer strong field enhancements. For this reason, plasmonic nanostructures are often referred to as optical antennas or nanoantennae.
Optical antennas can take various unusual forms and their properties are strongly shape and material depending. While strongly analogous to their conventional counterparts, there are crucial differences in a nanoantenna’s physical properties and scaling behaviour. Notably, metals are not perfect conductors at optical frequencies, and losses must be considered (the following chapter addresses the source and application of these losses explicitly). A wide variety of optical antenna geometries have been studied, ranging from single metal nanoparticles [25,26], to narrow-gapped dimers [27], and even to complex multicomponent Yagi-Uda like structures [28].

2.5 COMPUTATIONAL ELECTRODYNAMICS

High symmetry means that simple structures – including that of the small isolated single metallic sphere we have considered up until this point – exhibit a single plasmon resonance. If we turn our attention to more complex structures, such as antennas with very small gaps or arrays of plasmonic nanoparticles, we are faced with the breakdown of the simplistic dipole approximation as utilised from equation 2.33 onwards. These complex structures often yield multi-featured resonance spectra with field enhancements far higher than that offered by a single nanoparticle. To address these analytically, we must consider such notions as the hybridisation of elementary plasmons of simpler substructures [29], modification to the structure’s polarisability [30], and the aforementioned dark modes [24]. While many of these concepts are beyond the scope of this thesis, we will address adjustments to the polarisability and implications in the context of plasmonic losses in the following chapter. But it is sufficient to say now that for all but the most simplistic geometries, analytical solutions to Maxwell’s equations do not exist and we must turn to computational electrodynamics to numerically study plasmonic effects.

2.5.1 THE FINITE-DIFFERENCE TIME-DOMAIN METHOD

One such method of study is that of the finite-difference time-domain method (FDTD). It offers direct solutions of Maxwell’s curl equations (2.1b and 2.1d). Unlike our quasi-static approximation approach, the method employs no potentials but instead relies on volumetric sampling of the unknown electric field $E$ and magnetic field $H$ in and around the structure of interest, over a period of time. Overall, FDTD presents a marching-in-time procedure that simulates the continuous development of the EM wave in the finite spatial region modelled with sampled material data (typically in the format of a complex refractive index). As a time-domain method, the solutions provided can cover a wide frequency range with a single simulation.
The first FDTD method, introduced by Yee in 1966 [31], considers the geometric relation in the spatial sampling of the vector field components. Briefly, the algorithm decomposes Maxwell’s curl equations to a coupled set of finite-difference equations. It is reliant on the Yee lattice, which centres the $E$ and $H$ components in a meshed three-dimensional space such that every $E$ component is surrounded by four circulating $H$ components, and every $H$ component is surrounded by four circulating $E$ components. This is illustrated schematically in figure 2.7, which provides a simple picture of three-dimensional space being filled with an interlinked array of Faraday’s law (equation 2.1b) and Ampere’s law (equation 2.1d) contours.

Additionally, the Yee algorithm also centres the $E$ and $H$ components in time in a leapfrog arrangement: all $E$ computations in the modelled space are performed and stored in memory for a particular time using the previously stored $H$ data; all $H$ computations are then completed with this $E$ data and stored. This cycle continues until some defined time-stepping is concluded. This method for advancing both fields negates the need to solve simultaneous equations or use matrix inversion, while still obtaining second-order accurate solutions [32].

Throughout this thesis, Lumerical FDTD Solutions has been employed as a 3D FDTD-method Maxwell solver to determine the cross-sections, the field-profiles, and the local density of electromagnetic states associated with plasmonic nanoparticles.
2.5.2 THE FINITE ELEMENT METHOD

Section II of this thesis introduces both the Navier-Stokes equations and the heat-diffusion equations in the context of fluid flow and heating around plasmonic nanostructures, respectively. Because of their complexity, these equations only present a limited number of analytical solutions and we must turn to numerical methods to address them. For this reason, we introduce the finite element method (FEM).

The method formulates approximate solutions of partial differential equations (such as the equations mentioned above) either by eliminating any time derivatives completely and looking for steady state solutions to a set of algebraic equations, or by casting the equations into equivalent ordinary differential equations before solving. The method divides the domain into smaller, simpler regions – finite elements – in a simmer manner to the meshing procedure in FDTD studies; crucially, FDTD is most commonly implemented with Cartesian meshing whereas 3-dimensional FEM analysis conventionally employs tetrahedral meshing. A simple 2-dimensional comparison of FDTD and FEM meshes is illustrated in figure 2.7b. The simple equations that model each of the finite elements may be assembled into a larger system of equations that, through minimising some associated error, is solved to approximate a solution.

Perhaps the primary challenge with FEM analysis is the formation of an equation set that accurately approximates the equation of interest while maintaining numerical stability. That is, the errors in the initial data and any intermediate calculations do not accumulate to such a degree as to render results meaningless. Careful convergence testing is employed throughout to address this concern.
Both localised and propagating surface plasmons enable high mode confinement beyond the diffraction limit that provide a pathway to manipulate EM radiation at the nanometre scale. However, because the electric field penetrates significantly into nanostructured metals, we must also consider the high losses involved.

Consider first a simple one-dimensional optical cavity of a scale larger than the wavelength of the EM radiation contained within. Assuming no dispersion and no losses, the total energy density of the EM field can be expressed as

\[ U = \frac{1}{2} (E \cdot D + B \cdot H) \]  

Decomposing the energy density into its electric and magnetic contributions, we can note that every half-period of an oscillation of the EM mode within the cavity, energy is transferred from the magnetic field \( u_H \sim \frac{1}{2} \mu H^2 \) to the electric field \( u_E \sim \frac{1}{2} \varepsilon E^2 \) and back. Maxwell’s equations require that \( H = \sqrt{\varepsilon/\mu} E \) and therefore \( u_H = u_E \), indicating that energy is conserved when undergoing this transformation. Recall that within the near-field region surrounding a nanostructure, fields are predominantly electric in nature \([1]\). Therefore, reducing the cavity to a scale smaller than \( \lambda/2 \) renders self-sustaining oscillations impossible, and therefore the cavity must radiate energy. Through incorporating free-carriers into a simplistic Drude model – energy can now be stored in the form of kinetic energy \( u_K \sim \frac{1}{2} \varepsilon_0 (\omega_p/\omega)^2 \). The energy balance may be recovered by tuning the cavity’s geometry such that the radiation frequency and plasma frequency obey \( u_H + u_K = u_E \). Therefore, whilst confinement of the EM mode does allow us to beat the diffraction limit, this comes with the price of having to physically move electrons within the structure. The motion of these carriers cause energy to be lost at a rate proportional to the rate of scattering in the material.

### 3.1 Plasmon Damping in Large Nanoparticles

A quasi-static approximation may be taken when approximating the polarizability of plasmonic nanostructures, which takes the phase of the incident harmonically oscillating EM field to be constant over the volume of such nanostructure. When considering larger particles, however, retardation effects invalidate this approach as light no longer polarizes the nanostructure homogeneously.
As an explicit example, consider a metallic sphere. Expanding the first p-polarised mode of Mie's formulation of polarizability, we can reveal an extension to the polarizability of a sphere [30]:

\[
\alpha = \frac{1 - 10(\varepsilon_1 + \varepsilon_2)x^2 + O(x^4)}{\left(\frac{1}{3} + \frac{\varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right) - \frac{1}{30}(\varepsilon_1 + 10\varepsilon_2)x^2 - i \frac{16}{9} \varepsilon_2^2 x^3 + O(x^4)}
\]  

(3.2)

where \(x = \pi a / \lambda_0\) is the size parameter, \(a\) is the sphere’s radius, \(\varepsilon_1 = \varepsilon_1' + i \varepsilon_1''\) is the relative permittivity of the metal, and \(\varepsilon_2\) is the (complex) permittivity of the surrounding medium. Plasmonic resonance occurs when the polarizability itself experiences resonance, a phenomenon that is explicitly dependent on the particle size.

The second term of the denominator within equation 3.2, which is real for \(\varepsilon_1' >> \varepsilon_1''\), describes the energy shift due to retardation effects [10]. Intuitively, this may be understood through noting that with increasing size of the particle, the distance between charges bound to the structure increases. With this increase comes a decrease in the effective restoring force and a subsequent redshift in resonant frequency. The lengthy fourth-order terms are real and provide higher order corrections to the second-order terms and give rise to higher-order resonances.

The third-order term in the denominator is purely imaginary and represents the radiative damping of the system, which arises as the coherent electron oscillations decay directly into photons [33]. This occurs alongside non-radiative decay pathway in which the plasmon energy is transferred into electron-hole pairs via interband transitions from low-lying d-band to higher sp-conduction bands within the metal, or via intraband transitions within the conduction band. With increasing particle volume, the radiative pathway becomes dominant and gives rise to the broadening of the plasmon resonance [34].

The plasmon bandwidth can be related to the electron oscillation's coherent dephasing; rapid loss of electron motion gives rise to large bandwidths. Electron dephasing times of a few femtoseconds can be determined from the surface plasmon bandwidth, which strongly implies that the dominant relaxation process involves electron-electron collisions [35]. Both the radiative and non-radiative pathways may be accommodated into a simple two-level model allowing us to gather some physical insight into the phenomena. For a linewidth of a plasmon resonance \(\Gamma\):

\[
\frac{1}{\tau_2} = \frac{\Gamma}{2\hbar} = \frac{1}{2\tau_1} + \frac{1}{\tau_2^*}
\]  

(3.3)

Here \(\tau_2\) denotes the total dephasing time, \(\tau_1\) describes the population relaxation time (of both radiative and non-radiative processes), \(\tau_2^*\) is the pure dephasing time – that is, dephasing due to the change in wavevector but not
energy in a collision. Assuming a homogenous size distribution of nanoparticles in a sample, the dephasing time can be computed from the measured width of the plasmon absorption spectrum; various studies are in agreement that the dephasing times are – at most – on the order of 10 fs [36].

3.2 PLASMON DAMPING IN SMALL NANO PARTICLES

For smaller nanoparticles only a dipole term is significant and we can adopt a quasi-static approximation of the structure’s polarizability:

\[ \alpha = 4\pi\varepsilon_0 a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \]  \hspace{1cm} (3.4)

However, this fails to reflect the experimentally observed polarizability for very small nanoparticles; absorption completely disappears for diameters less than 2 nm due to electron density becoming very small. We should however take the notion of bulk-like electronic bands and associated optical properties with some caution as such small scales.

Kreibig and von Fragstein proposed that within such small particles, the mean free path is limited by the nanoparticle’s physical dimensions and electron-surface scattering is enhanced [37]. In gold and silver, typical mean-free paths are on the order of 10 nm in length. In smaller structures, the ballistic electrons would then reach the surface quicker than in a larger particle. Both inelastic and random elastic scattering events serve to reduce coherence in the plasmon oscillation, so the linewidth of the oscillation broadens with decreasing particle size.

We can formulate a mathematical description of this phenomenon by invoking a free-electron Drude model of permittivity. The damping constant \( \gamma \) is equal to the plasmon absorption bandwidth \( \Gamma \) in the case of a perfectly free-electron gas in the limit \( \gamma \ll \omega \), and may then be related to the individual lifetimes (denoted by \( \tau \)) of all electron scattering processes. In the bulk, these are predominantly electron-electron, electron-phonon, and electron-defect, so we can define the bulk damping constant \( \gamma_0 \) as

\[ \gamma_0 = \tau_{e-e}^{-1} + \tau_{e-p}^{-1} + \tau_{e-b}^{-1} \]  \hspace{1cm} (3.5)

The full damping constant, including an electron-surface scattering term, is then given as

\[ \gamma = \gamma_0 + \frac{Av_F}{a}, \]  \hspace{1cm} (3.6)

where \( A \) is a parameter dependent on the specific details of the scattering process (e.g. diffuse or isotropic scattering), \( a \) is the radius of the NP, and \( v_F \) is the Fermi velocity of the conduction electrons. This model has been used to successfully explain the experimentally observed \( 1/r \) dependence of the
plasmon bandwidth as a function of size [38]. A variety of other approaches exist including calculation of the optical response by using quantum mechanical approaches [39], by adopting a jellium model [40], or by incorporating band structures into a size-dependent dielectric function.

Experimentally, comparison between small nanoparticles prepared by different chemical methods is difficult as the capping ligands surrounding the otherwise identical particles can drastically affect the plasmon bandwidth and position [41]. Persson developed a model in which the empty LUMOs of the acceptor molecules on the NP surface may couple to the free electrons in the metal’s conduction band [42]; after plasmon resonance excitation, carriers can transfer back and forward between the donor and acceptor levels causing loss of coherence with the remaining excited electrons and a subsequent broadening of the plasmon bandwidth. This so-called chemical interface damping has been verified to some extent by Hövel et al. for silver nanoparticles deposited on SiO$_2$ substrates and within SiO$_2$ matrices, wherein they observed the predicted plasmon bandwidth broadening [43].

3.3 ABSORPTION OF ELECTROMAGNETIC QUANTA IN METALS

We now further discuss the non-radiative decay pathway of a plasmon; although its presence is evident in the absorption cross section of a nanoparticle, we have not yet addressed the underlying physical mechanisms. Consider the absorption of a photon by a metal described by a simple band structure as in figure 3.1. Take two states with wavevectors $k_1$ and $k_2$, and energies $E_1$ and $E_2 = E_1 + \hbar \omega$ below and above the Fermi level $E_F$, respectively. The two momenta’s magnitudes differ by $\Delta k_{1,2} > \Delta k_0 \sim \omega v_F$ where $v_F$ is the Fermi velocity (around $10^6$ ms$^{-1}$ in metals). This momentum difference is typically larger than that provided by a photon [1].

Figure 3.1a illustrates a scenario in which a phonon or lattice imperfection with wavevector $q_{ph}$ assists absorption. The induced carriers from absorption processes are considered ‘hot’ carriers if their energies are larger than thermal excitations at ambient room temperatures, approximately 25 meV [44]; this phonon-assisted process results in two hot-carriers – a hot-electron and a hot-hole. The probability of phonon or defect assisted absorption is proportional to $\gamma_{ph} \omega_F^2 / \omega^2$. It is Fermi’s golden rule that gives rise to this large value due to the huge density of available states above the Fermi level. Electron-phonon scattering on a monometallic particle, however, plays a relatively minor role, because such phonons involve atoms of the same charge and do not possess electrical multipolar moments [45].
Electron–electron scattering can also give rise to absorption. Figure 3.1b shows two scattered electrons transitioning from states \( k_1 \) and \( k_2 \) to \( k_3 \) and \( k_4 \) above the Fermi level. This Umklapp scattering process conserves momentum with the inclusion of the reciprocal lattice vector \( G \):

\[
  k_3 + k_4 = k_1 + k_2 + G .
\]  

(3.7)

Energy conservation indicates that

\[
  E_3 + E_4 = E_1 + E_2 + \hbar \omega
\]

(3.8)
and, therefore, the incident photon energy is shared between four carriers. Consequently, this process does not create especially hot carriers and thus – in the context of our discussion – is not particularly useful [1].

Figure 3.1d illustrates interband absorption from the d to the s-band in the metal. This process becomes significant in gold below around 600 nm and in silver below around 400 nm. The hot-hole formed deep in the d-band, whilst very energetic, may not be effectively harvested due to its high effective mass and low velocity. The electron meanwhile is typically promoted to an energy value very close to the Fermi level, so is not regarded as hot.

The final mechanism of absorption, and the most relevant to our discussion, is that of direct absorption or Landau damping. This quantum mechanical process occurs when the phase velocity of the surface bound wave becomes comparable to the thermal speed of the electrons [46]. This arises from the confinement of the surface plasmon mode: modes inside the metal significantly shorter than half the wavelength of the incident photon will include spatial frequencies larger than \( \Delta k_0 \). They therefore can undergo the diagonal direct absorption illustrated in figure 3.1c.

The absorption via Landau damping is dependent of the scale of the plasmon mode and becomes comparable to the previously mentioned bulk contributions when the mode is around 10 nm [1], which has two significant consequences. Firstly, this confinement dependent loss restricts our ability to focus light and places a limit on the maximum attainable Purcell factor [47]. And secondly, even if an ideal metal with no bulk losses existed, confinement dependent absorption means losses are unavoidable.

Landau damping is the preeminent mechanism for generating hot carriers. The average energy of the each hot carrier is half the energy of the incident photon and the angular distribution is relatively directional (factor of 4). Further, the carriers are all generated right at the surface and thus are capable – provided they have enough kinetic energy in the forward direction – of being emitted. The rate of Landau damping surpasses the rate of phonon and defect assisted damping when the mode penetration (or the entire nanoparticle size) becomes less than the mean free path. Thus, by exploiting the geometric tunability of LSPRs of metal nanoparticles, it should then be possible to position the plasmon frequencies where hot carrier production is maximised.

### 3.4 Non-Radiative Plasmon Decay

Both hot-electrons and hot-holes can be employed in chemical and physical processes. Their capacity to do so however is limited by rapid relaxation of the carrier’s energies into heat. The hot-carriers generated from plasmonic decay will quickly redistribute their energies amongst many lower energy carriers.
We have now discussed that, following the excitation of a LSPR (figure 3.2a), the plasmon decays into hot-carrier pairs on the timescale $\tau_L$ ranging from 1 to 100 fs. Given that the energy of an LSPR is typically smaller than the work function of metals used in the field of Plasmonics, hot-electrons will take on energies from the Fermi level $E_F$ up to $E_F + \hbar \omega_{LSPR}$. Figure 3.2b illustrates the highly athermal distribution of electron-hole pairs as a result of Landau damping.

The number of hot-carriers that form after the decay of a single plasmon is uncertain. Some argue that given the transition matrix element for pair formation is small, the most likely product of plasmon decay is a single pair [48]. Similarly, some argue that since there is evidence that a single electron can launch a plasmon [49] and that non-radiative quenching of the electronic excitation of molecules near plasmonic nanoparticles occurs (thus suggesting LSPR conditions can be met by a singular electronic molecular transition), the inverse process can be presumed to be true also. By contrast, others argue that the absorption cross section of a plasmonic nanoparticle can be hundreds of times larger than that of a single electron transition in other highly absorbing molecules; the oscillator strength is therefore significantly higher in a LSPR.
than that of a single-electron transition. The quantum-mechanical Thome-Reiche-Kuhn sum rule notes that the oscillator strength of all possible transitions sum to the number of that molecule’s electrons and therefore many hot-carriers can be produced from plasmon decay [3].

Sundararaman et al. recently combined experimental dielectric functions with electronic states calculated from first principle density functional theory to estimate the initial distribution of hot carriers in commonly used plasmonic materials [50]. Figure 3.3 indicates the permitted transitions of electrons and resultant hot-carrier energy distributions. Though they go on to investigate geometry effects through considering thin metallic films of various thicknesses, these theoretical results were determined for surface plasmon decay on an infinite plane. Manjavacas et al. recently began work in developing a theoretical model for plasmon-induced hot-carrier generation and applied it to 3-dimensional silver nanoparticles and nanoshells [51]. Their work, though incomplete, provides the beginnings of a solid theoretical background for understanding hot-carrier generation in realistic nanostructured geometries.

Permitting they are not first harvested, the particles redistribute their energy amongst lower energy electrons via electron-electron scattering following hot-carrier generation (figure 3.2c). In this process, hot-electrons above the Fermi level collide with an electron below, quickly leading to thermalisation of carriers where all possess energies only slightly above the Fermi level [1]. Time-resolved studies for extended metal surfaces suggest relaxation times $\tau_{el}$ of
around 100 fs to 1 ps, in which an initial Fermi-Dirac distribution of energies forms, characterized by a very large effective electron temperature \[52\].

Finally, the heat from carrier collisions is transferred to the material surrounding the metallic nanoparticle (figure 3.2d). This is highly dependent on the NP material, size, and the thermal conductivity properties of the surrounding environment, but has been shown to take from 100 ps to 10 ns \[44\].

### 3.5 The Role of Plasmon-Mediated Hot-Carriers

A trade-off between loss and localisation has limited the widespread adoption of plasmonics into integrated photonics. There is a large effort to develop strategies that mitigate these losses, such as the design of new plasmonic materials, using materials that exhibit optical gain \[53\], and employing advances in nanofabrication techniques \[54\]. The discussion now, however, will turn to the similarly large effort to embrace these losses and put them to use in such applications as catalysis and localised heating.

#### 3.5.1 Solid State Collection

Metal–semiconductor (M-S) junctions formed at the interface exhibit either rectifying or non-rectifying properties: the latter gives rise to an Ohmic contact, while the former results in a Schottky junction. Fowler theory for internal photoemission \[55\] has successfully described the transport of hot-carriers over Schottky barriers for nearly a century. The semi-classical model considers photoexcited electrons incident on the potential barrier at the M-S junction. Carriers with energy less that the Schottky barrier height (\(\phi_B\)) are reflected; carriers with energies higher are transmitted.

Figure 3.4a illustrates a Schottky barrier formed from an n-type semiconductor and a metal upon contact (plasmonic p-type Schottky devices also exist \[56\]). The metal absorbs an incident photon of energy \(\hbar \nu\) and launches a plasmon. Hot-electrons formed from the plasmon decay are transiently promoted to an energetic state above the Fermi level. The hot-electron may move towards the M-S interface and, assuming the energy of the hot electron exceeds the Schottky barrier, it may pass into the semiconductor and a photocurrent will be detectable. This is not however the complete picture: we must also consider momentum. It is often assumed that hot-electrons may be considered free with an isotropic initial momentum, which is not unreasonable for a semi-infinite planar interface due to the large wavevector mismatch between the initial plasmon and the generated hot-carrier \[57\]. For finite nanoparticles however, the carriers are bound to the structure and require more rigorous treatment, considering the electron dispersion within the metal \[58\].
Only the normal component of the momentum changes as the carrier passes the interface, suggesting that a sufficiently small tangential momentum is required such that the carrier’s kinetic energy contribution in the semiconductor must be less than the excess energy above the Schottky barrier; carriers with a larger tangential momentum component undergo reflection. Consider the constant energy contour connecting all possible final momentum states \( k \) for a given kinetic energy \( E_K \):

\[
E_K = \frac{\hbar^2}{2m^*_e} \left( k_{ix}^2 + k_{iy}^2 \right)
\]  

where \( m^*_e \) is the effective mass of the electron and the subscript \( i \) refers to either the metal or the barrier. Figure 3.4c illustrates the height of Fermi levels for commonly used combinations of plasmonic metals and semiconductors; the band offset with the semiconducting material illustrated in figure 3.4b gives rise to different sized contours (circles for free-electron materials) and therefore to an escape cone around normal incidence of solid angle \( \Omega \). For angles beyond \( \Omega \), total internal reflection occurs.

An early example of using hot-carriers from plasmon decay to induce a photocurrent over a Schottky junction was provided by Knight et al. [8]. This was accomplished by fabricating a gold nanoantenna on a silicon substrate, where an M-S contact is formed at the interface. In this configuration, the generated photocurrent is not restricted to the photon energies above the semiconductor bandgap, but to photon energies above the Schottky barrier height (figure 3.5a-c). Such a device can therefore detect light well below the semiconductor bandgap with no need for an applied bias voltage.
To resolve plasmon-induced and photoexcited carriers generated within the same device, Zheng et al. extended upon this work using a nanowire-based device on a wide-bandgap semiconductor: gold nanowires on TiO$_2$ provide a Schottky barrier, whilst gold nanowires with a thin titanium adhesion layer provide an Ohmic barrier (figure 3.5d,e) [60]. They demonstrate that, with the Schottky device, the photocurrent responsivity may be determined by integrating the enhancement in electric field over a volume within the electron’s mean-free path on the surface of the plasmonic NP. Similarly, for an Ohmic device, the responsivity may be calculated by integration of the gold’s imaginary permittivity over the same volume.
Knight et al. overcame some of the aforementioned limitations on the permitted momentum states of the hot-carriers by embedding plasmonic nanostructures within a semiconductor, effectively forming a 3D Schottky barrier enabling ballistic electron movement across multiple interfaces [61] (figure 3.5h-k). Doing so increased the responsivity of the device to 25 times that of a planar diode. These results suggest that 3D Schottky barriers may be key in optimising plasmonic hot-carrier devices.

In the above examples, careful consideration of band alignment between the metal work function and the conduction bands of the semiconductor is required to optimise the device's efficiency. Recent work (figure 3.5l) has however has demonstrated the direct formation of a hot-electron in the conduction band of the semiconductor following plasmon decay and a corresponding hole in the metal nanoparticle [62]. This interfacial charge transfer mechanism requires further theoretical and experimental investigation but could present an exciting opportunity for plasmonic hot-carrier devices.

### 3.5.2 PLASMON-ENHANCED CATALYSIS

The injection of hot-carriers produced by plasmon decay directly into molecules adsorbed at the surface of the structure that supported the plasmon resonance has recently become an active area of research. Hot-electron induced femtochemistry at surfaces is a broad class of chemical reactions that have been investigated in various contexts, including those in which the hot-carriers are generated through non-plasmonic means [63].

The general proposed mechanism for instigating plasmon-enhanced catalysis involves the injection of a plasmonic hot-electron from the metal into the antibonding state of an adsorbed molecule (figure 3.6a). Similarly, the production of hot-holes following plasmon decay means that electron transfer from the highest occupied molecular orbital of an adsorbed molecule to the NP becomes possible. The Fermi-Dirac distribution describes a continuous energy distribution of excited electrons around the Fermi level. At significantly short timescales – such as that of the formation of a non-thermal hot-electron population following Landau damping in planar structures – it is only the adsorbate resonances that are near the Fermi level that may be populated [64]. Planar extended surfaces therefore are not especially useful for plasmon-enhanced catalysis.
Due to such effects as reduced electron-electron scattering and increased confinement, the lifetime of the non-thermal hot-electron population in nanostructured materials is however much longer [51]. Nanoparticles are therefore more suited for state-selective electron occupation of adsorbate resonances, enabling us to selectively desorb or dissociate an adsorbate on that nanoparticle’s surface. We should note however that the resultant electronic distribution (as in figure 3.3) suggests that, due to the high concentrations of low energy electrons, this indirect charge-transfer mechanism would preferentially favour interactions involving acceptor states with energies close to the Fermi level. This seems to imply that the indirect mechanism limits the opportunity to selectively target specific orbitals for photochemical reactions [65].

Alternatively, we note that there is also a direct charge-transfer mechanism (figure 3.6b). The above indirect mechanism assumes that hot-carriers first form on the surface of the nanoparticle and are transferred to the adsorbate; the direct mechanism, sometimes referred to as chemical interface damping, involves plasmon-mediated enhancement of the transition matrix between states localised on the adsorbate [66]. Here, plasmons interact with the accessible adsorbate states, thereby scattering the adsorbate charge carriers. Yan et al. recently supported this alternative mechanism with time-dependent density functional theory measurements, demonstrating that hydrogen adsorbed on a silver nanoparticle surface dampens plasmon oscillations, enhancing electron excitations from bonding to antibonding orbitals on the molecule [67]. This seemingly comes as a result of there being a high density of electronic states corresponding to the particular transition at a photon energy corresponding to the LRPR of the nanoparticle.

Figure 3.6 Charge-transfer mechanisms in a metal/adsorbate system. a, Indirect charge transfer in which plasmon decay results in a non-thermal electron distribution. Those electrons at or above the energy level of the lowest unoccupied adsorbate orbital may transfer into such an orbital, permitting catalysis. b, Direct mechanism of charge transfer where plasmon decay excites electron from the highest occupied adsorbate state to a more energetic unoccupied state directly. c, Alternative direct mechanism in which hot-electrons transfer directly from the metal into the adsorbate’s unoccupied acceptor state. Figures adapted with permission from ref. [65].
Similar to the interfacial solid-state charge transfer mechanism discussed at the end of the previous subsection, a final mechanism involves direct charge transfer in which hot-carriers are injected directly into the adsorbate acceptor state without first occupying available high energy metallic states (figure 3.6c) [68].

Several studies of chemical processes induced by plasmonic hot-carriers are illustrated in figure 3.7. An early significant work by Christopher et al. observed various oxidation reactions catalysed by silver, including NH₃ oxidation, CO oxidation, and ethylene epoxidation on nanostructures [69]; it was demonstrated for the first time that metallic nanostructures are able to yield chemically useful hot-electrons.

Plasmon enhanced catalysis is not limited to only silver structures: a 2012 study from Mukherjee et al. reported dissociation of hydrogen molecules adsorbed on gold nanoparticles supported on TiO₂ substrates [70]. Exciting the gold nanoparticle’s LSPR produces hot-electrons of energy sufficiently high as to occupy the H₂ antibonding orbital and trigger dissociation. This was verified to be plasmon induced and not simply a thermal effect by observing the production rate of HD molecules following resonant illumination of nanoparticles when exposed to a mixture of H₂ and D₂ molecules (figure 3.7a-c). The same group extended this study and looked into the role of the supporting substrate. In replacing TiO₂ with SiO₂ (a much higher bandgap semiconductor), it was found the reactivity increased by two orders of magnitude (figure 3.7c), and that the conduction band of the semiconductor acts as an electron acceptor, limiting the number of hot-electrons available for dissociation [71].

The previous studies involved hot-electron transfer to antibonding adsorbate orbitals; hot-hole catalysis involves electron transfer from occupied adsorbate orbitals into states in the metal below the Fermi level that are transiently unoccupied. Jin et al. announced the surprising discovery that silver nanoprisms may be synthesised through plasmon excitation in smaller silver seed particles [72]. Numerous follow-up studies from this group and others have elucidated some of the finer details [73,74]: it appears that under resonant illumination hot-holes in the seed nanoparticle are occupied by electrons from citrate ions in solution, yielding negatively charged nanostructures (the accompanying plasmon-induced electron remains in an elevated energy state). Positively charged silver ions in solution are then reduced at the nanoparticle surface via Coulomb forces resulting in prism growth (figure 3.7d, e). Though very few studies that concern plasmon-derived hot-hole driven chemistry exist, we should note that the broad application to various forms of oxidation chemistry is an exciting prospect within plasmonics.
Devices that look to fully exploit hot-carrier yields following plasmon decay must consider both half reactions within the redox cycle. Recent work from

Figure 3.7 Examples of plasmon-induced hot-carrier catalysis. a, Schematic illustrating the hot-electron induced photodissociation of H₂ by transfer of a hot-electron into the antibonding orbital of an adsorbate molecule, resulting in the formation of H₂⁻ at the gold NP surface. b, Comparison of light-induced HD production (grey) relative to that produced by the equivalent thermal response with no illumination (red). c, as in b but replacing the TiO₂ substrate with SiO₂. Note the increase in the vertical axis scale depicting rate of HD production. d, Hot-hole transfer from a photoexcited silver NP to the highest occupied molecular orbital of an adsorbed citrate molecule, resulting in citrate oxidation reduction of surrounding Ag⁺ ions, and e, NP growth into nanoprisms. f, Schematic of the cross section of a photosynthetic unit capable of splitting water. The inner core is a gold nanorod, which is capped with TiO₂ and platinum NPs to serve as a hydrogen evolution catalyst. Cobalt-based material on the sides serve as oxygen evolution catalysts. g, Measured O₂ and H₂ products over time from the device depicted in f illuminated at 1.5 suns. h, Architecture of a broadband metal-semiconductor-NP absorber where TiO₂ is positioned between gold NPs and a gold film. i, Band diagram illustrating the working principle the device depicted in h: upon plasmon decay, hot-electrons in the NPs are injected into the TiO₂ and transferred to the platinum counter-electrode to enable catalysis. Hot-holes meanwhile oxidise methanol in solution. Figure a,b, reproduced with permission from ref. [70]; c, from [71]; d, from [74]; e, from [72]; f, g, from [75]; h,i, from [76].
Mubeen et al. is particularly significant given that their developed device generates both plasmon-induced hot-electrons and hot-holes, which are then utilised to split water [75]. Furthermore, it is able to do so using only solar illumination. Figure 3.7f illustrates the device schematically: each gold nanorod in an array that serves as a plasmonic antenna is capped with crystalline TiO$_2$, which gives rise to a Schottky barrier (as discussed in the previous section). Platinum nanoparticles are deposited on top of this capping layer, and a cobalt based oxygen evolution catalyst (Co-OEC) is deposited on the side of each rod in the array. When illuminated at resonant wavelength, the plasmon supported by the rod decays and the hot-holes are transported through the Co-OEC and dissociate water molecules to O$_2$ gas and positively charged hydrogen ions. Simultaneously, hot-electrons are injected over the Schottky barrier and transported through to the platinum nanoparticles. When submerged in water, the platinum layer permits reduction of the positively charged hydrogen ions to form H$_2$ gas. The device can evolve hydrogen for more than 66 hours with no efficiency decrease and, although it exhibits lower solar-to-hydrogen efficiency (around 0.1%) than other non-plasmonic devices, provides an exciting example of the practical implementation of plasmonic hot-carriers for alternative sustainable fuel production.

Other examples of devices that combine carrier transfer between metal and adsorbate and between metal and semiconductor include that devised recently by Ng et al. The group utilised a metal-semiconductor-nanoparticle structure to achieve broadband absorption from 600 to 1000 nm at efficiencies that exceed 90% [76]. Their device, upon visible light illumination and non-radiative plasmon decay, relies on hot-electron injection from gold nanoparticles to TiO$_2$ over a Schottky barrier. The structure is used as a photoanode within a photoelectrochemical cell as illustrated in figure 3.7i. The hot-electrons from the nanoparticle are transported into accepting states of the TiO$_2$ and then on to a platinum counter electrode to reduce hydrogen ions in solution. Hot-holes are occupied through oxidation of methanol (in which the structure is immersed) to ethanol and isopropanol. With a quantum yield for electron injection of over 24%, the device signifies significant advancements in plasmon-based opto-electronic devices.

3.5.3 HEAT

As previously highlighted in figure 3.2, carrier relaxation and thermal dissipation follow the decay of a plasmon and lead to significant heating of the nanostructure and its surrounding environment [52]. Indeed, perhaps the most widely utilised aspect of plasmonic losses is that of plasmonic heating. Many have embraced this phenomena and put it to use in such practical plasmonic applications as modification of a polymer surface [77], chemical separation in
nanofluidics [78], and local manipulation of phase transitions [77]. Here we highlight just a few of these exciting developments.

Despite having been in use for nearly 50 years [79], nanoparticles are increasingly finding new applications in biomedical research. Plasmon enhanced photothermal cancer therapy is one particularly promising application: this employs nanoparticles in which the plasmon resonance is tuned via geometric or material adjustments to the near-infrared spectral region. Within this window, light is able to penetrate much deeper into living tissue. The organism is injected with the functionalized nanoparticles, which assemble within the tumour. A laser is then used to illuminate the subject, and the local thermal heating induces hyperthermia, resulting in cell death and tumour remission (figure 3.8a) [80]. The large absorption cross section associated with the nanoparticle’s LSPR means that the intensity of radiation required relative to other photothermal methods is very low. The requirement to heat only locally gives rise to large increases in speed and control, with an accompanying reduction in cost.

Plasmonic heat loss can be employed to grow nanostructures. Figure 3.8b schematically illustrates plasmon-assisted nanowire growth wherein a gold nanoparticle catalyses the formation of a silicon nanowire [81]. In the work by Cao et al., plasmon-induced local heating of gold nanoparticles atop a silica substrate allow the nanoparticle to decompose a precursor gas and initiate chemical vapour deposition (CVD) in highly localised positions. The heating was provided by a focused laser beam at 532 nm, close to the resonant frequency of the NP. This method can be conducted with laser intensities of just a few milliwatts and therefore can be over 5 orders of magnitude more efficient.

Figure 3.8 Physics and applications of hot-electron induced heating. a, Upper: mouse with subcutaneous prostate cancer tumour on same day as treatment with plasmon-enhanced photothermal therapy. Lower: 10 days after treatment. b, Plasmon-assisted nanowire growth in which a continuous-wave laser at low power heat the catalytic metallic NPs, inducing semiconductor nanowire growth. Inset: SEM image of such a nanowire. c, Schematic of NP-enabled steam generation: NPs absorb light and heat to temperature above the boiling point of the fluid vapour forms around the surface, and the complex moves to the surface of the liquid where steam is released. Figure a, reproduced with permission from ref. [80]; b, from [81]; c, from [82].
than conventional CVD techniques in which heating of the entire substrate is required.

Neumann et al. recently demonstrated the ability of absorptive nanoparticles dispersed in water to generate steam upon solar illumination (figure 3.8c). Silica-cored, gold-shelled nanoparticles were fabricated at such a size that absorption was present across the entire solar spectrum. Focusing sunlight onto the solution results in direct steam generation as, when appropriately illuminated, nanoparticles can reach temperatures well above water's boiling point [82]. This process occurs at notably high efficiencies, with only 20% of the incident energy going the heating of the bulk fluid solution. This technique may be applied as a means of solar distillation; that is, using sunlight to separate various fluids within a mixture, and therefore has significant potential for use in a large variety of energy relevant applications.
II HEATING & PLASMONICS
4 PLASMONIC OPTICAL PRINTING

The previous chapter introduced the notion that the enhanced light absorption supplied by metallic nanostructures turns them into effective nano-sources of heat, remotely controllable using only light. They therefore present an unprecedented method of controlling thermal-related phenomena at the nanoscale. Here we look at some of the underlying physics beneath this nanoscale temperature increases and its corresponding effects on the nanofabrication technique of optical printing.

4.1 OPTICAL HEATING

The power absorbed by a nanoparticle can be expressed simply as a function of the absorption cross-section:

\[ Q = \sigma_{abs} I \]  \hspace{1cm} (4.1)

where \( I \) is the irradiance of the incoming light. In the case of a plane wave (which is often a suitable approximation when considering a single nanostructure), \( I = n_s c_0 e_0 |E_0|^2/2 \).

Alternatively, one may derive the heat generation from the heat power density \( q(r) \) within the nanoparticle, such that \( Q = \int_V q(r) dV \), where the integral considers the nanoparticle volume, \( V \). It is the Joule effect that gives rise to this heat, and therefore the density may be written as:

\[ q(r) = \frac{1}{2} Re [J^*(r) \cdot E(r)] \] \hspace{1cm} (4.2)

where \( J \) is the complex amplitude of the electronic current density inside the structure. Given that \( J(r) = i\omega P \) and \( P = \varepsilon_0 \varepsilon(\omega) E \), we can cast the heat density as

\[ q(r) = \frac{\omega}{2} Im[\varepsilon(\omega)]e_0 |E(r)|^2 \] \hspace{1cm} (4.3)

The heat generated within a nanostructure is therefore directly proportional to the intensity of the electric field inside the metal; design of a nanostructure may then be carefully optimised to increase or decrease this property as desired.

This heat gives rise to a temperature distribution \( T(r) \) inside (4.4a) and outside (4.4b) of the nanoparticle, as determined by the solution to the heat transfer equation (see section 4.5 for further details):

\[ \nabla \cdot [\kappa(r) \nabla T(r)] = -q(r) \] \hspace{1cm} (4.4a)

\[ \nabla \cdot [\kappa(r) \nabla T(r)] = 0 \] \hspace{1cm} (4.4b)
where $\kappa(r)$ is the thermal conductivity of the medium in question (the metal or the surrounding substrate).

As an example, consider a spherical nanoparticle of radius $a$ under continuous illumination in a homogeneous medium of thermal conductivity $\kappa$; solving equations 4.4 leads to a temperature increase [9]:

$$\Delta T(r) = \frac{\sigma_{abs} I}{4\pi\kappa a}, \quad r < a$$  \hspace{1cm} (4.5a)  

$$\Delta T(r) = \frac{\sigma_{abs} I}{4\pi\kappa r}, \quad r > a$$  \hspace{1cm} (4.5b)

Figure 4.1 Electromagnetic response and heating of 60 nm diameter gold nanoparticle a, Scattering, absorption and extinction cross sections when immersed in water, and illuminated, calculated with Mie theory. b, Steady state temperature increase in and around the same 60 nm Au nanoparticle upon illumination with a 532 nm source with an irradiance of $I = 110$ kW·cm$^{-2}$. 
For a 60 nm diameter Au nanoparticle immersed in water, illuminated near plasmon resonance (at 532 nm) with an plane wave of intensity 1 mW·µm\(^{-2}\), the particle experiences an increase of approximately 50 °C (figure 4.1b).

This steady-state temperature profile is established very quickly; the typical duration of the transient regime, \(\tau_{tr}\), is independent of the temperature increase itself, but rather depends on the characteristic size of the system, \(L\)

\[
\tau_{tr} \sim \frac{L^2 \rho c_p}{3k}\]  

(4.6)

where \(\rho\) is the mass density and \(c_p\) is the specific heat capacity of the nanoparticle, respectively [83]. The particle-fluid system illustrated in figure 4.1b would therefore reach a steady state temperature profile in a timescale on the order of 4 ns.

4.2 FUNDAMENTALS

Optical printing is a versatile method of affixing nanoparticles from a colloidal synthesis to a substrate; optical forces are used to select and position the nanoparticles and van der Waals attraction is used to bind the structures to the substrate. Introduced as a method of fabrication by Urban et al. in 2010 [84], their seminal work demonstrated the practicality of printing single spherical gold nanoparticles with a positioning precision of 50 nm without the need for prior 3-dimensional trapping.

Briefly, the method utilises a positively-charged colloidal suspension of CTAB-coated Au nanoparticles; the equal polarity of surface charges prevents the particles from binding in solution. Similarly, the substrate is functionalised with a layer-by-layer deposition of the cationic polyelectrolyte PDADMAC, which serves to prevent unwanted binding of the particles to the surface. The total interaction between the substrate and the nanoparticles is then given by as the sum of the electrostatic repulsion \(F_{elec}(z)\) and the van der Waals attraction \(F_{vdw}(z)\), which may be determined using the classical Derjaguin-Landau-Verwey-Overbeek formalism [85] of differentiation of the interaction energies between a charged surface and charged sphere:

\[
F_{elec}(z) = \frac{\pi \varepsilon a k}{2A a^3} \left( \zeta_{surf}^2 + \zeta_{NP}^2 - 2\zeta_{surf}\zeta_{NP} e^{\varepsilon z t} \right) (\cot(zt) - 1) \]  

(4.7a)

\[
F_{vdw}(z) = \frac{2A a^3}{3z^2(z + 2a)^2} \]  

(4.7b)

where \(z\) is the perpendicular distance of the nanoparticle to the substrate, \(\zeta\) is the zeta potential, \(\varepsilon\) is the permittivity of the surrounding medium, \(A\) is the Hamaker constant, and \(t^{-1}\) is the thickness of the electric double layer.
Figure 4.2c illustrates the magnitude of these forces for typical experimental conditions ($\zeta_{NP} = 30$ mV, $\zeta_{surf} = 30$ mV, $A = 2.5 \times 10^{-20}$, $t^{-1} = 2.2$ nm); an effective potential barrier for the nanoparticles is then formed. Optical printing relies on sufficient optical forces from an incident focused laser to overcome this barrier and affix the particle to the substrate. In utilising a laser source tuned to the plasmon resonance of the colloidal nanoparticles, one has the advantage of enhanced interaction with incoming light.

Given that optical forces decrease rapidly with distance to the focal plane (see the following subsection), only nanoparticles sufficiently close to the focal volume of the incident laser beam experience a force adequate to overcome Brownian motion and the aforementioned potential barrier. Simply regulating the laser power is sufficient to change the size of this active focal volume. Urban et al. employed dark field microscopy to monitor this stochastic process and determine when the nanoparticle was stabilised (and therefore printed), after which the substrate is shifted radially to a pre-determined location and the process is repeated. In this manner, one is capable of producing nanoscale devices and circuitry with distinct nanoparticles.

4.3 Optical Forces

When light is incident on a body, it is either absorbed or scattered; the time-averaged force on the particle due to the field will be dependent on the nanoparticle and the illumination laser itself. Explicitly, the time averaged field
momentum is zero when averaged over one complete oscillation; the time-averaged force \( \langle F \rangle \) on a particle due to a harmonic field is then due solely to a mechanical force, which may be determined though integration of Maxwell’s stress tensor \( \mathbf{T} \) over a closed surface \( S \) surrounding the particle [11]:

\[
\langle F \rangle = \int_S (\mathbf{T}(r, t)) \cdot \mathbf{n}(r) ds
\]

(4.8)

where \( \langle \ldots \rangle \) denotes the time average, and \( \mathbf{n} \) the unit vector normal to \( - \) and \( ds \) is an infinitesimal surface element of \( - \) the particle surface.

For a harmonic EM wave incident on a particle immersed in a (non-dispersive) medium of permittivity \( \varepsilon \) and permeability \( \mu \), Maxwell’s stress tensor takes the form:

\[
\mathbf{T} = \left[ \varepsilon_0 \varepsilon \mathbf{E} \mathbf{E} + \mu_0 \mu \mathbf{H} \mathbf{H} - \frac{1}{2} \left( \varepsilon_0 \varepsilon E^2 + \mu_0 \mu H^2 \right) \mathbf{I} \right]
\]

(4.9)

where the notation \( \mathbf{E} \mathbf{E} \) denotes the outer product, and \( \mathbf{I} \) the unit tensor.

The above equations are of general validity, and therefore allow calculation of the optical forces on any arbitrary geometry. Importantly, the fields used in the calculations are self-consistent fields of the problem, that is, they are a superposition of the scattered and incident fields. It is then necessary to solve first for such fields, which – for anything but the simplest of geometries – requires the use of such computational methods as FDTD or FEM.

One such simple geometry, where an analytical solution is available, is that of a small spherical nanoparticle. For a particle of a size on the same order as the incident monochromatic wavelength, the time-averaged radiation force takes the form of the non-relativistic Lorentz force:

\[
\langle F \rangle = \frac{1}{4} \varepsilon_0 \varepsilon \alpha' \nabla (E^* E) + \frac{1}{2} \varepsilon_0 \varepsilon \alpha'' \text{Im} \left[ \sum_i E_i^* \nabla E_i \right]
\]

(4.10)

where \( \alpha' \) and \( \alpha'' \) are the real and imaginary parts of the nanoparticle’s complex polarizability, the superscript \( * \) indicates the complex conjugate, and the subscript \( i \) runs over all three spatial dimensions. Here we have assumed that the only field of interest is the incident EM field given that the dipole is insufficient in strength to disturb the incoming light.

We may decompose the above equation into a sum of the so-called gradient force \( \langle F_{\text{grad}} \rangle \), and the scattering force \( \langle F_{\text{scat}} \rangle \):

\[
\langle F_{\text{grad}} \rangle = \frac{1}{4} \varepsilon_0 \varepsilon \alpha' \nabla (E^* E)
\]

(4.11a)

\[
\langle F_{\text{scat}} \rangle = \varepsilon_0 \varepsilon \alpha'' \text{Im} \left[ \sum_i E_i^* \nabla E_i \right]
\]

(4.11b)
The gradient force derives from the gradient of the incoming laser's intensity profile. Any particle that may be polarized is then accelerated towards the position of maximum intensity of the incident beam, thus enabling optical trapping in all three dimensions. The scattering force, however, is representative of the momentum transfer to the nanoparticle from the external field by both scattering and absorption and serves to push the particle along the optical axis.

As evidenced in equations 4.11, both components of the optical force are dependent on the nanoparticle's size, shape, and composite material. In tuning these parameters along with the illumination wavelength and beam shape, we have control over which of the force components dominates; for systems in which \( \langle F_{\text{scat}} \rangle \ll \langle F_{\text{grad}} \rangle \), the particles may be efficiently stabilised in the focal volume of the beam. Conversely, by illuminating spherical particles near their plasmon resonance, the imaginary component of the polarizability typically gives rise to a strong scattering force, transporting the particle along the beam. Figure 4.2b illustrates this concept schematically.

Many conventional optical printing setups – including our own – utilise a focussed Gaussian beam, for which the field at a distance \( z \) from the beam's focal plane and at a radial distance \( r \) from the optical axis, may be expressed as

\[
E(r, z) = E_0 \frac{w_0}{w(z)} e^{-r^2/w(z)^2} e^{i(kr^2/2R(z))} e^{i(kz-\omega t)} e^{-i\eta(z)}
\]

(4.12)

where

\[
w(z)^2 = w_0^2 \left( 1 + \left( \frac{z}{z_0} \right)^2 \right) \quad (4.13a)
\]

\[R(z) = z \left( 1 + \left( \frac{z}{z_0} \right)^2 \right) \quad (4.13b)
\]

\[\eta(z) = \tan^{-1} \left( \frac{z}{z_0} \right) \quad (4.13c)
\]

Here we have defined the *Rayleigh range* \( z_0 = \pi w_0^2 \sqrt{\varepsilon} / \lambda \) – the distance along the beam at which the cross-sectional area is double that relative to the focus, where the beam radius is given by \( w_0 = \lambda / (NA \pi) \). Additionally, we have introduced *Guoy’s phase* \( \eta \), which results in an increase in the apparent wavelength near the waist, and \( R \) that describes the radius of curvature of the wavefront [16]. A schematic figure illustrating the geometric significances of these quantities is included in Appendix A2.

In combining equations 4.11 and 4.12, we arrive at expressions for the magnitudes of the radial and \( z \)-components (denoted by the subscripts \( r \) and \( z \), respectively) of both the gradient and scattering forces for a paraxial focussed Gaussian laser beam.
With these equations, we are then equipped to estimate the forces upon individual nanoparticles during the optical printing process. Figure 4.3 illustrates the expected optical force profile using a Gaussian focused beam with an intensity of 10.4 mW·µm⁻² (a value chosen to correspond to upcoming experimental conditions).

4.4 LIMITATIONS OF CURRENT PRINTING METHODS

Though the printing method is reliant on many elements of classical optics, the positional accuracy is not strictly dependent on optical diffraction. Urban et al.’s seminal paper noted a precision of 50 nm when printing 80 nm Au nanoparticles [84] (figure 4.4), and that an increase in laser power leads to a larger deviation from the intended printing position. In contrast to this, a study by Guffey & Scherer [85], in which they optically print slightly smaller (~50 nm) Au nanoparticles using off-resonance illumination, determined that an increase in laser power gives rise to a decrease in printing error.

Some of the ambiguity as to whether these precision values can be attributed to some fundamental limit or to the chosen experimental parameters was removed though a systematic investigation by Gargiulo et al. of the accuracy of immobilising a single nanoparticle [86]. Through addressing the printing as a

![Figure 4.3 Total optical force upon a 60 nm Au nanoparticle, illuminated at 532 nm with a beam irradiance of \( I = 10.4 \text{ mW·µm}^{-2} \), a diffraction limited beam waist of \( w_0 = 266 \text{ nm} \). Streamlines indicate direction of force vector; colour scale indicates magnitude. Scale bar: 100 nm.](image-url)
function of such experimental parameters as the laser power and wavelength, and the nanoparticle material, it was found that two separate regimes of printing may be identified depending on whether illuminating on- or off-resonance. Off-resonance, precision is essentially independent of laser power and poorer than the best achieved using resonant illumination. On-resonance, the smallest error is produced by printing at the lowest possible laser power, down to the threshold power at which optical forces are insufficient to overcome the electrostatic repulsion barrier.

Alongside the error in printing a single nanoparticle at a desired position is the limit in attainable resolution when printing two particles in close proximity. An insurmountable inter-particle separation of around 300 nm limits the ability to fabricate circuits of connected nanoparticles and coupled plasmonic nanostructures [87].

Bao et al. addressed this limitation of lateral resolution with a systematic study in which they employed line traps to print chains of 200 nm Ag nanoparticles using an off-resonant 800 nm laser beam [88]. As illustrated in figure 4.5a, the study indicated three distinct regimes of printing when varying the distance between columns of nanoparticles: a non-interacting regime, where the printing is independent of previously printed chains (for desired distances greater than 600 nm); an interacting regime, within which a decrease in chain separation yields an increase in deviation from this set value (for distances down to 250 nm); and, finally, a regime in which printing accurately becomes impossible (for distances shorter than 250 nm). This inter-particle interaction
was attributed to optical binding, a phenomena that gives rise to optical forces upon the illumination of already printed nanoparticles; the subsequent scattered light interferes with the incident field and creates energetically favourable positions at large distances from the fixed nanoparticle [87,89,90].

During the optical printing process, both the approaching and the fixed nanoparticles become polarized, with the induced dipole parallel to the electric field. Given that the near fields produced by a radiating dipole are dependent on the orientation of such dipole, one might expect that the interaction between particles is dependent on the polarization of incident light. A computational study performed by the Chvátal group, OMITEC at the Institute of Scientific Instruments of the Czech Academy of Sciences, however, illustrated that, for a fixed particle 200 nm away from the desired position of a second particle (recall that the experimental limit is approximately 300 nm), the influence of the fixed particle is not strong enough to prevent printing regardless of incident
polarization. Figures 4.5a-b illustrate that for both polarizations, the optical binding interaction force is at least one order of magnitude weaker than the optical force exerted upon the nanoparticles by the laser beam.

To complement the above study, the Stefani group, CIBION at the Universidad de Buenos Aires, addressed the same system experimentally: 60 nm Au nanoparticles were printed in an attempt to fabricate dimers of a variety of inter-particle gap sizes, using both a parallel and perpendicularly polarized 532 nm laser beam. Figure 4.6a-b indicates the resultant dimer geometries: it is clear that separation of less than around 250 nm is impossible and that the results are independent of the orientation of the nanoparticle dimer.

Computational calculations of optical binding forces, alongside the experimental observation that the limitations of optical printing are independent of the beam polarization, indicate that light-induced repulsions may not be attributed to optical binding. Urban et al. noted that "[additionally], because the already printed nanoparticle is still illuminated by the laser, it can heat up and create convective currents, disrupting the path of the second nanoparticle". We must then address the absorption and subsequent heating of the printing nanoparticles if we are to develop strategies to overcome this limitation and become capable of fabricating arrays of any arbitrarily given inter-particle separation.

Figure 4.6 Attempts at linking silver nanoparticles with optical printing. a, Nanoparticle intercolumn separation vs piezo controlled step sizes (Δx). Inset: representative optical images of the deposited arrays for various step sizes: i, Δx = 0.3 μm; ii, 0.4 μm; iii, 0.45 μm; iv, 0.5 μm; v, 0.7 μm; vi, 1 μm. The size of optical images as insets are 3.1 × 2.5 μm. b, FDTD map of the force exerted by the central pair of 200 nm diameter Ag nanoparticles (the grey spheres) on a new 200 nm Ag nanoparticle in water illuminated by a plane wave (800 nm vacuum wavelength). The polarization is along the x-axis. The direction of each arrow denotes the direction of the optical force when the third nanoparticle is located at the midpoint of the arrow. The colours of the arrows represent the value of electrodynamic forces as shown by the scale bar. The direction indicates the (local) direction of the force with respect to the pair of fixed particles. The dashed circle represents the equilibrium position of the newly added nanoparticle.
4.5 HEAT DISSIPATION

The optical printing system in question utilises a Gaussian focussed laser beam, and thus the total generated heat upon illumination may be given as determined through equation 4.1 as

\[
Q(r) = \sigma_{abs} \frac{2P}{\pi \omega_0^2} \exp \left[ -\frac{2r^2}{\omega_0^2} \right]
\]  

(4.15)

Combining equation 4.15 with 4.4 (and ignoring the substrate) yields the temperature increase of the fixed particle as a function of the separation between the centres of the beam and the nanoparticle \(d\):

\[
\Delta T(d) = \frac{\sigma_{abs} P}{2\pi^2 \kappa \omega_0^2} \exp \left[ -\frac{2d^2}{\omega_0^2} \right]
\]

(4.16)

By taking the surrounding medium to be uniform, it is relatively simple to calculate the temperature increase. Figure 4.7 illustrates the solution to equation 2.16 for 60 nm diameter nanoparticles of both Au and Ag immersed completely in water illuminated by a 532 nm Gaussian beam with a waist diameter of 265 nm.

Notably, the temperature increase for the Au nanoparticle up to a particle-beam separation of 250 nm, remains above 100 °C; while this may initially appear unphysical, one must note that the fields decay rapidly with increasing distance and that it has been observed experimentally that water can be superheated well above water's boiling point in small volumes [91-93]. Additionally, this steady-state approximation takes the surrounding medium

![Figure 4.7](image)

Figure 4.7 Surface temperature increase of a 60 nm (Au or Ag) nanoparticle in water as function of the distance, \(d\) to centre of a Gaussian beam of wavelength 532 nm, with a waist of \(\omega_0 = 265\) nm and power of \(P = 1.2\) mW, calculated using equation 4.16 with a thermal conductivity of \(\kappa = 0.58\) Wm\(^{-1}\)K\(^{-1}\).
to be stationary and neglects to include the formation of convection cells in the liquid.

This transient time for the temperature profile to reach a steady-state, as given by equation 4.16, can be calculated using the density, specific heat capacity, and the thermal conductivity of water ($\rho = 10^3$ kgm$^{-3}$, $c_p = 4.18 \times 10^3$, $\kappa = 0.58$ W·m$^{-1}$K$^{-1}$, respectively) as approximately $\tau_{tr} \sim 25$ ns. This time interval is significantly shorter than the characteristic time of a single printing event in the optical printing process, and therefore the temperature is established effectively instantaneously after switching the laser on.

Different heat dissipation schemes were tested in order to determine if the light-induced repulsions evident in optical printing are caused by local increases in temperatures surrounding printed nanoparticles. A first study examined the role of thermal conductivity within the supporting substrate. Glass – as used in the aforementioned printing trials – with a thermal conductivity of $\kappa_{glass} \sim 1.3$ W·m$^{-1}$K$^{-1}$, was replaced with sapphire, a material with a conductivity of $\kappa_{sapphire} \sim 20$ W·m$^{-1}$K$^{-1}$. We hypothesised that this twenty-fold increase in conductivity would, under steady state conditions, result in a lower temperature in and around any existing printed nanoparticles. Additionally, sapphire is transparent in the optical regime and thus permits the dark field imaging required for the described printing method.

The above discussion of the temperature profile within a homogenous thermal conductivity is obviously not applicable to our printing system. Instead we must evaluate the temperature evolution for a more complicated geometry – i.e. that with a substrate – utilising numerical methods.

In the absence of any phase transformation, the temperature distribution inside optically stimulated nanoparticles may be described by the heat transfer equation:

$$\rho(r)c_p(r) \frac{\partial T(r, t)}{\partial t} - \kappa(r)\nabla^2 T(r, t) = q(r, t)$$

(4.17)

where, once again for emphasis, $q$ is the power density inside the nanoparticle, originating through the Joule effect. All parameters are described by the spatial coordinate $r$. The temperature profile inside the structure is typically very uniform despite the non-uniformity of the heat source term $q$ due to the large magnitude of the thermal conductivity of gold relative to water [9].

Outside of the structure, this heat source term vanishes but we must include a term to handle the convection of the fluid:

$$\rho(r)c_p(r) \left[ \frac{\partial T(r, t)}{\partial t} + \nabla \cdot (T(r, t)v(r, t)) \right] - \kappa(r)\nabla^2 T(r, t) = 0$$

(4.18)

where $v(r, t)$ is the fluid velocity field and $\nabla \cdot (Tv)$ is the additional (non-linear) convective term.
For the geometry in question, we can determine the electromagnetic losses through solving Maxwell’s equations with appropriate boundary conditions. We have solved these and the above equations 4.17 and 4.18 using finite element simulations; COMSOL Multiphysics, which provides the ability to solve coupled partial differential equations, was chosen for its ease of implementation and reliability.

In our simulations, we have taken the electromagnetic losses in the nanoparticles as the only heat source. Furthermore, as we have assumed that the electromagnetic cycle time is short compared with the thermal time scale (the adiabatic assumption), we may then initially neglect the role of convection and decouple the temperature and velocity calculations. In this way, we may first solve for the temperature profile and then for the fluid velocity (we shall justify this assumption more comprehensively in section 4.6.1).

To take into account heat dissipation in our simulation domain, we implement a heat flux node across the outer boundaries, defined by the equation \( q_\theta = h(T - T_{ext}) \), where \( h \) is the heat transfer coefficient of each medium, dependent on the geometry, material and the ambient flow conditions, \( T_{ext} \) is the external temperature (assumed to be the same as the initial temperature of the system), and \( T \) is the temperature of the system. The heat transfer coefficient \( h \) can often be estimated by dividing the thermal conductivity of the convection fluid by a length scale [94]. The permittivity of gold was taken from Johnson & Christy [13], while the remaining temperature dependent material parameters were taken from the COMSOL library.

Figure 4.8 illustrates the temperature profiles around 60 nm Au nanoparticles in water fixed atop glass and sapphire substrates illuminated at 532 nm with an irradiance of 1 mW·µm\(^{-2}\). It is clear that the superior thermal conductivity gives rise to far lower particle, fluid, and substrate temperatures – approximately 3 times lower than evident with a glass substrate.
Optical printing of 60 nm Au nanoparticles was experimentally tested utilising the same protocol as described in section 4.2. The first noticeable fact was that the minimum laser power required to overcome electrostatic repulsion between the negatively charged particles and negatively charged polyelectrolyte layer and to enter the van der Waals attraction regime was approximately 2.4 times lower than required when using glass substrates; for sapphire the threshold power was found to be $P_{th} = (0.45\pm0.06)$ mW. We can justify this via two notions: firstly, that the assembly of the polyelectrolyte differs when on sapphire compared to when on glass, resulting in a lower superficial charge; and secondly, that there exists a short-ranged thermophoretic attraction between the heat-releasing particles and the heat-conducting substrate, as discussed by Dolinsky & Elperin [95].

Figure 4.9a illustrates attempts to print Au-Au nanoparticle dimers on sapphire (recall figure 4.6b for a glass substrate comparison). Dimers were fabricated with separations ($d$) ranging from 60 to 600 nm (with a separation of 60 nm resulting in connected 60 nm nanoparticles). SEM imaging allowed us to determine the experimentally achieved separations ($d_{exp}$); while dimer printing was impossible on glass for distances below 250 nm, printing was achievable for any desired separation on sapphire. However, for separations below around 100 nm, the achieved separation is larger than the desired value. When attempting to print connected nanoparticles ($d = 60$ nm, figure 4.9a inset), one
is able to print two particles in a reasonably well-defined orientation, albeit with separations of $d_{exp} = (211 \pm 12)$ nm.

### 4.5.2 HEAT DISSIPATION OF NANODISKS

We can suppose that by simply changing the printing substrate, we efficiently reduce the temperature of the system and decrease the achievable inter-particle separation in the optical printing of nanoparticle dimers. If indeed it is the increase in thermal conductivity of the substrate that permits this, it is then reasonable to suggest that an increase in the contact area between nanoparticle and substrate should further enhance heat dissipation. Figure 4.10 illustrates the expected steady-state temperature profile around nanodisks, as calculated using equation 4.18.

While spherical nanoparticles have a limited contact area with a supporting substrate (simplistic schematics unrealistically depict a single infinitesimal point of contact), nanofabrication techniques allow us to construct geometries with extended contact areas. To test this hypothesis, Au nanodisks were fabricated via top-down methods onto sapphire substrates.

Dr Toshihiko Shibanuma assisted in the fabrication of Au nanodisks using electron beam lithography. Briefly, positive tone resist PMMA (poly(methyl methacrylate)) was coated onto a sapphire substrate and baked at 180 °C for 5 minutes. The substrate was exposed to an electron beam, which patterned the resist with nanodisk masks of 70, 100, and 150 nm diameter before a development procedure utilising MIBK (methyl isobutyl ketone) and IPA (isopropanol) in a 1:3 ratio. The patterned nanostructured substrate was covered with a 2 nm chromium adhesion layer and a 50 nm gold film deposited by thermal evaporation. Subsequent PMMA removal via an acetone lift-off procedure yielded arrays of gold nanodisks.
Figures 4.11a and 4.11b exhibit the dark field scattering and representative SEM images for the 70 nm and the 150 nm Au disks on a sapphire substrate before printing. Figures 4.11c and 4.11d highlight the calculated absorption cross-sections and the expected temperature increases upon experimental illumination of disks on sapphire in comparison to spheres on both glass and sapphires. These spectra were determined through solving Maxwell’s equations and the heat diffusion equations (equations 4.18) explicitly with COMSOL. It is clear that despite the increased volume of the nanodisks and the increased absorption cross-sections at the printing wavelength, the expected temperature increase is envisaged to be up to around 5 times smaller than expected with spherical nanoparticles.

The schematic depicted in figure 4.12a illustrates the experimental printing procedure; 60 nm diameter Au nanoparticles were printed in proximity to the pre-fabricated Au nanodisks, with a set gap defined as the desired separation between nanoparticle centre (which is also the centre of the Gaussian beam) and nanodisk surface (unlike in the previous sections where we considered centre to centre separation). After printing, SEM images were taken to determine the experimentally achieved gap ($G_{exp}$) and the deviation of desired behaviour.
Figure 4.1 displays dark-field images after printing for the case of a 70 nm Au nanodisk and a 60 nm Au nanoparticle for a range of set gaps. Inset is a representative SEM image and dark-field spectra of a disk-particle dimer fabricated with a 0 nm set gap; while the dark-field image is clearly diffraction limited, the resultant structure has been fabricated with sub-diffraction resolution. It does not however achieve the separation as desired with the set gap. The twin-peaked dark-field spectra clearly indicates the presence of a dimer system.

Figure 4.12d plots the results of experimental attempts to perform optical printing with all geometries of nanodisks for a range of set gaps; this was possible for all gaps and disk sizes, albeit with some deviation from desired behaviour at small set gap values. Negative values of set gap here represent attempts to print nanoparticles atop of the disks; printing was achieved, but on top of the substrate rather than on the disk itself. As can been seen with
reference to the dashed lines, printing next to nanodisks allows us to beat the minimum achievable gap sizes attainable when printing two nanoparticles on glass and on sapphire (300 and 100 nm, respectively). It is then clear that through the engineering of the heat dissipation capability of nanostructures, we can more effectively control the capability of plasmonic optical printing.

4.5.3 HEAT DISSIPATION DISCUSSION

These experimental results provide additional evidence against the proposed repulsion mechanisms that invoke scattered light as noted in section 4.4: at 532 nm, the scattering cross-section of a 60 nm Au nanoparticle and a 70 nm Au nanodisk are comparable in magnitude and yet printing resolution is far higher for the case of the disk. Similarly, the 150 nm nanodisk has a scattering cross-section some 7 times larger than the 60 nm nanoparticle yet permits the highest resolution (and thus smallest repulsion) of any of our tested systems.

Figure 4.13 depicts a comparison of all aforementioned trials of plasmonic optical printing with a variety of methods of heat dissipation. Here we plot the deviation between the (desired) set gap and the experimentally verified achieved gap against the expected temperature increase of the nanoparticle. COMSOL simulations allowed up to determine this expected temperature increase; the beam intensity was varied throughout the simulations to reflect the notion that at a predefined set-gap the particle already on the substrate would be illuminated with the tail of the Gaussian beam rather than with the peak intensity. Spatially, the intensity at the substrate surface varies as
\[ I(r) = I_0 \exp \left( -\frac{2r^2}{w_0^2} \right) \]  

(4.19)

where \( I_0 \) is the intensity at the centre of the beam, \( w_0 \) is the beam waist diameter (266 nm for the 532 nm laser in use here), and \( r \) is the radial distance from the centre of illumination. It follows that the temperature increase of nanoparticles under illumination with the Gaussian tail is smaller than the expected increase had that particle been illuminated at a zero set-gap.

The threshold between impossible and possible printing is consistent with the boiling point of water. Interestingly, despite the diversity of the geometries in use during the printing trials, we can group the printing error vs. expected temperature increase into distinct clusters: temperature does indeed appear to be a key parameter in the prediction of the accuracy of optical printing.

4.6 **Nanoscale Fluid Dynamics & Heat Transfer**

We now have strong experimental evidence that it is the heating of the stabilised particle on the substrate upon illumination with the printing beam that gives rise to positioning errors during the optical printing of dimer-like structures. The underlying repulsion mechanism still, however, remains unclear. We shall now address convection, thermophoresis, and thermosmosis as three possible governing mechanisms.

4.6.1 **Navier-Stokes & Simplifications**

With the previously discussed calculated temperature increase of illuminated nanoparticles, we are equipped to tackle the general equation governing the profile of the fluid velocity surrounding the structure, the Navier-Stokes equation:

\[
\frac{\partial \mathbf{v}(r, t)}{\partial t} + (\mathbf{v}(r, t) \cdot \nabla) \mathbf{v}(r, t) = \nu \nabla^2 \mathbf{v}(r, t) + f_{th}(T(r, t))
\]  

(4.20)

where \( \nu \) is the kinematic viscosity of the surrounding fluid, \( \mathbf{v} \) is the velocity of the fluid, and \( f_{th} \) represents the thermal force per unit mass due to a non-uniformity in the temperature profile. Using the Boussineq approximation allows us to solve non-isothermal flow without the need to tackle the full compressible forms of the Navier-Stokes equations, and is valid when density variations are small and thus have no effect on the flow field other than to give rise to a buoyancy force [83]. This thermal, buoyancy force term takes the form

\[
f_{th}(T) = \beta(T) g \delta T(r, t) \hat{z}
\]  

(4.21)

where \( \beta \) is the thermal expansion coefficient of the fluid, \( g \) is acceleration due to gravity, \( \delta T \) is the temperature increase at position \( r \) and time \( t \), and \( \hat{z} \) is the upwards unit vector (perpendicular to the substrate).
If we neglect the non-linear convective terms in the above equation 4.20 (as we shall justify shortly), the equation takes the mathematical form of a diffusion equation – just as with our heating equation 4.18. An estimate of the timescales associated with these two equations are then, respectively:

\[ t_T = \tilde{L}\rho c_p/\kappa \]  
\[ t_v = \tilde{L}/\nu \]  

(4.22a)  
(4.22b)

where \( \tilde{L} \) is a characteristic length scale of the plasmonic structure in question, and \( t_T \) and \( t_v \) denote the characteristic time required to reach a steady temperature and a steady velocity profile, respectively. In general, with nanoplasmonics experiments, these time scales are of a similar magnitude, on the order of 1 ns to 1 \( \mu \)s. In our case, the length scale is approximately 60 nm and the fluid in question is water; this gives \( \tilde{t}_T \sim 25 \) ns and \( \tilde{t}_v \sim 5 \) ns.

As we are now interested in a steady-state solution to the Navier-Stokes equation, let us then drop the time dependency and consider each remaining term: \((v \cdot \nabla)v\) is a convective term, \(\nu \nabla^2v\) describes diffusion, and \(f_{th}\) the force. We might then ask if it is the diffusive or the convective term that is dominant; equating the orders of the magnitude for each reveals that convection becomes dominant only at temperatures approaching the order of \(10^6 \) K – values clearly not found in our experimental system. A simple equivalence of the diffusive and force orders of magnitudes gives a characteristic order of magnitude of the velocity given a temperature increase of \(\delta T\):

\[ \tilde{V} = \tilde{L}^2\beta g \delta T/\nu \]  

(4.23)

which – using a thermal expansion coefficient of \(\beta = 10^{-4} \) K\(^{-1}\) and a temperature increase of \(\delta T = 50 \) K – yields a thermal-induced fluid velocity on the order of \(\tilde{V} \sim 1 \) nm\(\cdot\)s\(^{-1}\).

A fundamental characteristic in the analysis of fluid flow is the Reynolds number, which describes the ratio between inertial and viscous forces. We can calculate this through comparison of the order of magnitude of the non-linear convective term \((\tilde{V}^2/\tilde{L})\) to that of the diffusion term \((\eta \tilde{V}/\tilde{L}^2)\):

\[ Re = \tilde{V}\tilde{L}/\nu. \]  

(4.24)

Small Reynolds numbers (< 0.1) indicate laminar fluid flow that is governed by viscous forces; our system typically exemplifies flows with values around \(Re \sim 10^{-9}\).

Additionally, the Rayleigh number, \(Ra\), quantifies whether it is heat diffusion or heat convection that is dominant. We may calculate this through comparison of the order of magnitude of the terms within the (steady-state) heat diffusion equation 4.18. Recall that \(\rho c_p \nabla(\delta T)\) gives a fluid convection term on the order of \(\rho c_p \delta T \tilde{V}/\tilde{L}\), while \(\kappa \nabla^2 T\) represents thermal diffusion, on the order of \(\kappa \delta T/\tilde{L}^2\), and thus
\[ Ra = \rho c_p \bar{V} L / \kappa. \]  

(4.25)

A Rayleigh number much smaller than 1 indicates that it is diffusion that dominates with respect to convection after a temperature profile has been established; in our case, we achieve Rayleigh numbers around \( Ra \sim 10^{-8} \).

The above discussion leads us to conclude that with our plasmonic optical printing experiments, it is heat diffusion and not fluid convection that governs the resultant temperature distribution. The temperature profile reaches a steady-state in a timescale such that the slow fluid velocities present are incapable of distorting it. Our handling of the non-linear convective term back in section 4.5 is then completely justified.

Additionally, we should briefly consider Marangoni convection, which is induced by a surface tension differential on a gas–liquid interface in the presence of a temperature gradient. In the context of our experiments, one might expect the presence of such a convective force given the possible formation of bubbles upon heating. It was recently observed by Ito et al. that with bubble formation around a hot Au nanoparticle, Marangoni convection can present a force 6 orders of magnitude larger than that found with natural convection [96]. However, the temperature threshold for bubble formation in systems similar to our own has been found to be around 600 K [91,92,97,98]. Corroborated by the fact that we observe no visible bubble formation, it is then highly unlikely that Marangoni convection is at play here.

We can then finally obtain simplifications to equations 4.18 and 4.20 that allow us to computationally evaluate both the temperature and the fluid velocity profiles, respectively, around a heated nanoparticle:

\[
\frac{\partial T}{\partial t} - \frac{\kappa}{\rho c_p} \nabla^2 T = 0 \tag{4.26a}
\]

\[
\frac{\partial \mathbf{v}}{\partial t} - \nu \nabla^2 \mathbf{v} = \mathbf{f}_{th} \tag{4.26b}
\]

Importantly, the problem of computing the temperature profile and the velocity profile evolutions is non self-consistent. That is, we can solve equation 4.26a to obtain the temperature before determining the velocity with equation 4.26b. In the steady-state, these equations take the form of the Laplace and the Poisson equations, respectively.

**4.6.2 THERMOPHORESIS & THERMOS-Osmosis**

Having ruled out both natural and Marangoni convection, we then propose a mechanism that is reliant on thermally induced flow phenomena that arise due
to non-uniform temperature profiles at solid-liquid interfaces. There exist two such boundaries in our system: the fluid-substrate interface, and the fluid-nanoparticle interface. In the following discussion we utilise the notion that we are working in the regime of Stokes flow, and as such, we are justified in taking the spherical, colloidal particles of radius $a$ to obey Stokes' law of frictional drag in the fluid. Forces on the particle may then be computed from the surrounding fluid velocity profile, $v$, via

$$ F = 6\pi \rho \nu a v $$

(4.27)

For a suspended particle in a non-isothermal solvent, the induced force induces migration of the particle and is known as thermophoresis, as illustrated in figure 4.1a. For dilute concentrations of migratory particles, it is commonly assumed that the thermophoretic drift velocity $v_{TP}$ depends linearly on the external temperature gradient $\nabla T$ with the thermodiffusion (or, more accurately, the thermophoretic mobility) coefficient $D_T$ as the proportionality constant:

$$ v_{TP} = -D_T \nabla T $$

(4.28)

Quantitative computation of thermophoretic forces is difficult however due to the scarcity of $D_T$ values – particularly for metallic nanoparticles and systems with temperature gradients as high as those expected with optical printing. Piazza & Parola recently reviewed thermophoresis within colloidal suspensions, and it can be noted than most $D_T$ values fall within the range of $10^{12} - 10^{11} \text{m}^2\text{s}^{-1}\text{K}^{-1}$. Notably, the sole study reviewed concerning heat conducting nanoparticles (albeit a study performed with fullerenes in toluene) employed a value of $D_T = 4.5 \times 10^{-11} \text{m}^2\text{s}^{-1}\text{K}^{-1}$. Figure 4.15a demonstrates a typical simulated thermophoretic force map as calculated using equation 4.20, the aforementioned simulated temperature profiles, and the Stokes drag equation.

Figure 4.14 a, Schematic of the thermophoretic force. A temperature gradient in the fluid pushes the NP away from the hot source. b, Schematic of the thermo-osmotic force. A temperature gradient in the surface induces a slip velocity in the fluid. This induces a thermo-osmotic flow that exerts a drag force to the suspended NP.
4.27. The nanoparticle undergoing printing tends to be repelled from the hot fixed nanoparticle on the substrate.

Temperature gradients along the fixed substrate, meanwhile, induce a long ranged movement of fluid known as thermos-osmotic flow [99], again illustrated in figure 4.14b. It is the solid boundary that exerts additional forces on the fluid: the excess specific enthalpy \( h \) in the boundary layer results in a creep flow parallel to the surface, with the given effective thermo-osmotic slip velocity of [100]

\[
v_{\text{RO,slip}} = -\frac{1}{\eta} \int_0^\infty z h(z) \frac{\nabla T}{T} \frac{\nabla T}{T} \equiv \frac{\nabla T}{T} = \left(4.29\right)
\]

Enthalpy excess, \( h > 0 \), gives rise to a negative thermo-osmotic parameter (also known as the mechanocaloric cross-coefficient \( \chi \)) and is indicative of flow from hot to cold. The parameter \( \chi \) is not easy to predict, in part because the excess of enthalpy for an assembly of polyelectrolytes is, in principle, a complicated quantity with several contributions. It is reasonable to speculate that the main contributions are due to surface charges in the electric double-layer. In this case, the Debye–Hückel approximation [101] allows us to estimate the excess enthalpy in the electric double-layer

\[
h(x) = -\frac{1}{2} \varepsilon \frac{\zeta^2}{\Lambda^2} \exp \left[ -\frac{2x}{\Lambda} \right] = \left(4.30\right)
\]

Where \( \varepsilon \) is the permittivity of the layer, \( \zeta \) is the surface zeta potential, and \( \Lambda \) is the so-called Debye length. Comparison with equation 4.29 results in an expression for \( \chi \) of

\[
\chi = \frac{\varepsilon \zeta^2}{8\eta} = \left(4.31\right)
\]
which, using a value of $\zeta = -37$ mV for the PDADMAC polyelectrolyte layer (though this value refers to coated silica beads, so must be taken with some caution) gives a value of $\chi = 1.2 \times 10^{-10}$ m²·s⁻¹. This approach was adopted for charged micelles [102], for bare glass [99], for proteins [103], and it is compatible with the salinity dependence found for Janus particles [104]. Our estimated value is of a similar order of magnitude to those described; in our case, the positive sign of $\chi$ suggests a surface flow the hotter region.

We simulate the effect of thermo-osmosis in the optical printing process through the inclusion of an additional boundary condition in the search for a steady-state solution to the applicable equations within COMSOL; we explicitly impose equation 4.29 as the velocity at the substrate-fluid interface, which – alongside equation 4.27, gives rise to such thermos-osmotic force profiles as illustrated in figure 4.15b. Mass continuity in the flow cell here requires the formation of convection-like fluid cells with closed streamlines.

We expect both phenomena to be present during the optical printing process; temperature fields around a hot nanostructure typically decay in less than 100 nm (recall figure 4.7), therefore extreme temperature gradients as high as $10^9$–$10^{10}$ K·m⁻¹ are produced, leading to enhancement of both thermophoretic and thermo-osmotic interactions.

4.6.3 FLUID DYNAMICS PARAMETER OPTIMISATION

Let us briefly recap where we currently stand with regards to the simulations of fluid dynamics applicable to optical printing of plasmonic nanoparticles. We can model the temperature profile around a stationary (already printed) nanoparticle that is heated by a nearby Gaussian laser beam. Thermal gradients give rise to thermophoretic and thermo-osmotic induced forces on a second nanoparticle suspended in solution with the same Gaussian beam. This laser also imparts a variety of optical forces upon the suspended nanoparticle.

We are therefore equipped to address the experimental observation that some repulsive mechanism serves to prevent the suspended particle from approaching the static particle. Additionally, the printing accuracy is maximised and thus the repulsive mechanism is seemingly minimised when the thermal conductivity of the system is increased and the temperature is decreased. The total force is a summation of the optical, thermophoretic, and thermo-osmotic forces, which can be determined with just two free parameters for each printing conditions: the thermodiffusion coefficient $D_T$ and the thermos-osmotic parameter for the substrate-fluid interface $\chi$ (note that we can use our previous estimation of $\chi \sim 10^{-10}$ m²·s⁻¹ as a starting point). A representative map of the total force is illustrated in figure 4.16a.
We initially looked for a set of parameters \([D_T, \chi]\) that most accurately reflected the experimentally observed printing results. Given that it is the polyelectrolyte that is in direct contact with the boundary layer of fluid, we expect both PDADMAC on glass and sapphire to share a value of \(\chi\). Additionally, given that \(D_T\) refers to the diffusion of a single nanoparticle in fluid, we can similarly look for a common value. By noting that a nanoparticle in suspension undergoing printing will tend to follow a streamline of the total force until it reaches the substrate (as illustrated in figure 4.16a), we can simulate the trajectory for a nanoparticle (an example is given in figure 4.16b). Repeating this process for a range of \([D_T, \chi]\) pairs gives us a set of error values (\(\Delta\)) corresponding to the

![Figure 4.16 Parameter acquisition through comparison of simulated nanoparticle trajectories and experimentally observed nanoparticle separations.](image)

- **a**, Representative total (optical + thermophoresis + thermo-osmosis) force acting on a 60 nm Au NP for positions around a fixed Au NP. Streamlines indicate the direction of the net force and the colour scale indicates its magnitude. 
  - **b**, Simulated trajectories of the NPs corresponding to different values of \([D_T, \chi]\). The red line indicates the position of the centre of the beam. The green star marks the experimentally measured position and the red star the predicted position for each set of parameters; the distance between both is the printing error, \(\Delta\).
  - **c**, Predicted error \(\Delta\) as a function of parameters \([D_T, \chi]\) for a NP on sapphire and a set gap of 50nm. White squares indicate that the final position of the trajectory is not on the substrate. \(D\), average error \(\bar{\Delta}\) for each parameter set, determined through averaging all experimental conditions. Minimum \(\bar{\Delta}\) corresponds to \([D_T, \chi] = \{4.3\times10^{-12} \text{ m}^2\text{s}^{-1}\text{K}^{-1}, 3\times10^{-9} \text{ m}^2\text{s}^{-1}\}\).
By repeating this process for every experimental condition – that is, nanoparticles on glass, on sapphire, and nanodisks on sapphire – for each attempted set gap, we can determine a set of average errors, $\Delta$. The set of values that give the minimum error was then chosen as representative of all of our systems, which was given by $[D, \chi] = [4.3 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \text{K}^{-1}, 3 \times 10^{-9} \text{ m}^2 \text{s}^{-1}]$.

Figure 4.17 displays the total force maps calculated using these optimised thermos-osmotic and thermophoretic parameters for a 60 nm Au nanoparticle being printing near to a static 60 nm Au nanoparticle on functionalised glass and sapphire and near to a 70 nm diameter Au nanodisk on functionalised sapphire. The printing beam’s centre is depicted with a solid white vertical line, and it’s junction with the substrate can be interpreted as the desired printing position.
For a 50 nm set gap in the case of a nanoparticle on glass (figure 4.16a), recall that printing was impossible. Indeed, the simulated trajectories point away from the static nanoparticle. By exchanging the substrate material to sapphire, printing was possible, but at a distance larger than desired. Simulations indicate (figure 2.16b) just this – while the trajectory streamlines do meet the substrate, they do so at a larger distance than that described by the centre of the printing beam. The most effective thermal dissipation method was that conceived, employing nanodisks for their increased substrate contact area, gave rise to the smallest errors in printing; figure 4.16c illustrates this concept.

For larger set gaps (240 nm here), temperature increases in our static nanoparticle are not as significant and therefore the magnitude of both thermos- osmotic and thermophoretic forces are dwarfed by optical forces. The trajectories (figure 4.17d-f) are then effectively undisturbed by these thermofluidic phenomena and printing can proceed as desired (reflecting the adherence to the $y = x$ line in figure 4.9b for larger $d$ values).

Notably, during our parameter optimisation procedure, it was found that the forces that arise due to thermophoresis are significantly larger than those due to thermos-osmosis. While the chosen values quantitatively reproduce experimental observations, by eliminating all thermos-osmotic effects (that is, setting $\chi = 0 \text{ m}^2\text{s}^{-1}$) the resultant trajectory maps are practically equivalent (particularly when considering experimental errors). We therefore conclude that thermos-osmosis is not likely to be a relevant phenomenon during the optical printing process.

We conclude this section by highlighting that the results presented here are, to our knowledge, the first to address both thermos-osmosis and thermophoresis in the context of optical printing. Thermofluidic phenomena at the nanoscale are not widely understood, particularly when handling such large temperature gradients as presented with optical printing. While this work assists in the manipulation of nanostructures during printing, it is anticipated that the deeper comprehension gained can assist also in other fields.

4.7 CONNECTED NANOPARTICLES ON GRAPHENE

The previous subsections have served to highlight that through the effective engineering of the thermal dissipation of an optical printing system, one can achieve smaller dimer gap sizes. It follows then that by increasing the thermal conductivity of the substrate to values beyond that even of sapphire, we might reduce the gaps and experimental errors even further. Graphene presents a suitable candidate; it has been reported that its absorption at 532 nm is just 2.3 % and its thermal conductivity is as high as 5000 $\text{W} \cdot \text{m}^{-1}\text{K}^{-1}$ [105,106].
Dr Ianina Violi at Centro de Investigaciones en Bionanociencias (CIBION), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina, fabricated a sapphire substrate topped with thin films of reduced graphene oxide (rGO). A Langmuir–Blodgett trough was used for the deposition of graphene oxide, which was then reduced at 600 °C under high vacuum conditions to obtain negatively charged rGO thin films of a thickness of just one or two atomic layers. Electronic conductivities as large as $10^5$ Sm$^{-1}$ were found using the same method on silicon substrates. Both Raman and X-ray photoelectron spectroscopies were used to observe the homogeneity of the sample across the substrate. Figure 4.18b illustrates a typical Raman spectra, with the peaks at 1330 cm$^{-1}$ and 1600 cm$^{-1}$ corresponding to the D and G bands of rGO, respectively. 2 minutes of 532 nm laser irradiation at a peak power of 1 mW was found to not damage the sample in any way. Additionally, the surface functionalisation step as described in section 4.2 was not necessary as, after 2 hours of observation, no nanoparticles were found to spontaneously attach to the negatively charged surface. It was found that the rGO sheet was not homogenous as indicated through the variation of laser powers required to overcome the electrostatically repulsive barrier and therefore variations in the surface charge density.
FE-SEM images and dark-field spectra, such as those displayed in figure 4.17e, demonstrate the effectiveness of this thermal-dissipation method. With a set-gap of 0 nm, it was found that it was possible to connect two distinct Au nanoparticles.

4.8 CONCLUSIONS

Obtaining high accuracy is the positioning of nanoparticles is one of the foremost open challenges in the top-down fabrication of nanostructured devices. Optical printing of plasmonic nanoparticles is a novel technique that permits the direct assembly of intricate structures from colloidal origins. It has been shown to allow the fabrication of large-scale complex geometries of arbitrary design with no need for time-consuming prior surface patterning.

The experimental set-up of an optical printing system was conducted by Dr Julian Gargiulo and colleagues in CIBION, Buenos Aires; the full automation and mechanical stability enabled thorough investigations in some of the fundamental open questions associated with the printing method. Particular focus here has addressed the issue of the inability to print nanoparticles at inter-particle distances of anything less than 300 nm in a controlled manner. Experimental observations and numerical calculations indicated that the printing beam heats particles already upon the substrate for such small defined gaps. By increasing the thermal dissipation of the system, it was found that this minimum gap size could be reduced.

By coupling the thermal diffusion equation and the Navier-Stokes equation for our system, we were able to computationally study the temperature-induced nanoscale fluid dynamics at play here. It was found that the forces induced by thermo-osmosis – those due to temperature gradients at the substrate-fluid interface – were dwarfed by the forces imparted upon the printing particles by the laser beam and the thermophoretic forces induced by temperature gradients in the fluid itself. We report – to the best of our knowledge – the first reliable value of the thermophoretic diffusion coefficient a metallic nanoparticle in colloidal suspension: $D_T = 4.3 \times 10^{-12} \text{ m}^2\text{s}^{-1}\text{K}^{-1}$. 


III PLASMONICS & SUPER-RESOLUTION IMAGING
At the heart of this thesis is the interaction of light with nanostructured systems. Until now we have simply looked at the interaction with relatively simple metallic structures, addressing the dissipation of heat in such systems.

If however we reduce the size of the structure under scrutiny, quantum mechanical laws come into play; continuous absorption and scattering of light is replaced with resonant interactions, initiated when the incident photon energy matches that of discrete electronic energy levels within the system. Crucially, for many molecules and small nanoparticles, these resonances are positioned in the optical regime. These resonant light-matter interactions can, in many cases, be approximated as a quantum two-level system in which transitions occur only between levels whose energy gap matches that of the incident photon.

Recall figure 3.2; the absorption of a photon into the structure's lattice, via Landau damping, induces a highly athermal population of charge carriers. One might then look to utilise these highly energetic electrons and holes for purposes other than heat generation. Here we investigate the combination of plasmonic hot-carriers and fluorescence – namely, super-resolution fluorescence, wherein we exploit the quantum mechanical resonant light-matter interactions in systems involving plasmonic nanoparticles and fluorescent molecules.

5.1 Fluorescence

The lowest energy resonant transition in an organic molecule occurs between the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO), though all electronic states involved have a large number of harmonic-oscillator-like vibrational states superimposed [11]. The Born-Oppenheimer approximation notes that due to the large mass of the nuclei relative to the orbital electrons, the electrons follow the vibrational motion of the nucleus instantaneously and therefore the total wavefunction may be written as a superposition of purely vibrational and electronic wavefunctions. At room temperature, the thermal energy is far smaller than the separation between vibrational states and thus the excitation of the molecule starts from the electronic ground state.

Fluorescence is simply the radiative relaxation from the higher to lower energy states. The energy states of a simple fluorescent molecule (or a fluorophore) are illustrated in figure 5.1. Transitions between the ground state $S_0$ and the first
electronic excited state $S_1$, are permitted upon absorption and emission of a photon corresponding to the energy difference between states $\Delta E$, which may be related to the photon’s wavelength, $\lambda$, via the Planck-Einstein relation:

$$\Delta E = \frac{hc}{\lambda}$$  \hfill (5.1)

where $h$ is Planck’s constant, and $c$ is the speed of light in the medium.

This initial excitation does not necessarily result in population of the lowest excited state $S_1$, rather, we often see transitions to vibrational levels corresponding to higher energy states ($S_n$ with $n > 1$). In these scenarios, Kasha’s rule indicates that fast internal relaxation (on the order of $10^{-14}$ s) drops the molecule into the lowest vibrational state of that energetic state before dropping to lower electronic states. Fluorescence emission of a photon of energy $h\nu_2$ occurs upon relaxation of the electron back to ground state $S_0$. Dashed lines indicate the possibility of non-radiative decay between electronic states. Spin-orbital coupling may induce intersystem crossing to the first triplet state $T_1$, which – upon relaxation – may give rise to a phosphorescent photon of energy $h\nu_3$.

The energy of the photon emitted via radiative decay of the molecule is always lower than that of the incident light due to non-radiative internal losses involved in the decay through vibrational levels to $S_0$. This Stokes shift results in the emission being red-shifted relative to the excitation with the emission spectrum comprising a sum of Lorentzians corresponding to all possible decay pathways in the ground state vibration levels. The timescale of this fluorescence process is on the order of some nanoseconds [11].

Figure 5.1 An example Jablonski energy level diagram, highlighting some of the pathways available in a fluorescent system. Upon absorption of a photon of energy $h\nu_1$, the system can be excited from the electronic ground state $S_0$ to a higher state (here, $S_1$). Kasha’s Rule requires the molecule drops into the lowest vibrational state of the electronic state before dropping to lower electronic states. Fluorescence emission of a photon of energy $h\nu_2$ occurs upon relaxation of the electron back to ground state $S_0$. Dashed lines indicate the possibility of non-radiative decay between electronic states. Spin-orbital coupling may induce intersystem crossing to the first triplet state $T_1$, which – upon relaxation – may give rise to a phosphorescent photon of energy $h\nu_3$.
Relaxation of the molecule is not always radiative, but may also occur non-radiatively via collisions and vibrations that lead to heat generation. With the condition of weak excitation, that is, far from saturation of the excited state, each fluorophore may be described by its quantum yield $Q$, which is the ratio of the radiative decay rate $\gamma_r$ to the sum of the total decay rate:

$$Q = \frac{\gamma_r}{\gamma_r + \gamma_{nr}}$$  \hspace{1cm} (5.2)

where $\gamma_{nr}$ is the non-radiative decay rate, which is composed of the multiplicity of process that lead to decay to the group electronic state. The total decay rate $\gamma = \gamma_r + \gamma_{nr}$ defines the lifetime $\tau = 1/\gamma$ of the excited state. Generally, the fluorescence emission is not dependent solely on the molecular properties but also on the local environment of the fluorophore.

5.1.1 FLUORESCENCE BLINKING

Figure 5.1 also highlights the process of intersystem crossing within a fluorescent molecule. This less common (though still significant) phenomena originates due to non-negligible spin-orbital coupling in the molecule and results in a finite torque acting on the spin of the electron in the excited state [11]. This gives rise to the occasional flipping of the spin of such an electron, and a change of the total spin of the molecule from 0 to 1. The three possible orientations in an external magnetic field lead to a triplet of eigenstates. The triplet state’s energy is typically lower than that of the singlet due to the increased distance between electrons as per Hund’s rule [107].

Having undergone intersystem crossing to a triplet state, the molecule may decay via phosphorescence into the singlet ground state. This spin-forbidden transition are kinetically unfavourable, so only proceed at significantly slower time scales – in some cases on the order of minutes or even hours. Due to occupation of this long-lived state, a time-trace of fluorescence emission displays high count rates of singlet-singlet transitions followed by dark periods of singlet-triplet transitions. This fluorescence blinking is commonly observed when studying single fluorescent molecules.

After a prolonged period of successive excitation and emission, fluorescent molecules will cease to fluoresce at all. This photobleaching process is typically as a result of some photochemical alteration to the structure of the molecule itself; this is often attribution to interaction with highly reactive singlet oxygen, which interrupt the conjugated or aromatic system of many molecules [108].

5.1.2 PLASMONICS & FLUORESCENCE

Purcell demonstrated that the lifetime of excited atomic states is critically dependent on the environment and the inner properties of the atom [109]. The
fluorescence processes of both excitation and emission, due to the interaction of the fluorophore with the surrounding environment, may be modified through alteration of the local EM field. As seen in chapter 2, plasmonic nanoparticles offer intense near-field intensity enhancements that form the basis of plasmon-enhanced fluorescence (PEF).

The molecule is typically far enough away from the metal surface to avoid quenching of the excited state and therefore it can be assumed that the non-radiative decay rate is not affected strongly by the presence of the nanostructure [110,111]. The enhanced local field around the structure does however increase the radiative decay rate; PEF gives rise to enhancements of fluorescent emission that scales as $E^2$ [28].

With extinction cross sections several orders of magnitude larger than those of molecular fluorophores, plasmonic nanoparticles are capable of facilitating
coupling between the frequencies emitted by the fluorophore and the resonance of the metal structure. This gives rise to the emission of light with enhanced intensity at the same frequency as the fluorescence. At resonance, this effect is most prominent – when the LSPR overlaps with the molecular absorption and emission spectra, we achieve the highest fluorescence enhancement factor [2].

The emission enhancement arises in unison with the plasmonic nanostructure’s effect of the local density of states (LDOS) in its vicinity [111,112]. Upon relaxation back to the electronic ground state, the fluorescent photon is emitted into one of the available states available; the number of such states in vacuum is a function of the frequency of the emitted photon. The plasmonic particle serves as a resonant cavity that introduces a new strong decay channel for the emitter; if a fluorescent emitter is placed close to the metal surface, the final density of states will have a peak positioned spectrally at the same location as the LSPR wavelength (see figure 5.2) [21].

Through calculation of the radiative transition rate using Fermi’s golden rule [113], we can compare the radiative decay rate for the emitter in free space to that when placed (in this case parallel to the field direction) in a simple plasmonic cavity (modelled as a cavity supporting just a single Lorentzian-like mode):

$$ F_P = \frac{\gamma_r}{\gamma_{r,\text{free}}} = \frac{3}{4\pi^2} Q \left( \frac{\lambda^3}{n^2 V} \right) $$

(5.3)

where $F_P$ is known as the Purcell Factor, $Q$ is the quality factor of the plasmonic resonator, and $V$ is the plasmonic mode volume. The ability to concentrate EM fields into sub-wavelength volumes means that, despite relatively low $Q$ values on the order of 10 – 100 [21], plasmonic nanostructures very effectively manipulate the decay rate of fluorescent emitters. We shall shortly return to the concept of the LDOS in our discussion of super-resolution microscopy.

One notable study into PEF employed chemically synthesised gold nanorods to give fluorescence enhancements of up to 1100 times [114]. A fluorescent dye was chosen such that the absorption had a significant overlap with the LSP of gold nanorods and the excitation laser at 633 nm. A subsequent study from the same group using super-resolution microscopy looked at resonantly-coupled single-molecule, nanorod hybrids. They concluded:

"The study unravelled the dominating role of the nanorod antenna in the coupled molecular emission to the optical far field. Such observations emphasize the nanorod’s dual roles to enhance fluorescence signals and to dominate the fluorescence emission at the far field via efficient coupling. The results emphasize the role of plasmonic nanostructures as optical antennas in the plasmon-enhanced microscopy on a resonantly coupled optical system. The antenna effects have to be
The study then highlights the notion that through efficient coupling, the nanostructure not only enhances fluorescent signals, but also the emission into the far-field.

5.2 A BRIEF LOOK AT MICROSCOPY

The first optical microscopes were invented in the 16th century in the Dutch Republic, though until the mid-18th century the lenses in use were made by trial-and-error methods with a limited theoretical understanding of their working principles [115]. By the end of the 19th century, Ernst Abbe, Carl Zeiss, and Otto Schott had developed the mathematical groundwork for image formation theory and lens aberrations that facilitated the design of far more accurate optical systems. In doing so, they established the spatial resolution of around half a wavelength for any system as caused by the diffraction of light.

Though techniques such as scanning tunnelling microscopy [116] and electron microscopy [117] have been successful in achieving sub-nanometre resolution due to the short de Broglie wavelength of the electrons, this comes at the cost of invasiveness, which is particularly undesirable for live-cell imaging. Similarly, atomic force microscopy [118] and near-field optics [119] have gone beyond the spatial resolution limit through working in the near-field of the structure under study, but are only capable of examining the topography of the system. Far-field super-resolution techniques, developed over the past 20 years, have been successful in obtaining a non-invasive optical method of imaging structures smaller than the historical diffraction limit, and do so by using the previously discussed photophysical properties of fluorophores. In 2014, the Nobel Prize in Chemistry was awarded to Eric Betzig, Stefan Hell, and William

![Figure 5.3 Schematic of image formation with a compound microscope.](image)

- $O$: objective lens, $TL$: tube lens, $E_0$: excitation plane wave, $f_0$: focal length of objective lens, $f_{TL}$: focal length of tube lens, $\Delta r$: separation between two radiating dipoles in the object plane, $M\Delta r$: separation between images of two radiating dipoles in the image plane, where $M$ is the system magnification. Also illustrated is the combined point-spread function in the image plane; if the two point sources can be distinguished based on the image pattern, they are said to be optically resolved.
Moerner for "the development of super-resolved fluorescence microscopy", taking "optical microscopy into the nanodimension" [120].

Far-field optical microscopes utilise propagating light and lenses to form an image of an object. Figure 5.3 illustrates the basic working principle of a compound (as opposed to a single-lens) microscope: the sample is positioned at the focal plane of the objective lens such that emitted light within the lens’ angular aperture is collimated. Light is refocused with the tube lens onto some detector positioned at the lens’ focal plane. Geometric optics allows us to calculate the (lateral) magnification $M$ of the optical system as

$$M = \frac{\Delta r'}{\Delta r} = -\frac{f_{TL}}{f_0}$$  \hspace{1cm} (5.4)

where $\Delta r$ and $\Delta r'$ are the distances between two points in the object and image plane, respectively, and $f_0$ and $f_{TL}$ are the focal distances of the objective and the tube lens, respectively.

Of particular importance throughout this discussion is the numerical aperture of an objective lens:

$$NA = n \sin \alpha$$  \hspace{1cm} (5.5)

which is a function of $\alpha$, the half angle of the maximum cone of light collected by the lens, and $n$, the refractive index of the immersion medium. An objective with a high NA is then capable of gathering a large amount of light from the sample under study and allows the user to resolve fine specimen details.

Abbe’s formulation for the diffraction limit of an optical system considers the paraxial point-spread function of two dipoles with axes perpendicular to the optical axes. The distance $\Delta r$ between the dipoles in the object plane is magnified by the factor $M$ and mapped to the image plane to give a new separation distance of $M\Delta r$. The minimum separation is then defined as the distance between two point-spread functions for which the maximum of one coincides with the first minimum of the second [11]:

$$M \min[\Delta r] = 0.61 \frac{\lambda}{NA}$$  \hspace{1cm} (5.6)

where the preceding constant factor is related to the angular position of the first minimum of the Airy disk – formed via Fraunhofer diffraction through a circular aperture.

The intensity of the Airy disk at $z = 0$ – the observation plane – may be expressed as

$$I(\theta, z = 0) = I_0 \left(\frac{2J_1(x)}{x}\right)^2$$  \hspace{1cm} (5.7)
where $x = 2\pi NA r/M\lambda$ is a function of angle between the observation point and the optical axis of the circular aperture, $a$ is the radius of the aperture, $I_0$ is the maximum intensity at the centre of the pattern, and $J_1$ is the Bessel function of the first kind of order one. This Airy disk is well approximated by a Gaussian function, which is mathematically much simpler to work with. The intensity distribution of such a Gaussian approximation is given as

$$I(r, z = 0) = I_0 \exp \left(-\frac{2r^2}{w_0^2}\right) \tag{5.8}$$

where $w_0$ is the $1/e^2$ width of the beam in the radial direction (as introduced in section 4.3). Figure 5.4 illustrates a normalized comparison between the two functions.

### 5.3 Fluorescence Microscopy

Fluorescence microscopy utilises fluorescent compounds as the contrast mechanism in the acquisition of images. We can classify microscopes, broadly speaking, according to their excitation and detection methods: Figure 5.4a illustrates the working principle of a conventional wide-field fluorescence microscope. A dichroic mirror is used to reflect the source light (a laser beam in the context of our discussion) towards the sample of interest. Focussing at the back focal plane of the objective ensures that the light is in focus when...
impinging upon the sample. Fluorescence within the sample is initiated and a fraction of the emitted light passes back through the objective, and is now transmitted through the dichroic mirror and focuses with a tube lens onto some form of detector (typically a CCD camera). It is common practise to include an emission filter before detection that serves to collect only light of the wavelengths of interest [107].

Wide-field microscopy illuminates a large portion of the sample, and thus the collected light is an integration of a large number of fluorophores; confocal microscopy, however, focuses the light source to a diffraction limited spot, and employs a pinhole to block all light that arrives at the detector that is out of focus (figure 5.5b). This enables a drastic reduction in unwanted background fluorescence, but does so with the added complexity of having to spatially scan the sample simultaneously with the focused illumination spot and the spot at the detector [107].

5.3.1 TOTAL INTERNAL REFLECTION FLUORESCENCE MICROSCOPY

Total internal reflection fluorescence (TIRF) microscopy is a variant of wide-field fluorescence microscopy that exploits the properties of evanescent EM fields to study fluorophores only in the highly localised region near a substrate interface. Introduced in 1981 by Daniel Axelrod, the first applications of the method involved targeted investigation of various phenomena at cell membranes, but has since found use in monitoring the fluorescence of single
molecules \[^{121,122}\]. We shall utilise TIRF microscopy extensively in chapter 7, so we shall devote some time here to understanding the underlying principles.

Consider an EM wave described by the electric vector \( E_i \) impinging upon the boundary between two optically transparent, isotopic media with refractive indices \( n_i \) and \( n_t \). Some of the wave is transmitted and some is reflected, which we shall denote as \( E_t \) and \( E_r \), respectively. Taking the waves to be monochromatic planar harmonic waves, we can describe them as

\[
E_i = E_{0i} e^{i(k_i r - \omega_i t)} \quad (5.8a)
\]

\[
E_t = E_{0t} e^{i(k_t r - \omega_i t + \varphi_t)} \quad (5.8b)
\]

\[
E_r = E_{0r} e^{i(k_r r - \omega_i t + \varphi_r)} \quad (5.8c)
\]

where \( E_0 \) is the maximum amplitude of the wave, \( \varphi \) is any phase change relative to \( E_i \), \( r = (x, y, z) \) is the spatial vector, and the subscripts \( i, t \) and \( r \) denote incident, transmitted, and reflected components, respectively.

Various field continuity conditions must be fulfilled at the interface (recall section 2.3), notably the restriction that the tangential component of \( E \) must be continuous across the boundary. It is then possible to derive the familiar Snell's laws describing the relationship between the angles of incidence \( \theta_i \), refraction \( \theta_t \), and reflection \( \theta_r \):

\[
n_i \sin \theta_i = n_t \sin \theta_t \quad (5.9a)
\]

\[
\theta_i = \theta_r \quad (5.9b)
\]

If we take the wave to be propagating from a higher to a lower refractive index material (from glass into air, for example), there exists a **critical angle** given by \( \theta_c = \sin^{-1}(n_t/n_i) \), beyond which no light is transmitted but instead **totally internally reflected**. If we simplify the geometry of the system such that the

![Figure 5.6 Plane waves at the boundary between two media. The electric field of a, s- and b, p-polarised plane waves are polarised perpendicular and parallel, respectively, to the plane of incidence. The electric (\( E \)) and magnetic (\( H \)) field components of the incident \( i \), reflected \( r \) and transmitted \( t \) waves are orthogonal to each other and to the direction of propagation \( k \). From Snell's laws, \( \theta_i = \theta_r \) and \( n_i \sin \theta_i = n_t \sin \theta_t \), where \( n \) is the material's refractive index.](image-url)
interface sits at the plane $z = 0$, and $y = 0$ describes the plane of incidence—that is, there is no $y$-component in any of our fields. Such a system is illustrated in figure 5.6.

The projection of the transmitted wavevector then takes the form

$$\mathbf{k}_t \cdot \mathbf{r} = k_{tx} x + k_{tz} z$$

which, using Snell’s law (equation 5.9a), may be decomposed as

$$k_{tx} = k_t \frac{n_i}{n_t} \sin \theta_t$$

$$k_{tz} = \pm k_t \left( 1 - \frac{n_i^2}{n_t^2} \sin^2 \theta_t \right)^{1/2}$$

With the restriction that totally internally reflected light obeys $\sin \theta_i > n_i/n_t$, the wavevector in the $z$-direction can be shown to be wholly imaginary:

$$k_{tz} = \pm i \left[ \frac{k_t}{n_t} \left( n_i^2 \sin^2 \theta_i - n_t^2 \right)^{1/2} \right] = \pm i \xi$$

and the transmitted electric field then takes the form

$$\mathbf{E}_t = E_{0t} e^{\pm i \xi z} e^{i(\delta_t \sin \theta_i/n_t - \omega t)}$$

A positive exponential diverging to infinity is unphysical, so we may disregard the positive solution and take the amplitude of the transmitted wave to be $E_{0t} e^{-\xi z}$. Therefore, for any angles greater than the critical angle, we note that the field decays exponentially into the medium of the lower refractive index. Much like SPPs, these decaying fields propagate along the interface (in the $x$-direction in our case).

Let us now decompose the components of the transmitted evanescent wave — $E_{0t} = (E_{0x}, E_{0y}, E_{0z})$ — into components parallel and perpendicular to the incidence plane

$$E_{0y} = E_{0i}$$

$$E_{0x} = E_{0i} \cos \theta_t$$

$$E_{0z} = E_{0i} \sin \theta_t$$

By using Fresnel’s equations, which describe the relationship between the reflected and transmitted light at the interface, we are able to recast the above equations — more usefully — in terms of the incident electric field parameters:

$$E_{0y} = E_{0i} \frac{2 \cos \theta_i}{(1 - n^2 \sin^2 \theta_i)^{1/2}} e^{-i \delta_x}$$

$$E_{0x} = E_{0i} \frac{2 \cos \theta_i (\sin^2 \theta_i - n^2)^{1/2}}{(n^2 \cos^2 \theta_i + \sin^2 \theta_i - n^2)^{1/2}} e^{-i(\delta_x + \pi/2)}$$
\[ E_{0x} = E_{0i} \frac{2 \cos \theta_i \sin \theta_i}{(n^4 \cos^2 \theta_i + \sin^2 \theta_i - n^2)^{1/2}} e^{-i\delta_i} \]  

(5.14c)

where, for clarity, we have introduced \( n = n_L/n_i \) and we have simplified the perpendicular and parallel phase factors, respectively, as

\[
\delta_\perp = \arctan \left( \frac{(\sin^2 \theta_i - n^2)^{1/2}}{\cos \theta_i} \right) 
\]

(5.15a)

\[
\delta_\parallel = \arctan \left( \frac{(\sin^2 \theta_i - n^2)^{1/2}}{n^2 \cos \theta_i} \right) 
\]

(5.15b)

Interestingly, the presence of the perpendicular and parallel phase factors in the transmitted evanescent field gives rise to a longitudinal shift known as the Goos-Hänchen shift [123], arising due to the light travelling a short distance along the surface within the lower refractive index material before total internal reflection occurs back into the higher index material.

We can note that only when the incident EM field is perpendicular to the incidence plane (that is, s-polarisation) does the polarisation of the evanescent field become perpendicular to the \( x \)-direction of propagation. By contrast, if we excite the evanescent wave with p-polarised light – because \( E_{0x} \) and \( E_{0z} \) are 90° out of phase, the evanescent field becomes elliptically polarised in the incidence plane. The tip of the polarisation vector then rotates along the \( x \)-axis with a spatial period of \( x_0 \), which may be determined from equation 5.6 as

\[ x_0 = \frac{2\pi n}{k_i \sin \theta_i} \]

(5.16)

Figure 5.7c illustrates this phenomenon schematically.

If we turn now to the intensity of the EM fields in question, from equation 5.14, we note that the evanescent field at the boundary as a function of the incident field intensity may be given as

\[
I_{0\perp} = I_i \frac{4 \cos^2 \theta_i}{(1 - n^2)} 
\]

(5.17a)

\[
I_{0x} = I_i \frac{4 \cos^2 \theta_i (\sin^2 \theta_i - n^2)}{(n^4 \cos^2 \theta_i + \sin^2 \theta_i - n^2)} 
\]

(5.17b)

Interestingly, as illustrated in figure 5.6d, the intensity of the evanescent field may be several times higher than that of an incident wave when illuminated around the critical angle.

The system that we employ for TIRF microscopy is an objective-based system (as opposed to a prism-based TIRF system [124]), in which incident light is transmitted and reflected light is collected with the same objective as part of a custom-built inverted microscope. Efficient notch filters and dichroic mirrors must be chosen to prevent the reflected beam from reaching the objective; the
specular reflection is useful however for confirmation that we have achieved TIR conditions [125].

Recall from our discussion above that to achieve TIR, the incident EM wave must approach the substrate at an angle relative to the optical axis larger than the critical angle \( \theta_c \). Additionally, we must have a light source that is collimated else only a fraction of the waves meet this angular requirement. This may be achieved through first focusing the incident light at the centre of the back focal plane of the objective; the beam then exiting the objective is parallel the optical axis. By then translating the focus of the beam in the back focal plane, we are able to increase the value of \( \theta_i \) to a maximum value defined by the NA of the chosen objective.

Figure 5.7 The evanescent field considering an optical system comprising an objective where the lens, cover slip, and index matching immersion oil have a refractive index of \( n_i = 1.51 \) and the sample is immersed in water (\( n_t = 1.33 \)), illuminating at \( \lambda_0 = 561 \) nm. The vertical dashed lines indicate critical angle, which for this system is \( \theta_c = 61.7^\circ \). a, The evanescent field depth reduces as the angle of incidence increases. b, The intensity of the evanescent field at the interface can be over five times greater than the incident field when illuminating close the critical angle. c, For an incident wave polarised in the \( xz \) plane (\( p \)-polarisation) undergoing TIR, the polarisation direction of the evanescent field rotates along the \( x \)-axis with period \( x_0 \). The polarisation of the evanescent field experiences a Goos-Hänchen shift with respect to the incident wavefronts of \( \delta \).
It is advantageous to employ an objective with as high an $NA$ as possible in TIRF microscopy given that the greater the $NA$, the greater the fraction of the peripheral area of lens that can be used; coupling the laser into the rear aperture is then a much simpler process. For an $NA \geq 1.45$, index-matching immersion oil is used ($n_{oil} = 1.51$), which matches the index of glass lens and cover slip and allows light to pass freely with no unwanted reflections at the interface. One must take care when combining light sources as each wavelength experiences a different penetration depth (recall figure 5.7b); here, it is advantageous to use an apochromatic objective and chromatically corrected optics.

Since its advent, TIRF microscopy has found numerous applications in cell biology [125-127]. In particular, the noted field intensity increase in the near vicinity of the interface significantly improves both the signal-to-noise and the signal-to-background ratios relative to conventional fluorescence microscopy [128]. In more recent years, TIRF microscopy has been employed in combination with plasmonics to further amplify fluorescence signal [2,129-132]. We shall turn our attention to one particular use of combinatory TIRF and plasmonics shortly.

5.4 SUPER-RESOLUTION MICROSCOPY

Recall equation 5.6, outlining Abbe’s limit for the minimum resolvable separation between two point dipoles. The highest resolution of an optical microscope with a very high numerical aperture ($NA = 1.45$) looking into the blue region of the EM spectrum ($\lambda \sim 450$ nm), is approximately 200 nm. A resolution of 200 nm has become increasingly inadequate as researchers look to study increasingly smaller structures.

Figure 5.8 TIRF microscopy experimental setup. Fluorescence is excited and emission is collected from the same side of the sample. The $NA$ of the objective define the range of incident angles that may be used – between $\theta_i$ and $\alpha$. High $NA$ objectives typically employ index-matching oil. Collimation of the excitation beam is ensured by focusing off-axis at the back-focal plane.
Classical fluorescence microscopy, including the use of TIRF, allows the user to monitor films of fluorophores fixed in position. In combination with plasmonic field enhancement, they provide a useful local probe of the field intensity [132]. The large concentrations, however, means that we lose information about single probes and instead collect the integrated effect of many fluorophores. Decreasing the density of fluorescent molecules gives a route to single-molecule detection but does not provide a method to overcome the limitations regarding Abbe’s diffraction limit; any information pertaining to structural features smaller than this limit is lost. To study smaller structures, we must turn to super-resolution microscopy techniques. For the purpose of this discussion, it is useful to categorise super-resolution methods into either true or functional techniques [133].

True super-resolution techniques are those that directly yield images with features smaller than the diffraction limit. A wide variety exist, including 4Pi microscopy [134], spatially modulated illumination [135], and structured illumination microscopy [136], but perhaps the most relevant pertaining to plasmonic systems is that of scanning near-field optical microscopy (SNOM). Here, a hollow nano-tip is used as an aperture through which an excitation laser is focused. Upon exiting the tip, and before diffraction sets in, the evanescent light in the near-field spans a region on the same scale as the aperture itself – often just a few nanometres in diameter. In scanning the tip across a sample, all collected light in the far-field at any one moment in time can be attributed to only the region of excitation under the tip, allowing one to construct a map of the sample’s optical response.

SNOM has been successful in resolving features less than 5 nm in size [137,138], but to do so requires expensive, bespoke setups. In combination with plasmonic systems, one must also consider the perturbation to the plasmonic response due to the presence of a conducting nano-tip in the near-field. The often non-invasive nature of functional super-resolution techniques allows us to overcome these limitations. These techniques do not directly increase the resolution of an optical system, but instead rely on the sparsity of active fluorescent probes in space such that light collected in the far-field after a single fluorescent event may be attributed to a region on the order of the excitation size.

Again, a wide variety of these techniques exist, including ground state depletion [139], saturated structured illumination microscopy [140], and stimulated emission depletion (STED) [141]. STED utilises stimulated emission to turn off the spontaneous fluorescence emission of molecules by overlapping a focused excitation beam with a toroidal-shaped beam that de-excites emitters to the ground state everywhere except the central region. This provides a theoretically diffraction-unlimited resolution in the transverse plane through the reduction of the width of the point spread function. It has
been shown that such a functional super-resolution technique gives rise to experimental resolutions of less than 10 nm [142]. Notably, in more recent years, the technique has found use in combination with plasmonic nanoparticles [143]. It is however an optically complex method, which requires great care in the alignment of the two beams; the use of plasmonic structures complicates this further due to local distortions of both illumination and depletion beams.

**5.4.1 STOCHASTIC SUPER-RESOLUTION MICROSCOPY**

Of particular relevance to this work is a subset of functional techniques known as *stochastic super-resolution microscopy*. An array of techniques exist that can be classified under this title, but all rely on the same underlying principle: spatially separate fluorescent emitters are used over extended periods of time to gradually resolve the underlying structure. Figure 5.9 illustrates this concept schematically.

It is necessary to modulate the emission of a large number of emitters such that only a single molecule is active within a diffraction limited spot at a given time. Upon acquisition of this diffraction limited spot, localisation is performed by...
fitting to a model function – typically a point-spread function or a Gaussian (recall the close proximity of the two as illustrated in figure 5.3). The position of the fitted peak is then taken to correspond to the position of the emitter.

Experimentally, care is taken to select fluorophores that may be controllably modulated between non-emissive and emissive states, including through the formation of metastable dark states and through diffusive techniques [144-146].

5.4.2 SUPER-RESOLUTION IMAGING OF REACTIONS ON PLASMONIC NANO PARTICLE SURFACES

Here we shall briefly narrow our discussion to stochastic super-resolution techniques that have been utilised to image plasmonic nanostructures, though I do direct the reader to the recent review from Willets et al., that comprehensively covers the topic [147]. Direct stochastic optical reconstruction microscopy (dSTORM) operates through placing a large number of fluorescent molecules surrounding a plasmonic nanostructure into the dark triplet state, where the lifetimes can exceed hundreds of milliseconds. The use of self-assembled thiols on the metal surface introduce an additional metastable state that is reached through the triplet state and serves to extend the ‘off’ state further [148]. Uji-i and colleagues monitored the fluorescent Alexa647 dye when bound to silver nanowires [149], and took care to note that the strong laser intensities used to deplete the ground state should be carefully chosen so as to not damage the structure of the plasmonic nanostructure.

Photoactivation localisation microscopy (PALM) and the related strategy stochastic optical reconstruction microscopy (STORM) both employ a photoactivation laser to modify the chosen fluorophore (typically variants of fluorescent proteins with PALM and organic fluorophore pairs with STORM [150,151]) to a fluorescent state before a second laser is used to excite the fluorescence. Low intensities in the former ensure that only a small number of molecules are activated, ensuring the criteria of spatially separated fluorescent events is met. Aramendía and colleagues recently used such a twin-laser strategy to study the conversion of spiropyran to the fluorescent merocyanine state on the surface of gold nanorods [152].

PALM and dSTORM are limited in that once all fluorescent molecules bound to the substrate of interest are quenched, no more measurements may be taking. Point accumulation for imaging in nanoscale topography (PAINT) rectifies this through the use of rapidly diffusing fluorophores [153]: upon adsorption to the sample (either through random electrostatic means or through controlled binding [154]), the fluorophore is immobilised and a diffraction limited emission spot may be observed. Desorption or photobleaching returns it to the non-emissive state, and the process may be repeated indefinitely. Care must be taken to consider the background fluorescence emission from detached probe
molecules that are not always easily uncoupled from that of active, surface-bound fluorophores.

Notable recent studies from Chen and colleagues have utilised the PAINT technique (or variants thereof) to investigate the intricacies of plasmonic catalysis [155-157]. Plasmonic nanoparticles have been observed to catalyse the modification of non-fluorescent molecules into fluorescent forms; for example gold nanorods have been seen to catalyse the formation of the fluorescent molecule Resorufin from the non-fluorescent dye Amplex Red in the presence of hydrogen peroxide through oxidative deacetylation [155]. In combination, super-resolution imaging and plasmonics both enhance our understanding of fundamental nanoscale phenomena and allow us to drastically improve the imaging method’s performance.

5.4.3 LOCALISATION ERRORS WITHIN SUPER-RESOLUTION MICROSCOPY

Super-resolution imaging of plasmonic systems is reliant on the fitting of some localisation function to the diffraction-limited emission, taking the centre of the fitting to correspond to the exact position of the emitter itself. Recall the use of a 2-dimensional Gaussian model fitting as described in section 5.2; this in itself is an approximation to the idealised point spread function of emission from a dipole, and thus there exist inherent errors in localisation. Indeed, a study by Uji-I and colleagues highlighted the significant modification of the point spread function when the fluorophore is placed in the vicinity of a silver nanowire, indicating clearly that a single Gaussian fit is often inappropriate [149]. If we consider the use of fluorophores in collaboration with plasmonic nanostructures, further localisation errors set in due to such mechanisms as image dipole formation [158,159] and plasmon-molecule coupling [160-162], which we shall turn to discussing now.

Early papers that studied the combined use of plasmonics and super-resolution techniques neglected to consider the interaction between the emission and the plasmonic system itself [163,164], which has since been shown to induce dramatic distortions in the localisation. As we have seen in chapter 2 of this thesis, plasmonic nanostructures are capable of behaving as nanoantennas; nearby fluorophores, rather than emit uninhibited to the far-field, can couple into the plasmonic modes of the nanostructure itself and the detected light then originates from either the plasmonic source or from some position corresponding to a convolution of the molecule and the nanostructure. This is illustrated schematically in figure 5.9. A numerical study from Ausman & Schatz looked into this phenomenon through considering a single dipole placed at various positions upon a nanoparticle’s surface. It was found that the emission into the far-field could not be attributed solely to the nanoantenna of the dipole itself, but rather a convolution of the two [161].
Experimentally, the same principle was verified in a study by Biteen and colleagues, in which they considered the emission from Cy5.5 molecules upon the surface of gold nanodisk antennas through a PAINT approach. Despite no functionalisation of the nanostructures to promote binding of the molecules, the most dominant centre of fluorescent emission was the centre of the disk itself. Additionally, there existed a “depletion zone” surrounding the disk in which activity was significantly diminished relative to other regions. Together, these observations corroborate the proposal that fluorescent emission is coupled into and re-radiated from the nanoantenna [162].

We can begin to quantitatively unravel the modification to the emissive properties of any dipole placed in the vicinity of a nanostructure by considering the formation of induced image dipoles, which serve as a second source of emission that may destructively or constructively interfere with emission from the original dipole [159]. This mirage effect may be modelled accurately using full-field numerical simulations and has been experimentally verified to be dependent on the spectral properties of the plasmonic nanostructure, the fluorophore emission frequency, and the relative orientation and position of the fluorescent emitter [158].

The final source of localisation error that we shall consider here is that induced by the weak photoluminescent properties inherent to the plasmonic materials.
commonly used. Both silver and gold exhibit weak luminescence upon excitation [165,166]. Although the underlying mechanisms remain unclear, Lin et al. attribute the phenomena, when illuminating at plasmon resonance frequency, to the radiative recombination of hot-electrons following intraband transitions [165]. The emission may then be convolved with the fluorescent molecule’s own emission, distorting the apparent position of the fluorophore. Methods exist to counter this concern, including those reliant on the notion that the rapidly modulating emission from fluorophores is easily distinguished from the stable nanostructure luminescence; it is often sufficient to first take a background, diffraction-limited image in the absence of fluorescent probes that can be subtracted from final images. Raw background subtraction, while computationally simple, may not adequately address sample drift – even a single pixel drift over the course of image acquisition can contribute to significant localisation errors [167]. Alternatively, one may choose to fit the background image with some model function to identify the nanostructures and handle subsequent fluorescence image frames individually [168]. We note here however that the spatial origin of the plasmonic structure’s luminescence often serves as a useful fiducial marker in aligning either successive frames in a stack of super-resolution images or entire frame stacks with one another [169]
With the ever-increasing demand for energy and the decline of fuel reserves, catalysis is one of the key technologies capable of inflicting change. Heterogeneous catalysts play a hugely significant role in the chemical manufacturing industry due to their ability to lower the activation barriers required for a wide variety of reactions. With rapid advances in nanotechnology, new nanostructured catalysts have emerged [170-172]. Catalytic activity is directed by the surface properties of active sites of such nanostructures, and as such, the study of reaction kinetics is vital for understanding such surface processes as adsorption, reaction, and desorption [173-175].

Plasmonic photocatalysis has recently expedited progress in enhanced catalytic activity under visible light illumination. Typical plasmonic photocatalysis employs plasmonic nanoparticles dispersed within conventional semiconductor photocatalysts or plasmonic nanoparticles functionalised with charge-carrier-accepting adsorbate molecules. They utilise both the enhanced absorption facilitated by the LSPR and the formed interfacial junction to enforce charge separation [176]. While plasmonic photocatalysis offers a direct means of accessing a diverse array of reaction pathways that would otherwise be unattainable [157], the surface modification introduces structural complexity and an increased difficulty in deciphering the properties of the charge-carriers involved.

Within the literature of plasmonic photocatalysis, four dominant process have been proposed: direct transfer of charge-carriers from the metal to the semiconductor or adsorbate; indirect transfer, mediated by the LSPR; localised heating of the nanoparticle; and radiative transfer of photons from the metal to (and absorption within) the semiconductor or adsorbate, generating electron–hole pairs [69,177-186]. Here, we aim to provide a systematic study of the fundamental physical mechanisms of plasmonic photocatalysis involving direct hot-carrier production in silver nanoparticles and transfer to an adsorbed molecule; the other mechanisms are beyond the scope of this discussion and I direct the reader to recent reviews from Hou & Cronin [176], Zhang et al. [187], and Hesari et al. [157] for a comprehensive overview of the field.

6.1 MATERIAl SELECTION

Over the last 10 years or so, Chen and co-workers have intensively studied the kinetics of nanoparticle-catalysed (non-plasmonic) reactions with single-
molecule turnover resolution. They have investigated the reduction of the weakly-fluorescent dye resazurin to the highly fluorescent product resorufin. Their experimental approach is reliant on immobilised Au-nanoparticles, separated by distances much larger than the diffraction limited spatial resolution as described in detail in the previous chapter. By flowing the fluorescent molecule in solution above the nanostructures (at a suitably low concentration) in the presence of hydroxylamine in an aqueous solution, single conversion events may be detected through use of TIRF microscopy [188].

To the best of the author’s knowledge, nobody has studied the use of the plasmonic properties of silver to facilitate such a reaction. Silver is unique in its marked ability to tune the resonance peak through geometric modification. Additionally, its ‘green’ credentials are particularly desirable [189]; it readily absorbs naturally available sunlight; it is stable under typical reaction conditions; it is readily available and reusable; and it is has a low toxicity (indeed, it has been used throughout history for its anti-microbial properties [190]).

6.1.1 SILVER IN PLASMONIC CATALYSIS

A particularly relevant example of the use of plasmonic silver nanoparticles in a thermocatalytic reaction (that is, a reaction where it is the temperature that facilitates enhanced rates) is that reported by Christopher and colleagues. Low-intensity photon flux (on the order of solar intensity) was used to drive catalytic oxidation of ethylene adsorbed on the silver surface, which was found to be enhanced relative to the case of using only thermal stimulus [69]. Though their studies indicate that surface plasmons are responsible for the transfer of energetic electrons, further mechanistic analysis is required to address whether it is the formation of energetic hot-electrons on the silver surface and the subsequent transfer to the adsorbate that mediates the reaction, or if it is due to the direct interaction of the surface plasmons with the adsorbate [191,192].

In a recent study from Wu et al., the plasmonic properties of Ag nanoparticles were used for the reduction of graphene oxide (GO) to reduced graphene oxide [193]. Under visible light illumination, the induced LSPR in the Ag nanoparticle decays and the hot charge carrier products are injected into the conduction band of the GO layer. Simultaneously, the oxidation of the Ag nanoparticles is countered with the transfer of holes to an electron donor (dimethylformamide in this instance). Compared with conventional chemical reduction of GO, this method is far more environmentally friendly and easily controllable with simple illumination, further highlighting the beneficial role Ag nanoparticles are poised to play in catalysis.
Jurasekova and co-workers recently exhibited catalysis with plasmonic silver nanoparticles in the redox of ABTS (2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) – a compound typically used in cell biology to evaluate the free radical trapping capacity of antioxidant compounds and complex mixtures such as biological fluid, beverages, and foods [194]. Specifically, they highlighted the pronounced formation of radical ABTS cations in the presence of both silver nanospheres and silver nanostars, attributing the high reactivity to hot-spots on the plasmonic structure’s surface. Monitored with Raman spectroscopy, they note that the findings suggest that ABTS could be employed as an agent to further investigate the interfacial and plasmonic properties of silver nanoparticles.

This thesis considers the catalysis of the same molecule as that studied by Christopher et al [69], but reports – for the first time – the catalysis facilitated by plasmonic activity alone. That is, simply supplying additional energy through heating the system – as addressed in the context of non-plasmonic catalysis of the same molecule by Chen et al – is incapable of facilitating the reduction of the adsorbed molecule. Through hot-electron production within Ag nanoparticles and transfer into such an adsorbate, we are capable of demonstrating a model platform indicating the possibility of such a reaction.

### 6.2 Ensemble Hot-Carrier Mediated Dye Conversion

We carried out ensemble-level fluorescence measurements to determine the activation energy required for the reduction of resazurin to resorufin when in the presence of plasmonic Ag nanoparticles. Initial UV-Vis measurements, as illustrated in figure 6.1a, indicated the plasmon for the 60 nm Ag nanoparticles in use can be resonantly excited at wavelengths around 430 nm; we employ a 405 nm CW laser for exactly this purpose. Additionally, the absorption of the dyes was determined in order to ensure efficient excitation of fluorescent states, allowing us to determine when conversion has occurred. Resazurin and resorufin exhibit absorbance peaks at 602 and 572 nm, respectively. All UV-Vis measurements throughout were performed with an Agilent Cary 60 UV-Vis spectrophotometer.

Dye conversion may be confirmed through the increase and accompanying decrease in the fluorescence emission peaks of resorufin and resazurin, respectively. Figure 6.1b illustrates the profile of such peaks. Note that the normalisation procedure performed here is simply to highlight the shape and position of the peaks; the intensity of resazurin fluorescence is significantly higher than that of resorufin.
Recall that we previously noted that dye resazurin is weakly fluorescent; we should clarify the large magnitude of the 630 nm peak relative to that of resorufin’s 570 nm peak. The illustrated fluorescent spectra are representative of highly concentrated resazurin, which inevitably is accompanied with a small quantity of converted resorufin. The large number of weakly fluorescent molecules here gives a similar fluorescent emission to the small number of highly fluorescent molecules. This can be verified through considering the absorption spectra. Resazurin and resorufin exhibit absorbance peaks at 602 and 572 nm, respectively, with comparable extinction coefficients [195].

Figure 6.1 Fluorescent properties of resorufin and resazurin. a, Normalised UV-Vis absorption spectra (solid lines) of non-fluorescent redox dye resazurin (blue) and fluorescent redox product dye resorufin (red). For comparison, the absorption spectrum of 60 nm silver nanoparticles is also plotted. b, Normalised fluorescent emission (dashed lines) in the visible spectrum following 530 nm excitations of resazurin (blue) and resorufin (red).
(47000 M⁻³cm⁻¹ and 56000 M⁻³cm⁻¹); our measured absorbance spectra indicate the dominating presence of resazurin.

The aqueous catalytic reactions were monitored with an Agilent Technologies Cary Eclipse Spectrophotometer, and conversion was initiated through illumination with a Coherent 405 nm Cube CW laser, expanded with a telescope. Expansion of the beam was performed to allow large-area excitation of plasmons and thus production of hot-electrons, to perform the experiment at power densities that would not denature the dyes or lead to nanoparticle deformation, and to ensure that the power density falling upon the nanoparticles is somewhat more uniform than if a focused beam at a correspondingly lower peak power was used.

The Gaussian shape of expanded beam was profiled using a custom knife-edge system that allows the 1/e² beam width to be extracted from measurement of the total power falling on a power meter (here, a Thorlabs Optical Power Meter) upon translation of the knife edge across the beam's diameter. A full derivation of the function relating the measured power \( P \) to the knife-edge translation position \( x \) is given in Appendix A2, but it suffices here to note the power obeys

\[
P(x) = \frac{P_{\text{tot}}}{2} \left( 1 - \text{erf}\left(\frac{\sqrt{2}x}{w_x}\right) \right)
\]

where the 1/e² beam width is given by \( w_x \) and \( P_{\text{tot}} \) is the total power detected by the power meter when the knife is fully removed. Figure 6.2 illustrates

![Figure 6.2](image)

**Figure 6.2** Knife-edge beam profiling. **a**, normalised power measurements upon translation of knife-edge across expanded Gaussian 405 nm laser beam. Fitting has been performed to equation 6.1. **b**, Gaussian intensity profile of beam with characterising parameters as determined with the fitting of **a**.
experimental fitting to this function, and the resultant Gaussian intensity profile of the beam.

Control experiments were performed to monitor the stability of the Ag nanoparticles when exposed to extended periods of illumination. The aqueous solutions of Ag nanoparticles and resazurin were contained in Hellma Analytics fused quartz cuvettes, chosen for their transparency all the way from the UV into near-infrared. The solution was placed into the 2 mm narrow channel; the bold black line in figure 6b indicates this width in relation to the entire beam profile; the quoted intensities hereafter refer to the average intensity in this narrow region (that is, the intensities above the illustrated horizontal).

The temperature of the cuvette and the mixture of dye and nanoparticles was fixed with a Stuart magnetic stirrer and hotplate. Stirring with magnetic beads ensured that a uniform temperature was maintained throughout the entire volume of the cuvette; this was monitored with an RS PRO type K thermocouple. In order to maintain a constant concentration of reactants, the thermocouple directly into the dye-nanoparticle solution was decided against. Instead, an identical cuvette filled with an equal volume of water was placed directly next to the ‘active’ cuvette, and the temperature of this fluid was monitored. The validity of this quoted temperature value was assessed with control experiments ensuring that the bulk temperatures reported were not wildly different from the surface temperatures of the illuminated plasmonic nanoparticles (recall the discussion concerning plasmonic heating in section II).

Additional control experiments were performed to validate the claim that it is indeed hot-electrons that facilitate this reaction, and not due to an enhancement in the local fields upon excitation. FDTD simulations were performed using Lumerical’s FDTD Solutions in order to estimate both the field enhancements around the nanoparticles upon resonant illumination, and to determine the expected cross-sections of the particles. Specifically, the absorption cross-section was used to estimate the temperature increase in and around the nanoparticles upon illumination; we shall return to this notion more fully shortly.
6.2.1 MATERIALS

Resazurin, resorufin, hydroxylamine (NH$_2$OH), citrate-protected Ag nanoparticles and Au nanoparticles (60 nm) in aqueous buffer were all obtained from Sigma Aldrich (Milwaukee, WI). All chemicals were prepared and used as received. Milli-Q grade water (18.2 MΩ·cm) was used in all experiments.

6.3 RESULTS & DISCUSSION

Figure 6.3 illustrates a representative set of data acquired for one experimental condition: an initial colloidal mixture of Ag nanoparticles and resazurin is illuminated near resonance; the fluorescence emission of the ensemble sample is tracked in time, and presents a decrease in the resazurin peak (centred at 630 nm) and a corresponding increase in the resorufin peak (centred at 584 nm). Fluorescence was excited at 520 nm and monitored from 530–800 nm; these wavelengths were chosen so as to fully capture the two clear peaks, and although the excitation does not coincide with the peak of fluorophore absorption (560 nm [196]), it was found to give a reliable quantity of fluorescent emission.

In this particular case, we have used resazurin at an initial concentration of 5 µM and Ag nanoparticles at a concentration of 20 pM with milliQ water (of resistivity 18.2 MΩ·cm) as a solvent. 405 nm illumination here was sustained...
throughout at an average beam intensity of 308.6 mW cm\(^{-2}\). We shall shortly justify this chosen beam intensity and the chosen concentrations. The sample was stirred using a magnetic stirrer rotating at 125 RPM and the temperature here was maintained at 24.7 °C (that is, room temperature).

Here, we have subtracted the scattering from the Ag nanoparticles, which was measured in the absence of any resazurin. It was found to introduce a decaying tail that dropped to negligible values at wavelengths longer than 550 nm, such that subtraction from the spectra make no discernible change to the intensity of the two fluorescent peaks.

Here we introduce the chemical structure of the dyes in use. Both resazurin and resorufin are phenoazin-3-one dyes, with similar chemical structures aside from the absence of a single oxygen atom in the case of the latter (see figure 6.4). Reduction of resazurin yields resorufin. The photophysics of the dyes have not been extensively explored in the literature, but Encinas and colleagues have detailed some properties particularly relevant here [198]. At 602 nm, resazurin's absorption intensity increases linearly with the concentration in the range of 0.5–20 µM, indicating that aggregation is not appreciable. The quantum yield in an aqueous solution was found to be 0.11 and 0.74 for resazurin and resorufin, respectively.

Figure 6.4 Structural and redox properties of resazurin and resorufin. a, Chemical structure of resazurin and resorufin. b, Cyclic voltammetry of 1.50 mM resazurin (blue), indicating its reduction to resorufin, and of 0.27 mM resorufin (red), indicating its oxidation to resazurin. Figure adapted from Chen et al. [197].
Table 6.1 summarises the study’s findings. The rather long lifetime of resorufin, in comparison to that of resazurin, is in agreement with the high fluorescence quantum yield. These values give inherent radiative rate constants for the emitting states of resazurin and resorufin of $1.2 \times 10^8 \text{s}^{-1}$ and $2.5 \times 10^8 \text{s}^{-1}$, respectively, which are consistent with a highly allowed $\pi \pi^*$ electronic transition [198].

Numerous studies have reported the two-electron irreversible reduction of resazurin to resorufin. Cyclic voltammetry recently reported by Chen et al. [197] (recall figure 6.4b) notes that resazurin, at a peak potential of $-0.18 \text{V}$ reduces to resorufin. Additionally, resorufin may further reduce (reversibly) to hydroresorufin, though this is not fluorescent so does not affect our measurement system [199]. Integration under the curves confirms that the reduction of resazurin to resorufin is a two-electron process. Notably, the same study (and further confirmation with density-functional theory calculations) allows approximation of the HOMO and LUMO of resazurin relative to the normal hydrogen electrode, found to be $0.99 \text{V}$ and $-0.34 \text{V}$, respectively.

To ensure that the reduction of resazurin to resorufin is indeed induced solely by energetic carriers following plasmonic excitation of nanoparticles, we performed a series of control experiments. Here we discuss and rule-out the possibilities that the reduction is simply a photoreaction, that it is temperature induced, and that it is solely field induced.
6.3.1 **CONTROL 1: VERIFICATION THAT IT IS NOT SIMPLY A PHOTOREACTION**

In order to confirm that conversion only occurs in the presence of plasmonic nanostructures, the experiment was also performed in the absence of silver.
nanoparticles. Figure 6.5a displays the temporal change in fluorescent spectra over the course of 4 hours of 405 nm illumination with an intensity of 308.6 mW cm\(^{-2}\), with the solution maintained at 24.7 °C.

Here we have reported the data without any normalisation (but with the aforementioned background subtraction), which clearly illustrates a drop in the intensity of both peaks. This can be attributed to chemical decomposition of the dyes in aqueous solutions, which has been observed under exposure to room lighting [196]. For the concentrations of dyes under investigation, the effect is only evident at the highest chosen laser intensities; room lighting does not have a discernible effect (see figure 6.5a).

Note the rate of change of the fluorescence intensity for the 584 nm resorufin peak and the 630 nm resazurin peak were calculated to be \(-7.65 \times 10^{-4}\) s\(^{-1}\) and \(-1.52 \times 10^{-4}\) s\(^{-1}\) (inset figure 6.5a, & 6.5b). The ratio of the two is comparable to the ratio of the two dye's quantum yields (5.03 v. 6.7) and therefore we suspect that an equal number of resorufin and resazurin molecules are denatured upon intense 405 nm illumination.

What is significant here however is the absence of an increase in the resorufin peak centred at 570 nm. That is, we have no dye conversion induced solely by light.

6.3.2 TEMPERATURE-INDUCED FLUORESCENCE DECREASE

It should be noted that even in the absence of illumination, the fluorescent signal of both dyes when accompanied by Ag nanoparticles tends to drop gradually in time when working at elevated temperatures. Figure 6.6b illustrates the fluorescent signal decay upon heating the reaction solution to 42.6 °C over the course of two hours; for comparison, figure 6.5a highlights how this effect is not evident for room temperature experiments (a very slight increase in fluorescence is present here however, which we attribute to a slight increase of dye concentration upon evaporation of the solvent).

Note that the absorption spectra of a 20 pM solution of Ag nanoparticles before and after three hours of heating at 63.4 °C experiences a slight broadening and a redshift, as illustrated in figure 6.7a. This is perhaps indicative of an increase in nanoparticle size. Figure 6.7b depicts the expected absorption cross-section across the same wavelength range for silver nanoparticles of increasing diameter in water, as calculated with Mie theory. The narrowness of the simulated resonance peaks is due to the consideration of the response of just a single particle size; the broadness in experimental data comes from an inevitable range of diameters in colloidal nanoparticle solutions. We then suspect aggregation or growth of nanoparticles is occurring at raised
temperatures. With this increase in size, the fluorescence emission of both resorufin and resazurin undergoes collisional quenching (recall figure 6.5b).

6.3.3 DATA NORMALISATION PROCEDURE

We have seen that the detected fluorescent signal is reduced by two separate phenomena: quenching due to modification of nanoparticle size at elevated temperatures; and denaturing of the chemical structure with intense illumination. If we were to normalise each set of fluorescence traces in time to
the total fluorescence detected (that is, such that the bound area in each case is set to 1), we fail to take into account the notion that resorufin is significantly more fluorescent than resazurin - if a single resazurin molecule is converted to resorufin, the total fluorescence emission from the reaction solution should increase.

However, we encounter an isoemissive point in room temperature traces with no or very low intensity 405 nm illumination. Figure 6.8 demonstrates the fluorescence emission at room temperature upon 405 nm illumination at an intensity of 63.7 mW·cm⁻², where the inset highlights the isoemissive point around 613 nm (for clarity, the data in the inset has been smoothed using a weighted linear least squares and a 2nd degree polynomial model, using a span of 5% of the total number of data points).

This is indicative of a particular wavelength in the spectrum of both resazurin and resorufin where fluorescence emission is of an equal intensity. We may then scale all spectra taken at higher temperatures such that all traces share this isoemissive point, allowing us to correct for the uniform fluorescence intensity decrease due to nanoparticle aggregation.

To account for the asymmetric fluorescence intensity, decrease when the reaction solution is exposed to high field intensities, we shall correct the
spectra by the wavelength-dependent rates of fluorescence decrease as illustrated in figure 6.5b.

6.3.4 CONTROL 2: VERIFICATION IT IS A PLASMON-RELATED REACTION

Verification that the conversion only occurs when we are exciting the localised surface plasmon resonance of the silver nanoparticles was also performed. Figure 6.6a illustrates the constant fluorescence signal of a 5 µM resazurin and 20 pM Ag nanoparticle solution over the course of an hour. Again, the sample temperature was maintained at 24.7 °C. Significantly, this experiment was performed in the absence of 405 nm laser light, and therefore indicates that the conversion from resazurin and resorufin only proceeds in the presence of both plasmonic nanoparticles and light that induces resonant plasmon formation.

Recent work from Chen et al. has addressed the photocatalytic role of both Pd and Au nanoparticles (and PdAu composite particles) in reducing resazurin to resorufin [197]. They illuminate reactant solutions with both 488 nm and 532 nm light at comparable intensities to that employed here. Their work notes that both materials can catalyse the reaction, but only with 532 nm illumination; 488 nm, despite being capable of exciting metal valence electrons, does not catalyse the reaction. Resazurin does not absorb light at 488 nm and therefore this conversion invokes direct photoexcitation of resazurin rather than that of the metal. Our system is different in that conversion is seen with
405 nm light and therefore we suspect hot-electrons are reducing the non-fluorescent dye.

6.3.5 CONTROL 3: VERIFICATION THAT IT IS NOT A PLASMONIC THERMALLY INDUCED REACTION

One might suspect that it is the heating of the plasmonic nanoparticles that facilitates dye conversion. Recall equation 4.5, which gives an approximate temperature increase for a spherical nanoparticle illuminated under continuous illumination in a homogeneous medium. Applying this function to an individual 60 nm Ag nanoparticle in water with a power intensity of 308.6 mW·cm$^{-2}$ (as used in the experiments), we envisage a surface temperature increase of approximately $\Delta T = 5.4$ K.

Figure 6.9 Absorption and heating of illuminated 60 nm Ag nanoparticle. a, Simulated absorption and scattering cross-section of nanoparticle in water. Note that our experimental 405 nm excites the localised surface plasmon resonance of such a nanoparticle. b, Steady state temperature increase in and around the same 60 nm Ag nanoparticle upon illumination with a 405 nm source with an irradiance of 308.6 mW·cm$^{-2}$. Thermal conductivity of 0.591 Wm$^{-1}$K$^{-1}$ (water) used [202]. Scale bar: 100nm.
increase on the order of just $10^{-4}$ K – an insignificant rise. Figure 6.9 shows the FDTD-simulated absorption cross-section for such a nanoparticle and the corresponding temperature profile upon illumination.

The above assumes an isolated nanoparticle, but recent studies have investigated heating due to collective nanoparticle effects [200]. Baffou et al. noted the marked temperature rise – some orders of magnitude greater than that above – when the convective heat dissipation of a single nanoparticle is absorbed by other nearby particles [201]. Notably, a recent study from Halas and co-workers observed steam generation upon solar illumination of a high concentration of Au coated SiO$_2$ nanoparticles. Simple Mie calculations indicate that the absorption cross-section of the core-shell particles in use within their work are on the order of $10^5$ nm$^2$ across the visible spectrum; the light intensities involved are on the order of $10^4$ mW·cm$^{-2}$ – higher than that employed in our own study. Their calculations (using our own equation 4.5) give temperature increases of just 0.04 K. Clearly this is in disagreement with the steam generation observed and may potentially be attributed to this collective heating effect hypothesised by Baffou.

Given that we require careful control of the surface temperatures involved in our experiments, it is of utmost importance to rule out such striking temperature rises. A second thermocouple probe was inserted into a solution of 20 pM Ag nanoparticles, illuminated with and without 405 nm laser illumination at the maximum power intensity used in this study.

Figure 6.10 Temperature increase control, monitoring the increase in temperature of a 60 pM aqueous solution of silver nanoparticles with (solid blue) and without (dashed red) illumination at 405 nm, 308.6 mW·cm$^{-2}$). Set temperature refers to the desired temperature as set on the hot-plate. Upper and lower bounds for each data set illustrate the temperature variation at the bottom and the top, respectively, of the quartz cuvette.
(308.6 mW cm$^{-2}$), and with a variety of set temperatures. Figure 6.10 displays the measured temperatures.

Note that here, the set temperature refers to the user-controlled set temperature of the hot-plate. The dotted upper and lower bounds to each data point are included to reflect the range of temperatres measured within the cuvette; for larger set temperaures, a slight steady-state temperature gradient forms. In the case of the illuminated sample, each circled datapoint refers to the average temperature measured with the thermocouple placed directly into the laser path.

We can conclude that the bulk solution temperature is not rising significantly due to collective plasmonic heating effects.

6.3.6 Control 4: Verification that it is not a plasmonic field intensity based reaction

Though we have highlighted that the conversion of resazurin to resorufin only occurs upon plasmonic excitation of the silver nanoparticles, as a final control, we have investigated if the conversion of reaction can be attributed solely to the enhancement in electric field around the nanostructures upon resonant illumination.

Figure 6.11 depicts FDTD calculated field intensity enhancements in and around a 60 nm diameter Ag nanoparticle suspended in water upon illumination at 405 nm. The silver material data was taken from CRC [203], and a mesh of 0.8 nm was constructed over the nanoparticle. As an aside, CRC data is preferable to Johnson & Christy's optical data as, with very small real refractive
Figure 6.13 Field-intensity control tests, experimental results.  

a, Temporal fluorescent intensity change of resazurin only, initial concentration 5 µM, illuminated at 308.6 mW·cm⁻².  

b, Temporal fluorescent intensity change of resazurin, initial concentration 5µM, with 20 µM Ag nanoparticles, illuminated at 20.6 mW·cm⁻².  

c, Magnitude of 584 nm fluorescent peak, corresponding to resorufin. Note that Ag nanoparticles are vital to ensure conversion of resazurin to resorufin.
indices, the FDTD simulations tend to converge very slowly. Very small mesh sizes allow one to overcome this issue, but at huge computational cost. Instead, it is advantageous to choose material fitting data that ensures the real index remains as large as possible (obviously, there are limits on this since the adjusted fit must still represent the material properties). For example, at 500 nm J&C report a real index of 0.05, while CRC gives an index around 0.25.

Within a shell of 10 nm around the nanoparticle surface, the average field intensity over all three planes is 14.9 times greater than that of incident wave. We can then rule out the notion that it is solely a field induced effect through a comparison of the dye conversion with and without nanoparticles, using 15 times higher power density in the latter case. This way, both systems exhibit the same magnitude of field intensity.

Experimentally, with 15 times higher beam intensity (308.6 mW cm$^{-2}$) in the absence of plasmonic nanoparticles, we saw no change in the peak fluorescence values. For lower beam intensities (20.6 mW cm$^{-2}$) but with nanoparticles, we see a slight but discernible increase in the peak intensity over time, indicative of the conversion of resazurin to resorufin. Figure 6.12 illustrates this. The lower magnitude of this conversion relative to that illustrated in figure 6.3, for example, is to be expected given the low laser power involved.

We are then in a position to hypothesise that the reduction of resazurin to resorufin here only proceeds in the presence of hot-carriers, induced upon resonant excitation and subsequent decay of localised surface plasmons in silver nanoparticles.

6.3.7 POWER & REACTANT CONCENTRATION DEPENDENCE

Recall from our discussion of plasmonic losses that with increased power absorbed by the nanoparticle at plasmonic resonance, the quantity of hot-charge carriers available increases correspondingly. A simplistic application of this notion to the experiments at hand would suggest that a greater laser intensity would therefore facilitate increased rates of dye conversion. Figure 6.13 demonstrates this. The dotted upper and lower bounds for each data set indicate an estimate of the standard deviation of the error in predicting future observations. As we are interested in the rate of production of resorufin, the initial fluorescence value is not of interest here; for clarity, the datasets have been offset.

Additionally, we have depicted the rate of resazurin consumption within our reaction solution. A simple comparison of the ratio of the rates of resorufin production and resazurin consumption (accounting for the approximately seven-fold difference in quantum yield), suggests that this is an 1:1 reaction.
Inset in each figure is the rate of the reaction against the intensity of illumination. Note that the rate refers to the fluorescence emission (in arbitrary units) per unit time, rather than the number of fluorescent molecules. With increasing laser intensity, both the production rate of resorufin and the consumption rate of resazurin seemingly obey quadratic power dependence (insets, figure 6.13). This suggests that the rate-limiting step of this plasmonic catalytic reaction is the absorption of photons in the nanoparticle.
So far, we have naively assumed that there is no rate-limiting process involved; the surface of each nanostructure may well be saturated at the chosen concentration of dye (5 µM), either due to the large number of dye molecules relative to nanoparticle surface area or to slow desorption kinetics.

Figures 6.14a and 6.14b depict the resorufin and resazurin peak increase and decrease, respectively, for initial resazurin concentrations of 2.5, 5, and 10 µM. The insets of these figures depict the variation of rates of fluorescence change with concentration. Note that these follow classic Langmuir saturation kinetics.
for heterogeneous catalysis [204], and it appears that the surface becomes saturated with active reactants around the concentration of 5 µM. This then further supports the claim that rather than conversion of free resazurin molecules, this is a process mediated by the hot-electron transfer from the nanoparticle surface itself.
6.3.8 Temperature Dependence

Figure 6.16a presents the change of the resorufin peak (584 nm) height in time over a range of temperatures. Additionally, we plot a control dataset, with peak heights taken from illumination of a sample at room temperature in the absence of nanoparticles. Figure 6.16b illustrates the corresponding decrease in resazurin peak (630 nm) height. Again, we are solely interested in the rates of conversion here, so we have spaced each dataset for clarity.

6.4 Activation Barriers

As a comparison to our novel Ag nanoparticle mediated plasmonic catalysis, we return to the previously mentioned studies of Au nanoparticle catalysed reduction of resazurin to resorufin in the presence of hydroxylamine that have been monitored at both the ensemble level and the single-molecule level extensively by both Chen’s and Fang’s research groups [197,199,205].

The reaction differs to that studied above in that it proceeds via reductive deoxygenation by hydroxylamine on the surface of Au nanoparticles and does so with no need for illumination. It is therefore not an example of plasmonic catalysis. The reaction kinetics are significantly different to the proposed kinetic mechanisms of the Ag plasmon-mediated conversion: in the case of Au catalysis, a resazurin molecule and a hydroxylamine molecule must adsorb at adjacent sites upon the nanoparticle surface.

The literature typically utilises Au nanoparticles far smaller than the nanoparticles we have used so far: a 2010 study by Zhou and colleagues addressed the size-dependence of the reaction kinetics, highlighting that with decreasing particle size, the binding affinity of the Au substrate decreases, concurrent with an increase in the reactivity of catalytic conversion [206].

Here we examine the conversion of an initial concentration of 5 µM resazurin on the surface of 20 pM Au nanoparticles of 60 nm diameter in the presence of a large excess of hydroxylamine (100 µM). Though the kinetics between the two reactions are significantly different, the same concentrations as with our silver experiments were chosen so as to provide a useful tool of comparison, particularly in the context of temperature dependence.

Figure 6.16 illustrates two typical fluorescence traces with excitation at 520 nm; 6.16a depicts room temperature conversion; 6.16b illustrates the significant increase in catalytic activity (note the change in fluorescence intensity scale) with increased reactant solution temperature. Notably, the reaction here proceeds at a far greater speed than the Ag nanoparticle counterpart. There appears to be no issue of nanoparticle aggregation at elevated temperatures, and thus there is no need to manually adjust for collisional quenching of the dyes. Furthermore, given that this reaction proceeds with no need for
Figure 6.6 Temporal fluorescent intensity of resazurin during conversion to resorufin with Au nanoparticles. Initial concentration of resorufin, 5 µM, concentration of 60 nm Au nanoparticles, 20 pM, in aqueous solution. Hydroxylamine added in large excess (100 µM) Solution was stirred throughout with a PTFE-coated magnetic bead.

a, Temperature of the solution maintained at room temperature (24.7 °C) throughout.
b, Temperature of the solution maintained at 49.5 °C.

illumination, the issue of light-induced denaturing of the chemical structure of the dyes as previously experienced is not of concern. The reported fluorescence intensities are then unmodified with no normalisation.
6.4.1 TEMPERATURE DEPENDENCE FOR GOLD

Unlike in the case with Ag nanoparticles, the hydroxylamine-mediated catalytic conversion of resazurin to resorufin on the surface of Au nanoparticles was found to be strongly dependent on temperature. Analogous to figure 6.15 from the previous subsection, figure 6.17 depicts the change in fluorescent intensity at 584 nm with increasing temperature. The dashed line represents a control experiment in which Au nanoparticles were incubated with resazurin at room temperature without the reductant, hydroxylamine; no discernible change in the 584 nm peak height was detected over the course of two hours. A further control experiment indicated that Au nanoparticles are required for the reaction to proceed.

A full study of the reaction kinetics involved is largely beyond this scope of this thesis; Han et al. reported extensively on single-molecule conversion but stopped short of ensemble level measurements, which they deemed to be complex due to particle-particle interaction [188]. I therefore direct the reader to the PhD work of Venkataramanan Ravi for a complete discussion of the relevant kinetics at the ensemble level [207]. Notably, it is found that the rate of conversion of resazurin to resorufin may be modelled on a Langmuir-Hinshelwood formulation, which is reliant on absorption of both resazurin and hydroxylamine at neighbouring sites before undergoing a bimolecular reaction.
This example exhibits a reaction rate that, when normalized by Au nanoparticle concentration, should display first-order dependence on Au nanoparticle concentration in the absence of particle-particle interactions.

The saturating nature of the Langmuir kinetics involved in the fluorescence observed in the conversion of resazurin to resorufin may be associated to the rate of such conversion via

\[ F(t) = F_\infty + (F_0 - F_\infty)e^{-kt} \]  

(6.2)

where \( F \) denotes the fluorescence at time \( t \), \( F_\infty \) is the saturation fluorescence, \( F_0 \) is the initial fluorescence, and \( k \) is the (temperature dependent) rate of the conversion. Fittings of each experimental dataset are depicted in figure 6.17. The fitting yields an average saturation fluorescence value of 143.1 ± 5.8, and an initial fluorescence value of 7.1 ± 1.3. The control sample (without the reductant hydroxylamine) has simply been fitted to a zero-order linear fit to highlight the lack of change in intensity over this timescale.

The measurement of these ensemble catalytic rates as they vary with temperature enables us to introduce the Arrhenius equation, which describes the temperature dependence of reaction rates:

\[ k = A e^{\frac{-E_a}{k_BT}} \]  

(6.3)

where \( E_a \) is the activation energy for the reaction, \( T \) is the temperature at which the reaction proceeds, and \( k_B \) is the Boltzmann constant [208].

Figure 6.18 Arrhenius plot of logarithm of reaction rate constant against inverse temperature. Considering the reaction with Au nanoparticles, there exists a clear downwards slope when a linear regression is determined, indicating a (positive) activation energy for the reaction on the AuNP surface of 0.77 eV. Fitting for the Ag nanoparticle data indicates a negative activation barrier of -0.75 eV, though the fitting is significantly poorer in this instance.
We may then plot the natural logarithm of the fitted reaction rates against the (inverse) experimental temperature, ideally resulting in a linear fit with a gradient of $-E_a/k_B$. Figure 6.18 depicts the temperatures, the fitted reaction rates, and the corresponding fit to the Arrhenius equation for both our silver and our gold nanoparticle experiments.

The Arrhenius plot for the Au nanoparticles follows that of a conventional temperature-dependent reaction; calculation from the gradient of the fitting yields an activation energy for the reaction of approximately 0.77 eV. This is largely comparable to the value determined by Ravi of 0.65 eV [207].

Fitting to the rate observed with plasmon activated Ag nanoparticles gives an activation energy of -0.75 eV. A negative activation energy is a valid concept that appears in chemical kinetics – these are typically barrierless reactions in which the reaction proceeds only upon the capture of molecules into some potential well. Temperature increases serve to reduce the probability of capture. In our case, we might interpret this as an increase in the desorption rate of resazurin upon the heated Ag surface before electron transfer can occur. However, the fitting accuracy in the case of the Ag nanoparticles is comparatively poor, so this value should not be taken as definitive. Rather, the significant conclusion here is that there appears to be no positive activation barrier for the reduction of resazurin to resorufin on Ag nanoparticles.

Notably, since starting this study, work from Halas et al. has been published in which they too introduce the concept of a light-dependent activation barrier in plasmonic photocatalysis, which accounts for the effect of light illumination on electronic and thermal excitations [45]. While this study differs in that it addresses plasmonic copper nanoparticles and their role in the catalytic decomposition of ammonia ($2NH_3 \rightarrow N_2 + 3H_2$), they too conclude that upon resonant illumination of the plasmonic nanoparticles, the activation barrier that habitually limits transfer of hot-carriers is reduced. Thus, both their and our findings are critically important in the design of energy-efficient plasmonic photocatalysts.

As discussed by Halas et al. hot-carriers can influence the energetics of adsorbed molecules and enhance the net reaction rate. We hypothesise that, like the NH$_3$ molecules in Halas’ study, the energy barriers of resazurin can be reduced by activating the adsorbed molecules through hot-carriers, in a variety of manners, along the reaction pathway.

Hot-carriers can transfer into adsorbed resazurin molecules and electronically excite the Ag–Rz surface species, thus enabling the O desorption process, thereby forming a resorufin molecule. The Ag–Rz bond activation then occurs through an excited state with a lower activation barrier. This process requires resonant excitation conditions between the excited state and the acceptor levels of the Ag–Rz surface species.
Following creation by plasmon decay, hot-carriers rapidly relax via electron-electron scattering and approach the Fermi level. As mentioned in earlier chapters, electron-phonon scattering on a monometallic nanostructure plays a relatively minor role as all such phonons involve atoms of the same charge and thus do not possess electrical multipolar moments [45]. Another possibility for activation of the Ag–Rz bond is inelastic electron-vibrational dipole scattering. Resonant conditions are not critical here and the process may occur permitted the hot-carriers possess energies greater than the vibrational quantum.
The purpose of the in-depth study of the ensemble conversion of resazurin to resorufin upon the surface of Ag nanoparticles was to assess its potential use in stochastic super-resolution imaging of plasmonic Ag nanostructures at the single molecule level. Extensive super-resolution work has been conducted into the study of heterogeneous catalysis upon Au substrates, including composite TiO2/Au particles [157], CdS/Au particles [209], bimetallic PdAu structures [197], and Al structures [160]. But, to the best of the author’s knowledge, no stochastic super-resolution studies have employed Ag substrates, which is surprising given Ag’s prominence in industrial catalysis [210]. Here we investigate the use of resazurin to probe the plasmonically active regions upon top-down fabricated Ag nanostructures.

Single-molecule reaction kinetics involving fluorescent molecules provide a novel method in understanding chemical kinetics through focusing on the variation in the temporal duration of non-emissive and emissive periods during a chemical reaction and present a useful means of deciphering dispersive kinetics ubiquitous in the aforementioned heterogeneous catalytic systems [173,211,212]. At the ensemble level, though we gather important information to the statistical averages of the reaction pathways at play, we lose sight into the catalytic variation across a single nanoparticle.

7.1 AG ANTENNA DESIGN

Recall from section 5.4.1 that localisation efforts are hampered when the emission of the chosen fluorescent dye overlaps with the response of the antenna. Given that we are using a dye with a broad absorption spectrum centred at around 573 nm and an emission spectrum centred at around 584 nm, Ag is advantageous in the sense that small Ag nanoantennae typically exhibit plasmonic resonance further into the blue end of the visible spectrum. Following a similar approach as taken by Mack and colleagues [160], FDTD studies were conducted upon Ag nanobar geometries to predict the absorption and scattering properties, the spectral position of the plasmon upon both plane-wave and TIRF illumination, and the local density of states of the system in the presence of an idealised dipole emitter.
A nanobar geometry was chosen as, upon consultation with experts in lithographic fabrication, the simple geometry was deemed to be experimentally realisable. Issues arose with excessive 405 nm excitation intensities that were found to cause damage to the nanobars (recall equation 5.17 that indicates that the field intensity at the interface can be over 5 times that of the incident intensity). We consequently moved away from 405 nm TIRF illumination,

Figure 7.1 TIRF considerations for super-resolution experiments. a, Geometry for conventional wide-field excitation of localised surface plasmon of an Ag nanobar, at the interface of SiO$_2$ and water, excited polarised in the longitudinal ($\hat{x}$) direction. b, Excitation of localised surface plasmon in TIRF configuration. $\theta_c$ denotes the critical angle; $s$ and $p$ correspond to the polarisation states; $\phi$ denotes the azimuthal angle (around the $z$ axis). Left excitation of the longitudinal mode with $p$-polarisation. Right excitation with $s$-polarisation. c, Absorption and scattering cross-sections of a 150×50×50 nm Ag nanobar with wide-field illumination. d, Cross-sections with TIRF illumination. Note the change in scale between the two cross-section plots. e, Field intensity enhancement profiles at 405 nm wide-field illumination – corresponding to the laser used to excite the plasmonic mode of the nanobar. Top: $xy$-plane. Bottom: $xz$-plane. Right: $yz$-plane. f, Enhancement profiles with TIRF excitation. Scale bar: 50 nm.
instead opting to illuminate the nanobar with wide-field optics. Figure 7.1a illustrates the two possible polarisation configurations we can excite.

The 561nm illumination was performed in TIRF configuration with unpolarised light given that we are not interested in selectivity of fluorophore orientation. Computational electrodynamic simulations, however, require some description of the incident polarisation and, given that we can excite the system in four possible manners with linearly polarised light in TIRF configuration (as depicted in figure 7.1b), the reported cross-sections (figure 7.1d) are given as superpositions of the relevant polarisations. The angle $\phi$ refers here to the azimuthal rotation around the $z$-axis, such that the $\phi = 0^\circ$ results correspond to the superposition of $s$- and $p$-polarised waves upon excitation when the incidence plane is aligned with the long axis of the nanobar (figure 6.15b, left). Similarly, $\phi = 90^\circ$ corresponds to the superposition when the incidence plane aligns with the width of the bar (figure 7.1b, right). Notably, at 561 nm, we expect to see negligible absorption within the nanobar for both $\phi$ angles and we expect an increase in scattering for the $\phi = 90^\circ$ case.

Figure 7.1c illustrates the cross-sections of a 150 nm Ag nanobar illuminated in wide-field illumination (as in figure 7.1a). Note that at 405 nm, we can excite at resonance with a beam with the polarisation vector aligned perpendicular to the long bar axis; exciting with parallel polarisation gives rise to the longitudinal plasmon around 900 nm. Indeed, the electric field intensity enhancement profiles (figure 7.1d, e) demonstrate the hot-spots in the corners of the antenna only upon perpendicular polarisation excitation. We then have a simple method of verifying plasmon-induced hot-electron catalysis: upon parallel polarisation we expect to see no production of hot-carriers and thus no resazurin conversion and thus no resorufin emission.

In section 5.4.2, we noted that dye emission may couple with the nanostructure’s local density of states, resulting in emission from a site that reflects neither the nanoparticle’s or the fluorophore’s accurate position. Mack et al. argue that adequately decoupling the total radiative decay rate enhancement of the system from the dye’s emission is sufficient to avoid this issue [160]. Decay rates of fluorophore’s in the near vicinity of the nanoantenna were simulated by adopting a Green’s function approach [11]. Consider the field $E(r)$ at position $r$ as determined by a dipole source at position $r_0$, which is of moment $\mu$ and immersed in a background of permittivity $\varepsilon_r$. The Green’s dyadic for this system is given by

$$\overline{G}(r, r_0) = \frac{E(r)c^2\varepsilon_0\varepsilon_r}{\omega^2\mu} \quad (7.1)$$

where $\omega$ describes the angular frequency of the source. $\overline{G}$ is a dyadic tensor, such that each orthogonal component may be calculated by using a single dipole source of known linear polarisation. The partial local density of states $\rho$
along such a direction may be determined from the imaginary part of the relevant $\mathbf{G}$ component. Consider a dipole oriented along the $x$ axis for example; the partial density of states in $x$ is given by

$$\rho_x(r, \omega) = \frac{6\omega}{\pi c^2} \text{Im}[G_{xx}]$$  \hspace{1cm} (7.2)

where $G_{xx}$ is the $x$-component of $\mathbf{G}$. This may then be used to determine the decay rate of a two-level system as per Fermi's Golden rule:

$$\gamma_x = \frac{2\omega}{3\hbar} |\mu|^2 \rho_x(r, \omega)$$  \hspace{1cm} (7.3)

The total decay rate for the system may be found by averaging over all three orthogonal dipole orientations. This may be then normalised with respect to the free-space spontaneous decay rate of the dipole $\gamma_0$ to give a measure of the enhancement provided by the nanoantenna:

$$\gamma = \frac{\omega^3 |\mu|^2}{3\pi \varepsilon_0 \hbar c^3}$$  \hspace{1cm} (7.4)

Figure 7.2 illustrates the simulated total decay rate of a broadband dipole source decomposed into the radiative and loss channels calculated via the above
equations where the fields were determined with FDTD simulations. The source is positioned into the area of the system exhibiting the greatest field enhancement upon 405 nm excitation (see figure 7.1e), as it is here we expect the greatest magnitude of hot-electron production [213]. The emission window of our own fluorophore (resorufin) is highlighted (580-600 nm). The radiative decay rate of resorufin when positioned near a 150×50×50 nm Ag nanobar on a SiO$_2$ substrate is expected to be roughly twice that found for an identical emitter in free-space. Mack et al. were able to overcome the issue of mislocalisation by combining an aluminium antenna plasmonically resonant at 405 nm and a dye with an emission peak at 575 nm. Simulations of their system highlight that a dipole placed into the plasmonic hot-spot experiences a radiative decay rate enhancement (at 575 nm) of approximately 4 times that of a dipole in free-space. We therefore expect that our own dye and Ag antenna are sufficiently decoupled and mislocalisation should not be a concern.

7.2 Antenna Fabrication

10×10 arrays of the previously discussed Ag nanobars were fabricated by Dr. Javier Cambiasso at Imperial College London. The samples were prepared following a single-step electron beam lithography writing step and a metal evaporation procedure.

Quartz polished coverslips (GPE Scientific) were cleaned in three steps of 5 minutes each under DI water, acetone, and isopropyl alcohol (IPA). Poly(methyl methacrylate) (PMMA), 950k A4 (Microchem) was spin-coated upon the sample at 3500 RPM for 1 minute, yielding a homogeneous film of around 200 nm thickness. A thin layer of the conductive material Espacer 300Z (Showa Denko Europe) – used to counter charging under the electron-beam – was spin-coated at 2000 RPM for 1 minute. The sample was then loaded into a Raith eLine and the structures were defied in the PMMA layer with a voltage acceleration of 20 kV, 20 mm aperture, at a working distance of around 10 mm, area step size 6 nm, and an area dosage of 100 mC·cm$^{-2}$. After writing, the samples were developed in a solution of 1:3 methylisobutyl ketone: IPA for 30 seconds, followed by a developer stopper of IPA for another 30 seconds. O2 plasma ashing was performed to remove any PMMA debris in the developed holes.

Silver was then evaporated in a Åmod system (Ångstrom Engineering Inc) at a low pressure of 7×10$^{-7}$ Torr, at a fast deposition rate of 30 Å·s$^{-1}$, resulting in a final thickness of 50 nm. Lift-off was performed by immersing the samples in acetone for 24 hours, followed by careful acetone and IPA rinsing before N$_2$ drying. We avoid using a molecular adhesion layer between the Ag and the quartz substrate to avoid any unwanted molecular interaction with the hot-carriers [60].
SEM imaging was then performed to determine final sizes. Figure 7.3 depicts representative SEM images of the fabricated Ag nanobars. For comparative purposes, identical geometry nanobars,

Samples were prepared for super-resolution fluorescent microscopy by affixing a flow chamber atop. Arrays of antennas were designed such that their position upon the slide corresponded to the spacing between individual flow chambers as on the Ibidi sticky-Slide VI 0.4. These chambers were chosen to enable simple sample flushing after measurement, so as to enable successive measurements with different dye concentrations upon the same antennas (allowing for direct comparison of plasmonic catalytic activity). Further, the chambers proved advantageous as they allowed work to commence on one array of antennas without potentially damaging other arrays on the same slide, thereby reducing fabrication needs. Before affixing, the slides were cleaned by plasma-ashing for 10 minutes with an Emitech K1050X at 40% power in an oxygen atmosphere. For the comparative Au nanobars, the Au samples themselves were also cleaned for 1.4 minutes at 40% power; while trialled on the Ag samples, it was found that this irreparably oxidised the Ag structures.

7.3 OPTICAL SYSTEM FOR DUAL EXCITATION SUPER-RESOLUTION MICROSCOPY

The super-resolution optical system was constructed around an inverted Nikon Ti-U microscope. Simultaneous excitation of the fluorophore and of the plasmon of the nanostructure was achieved through dual excitation: the former with a 561 nm constant wavelength (CW) Cobalt Jive with a maximum output of 200 mW; the latter with a 405 nm Coherent Cube (100 mW maximum output). A CFI Apo TIRF 100× oil-immersion objective (1.49 NA) was chosen to allow TIRF excitation of the sample.

Both incoming lasers were passed through polarization maintaining beam-splitters. The 405 nm beam was then passed through the relevant combination
of half-wave and quarter-wave plates (Thorlabs) to select the desired polarization orientation at the substrate. Each beam was expanded independently to achieve the low power intensities required using a telescope formed of two biconvex lenses (Thorlabs, N-BK7), and the two were combined using a 405 nm Semrock laser BrightLine® single-edge dichroic mirror, collimated and focused at the back focal plane of the objective. An adjustable UV-enhanced aluminium mirror (Thorlabs) permits angular modification of the two beams, such that TIRF conditions (recall section 5.3.1) are achievable through simply adjusting the kinematic mount.

The sample of interest was mounted on the mechanical stage of the microscope. The use of a piezoelectric stage for sample stabilisation was considered, but an algorithmic image processing approach was chosen instead (see the forthcoming discussion for more details) and thus was deemed unnecessary. Both a Semrock 405/488/561/635 nm BrightLine® quad-edge dichroic beamsplitter and 586/20 nm BrightLine® single-band bandpass filter were mounted within the microscope to enable excitation at 405 nm and
561 nm and emission collection in the narrow region of 580 – 600 nm (recall the emission spectrum of resorufin, the fluorophore of interest here, as depicted in figure 6.1) removing the possibility of sensor damage with laser light. An illustrative photograph of the optical setup is given in figure 7.4.

Fluorescent emission was, after spectral filtering, collected with an electron-multiplying charge-coupled device camera (Evolve 512 Delta, Photometrics). Such a camera operates through the conversion of photons to electrons, which are then accelerated, cascading through multiplication regions, and give rise to detectable currents; our own chosen camera is capable of converting around 90 % of all collected photons to detectable electrons. The camera comprises a 512×512 array of 16×16 µm$^2$ pixels. With a system magnification of 100×, each pixel should correspond to an area of 160×160 µm$^2$ in object space. Optimum imaging for these experiments was found to correspond to a readout bandwidth of 5 MHz at 16 bits with a preamp gain of 3 and an electron multiplying gain of 200. A typical acquired image consists of 40000 individual TIFF frames, each acquired over a 30 ms window. Open-source software Micro-Manager, itself reliant on the open-source ImageJ, was used to handle image acquisition.

The knife-edge technique used to determine the beam widths and thus the beam intensities was not appropriate here due to the significant decrease in
sizes relative to those concerned in section 6.3. Instead, a high-concentration solution of resorufin in combination with the fluorescent dye Pacific Blue was dropped into an unused flow chamber (that is, without any nanoantennae). This combination of dyes was chosen so as to enable imaging upon both 405 nm and 561 nm excitation. Care was not taken to assess the concentration of the dyes as the measurements were used solely to determine the beam diameter, though it is estimated that both dyes were on the order of 10 μM. The ImageJ plugin Open Beam Profiler was used to measure the Gaussian profile of the two laser beams. As can be seen in figure 7.5, the two beams were of comparable sizes, with the 405 nm and the 561 nm beams having FWHMs of 43.85 μm and 45.80 μm, respectively.

Pre-processing of the data was performed for two reasons: to remove the scattering of the antennas, and to correct for inevitable sample drift arising due to even slight vibrations of the optical bench. The scattering of the antennas, serendipitously, provides a useful means of stabilisation. Acting as fiduciary markers, the antennas scattering allows us to perform discrete Fourier transform registration upon image frames with respect to a chosen reference frame. The algorithm used was developed by Guizar-Sicairos and colleagues [214], and allows registration of two images with a 2-dimensional rigid translation to within a fraction of a pixel (we have specified to 1/100th of a pixel hereafter). The code uses selective up sampling by a matrix-multiply discrete FT, which dramatically reduces computation time and memory without sacrificing accuracy. Additionally, as previously mentioned, this has negated the need for hardware-based sample stabilisation. Figure 7.6 displays an example of a typical translational shift as recorded through image acquisition.

Large fiduciary markers of irregular geometries were fabricated in the corners of each nanoantenna array in order to assist alignment. However, the uniformity of the arrays of nanoantennae that we employed occasionally gave rise to errors in the registration, i.e. a column might be taken to correspond to a completely separate column in the following frames, thereby giving rise to a large undesired translation. Manual filtering of the frame alignment was therefore employed to remove any significant shifts; figure 7.6b illustrates a ± 0.5 pixel threshold above and below the average trend of the sample drift. The average trend was calculated using a local regression using weighted linear least squares and a 2nd degree polynomial model. Any frame which registered a translational shift lying outside of these constraints was disregarded from any subsequent analysis. Half a pixel (corresponding to 80 nm) was found to be a suitable value for these bounds as it effectively removed any erroneous misalignments while preserving slight shifts induced by fine-focussing of the sample during measurements.

We then determine the average intensity of each pixel over the course of the entire stabilised image and construct an average single frame. Given that we
enforce by requirement temporally separate fluorescent events to be able to reconstruct a final super-resolution image (recall section 5.4.1), this average image, to a good degree, exhibits only the scattering of the antennas. This average image is then subtracted from each individual frame of the stabilised stack, leaving an image stack displaying only the fluorescent events.

Super-resolution images were reconstructed from the stabilised, scattering corrected data based on localisation of single molecule fluorescent events through a stochastic means as described in the previous chapter. We chose to use the Picasso software suite provided by Jungmann and colleagues [215]. Though optimised for DNA-PAINT (that is, PAINT with binding of fluorophores mediated by complementary DNA strands [154]), this suite was found to be suitable for our own needs. Events are identified in each successive frame of the TIFF stack by translating a box of a set edge length (default value 7 pixels, or 1.12 µm) within which we expect the all diffraction-limited fluorescent emission to be contained. All locations where the intensity gradient exceeds some user-defined threshold are then defined as an event. Each identified event is then fitted to a symmetric point-spread function (or a closely approximated Gaussian) and the event’s properties are saved – the most useful of such properties being the fluorophore’s expected (sub diffraction-limit) position within the frame.

Using Picasso’s own rendering functionality, or through writing our own MATLAB codes, we arrive at a map of all fluorescent events. The fabricated samples were designed with either 6×6 or 10×10 arrays of identical nanoantennae, such that custom MATLAB codes could be used for statistical averaging. Briefly, the codes transmute the averaged single frame into a two-dimensional binary image with components defined as having an intensity of the mean plus one standard deviation of all pixel’s intensities; such components are the antennas. The centroid of each component is then defined as the centre of each antenna. The rotation of the sample relative to the camera, determined through comparison of the positions of two separate antennas in the same row or column, is applied and a region of (typically) 3 pixels around each antenna is drawn. All localised events falling within this drawn region are attributed to the antenna at its centre, and all 100 (in the case of the 10×10 array) regions are averaged with user-defined positional binning to yield a final, super-resolution map of fluorescent activity.

7.4 RESULTS & LIMITATIONS

Attempts at super-resolution maps formed through the methods as detailed in the previous sub-section were processed from a stack of 40000 individual image frames, acquired with and without 405 nm illumination at between 1.66 and 6.62 µW·µm⁻². A solution of resazurin at an original concentration of 25 nM was used, and fluorescence was excited with 561 nm TIRF illumination at
3.34 µW·µm² as described in section 7.3. It became clear here however that super-resolution imaging at the desired accuracy was not achievable. We can attribute to this to a variety of potential effects, which we shall address successively as follows.

It became clear that due care was required in setting the power of the 405 nm laser, which was used to excite the plasmon resonance of the nanobars, thereby facilitating hot-electron production and transfer to the resazurin molecules. SEM imaging of an array of 150×50×50 nm nanobars was conducted before and after 20 minutes of 405 nm illumination at 6.62 µW·µm² (the timescale for a typical imaging procedure). All other conditions, including the solvent (here, water) were kept constant. It was clear that there is some mechanism at work that serves to damage the structure of the antennas.

Initially, we hypothesised that the temperatures of the nanobars upon illumination might be too high. FDTD calculations of the absorption cross-sections of the nanobars, conducted with Lumerical FDTD solutions as discussed in preceding chapters, indicated that – upon direct incident illumination with 405 nm and TIR illumination with 561 nm, in all possible relevant polarisation states – yielded absorption cross sections on the order of 10⁻¹⁴ m² (recall figure 5.2). Taking a particularly simplistic model in which the power absorbed is equivalent to the cross-section of the nanobars, $\sigma_{abs}$, multiplied by the intensity of the incident beams, $I$, (that is, ignoring any mechanisms of heat-transfer), and taking the bar to have an effective radius $R_{eff}$, which may be considered as the radius possessed by a sphere on an equivalent volume, the temperature increase may be expressed as

$$\Delta T = \frac{\sigma_{abs}I}{4\pi\kappa R_{eff}}$$  \hspace{1cm} (7.6)

Where $\kappa$ is the thermal conductivity of the surrounding medium (water here). This model takes the temperature increase as that experience by a sphere surrounded in a homogenous medium (as in the previous chapter). While not ideal, it does indicate that temperature increases of the antennas are on the order of just 0.46 K, and therefore it is unlikely that temperature increases after the super-resolution measurements significantly.

As noted in section 7.2, during the preparation of Ag nanoantennae, plasma-ashing was not used in the cleaning process due to the potential of unwanted Ag oxide formation. It is common practise in super-resolution measurements to plasma-ash the substrates to remove any biological materials [154]. Our inability to do so introduces concerns regarding the presence of unwanted biological material on the slides throughout measurements. Further, unwanted residual material from the lithographic process may have still been present upon these samples. Numerous attempts were made at sample fabrication,
which involved extended soaking and washing in acetone (up to 72 hours) to remove such material, but this still was unable to rectify the issue.

Recent work by Sundaresan and colleagues [216] has partially elucidated the mechanism wherein Ag oxide forms on Ag nanoparticles. Whilst this is discussed in the context of electrochemical reactions, they conclude that “particle shape can change anistropically during electrodissolution based on the nature of surface oxide layer”. We then propose that the oxidation of our nanobars may be such as to significantly modify the plasmonic response. Indeed, the work of Grillet et al. indicates that a simplified Ag nanostructure becomes 16.5% oxidised (in terms of total volume of the structure) after approximately 4 hours of illumination; a time-scale not too dissimilar to the total illumination lengths employed in our study [217].

While not conducted here, it could conceivably be sensible to study the effect of Ostwald ripening on the structure of the Ag nanobars over extended illumination times; numerous recent studies have investigated the modification of non-spherical colloidal systems of nanoparticles in the presence of plasmonically resonant illumination lasers [218,219]. Based on the mechanisms disclosed within, it is conceivable that our nanostructures are ‘ripening’ to a geometry that significantly modified the plasmon resonances, thereby negatively affecting the localisation attempts.

Citrate passivation of the silver nanobars was attempted. Immediately after fabrication, the Ag nanoantennae were immersed in a solution of aqueous sodium citrate (at a concentration of 10 µM). This was performed in order to better replicate the conditions of the ensemble conversion, as discussed in section 6.3; here, the Ag nanoparticles as purchased are provided with sodium citrate used as a stabiliser. We hypothesised that the citrate passivation would inhibit the formation of Ag oxide upon the Ag nanobars surface. Localisation maps, however, were found to be just as poor with the use of citrate as without.

Interestingly, during control experiments, the image frames acquired for each experimental condition in the absence of any fluorescent dye indicated that, after 405 nm illumination and in the presence of 561 nm (then with no 405 nm illumination), there were more background fluorescent events than the case in which 561 nm was used without prior 405 nm illumination. We are uncertain as to why this is the case, but it appears that some form of photoreaction occurs with resonant illumination, potentially generating luminescent bodies. While we attempted to account for these events in the post-processing stage, this proved problematic as the number of fluorescent events induced in such a way was wholly unpredictable. Such events were not present in the experiments using Au nanobars. It may then be that this phenomenon may conceivably be attributed to the leaching of Ag ions from the Ag nanostructures. Further studies are currently being considered that elucidate this further.
With regards to the Au nanobars control experiments, these differed extensively from the experimental methods described above. The purpose of these trials was to provide a comparison for the catalytic activity of identical geometry nanobars fabricated from different metals. The Au nanobars were to be monitored with and without hydroxylamine (recall the extensive discussion of the catalytic reduction of resazurin in the presence of this molecule from the ensemble measurements).

Further, the aim was to assess and compare the locations on each Au and Ag nanobars that presented a site where the activation barriers were scalable and electron transfer could take place. It was expected that non-plasmonic catalytic activity upon the Au nanobars was to be uniform over the entirety of the surface, given that hydroxylamine was too uniformly situated over the entirety of the surface. In contrast, it was expected that only the regions of the Ag nanobars wherein plasmonic generation of the hot-electrons occurred would be illustrated in maps of catalytic surface activity. Polarisation dependence too would have been present with Ag nanobars; with Au nanobars the scaling of the energy barriers was expected to be polarisation-independent.

Figure 7.6f illustrates representative super-resolution catalytic maps of the conversion of resazurin to resorufin on Au nanobars in the presence (and the absence) of hydroxylamine.

Ultimately, it is clear that neither Ag nor Au nanobar arrays yielded catalytic surface maps that allow us to make any meaningful conclusion.

We hypothesise that a large source of error in these measurements – for both Ag and for Au experiments – arises from the diffusive nature of the fluorophores. Very rudimentary calculations invoking a simple one-dimensional approach to Fick’s second law of diffusion gives a diffusion length, $x$, of

$$x = 2\sqrt{Dt}$$  \hspace{1cm} (7.5)

where $D$ is the diffusion coefficient for the aqueous medium and $t$ is the timescale of diffusion [220]. For a molecule in water at room temperature, diffusion coefficients typically take a value on the order of $10^{-9}$ m$^2$s$^{-1}$. In the span of one super-resolution frame ($30$ ms), a free resorufin molecule would thus travel a distance on the order of $10$ µm. While this neglects to include any consideration of desorption kinetics and makes some simplistic assumptions, given that we seek precision on the order of tens of nanometres, this is still clearly an issue.
Figure 7.6  Super-resolution image analysis procedure. a, A TIFF stack of (typically) 40000 individual frames is acquired. b, A DFT-based algorithm is used to align each frame with a chosen reference frame (typically frame 1). Plotted here are the detected shifts in the x (blue) and the y (orange) direction over the course of 20000 frames. The dashed bounding lines are used to highlight any frame registrations where a shift of over half a pixel from the general trend of the stage translation has been detected. c, The mean pixel intensity for each pixel is acquired through averaging the drift-corrected image stack. d, The scattering of the antennas is removed by subtracting the acquired drift-corrected, mean image from each frame of the image stack. e, Fluorescent events are detected and filtered using the Picasso software suite [215]. The centre of each Gaussian-filtered event is highlighted here. f, The 6×6 array of antennas is divided into 36 individual regions, overlaid, and a 2-dimensional histogram of the locations of fluorescent events is acquired. g, For comparative purposes, a conventional wide-field image of the same area as outlined in f, is shown. Note the significantly increased resolution of the super-resolution image, outlining (roughly) the gold ICL logo, which comprises each antenna of the array.
Experiments are currently underway to sputter silica atop the nanobars immediately after fabrication. This, we hope, rectifies two issues of the current setup: the sputtering may proceed in the same evacuated chamber as the metallic deposition, and therefore there is a significantly decreased chance of oxidation of the structures before imaging. Additionally, sputtered silica is porous by nature and has been shown to significantly reduce diffusive times of molecules after desorption [167]. Despite the increased risk of quenching, it is suspected that the mesoporous silica shells should enable us to more accurately localise the fluorescent molecule.

7.5 CONCLUSIONS

Both ensemble and single-molecule kinetics of the reduction of resazurin to resorufin have been studied using a fluorescence approach.

With silver, colloidal nanoparticles, it has been observed – for what we believe to be the first time – the plasmon-decay-induced hot-electron transfer into absorbed resazurin molecules, facilitating the reduction to resorufin.

Through comparative studies with gold colloidal nanoparticles, with the reduction of the fluorophore facilitated chemically by hydroxylamine, we have determined through temperature-dependent measurements that the activation barrier of electron transfer is negligible for hot-electrons.

Ultimately, the catalytic kinetics at both the single-molecule and ensemble level must satisfy the same reaction mechanism. It is extremely difficult to deconvolute this information from ensemble measurements since much information related to the desorption energy and dynamics is lost. Single-molecule level measurements were then sought as these were expected to provide dynamic insight into the behaviour of each individual fluorescent molecule, and to allow the population of active molecules – and thus, the active regions of electron-transfer on the surface of plasmonic nanostructures – to be resolved with super-resolution accuracy and precision.

Unfortunately, material limitations inhibited progress, and the resultant super-resolution images were not sufficient to resolve the underlying nanostructured features, let alone sites of hot-electron transfer activity.
In this thesis, I have explored the interaction of light with plasmonic nanostructures. We began in chapter 2 with a theoretical approach to the underlying physical phenomena at play during the illumination of plasmonic nanostructures, beginning with a macroscopic application of Maxwell’s equations to arbitrary materials of arbitrary sizes and permittivities. Only then did we address metals explicitly: by considering the polarizability of bulk metals, we introduced the concept of a surface plasmon. Moving into geometries more pertinent to this discussion, we approached a three-dimensional nanoscale metallic structure with the approximation that such a structure sustains fields equivalent to that of a single oscillating dipole. A full treatment of the potentials and associated fields outlines that such structures sustain a 3-dimensional equivalent to the surface plasmon: the localised surface plasmon, which is resonant in nature. It is this phenomenon that pervades the remainder of this thesis.

Chapter 3 considers extensively the loss mechanisms associated with localised surface plasmon resonances; both “large” and “small” nanoparticles exhibit plasmon damping, wherein fundamental energy conservation arguments outline that plasmonic linewidths must broaden in time. But to where does this energy go? The absorption of photons in metals is addressed in this context, with a particular focus to Landau damping in which the energy of the photon is passed to energetic charge carriers – the hot-electron and the hot-hole. The timescales of evolution of these hot-charge carrier populations is discussed. And herein lies the difficulty in exploiting them: thermal dissipation sets in after around 100 ps or so.

This aforementioned thermal dissipation in the event of plasmonic hot-electron decay following resonant excitation of plasmonic nanoparticles is explored in chapters 4 and 5. Here, an experimental study was reported looking into the use of plasmonic nanoparticles and optical printing techniques. Previous work had indicated that in using plasmonic Au nanoparticles illuminated at resonance with a 532 nm laser source, there exists some sort of repulsion mechanism preventing multiple nanoparticles from being printed within close proximity. It was established that optical binding – a phenomena in which the scattering of light off a colloidal nanoparticle generates positions that are energetically favourable for another suspended nanoparticle to occupy – were not the source of this printing error. It was hypothesised and confirmed that instead the error was due to heat generation in the fixed nanoparticle on the substrate. Methods to overcome this limitation were proposed and tested,
including the use of substrates with a higher thermal conductivity, so as to more effectively dissipate induced heat from the nanoparticle.

A computational study into the induced fluid flow surrounding illuminated nanoparticles was conducted to corroborate the notion that it is indeed induced heat that prevents accurate optical printing of plasmonic nanoparticles. By simulating the thermal dissipation of Au structures comparable to those used in experimentation and coupling this to (simplified) Navier-Stokes equations of fluid flow, it was found that illumination induces circulatory currents in the vicinity of the illumination nanoparticle. We were then able to estimate the thermophoretic motion of nanoparticles suspended in the vicinity an illuminated nanoparticle through comparison to experimentally acquired separations in printed Au nanoparticle. This, in turn, gave rise to what we believe is the first thermoefficient of a metallic nanoparticle in colloidal suspension: \( D_T = 4.6 \times 10^{-12} \text{ m}^2\text{s}^{-1}\text{K}^{-1} \).

Chapter 5 introduces some of the relevant concepts in the field of fluorescence in an attempt to prepare for the discussion into plasmonic catalysis in chapter 6. Particular attention is drawn to the use of super-resolution microscopy; an extensive discussion is presented, outlining some of the intricacies of such techniques as total-internal reflection microscopy and stochastic super-resolution microscopy.

With regard to the losses associated with plasmonic as discussed in chapter 3, in particular the formation of hot-electrons, chapter 6 looks to exploit these carriers before thermalisation. A study into the conversion of the non-fluorescent dye resazurin to the highly-fluorescent product resorufin was performed. Such conversion occurs via the transfer of electrons and has been seen previously with Au nanoparticles (catalysed with the molecule hydroxylamine). We, instead, sought to convert the molecule using hot-electrons from the decay of localised surface plasmon resonances in – for the first time – Ag nanoparticles, illuminated at resonance with a laser source of 405 nm. Conversion was seen and temperature-dependent measurements allowed us to note that the plasmonic catalysis at play here was performed seemingly without an activation barrier. We then proposed that, unlike the chemical-mediated catalysis involving Au nanoparticles, a lack of temperature-dependence in the rates of fluorescence increase suggest that upon plasmonic excitation of the Ag nanoparticles, the electrons are promoted to a level wherein there is activation barrier that is negligible in value and easily overcome by these energetic hot-carriers.

The use of the dye resazurin in the aforementioned experiments was initially chosen with further super-resolution experiments in mind. Stochastic super-resolution imaging techniques were hoped to be used to identify the regions of Ag nanostructures that were catalytically active, allowing us to generate catalytic ‘activity’ maps. Such maps would allow intelligent design of
nanostructured catalyst for widespread industrial application. Unfortunately, unforeseen complications – predominantly associated with the choice of Ag as a catalytic material – limited the accuracy of the experimental techniques.

Comparative studies on Au nanobars of the same geometries as those used in the trials of Ag nanobars yielded marginally better results; we hypothesise that this was due to unwanted oxidation of the Ag structures and also due to the notion that – to avoid such oxidation – cleaning of the substrate with plasma-ashing was not possible.

Passivation of the Ag surface was attempted in an attempt to improve accuracy of the super-resolution localisation but was limited in success. Attempts are still ongoing into this route. Furthermore, attempts are currently being made into the use of porous silica shells around the nanostructures. We expect that, with Ag nanobars, the shells would be act in two beneficial ways: they should passivate the surface, thereby preventing oxidation; and they should prevent rapid diffusion of converted fluorescent molecules from the surface, thereby increasing the resolution and the accuracy of the super-resolution images.

Figure 8.1 illustrates some preliminary images acquired in the same manner as discussed in the previous chapter for 150 nm Au nanobars with a 12 nm shell of amorphous (and thus porous) SiO₂ shells. The Au nanobars were prepared with the same method as previously outlined, and the SiO₂ shells were deposited via sputtering under a high vacuum.

It appears that the SiO₂ shell has improved the resolution of the super-resolution images in comparison to those in the previous chapter. The number of detected fluorescent events is significantly higher with hydroxylamine than without indicating that, with hydroxylamine, we catalyse the dye conversion. It remains unclear, however, if this is associated with the reduction of the molecule diffusion times or some other unconsidered method of quenching reduction.

Figure 8.1 Super-resolution localisation EVENS of resorufin molecules around 150×50×50 nm AuNBs; illumination with 561 nm laser at 200 mW; initial resazurin concentration 0.5 µM. a. Parallel polarisation; 1 mM NH₃OH; number of detected fluorescent events, \( N = 4850 \). b. Perpendicular polarisation; 1 mM NH₃OH; \( N = 24392 \). c. Perpendicular polarisation; no NH₃OH; \( N = 4400 \). Note the colour scale differs in all three examples.
Notably, a previously unconsidered polarisation dependence has been uncovered; FDTD simulations indicated that the transverse mode sustained in the Au nanobars should not be resonant at 561 nm (the wavelength used to excite the fluorophore). It is feasible that the silica shell has modified the resonant properties of the nanostructures. Further studies introducing a 640 nm laser are being considered. In this manner, we may be able to probe the fluorophores while more effectively exciting the plasmon resonance of the Au nanobars. If effective, this too should allow us to move away from Ag and all associated fabrication complications. Of course, full FDTD simulations must be performed investigating the modification of the LDOS of the system given that 640 nm illumination was not considered in earlier investigations.

The initial purpose of this thesis was to explore the possibility of understanding and utilising hot-charge carriers arising from the decay of localised surface plasmons in metallic nanostructures. Ultimately, this was successful through the manipulation and channelling of heat induced from thermalisation of such carriers in Au nanostructure for the purposes of optical printing, and successful through the demonstration of hot-carrier induced plasmonic catalysis in the reduction of a molecular species. These insights into the phenomenon hopefully provide clear guidelines for devising idealised nanostructures for both colloidal nanoplasmonics and for plasmonic catalysis.
IV APPENDICES & BACKMATTER
26 Zhang, Q., Large, N. & Wang, H. Gold nanoparticles with tipped surface structures as substrates for single-particle surface-enhanced Raman spectroscopy: concave


Yan, J., Jacobsen, K. W. & Thygesen, K. S. First-principles study of surface plasmons on Ag(111) and H/Ag(111). Phys Rev B 84, (2011).


A1  CHOICE OF REDOX PROBES

Below are short descriptions of the most relevant properties of redox probes, each considered for use in the ensemble redox experiments and super-resolution experiments.

A1.1  CELLROX OXIDATIVE STRESS REAGENTS

CellROX oxidative stress reagents are fluorogenic probes designed to reliably measure reactive oxygen species (ROS) in live cells. The cell-permeable CellROX reagents are nonfluorescent or very weakly fluorescent while in their reduced state; upon oxidation, however, they become brightly fluorescent.

The resulting fluorescence can be measured using traditional fluorescence microscopy, high-content imaging and analysis, microplate fluorometry or flow cytometry. All of the CellROX reagents are very photostable when compared with traditional ROS detection dyes.

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CellROX® Green Reagent</td>
<td></td>
<td>DMSO</td>
<td>485</td>
<td>520</td>
</tr>
<tr>
<td>CellROX® Orange Reagent</td>
<td></td>
<td>DMSO</td>
<td>545</td>
<td>565</td>
</tr>
<tr>
<td>CellROX® Deep Red Reagent</td>
<td></td>
<td>DMSO</td>
<td>640</td>
<td>665</td>
</tr>
</tbody>
</table>

A1.2  DICHLORODIHYDROFLUORESCEIN DIACETATE

The cell-permeant 2',7'-dichlorodihydrofluorescein diacetate also known as dichlorofluorescin diacetate, is commonly used to detect the generation of reactive oxygen intermediates in neutrophils and macrophages. Upon cleavage of the acetate groups by intracellular esterases and oxidation, the nonfluorescent H₂DCFDA is converted to the highly fluorescent 2',7'-dichlorofluorescein (DCF).

Oxidation of H₂DCFDA is reportedly not sensitive to singlet oxygen directly, but singlet oxygen can indirectly contribute to the formation of DCF through its reaction with cellular substrates that yield peroxy products and peroxyl radicals. In a cell-free system, H₂DCF has been shown to be oxidized to DCF by peroxynitrite anion (ONOO⁻), by horseradish peroxidase (in the absence of H₂O₂)
and by Fe$^{2+}$ (in the absence of H$_2$O$_2$). Furthermore, the oxidation of H$_2$DCF by Fe$^{2+}$ in the presence of H$_2$O$_2$ was reduced by the HO• radical scavenger formate and the iron chelator deferoxamine. In addition, DCF itself can act as a photosensitizer for H$_2$DCFDA oxidation, both priming and accelerating the formation of DCF. Because the oxidation of DCF and H$_2$DCFDA appears to also generate free radicals, their use for measuring free radical production must be carefully controlled.

5-(and 6-)chloromethyl-2,7'-dichlorodihydrofluorescein diacetate, acetyl ester (CM-H$_2$DCFDA) is a chloromethyl derivative of H$_2$DCFDA that exhibits much better retention in live cells. As with other chloromethyl derivatives, CM-H$_2$DCFDA passively diffuses into cells, where its acetate groups are cleaved by intracellular esterases and its thiol-reactive chloromethyl group reacts with intracellular glutathione and other thiols. Subsequent oxidation yields a fluorescent adduct that is trapped inside the cell, thus facilitating long-term studies.

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$DCFDA</td>
<td><img src="image1" alt="H$_2$DCFDA" /></td>
<td>DMSO, DMF, or ethanol</td>
<td>492–495</td>
<td>517–527</td>
</tr>
<tr>
<td>Carboxy-H$_2$DCFDA</td>
<td><img src="image2" alt="Carboxy-H$_2$DCFDA" /></td>
<td>DMSO, DMF, or ethanol</td>
<td>492–495</td>
<td>517–527</td>
</tr>
<tr>
<td>Di(Acetoxymethyl Ester)</td>
<td><img src="image3" alt="Di(Acetoxymethyl Ester)" /></td>
<td>DMSO, DMF, or ethanol</td>
<td>492–495</td>
<td>517–527</td>
</tr>
<tr>
<td>CM-H$_2$DCFDA</td>
<td><img src="image4" alt="CM-H$_2$DCFDA" /></td>
<td>DMSO, DMF, or ethanol</td>
<td>492–495</td>
<td>517–527</td>
</tr>
</tbody>
</table>
A1.3 Aminophenyl fluorescein and hydroxyphenyl fluorescein

Developed by Nagano, 3’-(p-aminophenyl) fluorescein (APF) and 3’-(p-hydroxyphenyl) fluorescein (HPF) provide greater selectivity and stability than dichlorodihydrofluorescein diacetate (H$_2$DCFDA) for ROS detection. H$_2$DCFDA is probably the most commonly used reagent for detecting intracellular reactive oxygen species despite its lack of specificity and tendency to spontaneously photooxidize. The nonfluorescent H$_2$DCFDA becomes fluorescent in the presence of a wide variety of reactive oxygen species including, but not limited to, peroxyl (ROO•) and hydroxyl (HO•) radicals and the peroxynitrite anion (ONOO$^-$). In contrast, APF and HPF show much more limited reactivity and greater resistance to light-induced oxidation. Both of these fluorescein derivatives are essentially nonfluorescent until they react with the hydroxyl radical, peroxynitrite anion or singlet oxygen. APF will also react with the hypochlorite anion (~OCl$^-$), making it possible to use APF and HPF together to selectively detect hypochlorite anion. In the presence of these specific reactive oxygen species, both APF and HPF yield a bright green-fluorescent product (excitation/emission maxima ~490/515 nm).

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APF</td>
<td><img src="image" alt="APF Structure" /></td>
<td>DMF</td>
<td>492–495</td>
<td>517–527</td>
</tr>
<tr>
<td>HPF</td>
<td><img src="image" alt="HPF Structure" /></td>
<td>DMF</td>
<td>490</td>
<td>515</td>
</tr>
</tbody>
</table>

A1.4 OxyBURST Green reagents

Fc OxyBURST Green assay reagent was developed to monitor the oxidative burst in phagocytic cells. The Fc OxyBURST Green assay reagent comprises bovine serum albumin (BSA) that has been covalently linked to dichlorodihydrofluorescein (H$_2$DCF) and then complexed with purified rabbit polyclonal anti-BSA antibodies. When these immune complexes bind to Fc receptors, the nonfluorescent H$_2$DCF molecules are internalized within the phagovacuole and subsequently oxidized to green-fluorescent dichlorofluorescein (DCF).
OxyBURST Green H$_2$HFF BSA is a sensitive fluorogenic reagent for detecting extracellular release of oxidative products. This reagent comprises BSA that has been covalently linked to dihydro-2',4,5,6,7,7'-hexafluorofluorescein (H$_2$HFF), a reduced dye with improved stability. Unlike Fc OxyBURST Green assay reagent, OxyBURST Green H$_2$HFF BSA is not complexed with IgG.

Amine-reactive OxyBURST Green H$_2$DCFDA succinimidyl ester (2',7'-dichlorodihydrofluorescein diacetate, SE) acts as an alternative to Fc OxyBURST Green assay reagent and OxyBURST Green H$_2$HFF BSA. Following conjugation to amines, the two acetates of OxyBURST Green H$_2$DCFDA can be removed by treatment with hydroxylamine at neutral pH to yield the dihydrofluorescein conjugate. OxyBURST Green H$_2$DCFDA conjugates are nonfluorescent until they are oxidized to the corresponding fluorescein derivatives.

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OxyBURST® Green Assay Reagent</td>
<td>?</td>
<td>PBS</td>
<td>488</td>
<td>523</td>
</tr>
<tr>
<td>OxyBURST® Green H$_2$HFF BSA</td>
<td>?</td>
<td>PBS</td>
<td>488</td>
<td>530</td>
</tr>
<tr>
<td>OxyBURST® Green H$_2$DCFDA</td>
<td><img src="image" alt="chemical structure" /></td>
<td>DMF</td>
<td>492–495</td>
<td>517–527</td>
</tr>
</tbody>
</table>

### A1.5 DIHYDRORHODAMINE 123

Dihydrorhodamine 123 is the uncharged and nonfluorescent reduction product of the mitochondrion-selective dye rhodamine 123. This leuco dye passively diffuses across most cell membranes where it is oxidized to cationic rhodamine 123. Like H$_2$DCF, dihydrorhodamine 123 does not directly detect superoxide, but rather reacts with hydrogen peroxide in the presence of peroxidase, cytochrome c or Fe$^{2+}$. However, dihydrorhodamine 123 also reacts with peroxynitrite, the anion formed when nitric oxide reacts with superoxide.
A1.6 REDUCED MITOTRACKER PROBES

MitoTracker Orange CM-H₂TMRos and MitoTracker Red CM-H₂XRos do not fluoresce until they enter an actively respiring cell, where they are oxidized by reactive oxygen species to the fluorescent mitochondrion-selective probe and then sequestered in the mitochondria. Although CM-H₂TMRos and CM-H₂XRos are widely used as indicators of mitochondrial reactive oxygen species, their fluorescence cannot be unambiguously associated with the site of oxidant generation, as the cationic charge that drives their electrophoretic sequestration in active mitochondria is only present after the probe has been oxidized. This same caveat also applies to dihydrorhodamine 123 and dihydrorhodamine 6G (see above). Probes such as MitoSOX Red mitochondrial superoxide indicator (see above) resolve this ambiguity by having their oxidant response and mitochondrial localization functions associated with different structural elements.
A1.7 REDOX SENSOR RED CC-1 STAIN

RedoxSensor Red CC-1 stain (2,3,4,5,6-pentafluorotetramethyldihydrorosamine) passively enters live cells and is subsequently oxidized in the cytosol to a red-fluorescent product (excitation/emission maxima ~540/600 nm). Alternatively, this nonfluorescent probe may be transported to the lysosomes where it is oxidized.

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RedoxSensor™ Red CC-1</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>DMSO</td>
<td>540</td>
<td>600</td>
</tr>
</tbody>
</table>

A1.8 RESAZURIN

Resazurin is a proven cell viability indicator that uses the natural reducing power of living cells to the fluorescent molecule, resorufin. The active ingredient of resazurin is a nontoxic, cell permeable compound that is blue in color and virtually non-fluorescent. Upon entering cells, resazurin is reduced to resorufin, which produces very bright red fluorescence. Viable cells continuously convert resazurin to resorufin, thereby generating a quantitative measure of viability—and cytotoxicity.

<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resazurin</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Water</td>
<td>530-560</td>
<td>590</td>
</tr>
</tbody>
</table>

A1.9 DIHYDROETHIDIIUM (HYDROETHIDINE)

The superoxide indicator dihydroethidium, also called hydroethidium, exhibits blue-fluorescence in the cytosol until oxidized, where it intercalates within the cell’s DNA, staining its nucleus a bright fluorescent red.
<table>
<thead>
<tr>
<th>Redox Sensor</th>
<th>Chemical structure</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydroethidium (Hydroethidine)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>DMSO</td>
<td>518</td>
<td>605</td>
</tr>
</tbody>
</table>
Recall from chapter 4, equation 4.12, that the electric field of a focussed Gaussian beam, propagating the in \( z \)-direction may be described by:

\[
E(r, z) = E_0 \frac{\omega}{\omega(z)} \exp \left( -\frac{r^2}{\omega(z)^2} \right) \exp \left( i \frac{k r^2}{2 R(z)} \right) \exp \left( i k z - i \eta(z) \right)
\]  

(A2.1)

where

\[
w(z)^2 = w_0^2 \left( 1 + \left( \frac{z}{z_0} \right)^2 \right)
\]  

(A2.2a)

\[
R(z) = z \left( 1 + \left( \frac{z}{z_0} \right)^2 \right)
\]  

(A2.2b)

\[
\eta(z) = \tan^{-1} \left( \frac{z}{z_0} \right)
\]  

(A2.2c)

where \( z_0 = \pi w_0^2 \sqrt{\varepsilon}/\lambda \). Descriptions of the physical interpretations of these quantities may be found in section 4.3. Figure A2.1 below depicts the geometry of such a system.

Away from the waist, the beam spreads with a hyperbolic profile, with the asymptotes defining the far-field divergence of the beam such that the \( 1/e^2 \) radius in intensity distribution is given by

\[
\theta = \lim_{z \to \infty} = \frac{\lambda}{\pi \sqrt{\varepsilon} w_0}
\]  

(A2.3)

Figure A2.1 Gaussian beam properties at focus. Gaussian beam width \( w(z) \) as a function of the axial distance \( z \). \( w_0 \): beam width at focus; \( z_0 \): Rayleigh range; \( \theta \): far-field angular spread of beam.
Notably, all Gaussian beam properties are dependent solely on the size of the waist, $w_0$ and the wavelength $\lambda$. It is then possible to fully characterise a Gaussian beam (of known wavelength) by determining the size and location of the beam waist.

If we take the beam propagating in the $z$-direction to obey a mathematical Gaussian profile (now cast into Cartesian coordinates)

$$I(x, y) = I_0 e^{-2x^2/w_x^2}e^{-2y^2/w_y^2} \quad \text{(A2.4)}$$

where $w_x$ and $w_y$ correspond to the $1/e^2$ radii of the beam in the $x$ and $y$ directions, respectively, and $I_0$ is the peak intensity.

The total power of the beam is then given by

$$P_{\text{tot}} = I_0 \int_{-\infty}^{\infty} e^{-2x^2/w_x^2} \, dx \int_{-\infty}^{\infty} e^{-2y^2/w_y^2} \, dy = \frac{\pi}{2} I_0 w_x w_y \quad \text{(A2.5)}$$

In translating a knife-edge across the beam in the $x$-direction to position $X$, we reduce the measured transmitted power $P$, such that

$$P(X) = P_{\text{tot}} - I_0 \int_{-\infty}^{X} e^{-2x^2/w_x^2} \, dx \int_{-\infty}^{\infty} e^{-2y^2/w_y^2} \, dy$$

$$= P_{\text{tot}} - \frac{\pi}{2} I_0 w_y \int_{-\infty}^{X} e^{-2x^2/w_x^2} \, dx$$

$$= P_{\text{tot}} - \frac{\pi}{2} I_0 w_y \left[ \frac{\pi}{\sqrt{8}} + \int_{0}^{X} e^{-2x^2/w_x^2} \, dx \right]$$

$$= P_{\text{tot}} - \frac{\pi}{2} I_0 w_y \int_{0}^{X} e^{-2x^2/w_x^2} \, dx \quad \text{(A2.6)}$$

Making use of the substitution $u^2 = 2x^2/w_x^2$, we may recast the above into the form

$$P(X) = \frac{P_{\text{tot}}}{2} - \frac{\pi}{2} I_0 w_y \int_{0}^{\sqrt{2}X/w_x} e^{-u^2} \frac{u}{\sqrt{2}} \, du$$

$$= \frac{P_{\text{tot}}}{2} \left[ 1 - \operatorname{erf} \left( \frac{\sqrt{2}X}{w_x} \right) \right] \quad \text{(A2.7)}$$

where $\operatorname{erf}(a)$ is the error function. This is the result used in the main text.
%% 13/03/2018 preprocessing_tiffstab.m
%% This file performs sub-pixel alignment on a TIFF stack. Using
dftregistration.m, every frame is compared to the first frame and
adjusted accordingly to 1/100th of a pixel precision.
%% Any mislocalisations are calculated as frames shifting more than 0.5
pixels [80nm] relative to the previous frame.
%% Unsuccessful registration is defined as that which loses more than 80% or
%% of frames.
%% USER INPUT
%% file_sweep: '0' manually select single file for stabilisation
%% '1' sweep through all TIFFs in folder. Assumes that there
%% all folders containing image stacks to stabilise start with
%% either L or R (left/right), and that all image stacks
%% filenames finish with '_MMStack_Pos0.ome.tif'
clear
file_sweep = 0; % turn on/off file sweep
root_folder = 'C:\Users\tb311\Documents\Projects\04 Superresolution\Superresolution\2018-05-31 AgNB06';

%% 1 Declare options for saveastiff function
tiffoptions.append = 0; % don't simply add data to the end of TIFF
tiffoptions.message = 0; % turn off message-output in console
tiffoptions.overwrite = 1; % overwrite existing files if they exist
tiffoptions.big = 0; % use 64 bit addressing and allows for files > 4GB
max_shift = 0.5; % maximum permitted shift in image stabilisation (pixels)

%% 2 Select original TIFF image
if(file_sweep==0) % manually select single file
    [filename{1}, filepath{1}] = uigetfile('*.tif', 'Select original, unstabilised TIFF');
    source{1} = [filepath{1} filename{1}];
end
if(file_sweep==1) % automatically load multiple files
    filename = []; source = [ ];
    dirinfo = dir(root_folder); % root directory
dirinfo(~[dirinfo.isdir]) = []; % remove non-directories
subdir = cell(length(dirinfo),1);
% look through directory to identify useful folders ('L...' or 'R...')
for i = 1:length(dirinfo)
    thisdir = dirinfo(i).name;
    if strcmp(thisdir,'L',1) || strcmp(thisdir,'R',1)
        subdir{i} = thisdir;
    end
end
subdir = subdir(~cellfun('isempty',subdir));
% construct full filenames using subdirectories
for i = 1:length(subdir)
    filename{i,1} = subdir{i};
end
source(i,1) = fullfile(root_folder, subdir{i}, ['_MMStack_Pos0.ome.tif']);
end

% error-handling
for i = 1:length(source) % to catch mis-titled files
    if exist(source{i}, 'file') ~= 2
        disp(['Warning: ' filename{i} ' does not exist']);
        source{i} = [];
    end
end

source = source(~cellfun('isempty', source)); % remove links to files
that don’t exist
if isempty(source) == 1
    f = warndlg('No suitable TIFF stacks in designated folder.',
    'Warning!');
    waitfor(f);
end

% clean-up
clearvars -except filename source tiffoptions max_shift
end

%% 3 DFT image stabilisation
for i = 1:length(source)
    % 3.1 Load image
    timerVal = tic; % start timer
    source_image = loadtiff(source{i});
    disp(['Loaded image ' num2str(i) ' in ' num2str(round(toc(timerVal)))
    's']);
    [source_rows, source_cols, source_frames] = size(source_image);

    % remove first frame - camera leaves charge-like effect on frame 1 only
    if source_frames == 40000
        source_image(:,:,1) = [];
        source_frames = 40000 - 1;
    end

    % initialise empty arrays to populate with stabilised data
    stab_image = zeros(size(source_image), 'like', source_image);
    xy_shift = zeros(source_frames, 2); % list of xy shift values (in pixels)

    % 3.2 Stabilise each frame of loaded TIFF image relative to first
    frame
    % to 1/100th of a pixel
    % try parfor loop - need to optimise dftregistration code first
    timerVal = tic; % start timer
    for xx = 1:source_frames
        [stab_data_tmp, stab_image_xframe] =
        dftregistration(fft2((source_image(:,:,1))), fft2(source_image(:,:,xx)), 100);
        stab_image_xframe = uint16(abs(ifft2(stab_image_xframe)));
        stab_image(:,:,xx) = stab_image_xframe;
        xy_shift(xx,:) = stab_data_tmp(3:4);
    end
    disp(['Stabilised image ' num2str(i) ' in ' num2str(round(toc(timerVal)))
    's']);

    % 3.3 Fitting of xy-shift to idenfity outliers
    timerVal = tic; % start timer
    frames = (1:source_frames);

    % rloess smoothing, filter by average +- 1px shift
    x_avg = smooth(frames, xy_shift(:,2), 0.025, 'rloess');
    x_upp = x_avg + max_shift;
    x_low = x_avg - max_shift;

    % ...
y_avg = smooth(frames, -xy_shift(:,1), 0.025, 'rloess');
y_upp = y_avg + max_shift;
y_low = y_avg - max_shift;

% plot original data, smoothed data, and CIs
if(1)
    figure
    hold on
    h(1)=plot(frames, -xy_shift(:,2), 'DisplayName', 'x-shift', 'Color', [0 0.4470 0.7410]);
h(2)=plot(frames, -xy_shift(:,1), 'DisplayName', 'y-shift', 'Color', [0.8500 0.3250 0.0980]);
    plot(frames,x_avg,'w');
    plot(frames,x_low,'Linestyle','-.','Color',[0 0.4470 0.7410]);
    plot(frames,x_upp,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    plot(frames,y_avg,'w');
    plot(frames,y_upp,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    plot(frames,y_low,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    xlabel('Frame')
ylabel('Shift relative to frame #1 [px]')
    legend([h(1) h(2)], {'x-shift', 'y-shift'}, 'Location', 'NorthWest');
    print([filename{i} '.png'], '-dpng')
end

% remove data that exceed defined shift threshold
A = -xy_shift(:,2)>x_upp | -xy_shift(:,2)<x_low | -xy_shift(:,1)>y_upp | -xy_shift(:,1)<y_low;
stab_image = stab_image(:,:,A==0);

% error-catching - if >80% frames are shifted too much, stop
if(sum(A)>=0.8*length(A))
    disp(['Warning: unable to stabilise file: ' source{i}])
end

% plot data after removing erroneous points
frames_r = frames(A==0);
xy_shift_r = xy_shift(A==0,:);
x_low_r = x_low(A==0);
x_upp_r = x_upp(A==0);
x_avg_r = x_avg(A==0);
y_low_r = y_low(A==0);
y_upp_r = y_upp(A==0);
y_avg_r = y_avg(A==0);

figure
hold on
h(1)=plot(frames_r, -xy_shift_r(:,2), 'DisplayName', 'x-shift', 'Color', [0 0.4470 0.7410]);
h(2)=plot(frames_r, -xy_shift_r(:,1), 'DisplayName', 'y-shift', 'Color', [0.8500 0.3250 0.0980]);
    plot(frames_r,x_avg_r,'w');
    plot(frames_r,x_low_r,'Linestyle','-.','Color',[0 0.4470 0.7410]);
    plot(frames_r,x_upp_r,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    plot(frames_r,y_avg_r,'w');
    plot(frames_r,y_low_r,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    plot(frames_r,y_upp_r,'Linestyle','-.','Color',[0.8500 0.3250 0.0980]);
    xlabel('Frame')
ylabel('Shift relative to frame #1 [px]')
    legend([h(1) h(2)], {'x-shift', 'y-shift'}, 'Location', 'NorthWest');
    print([filename{i} '_remaining.png'], '-dpng')
end

disp(['Analysed image ' num2str(i) ' in ' num2str(round(toc(timerVal))) 's']);
%% 3.4 Save as stabilised TIFF file
saveastiff(stab_image, ['stabilised_' filename{i} '.tif'], tiffoptions);
end
%% Clean-up
if(0)
clearvars -except tiffoptions filename*_image
end

%% 17/04/2018 preprocessing_tiffantennapos.m
% This file determines the xy-coordinates of all suspected antennas and
% attributes event localisations to each of these.
interpolate = 0; % turn on for interpolation between antennas

%% 1 Estimate antenna positions from averaged TIFF image
% load averaged TIFF
[filename, filepath] = uigetfile '*.tif','Select original, averaged TIFF');
source = [filepath filename];
average_image = loadtiff(source);
% calculate antenna intensity threshold
intensity_reshaped = double(reshape(a
verage_image,[numel(average_image) 1]));
intensity_threshold = mean(intensity_reshaped) + 1 * std(intensity_reshaped);
% determine positions of some nanoantennas from average image
antenna_threshold = bwlabel(double(roicolor(average_image,intensity_threshold,max(max(average_image)))));
antenna_xy = regionprops(antenna_threshold,'Centroid');
antenna_xy = cat(1, antenna_xy.Centroid);
% plot intensity and suspected positions of nanoantennas
figure
imagesc(average_image);
axis equal
hold on
positions = plot(antenna_xy(:,1),antenna_xy(:,2),'rx');
brush on % manually select incorrect localisations in figure

%% 2 Manually remove incorrect localisations
brushed = logical(get(positions,'BrushData'));
unbrushed = ~brushed;
x_tmp = get(positions,'XData');
y_tmp = get(positions,'YData');
brushed_xy = [x_tmp(brushed),y_tmp(brushed)];
antenna_xy = [x_tmp(unbrushed),y_tmp(unbrushed)];
% Replot without incorrect localisations
close
figure
imagesc(average_image);
axis equal
hold on
positions = plot(antenna_xy(:,1),antenna_xy(:,2),'rx');
brush on

%% 3 Manually select first column
brushed = logical(get(positions,'BrushData'));
x_tmp = get(positions,'XData');
y_tmp = get(positions,'YData');
xy_col1 = [x_tmp(brushed),y_tmp(brushed)];
xy_col1 = sortrows(xy_col1,2); % sort rows in order of ascending y
ant1_xy = xy_col1(1,:); % position of antenna 1
% convert to polar coordinates, relative to antenna #1
xy_col1_shift = [xy_col1(:,1)-xy_col1(1,1), xy_col1(:,2)-xy_col1(1,2)];
coll_theta,coll_rho = cart2pol(xy_col1_shift(:,1),xy_col1_shift(:,2));
% determine average separation & angle relative to #1
col1_rho = col1_rho(end)/(length(col1_rho)-1);
col1_theta = mean(col1_theta(2:length(col1_theta)));

%% 4 Manually select first row
brushed = logical(get(positions, 'BrushData'));
x_tmp = get(positions, 'XData');
y_tmp = get(positions, 'YData');
xy_row1 = [x_tmp(brushed)',y_tmp(brushed)'];
xy_row1 = sortrows(xy_row1,1); % sort rows in order of ascending x

% convert to polar coordinates, relative to antenna #1
xy_row1_shift = [xy_row1(:,1)-xy_row1(1,1), xy_row1(:,2)-xy_row1(1,2)];
[row1_theta,row1_rho] = cart2pol(xy_row1_shift(:,1),xy_row1_shift(:,2));

% determine average separation & angle relative to #1
row1_rho = row1_rho(end)/(length(row1_rho)-1);
row1_theta = mean(row1_theta(2:length(row1_theta)));

%% 5 Estimate positions of full 10×10 antenna array
% array of antenna locations (unrotated, #1 at (0,0))
for i =1:10
    for j = 1:10
        ant_xy(i+(j-1)*10,1) = (i-1)*row1_rho;
    end
    ant_xy((1:10)+(i-1)*10,2) = (i-1)*col1_rho;
end

% set up rotation matrices
rot_theta = (row1_theta + col1_theta-pi()/2)/2; % average rotation of antennas
rot_matrix = [cos(rot_theta) -sin(rot_theta); sin(rot_theta) cos(rot_theta)];

% rotate & shift
rot_center = repmat([ant1_xy(1); ant1_xy(2)], 1, length(ant_xy))';
ant_xy_rot = rot_matrix*ant_xy';
ant_xy_rot = ant_xy_rot' + rot_center;

% plot on top of existing plot
plot(ant_xy_rot(:,1),ant_xy_rot(:,2),'wx')
Below are extracts of screenshots of the successful licensing applications for all relevant figures. Note that figures 3.3, 3.5 d-g, and 5.9 are available under Creative Commons Attribution 4.0 International Licenses and are therefore not considered below.

**Fig 3.4c**

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**Fig 3.5l**

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Fig 3.7d

Fig 3.7 a-b

Fig 3.7e
Fig 3.8a

Fig 3.7f

Fig 3.7h
Fig 3.8b

Fig 3.2

Fig 3.4a
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