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Quantifying the Thermal Contribution Towards Plasmonic Catalysis

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2 ABBREVIATIONS

Abbreviation:	Meaning:								
q	Heat Source Density $\left[\frac{W}{m^3}\right]$								
E	Electric Field $\left[\frac{V}{m}\right]$								
$E_{i}^{ext}(\omega)$	External Electric Field Amplitude $\left[\frac{V}{m}\right]$								
$\overline{\alpha}$	polarizability $\left[\frac{Cm^2}{N}\right]$								
P	Polarization $\begin{bmatrix} C \\ C \end{bmatrix}$								
Ī	Identity Matrix								
$\frac{1}{\overline{k}}$	wavenumber [1]								
R C	Wavenumber $\left[\frac{1}{m}\right]$								
C C	Relative Permittivity								
er	Relative Permittivity								
e_r	Imaginary Part of Polative Permittivity								
e _r	Imaginary Fart of Kelative Permittivity								
EO	vacuum Permittivity $\left\lfloor \frac{1}{m} \right\rfloor$								
Enp	Nanoparticle Permittivity $\lfloor \frac{1}{m} \rfloor$								
μ	Permeability $\lfloor \frac{11}{m} \rfloor$								
μο	Vacuum Permeability $\left[\frac{H}{m}\right]$								
)	Polarization Current $\left[\frac{C}{m^2s}\right]$								
δ	Volume Fraction								
€s	Surrounding Media Permittivity $\left[\frac{r}{m}\right]$								
ω	Angular Temporal Frequency $\left[\frac{\kappa \alpha \alpha}{s}\right]$								
ω _p	Plasma Frequency $\left[\frac{Rad}{s}\right]$								
ω ₀	Resonant Frequency $\left[\frac{Rad}{s}\right]$								
γ	Damping Rate $\left[\frac{Kg}{s}\right]$								
σ _{abs}	Absorption Cross-section [m ²]								
Р	Light Power Absorbed[W]								
Ι	Intensity $\left[\frac{W}{m^2}\right]$								
V	Volume [m ³]								
c _p	Thermal Capacity $\left[\frac{J}{Ka + K}\right]$								
0	Density $\left[\frac{Kg}{2}\right]$								
k	Thermal Conductivity $\begin{bmatrix} W \\ W \end{bmatrix}$								
n	nanoparticle interdistance $[m]$								
L	size of nanoparticle distribution [m]								
a	characteristic size of nanoparticles [m]								
a a	Thormal Diffusivity [^{m²}]								
α	Time Scale [s]								
E	Fluence of the Illumination [W]								
Г	Fluence of the multimation $\left[\frac{1}{m^2}\right]$								
V									
	Volumetric Heat Capacity $\left[\frac{1}{Kg*K}\right]$								
K	Equilibrium Constant								
A	Pre-exponent Factor								
Ea	Activation Energy []								
R	Universal Gas Constant $\left[\frac{J}{mol * K}\right]$								
Т	Temperature [K]								
n	Refractive Index								
k _{ec}	Extinction Coefficient								
h	Planck's Constant $\frac{1}{Hz}$								
β _j	Empirical Parameters,								
ν	Frequency $\frac{1}{s}$								
N	Number of Nanoparticles								
î	Number of Nanoparticles along one Axis								
Vr	Volume Ratio								
n _c	Number of Clusters								
IPDC	Closest Interparticle Distance								
IPDA	Average Interparticle Distance								

3 ABSTRACT

Plasmonic catalysis offers a potential to sustainably produce green fuels to store energy to bridge seasonal fluctuations of renewable energies. Plasmonic catalysts utilizes two different mechanisms to drive catalysis, resulting in improved efficiency, hot electron generation and photo-thermal effect. Hot electron generation allows for a reduction in required activation energy. Heat generation drives catalysis by modifying the reaction kinetics which can be explained using the Arrhenius law.

Calculating and measuring temperature of nanoparticle constellations is required to accurately evaluate the photothermal contribution towards catalysis. It is computationally expensive to accurately calculate the temperature profiles of large 3D nanoparticle constellations (mm scale). This is due to the required resolution being in the nanometer scale. Due to the nonpropagative nature of heat, accurately measuring the temperature of nanoparticle constellations at the nanoscale is a complex task. Limitations in accurately calculating and measuring temperature result in uncertainty of the contribution of the two different mechanisms towards catalysis.

Calculating temperature profiles of nanometer sized nanoparticle constellations is possible due to the reduced computational cost. We utilized an analytical approach to calculate temperature profiles. Understanding how temperature changes with increasing constellation size has led to scaling laws that accurately predict the temperature profile of large nanoparticle arrays.

Temperature profiles of perfect arrays and hyperclusters are studied. The scaling of temperature as a function of nanoparticle radius, volume ratio and volume are analysed. We found that the mean temperature scales in a linear manner with volume ratio, which holds true across different temperature regimes and for different nanoparticle radii. The temperature regime as a function of nanoparticle radius, volume ratio and nanoparticle arrangement are evaluated and discussed. We found that perfect arrays are good predictors of non-structured arrays and hyperclusters. When increasing volume and volume ratio, the delocalized temperature regime dominates, and the difference between perfect arrays and non-perfect arrays diminishes. This indicates that temperature profiles of large nanoparticle constellations can be predicted by calculating the temperature profile of a representative structured array (equal volume ratio).

Temperature as a function of volume is investigated. We present two scaling laws which allow for the scaling of the temperature profile of a nanoscale sized constellation to larger millimeter sized constellation. An analytical derivation to the scaling law is presented. An analytical scaling law allowing for the calculation of temperature as a function of relative volume is given. The impact of volume morphology on relative temperature and temperature regime is discussed. Limitations to said scaling laws, numerical errors induced by temperature regime and quality of mesh are discussed and solutions to counter act said limitations are provided. We demonstrate that the scaling laws correctly predict temperature profiles published in literature.

The proposed scaling laws allow for a significant reduction in computational cost to accurately simulate temperature profiles of large nanoparticle constellations. This allows for a significant improvement in the understanding of temperature profiles and thus the thermal contribution towards catalysis. The possible applications also extend past plasmonic catalysis to all other possible applications of 3D thermoplasmonics.

4 INTRODUCTION

Thermoplasmonics is the study of light absorption by nanoparticles and subsequent heat generation[1]. Thermoplasmonics has a wide range of applications ranging from chemistry and biomedicine to magnetic recording and hydrodynamics[2]. Plasmonic chemistry is driven by hot electrons, the ejection of excited electrons allowing for molecule dissociation, and thermal contributions, which increase the temperature (Joule heating) of the surrounding media allowing for the chemical process to occur following the Arrhenius equation.

Global warming being of greater importance now more than ever before has resulted in a push for renewable energies dominated by photovoltaics. Atmospheric CO_2 levels increased at a rate of 2.11 ppm during the years 2005 to 2014[3]. Since the industrial age, there has been an increase of 200 ppm of CO_2 emissions, equivalent to $3x10^{12}$ barrels of oil[3]. Increased carbon emissions have led to global warming which has adverse effects on the quality of life of humans, animals, and natural vegetation. Increased global awareness towards global warming has led to a growing desire and understanding of the need for a carbon-free economy resulting in an energy transition. The energy transition drives an increased push from fossil fuels, to renewable carbon resources, circular carbon flows[3][4] and a solar driven energy supply[3][5].

The most significant challenge of solar-based energy portfolios is the intermittency of solar energy. Daily fluctuations can be covered with batteries. However, seasonal fluctuations cannot be handled by batteries[5]. An attractive alternative to cover seasonal fluctuations is chemical energy storage[5]. Aiming for net zero emissions will not suffice as current carbon levels are already too high. It will therefore be necessary to reduce the carbon levels in the atmosphere which can be done through carbon capture. Storing the captured carbon can be done through the Sabatier process converting hydrogen and carbon dioxide into methane and water resulting in sustainable chemical fuels[3].

Heterogeneous catalysis is of significant importance in chemical, environmental and energy conversion processes[6]. Photocatalysis aims at utilizing light energy, in converting photons into electricity or fuels[6]. Due to low efficiency in the visible range, a significant portion of current photocatalysis involves the use of UV illumination instead of the cleaner visible range light which can be harnessed from sunlight[6]. Plasmonic nanoparticles have raised great promise in their ability to utilize visible light instead of UV for photocatalysis[6][7][8][9]. In 2003 it was first shown that noble metal nanoparticles could increase the efficiency of photocatalysis via the injection of hot electrons[6][10].

Nanoparticle driven catalysis has two leading effects: the thermal contribution, and the hot electron contribution. The goal of this thesis is to help understand and quantify the effects on catalysis of local temperature increase due to light absorption and subsequent heat generation. Further understanding the underlying mechanisms that drive catalysis on the nanoscale will allow for improvements in catalysis and help combat global warming.

Extensive theoretical and experimental work has been done in the past demonstrating both the hot electron effect and its capability to drive catalysis. In 1987, the idea of using gold nanoparticles (not under illumination, no light) was first pioneered by the works of Haruta[2][11]. Chen et. al in 2008 further enhanced heterogeneous catalysis by illuminating gold nanoparticles under laser illumination[12][2]. In 2010 Cronin et. al experiments quantified the photothermal contribution of illuminated nanoparticles towards catalysis compared to bulk heating reporting a gain of 2-3 orders of magnitude[2][13]. These experiments demonstrated the ability to utilize heat generated by nanoparticles to drive catalysis. Christopher et. al in 2011 demonstrated an increased reaction rate with the utilization of nanorods with bulk heating, relative to what would have been obtained through bulk heating without nanorods[14]. They proposed that the mechanisms that facilitated the reported 4 times higher yield was the hot electron contribution. However, uncertainty was raised as to whether the illumination was not just heating the sample as a temperature increase of 21[K] would account for the 4 times higher yield (bulk heating was at 450[K]). Cortés et al. in 2016 demonstrated that hot electrons contributed towards catalysis by having nanoantennas with no thermal contributions drive a chemical reaction[15]. Quantifying the contributions of the two mechanisms has remained elusive. Small increases in temperature are sufficient to account for reported increases in yield. Both mechanisms have been reported to drive catalysis independently of the other. Limitations in modeling and measuring of temperature has led to uncertainty of the temperature of samples. As both mechanisms cannot be isolated, there is uncertainty as to the contributions of the individual mechanisms towards catalysis.

Evolution in temperature measurement techniques will allow for more precise temperature measurement on the nanoscale and thus allow for accurate predictions on given reaction rates. Thermal imaging through optical phase analysis first proposed by Baffou et al. has allowed for accurate, high resolution temperature measurements in a label free manner[16]. Thermal imaging through optical phase analysis has allowed for accurate 2D temperature mapping. Nanophotonics Systems Laboratory, ETHZ, has developed the method to allow for temperature mapping as a function of depth allowing for 3D temperature mapping[17].

The thesis is structured in five sections:

- 1. Methodology: Introduction to numerical and experimental approach of the thesis
- 2. Theoretical Models: Introduction to the different numerical models used for calculating thermal profiles.
- 3. Temperature Simulations: Results, trends and scaling laws with regard to temperature scaling as a function of nanoparticle radius, and volume ratio for both arrays and hyperclusters.
- 4. Scaling Temperature as a Function of Volume: Introducing scaling laws that allow for the prediction of temperature profiles of large nanoparticle arrays.
- 5. Conclusion: Summary of findings with an extensive section suggesting further improvements.

The theoretical component will be used to accurately model and map temperature profiles within nanometer to millimeter temperature profiles. Theoretical models will be created to help understand 1D, 2D, and 3D nanoparticle arrays and their respective heat transfer. The experimental component will measure the temperature of a nanoparticle cluster. Understanding the thermal contribution towards catalysis will allow for a better understanding of the contributions of the individual mechanisms towards catalysis.

5 PHOTONICS

Photonics is the science of the generation and manipulation of light[1] setting forth concepts necessary to understanding thermo-plasmonics, utilizing light to generate heat. In the following subsections, electric permittivity and optical near field enhancement will be introduced. Electric permittivity describes the polarizability of a material allowing for the calculation of heat generation. Optical near field enhancement sets forth the basic concepts behind heat and hot electron generation.

5.1 Electric Permittivity

Electric permittivity ϵ describes the polarizability of a material in response to the applied electric field[1]. Electric permittivity cannot be considered a constant as it is frequency and material dependent[1]. Electric permittivity is given as

$$\varepsilon = \epsilon_r x \epsilon_0$$
 (1)

where ϵ_r is relative permittivity and ϵ_0 vacuum permittivity. The Drude-Lorenz model composed of driving, damping, and spring forces allows for the calculation of the relative permittivity of a given material[1]. Relative permittivity is a complex quantity that has both real (ϵ'_r equation 3) and imaginary (ϵ''_r equation 4) parts dependent on the plasma frequency (ω_p), resonant frequency (ω_0), and damping rate (γ). The relative permittivity is given as:

$$\epsilon_{\mathbf{r}}(\omega) = \epsilon_{\mathbf{r}}'(\omega) + i\epsilon_{\mathbf{r}}''(\omega)$$
 (2)

$$\epsilon_{r}'(\omega) = 1 + \frac{\omega_{p}^{2}(\omega_{0}^{2} - \omega^{2})}{(\omega_{0}^{2} - \omega^{2})^{2} + \gamma^{2}\omega^{2}}$$
(3)

$$\epsilon_{\rm r}^{\prime\prime}(\omega) = \frac{-\gamma \omega \omega_{\rm p}^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \tag{4}$$

Electrons are not bound to their respective nuclei in metals and therefore there cannot be a restoring "spring" force resulting in $\omega_0 = 0[1]$. Therefore, the above model can be simplified down as shown below[1]:

$$\epsilon_{\rm r}(\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2 + i\gamma\omega} \tag{5}$$

Permittivity can also be linked to refractive index (n, ratio of the speed of electromagnetic waves in a vacuum vs that in a given media). Permittivity as a function of refractive index is given as[1]

$$n = \frac{c}{\nu} = \sqrt{\frac{\epsilon\mu}{\epsilon_0\mu_0}} \tag{6}$$

where c is the speed of light in a vacuum, ν the speed of light in the given media, and μ the permeability. Assuming the media is not magnetic material, the permeability is equal to vacuum permeability ($\mu = \mu_0$) rustling in the simplification of equation 6 as shown below[1]:

$$n = \sqrt{\frac{\epsilon}{\epsilon_0}} = \sqrt{\epsilon_r} \tag{7}$$

The refractive index is generally a complex quantity and can be converted into the relative permittivity as shown below[1]:

$$\bar{n} = n + ik_{ec} \tag{8}$$

$$\epsilon_{\rm r}' = {\rm n}^2 - k_{\rm ec}^2 \tag{9}$$

$$\epsilon_{\rm r}^{\prime\prime} = 2k_{\rm ec} \, {\rm n} \tag{10}$$

5.2 Optical near field Enhancement under Illumination

As previously stated in section 5.1, electrons are not bound to their respective nuclei in metals. The potential energy distribution of a metallic lattice makes it energetically favourable for electrons to be non bound to an individual nucleus and therefore allowed to move freely around the lattice of nuclei[1]. Delocalized electrons constitute what is known as "sea of electrons"-"electron gas" giving metal its electric conductivity[1].

Upon illumination, the free electron gas oscillates at the frequency of the incident electric field[6]. This oscillation is further enhanced when the frequency of the electric field equates to that of the localised surface plasmon (plasmonic resonant wavelength)[6]. Due to the oscillation of electrons, the nanoparticle behaves like an electromagnetic dipole re-emitting light coherently at the same frequency[6]. Part of the light is scattered to the far field, the remainder is locally concentrated at the metal surface[6]. For certain nanoparticle geometries, the enhancement of the optic near field can be gigantic[6]. Optical intensity enhancements of several orders of magnitude are obtained at the extremities of nanoparticles (tips of nanorods), called hotspots[6]. Hot spots are expected to increase the yield of photochemical reactions near the surface of the nanoparticles[6].

6 THERMO-PLASMONICS

Plasmonic nanoparticles under illumination become heat sources due to light absorption in metals[2]. The incoming light, electromagnetic waves, are absorbed by the metal and remitted as thermal energy. This process is enhanced by the plasmonic resonance wavelength[2]. At the plasmonic resonance wavelength, the thermal dissipation can become quite large leading to deformation of the nanoparticle, melting of the nanoparticle, and/or boiling or melting of the surrounding[2]. Utilizing plasmonic nanoparticles under illumination to destroy cancer cells by hyperthermia was proposed by Pitsillides et al[18] and Hirsch et al[19] leading to the development of thermoplasmonics which now denotes the branch of plasmonics involving photothermal processes[2].

6.1 Heat Generation

Joule heating is responsible for heat generation from nanoparticles under illumination[2]. For nanoparticles, the resonant oscillation of the electron gas and subsequent interaction with the phonon of the nanoparticles is responsible for energy dissipation via Joule heating[6]. Heat generation can be separated into three steps[2][20][21]:

- 1. electron gas of the metal nanoparticle primarily absorbs part of the incoming light energy
- electron-phonon interaction transmits energy to the nanoparticle atomic lattice (Joule heating)
- 3. thermal energy is released to the surrounding resulting in the cooling of the nanoparticle

The heat source density can be defined as a function of electric field. The heat source density is given as[2]

$$q(r) = \frac{1}{2} Re[J^*(r) * E(r)]$$
(11)

where J*, the polarization current, denotes the complex conjugate of $J = -i\omega\overline{P} = -i\omega\epsilon_0\epsilon(\omega)E[2]$. Therefore, the heat source density can be simplified as shown below:

$$q(\mathbf{r}) = \frac{\omega}{2} \mathrm{Im}(\epsilon(\omega))\epsilon_0 |\mathbf{E}(\mathbf{r})|^2$$
(12)

It can be seen that the heat generation is proportional to the square of the electric field within the nanoparticle[2].

As previously stated, at the plasmonic resonance wavelength the thermal dissipation can become quite large. The plasmonic resonance wavelength is dependent on the geometry of the nanoparticle. Elongated thin morphologies, such as nanorods, have enhanced penetration of the electric field and are thus preferred in thermoplasmonics[2][22].

6.2 Absorption Cross Section

The absorption cross section of a particle is defined as the light power absorbed divided by the intensity, and is given as[2][23][24]

$$\sigma_{abs} = \frac{P}{I} = \frac{\overline{k}}{4\pi\epsilon_0} Im(\overline{\alpha}) - \frac{2}{3} \frac{\overline{k}^4}{(4\pi\epsilon_0)^2} |\overline{\alpha}|^2$$
(13)

where \overline{k} is the wavenumber and $\overline{\alpha}$ is the polarizability. The light power absorbed, is converted into thermal energy[2]. Other forms of energy dissipation such as fluorescence, the emission of light, and thermal radiation are negligible[2].

The two presented quantities, heat source density (q(r)) and absorption cross area (σ_{abs}) can be simply related as shown below[2]:

$$P = \int q(r) dr = q(r) * V = \sigma_{abs} * I$$
(14)

The above integration is over the nanoparticle volume[2].

6.3 Temperature Increase/Distribution

Most nanoparticles are immersed in dense media, liquids or solids. Therefore, the temperature distribution is governed by the heat diffusion equation given as[2][25][26]

$$q(\mathbf{r}) = \rho c p \frac{\partial T}{\partial t} - k \bigtriangledown^2 T$$
(15)

where ρ is the density, cp is the thermal heat capacity, t is the time, T is the temperature and k the thermal conductivity. The thermal conductivity of the nanoparticle is significantly higher than that of the surrounding media given the nanoparticle is made of metal. Therefore the nanoparticle can be assumed as having a uniform temperature[2]. Non-uniform temperatures can be achieved through elongated structures under non-continuous illumination[27][2]. Given the system is stationary ($\frac{\partial}{\partial t} = 0$) and no self-heating contribution occurs (q = 0), the diffusion equation can be simplified as shown below:

$$0 = \nabla^2 \mathsf{T} \tag{16}$$

The temperature of the surround for a spherical nanoparticle of radius a is given as[2]

$$\Delta T = \frac{\sigma_{abs}I}{4\pi rk}$$
(17)

where σ_{abs} is the absorption cross area, and I is the intensity. The temperature profile follows a $\frac{1}{r}$ decay[2]. Within the nanoparticle, the temperature is given as:

$$T = \frac{\sigma_{abs}I}{4\pi ak}$$
(18)

The temperature profile of a spherical nanoparticle can be seen in figure 1.



Figure 1: Temperature profile of a spherical nanoparticle with radius a. Reproduced with permission from Ref [2].

For simple shapes such as discs, ellipsoids, and rods, fictitious diameters have been calculated using the boundary element method and fitted by analytic methods[27]. The temperature can be calculated by using a correction factor[27][2], given as:

$$\Delta T = \frac{\sigma_{abs}I}{4\pi\beta ak}$$
(19)

$$\beta = 1 + 0.09657 * \ln(\frac{D}{d})$$
(20)

However, to obtain an adequate temperature profile, a thermal simulation of a nanoparticle should be completed[2].

6.4 Thermal Collective Effects in Plasmonics

Temperatures resulting from collective thermal effects can only be calculated using thermal simulations. The temperature increase of a specific nanoparticle is no longer solely dependent on its heat generation but also of that of surrounding nanoparticles as their temperature profiles overlap resulting in collective effects[2][28][29][23]. Two different regimes of temperature profiles are generated based on the geometry of nanoparticles: temperature confinement regime, also called localized temperature regime, where hotspots around each nanoparticle can be observed, or a delocalization regime where collective effects occur characterized by a temperature offset (difference between surrounding temperature and lowest temperature between nanoparticles) resulting in a uniform temperature profile[2][23]. The different regimes can be characterized by a non-dimensional number only dependent on geometric properties and are further explored in section 7. The following nondimensional number is only valid for 2D nanoparticle layouts, and is given as[2][23]

$$\zeta = \frac{p^2}{3La} \tag{21}$$

where p is the nanoparticle interdistance, L size of nanoparticle interdistance, and a the characteristic size of nanoparticles. If ζ is smaller than 1 then thermal collective effects dominate while if ζ is larger than 1, then the localized temperature regime dominates. Figure 2 shows a delocalized and localized temperature regime.



Figure 2: Temperature profiles based on different temperature regimes. (a) localized temperature regime. (b) temperature delocalized regime with dominant overall temperature offset resulting from thermal collective effects. Reproduced with permission from Ref [2].

6.5 Temperature Dynamics

The rate at which a nanoparticle reaches a stationary temperature profile once it is under illumination or disappears once no longer under illumination is of great importance and is given as[2][30]

$$\tau = \frac{L^2}{\alpha} \tag{22}$$

where α is the thermal diffusivity and L can be characterized as the diameter of a single nanoparticle where temperature localized regimes dominate or the size of a nanoparticle array where thermal collective effects dominate[2]. Equation 22 is only valid for rudimentary nanoparticles and setups. The equation is no longer valid when significant thermal resistance occurs at the surface of a nanoparticle (Kapitza resistance / thermal boundary resistance), which reduces the rate of thermal exchange between the nanoparticle and its surrounding[2][30]. This would be the case if a nanoparticle was coated. Coating nanoparticles is common practice if a nanoparticle is required to be exposed to high temperatures for a long period of time. Nanoparticles are embedded in insulators such as silica glass (SiO₂) to preserve their shape at higher temperatures. Conserving shape is required, since, as previously discussed, the peak absorption is found at the plasmonic resonance wavelength which is geometry dependent. If the geometry of the nanoparticle were to change, due to thermal deformation, the plasmonic resonance wavelength of the given nanoparticle would shift, resulting in decreased absorption. Insulators shift the plasmonic resonance wavelength and can reduce the absorption cross section of a given nanoparticle. However, the reduction in absorption cross section is still beneficial as it allows the nanoparticle to be exposed to higher temperatures for longer durations[31].

6.5.1 Heating Under Pulsed Illumination

Pulsed illumination (femto to nanoscale) is used to generate a very rapid and intense increase in temperature of a single nanoparticle with the intent to generate physical effects such as bubble formation[32][33] or pressure wave generation[2][34][35]. Heat generation under pulsed illumination is more complex compared to that of continuous illumination[2]. Heating under pulsed illumination can be separated into the same three steps as previously detailed in section 6.1[2][20][21]. The electron gas of the metal nanoparticle primarily absorbs part of the incoming light energy over a time scale equal to that of the pulse duration. Electron-phonon interaction occurs over a time scale equal to the time constant of electron-phonon interaction, τ_{ep} (for gold, $\tau_{ep} = 1.7[ps][36][37][38]$). Thermal energy release occurs over a time scale proportional to that defined in equation 22[2].



Figure 3: Absorbed power and temperature evaluations for continuous illumination(a) and pulsed illumination (b). Reproduced with permission from Ref [2].

Figure 3 shows the difference in power absorbed and temperature with regard to time for continuous (a) and pulsed (b) illumination.

The maximum temperature increase of a given nanoparticle under pulsed illumination is given as 23[2][30]

$$\Delta T = \frac{\sigma_{abs}F}{Vc_{\nu}}$$
(23)

where σ_{abs} is the absorption cross area, F the fluence of illumination, V the volume, and c_v the volumetric heat capacity. The expression is independent of the geometry of a given nanoparticle and is thus useful as a reference to obtain an order of magnitude for temperature increase under pulsed illumination[2]. For femtosecond pulsed illumination, the assumption that no heat is released during pulsed absorption can be made for particles larger than 40[nm][2]. As previously stated for continuous illumination, the temperature profile outside the nanoparticle follows a $\frac{1}{r}$ gradient. However, for pulsed illumination, it follows a $\frac{1}{r^3}$ gradient which is a significantly steeper temperature decay allowing for a greater temperature localization regime[2][30].

6.5.2 Temperature Microscopy Techniques

Measuring temperatures on the nano and microscale is a complex task due to heat having a nonpropagative nature, as opposed to light. For this reason, measuring the temperature of nanoparticles only dates back to 2009[2][16][39].

Temperature microscopy techniques such as a sharp hybrid tip as a nanothermocouple has been used[16][40][41]. Such an approach allows for spatial resolutions of 50[nm][16]. However, due to the proximity of the tip to the sample, it is considered a very invasive procedure[16]. Far-field optical measurement-based thermal microscopy techniques have been developed which are less invasive[16]. Such thermal microscopy techniques rely on fluorescence intensity[42][43], fluorescence polarization anisotropy[39][44], fluorescence spectroscopy[45][46][46], Raman spectroscopy[47], infrared spectroscopy[48], or X-ray spectroscopy[49][16].

The most common approach to measuring temperatures of nanoparticles is utilizing fluorescence compounds dispersed within the nanoparticle surrounding, through a liquid medium or by embedding it directly into the substrate[2][39][50][51][52][53][44][54]. Fluorescence properties are temperature dependent. Measuring fluorescence polarization anisotropy[55][39] was the first reported temperature mapping technique, however other physical properties such as fluorescence lifetime[53][44] and fluorescence spectra[50][51][52] have been used[2].

Slow readout rate[45][56][46][47], low resolution[48], lack of reliability[42][43], poor temperature sensitivity[47], or the necessity to modify the medium with fluorescent molecules or nanocrystals[42][43][39][44][45][56][46] are all limiting parameters making the techniques mentioned above only suitable for a specific case[16]. Thermal-variation of the refractive index of the medium of interest does not suffer from the limitations above and allows for quantitative real-time retrieval of the temperature with a submicrometric resolution[16]. As stated previously in section 5.1, the electric permittivity and refractive index have both real and imaginary parts as they are frequency and material dependent. Under illumination, nanoparticles and their surroundings are warmed up resulting in a change in refractive index over a typical length much larger than the given nanoparticle[16]. The change in refractive index due to change in temperature of a material can be calculated with the Taylor series, and is given as[16][57]

$$\Delta n = \sum_{j=1}^{N} \beta_{j} \Delta T^{j}$$
(24)

where n is the refractive index, β_j are empirical parameters, and T is the temperature. For temperature changes of up to 20[K] in water, the change in refractive index can be calculated with the first term of the Taylor series $\Delta n = \beta_1 \Delta T[16][57]$. Two phase images are taken, one before heating (control), one during heating. The difference between provides a measure for the spatial distribution of the optical path difference, $\delta l(x, y)$. The difference is due to the change in refractive index induced by the change in temperature. Using equation 25 the change in the optical path can be related to the change in temperature for point-like sources of heat, and is given as

$$\Delta T(\theta) = \frac{P}{4\pi kh} * \sinh(\frac{\delta l(\theta) 4\pi k}{P\beta})$$
(25)

where T is the temperature, P is the power absorbed, k is the thermal conductivity, h is Planck's constant, β_j are empirical parameters, and δl is the optical path length.

7 NANOPARTICLE ARRAYS

7.1 Temperature Increase/Distribution

As previously stated in equation 13, the absorption cross section of a particle is defined as the light power absorbed divided by the intensity. However, for particle arrays whose interdistance is at least 4-5 times larger than the particle diameter, intensity can be described as $I = \frac{n\epsilon_0 c|E_0|^2}{2}$ where n is the refractive index, ϵ_0 the vacuum permittivity, c the speed of light, and E_0 is the electric field. The absorption cross-section of a nanoparticle is given as[23][58][59]

$$\sigma_{abs} = \frac{P}{I} = \frac{2P}{n\varepsilon_0 c |E_0|^2}$$
(26)

where σ_{abs} is the absorption cross area, and P is the light power absorbed. As previously stated, the temperature at a given point away from a spherical nanoparticle can be calculated using equation 17. However, if a spherical nanoparticle is at an interface between two different media with two different thermal conductivities(k_1 and k_2), the thermal conductivity can be formulated as $\bar{k} = \frac{k_1+k_2}{2}$. The averaged thermal conductivity can be integrated into equation 26 which is given as[23]

$$\Delta \mathsf{T} = \frac{\sigma_{abs}I}{4\pi r\bar{k}} \tag{27}$$

where T is the temperature, σ_{abs} is the absorption cross area, k is the thermal conductivity, r is the distance to given location and I is the intensity. Calculating the temperature of non-spherical nanoparticles is not as straight-forward and requires the use of a Laplace radius, r_1 as shown below[23]:

$$\Delta T = \frac{\sigma_{abs}I}{4\pi r_l \bar{k}}$$
(28)

For an array, where not only the self-contribution of temperature (ΔT_j^s) generation needs to be considered but that of collective effects (ΔT_j^{ext}) , the temperature of a given particle j is given as[23]

$$\Delta T_{j} = \Delta T_{j}^{s} + \Delta T_{j}^{ext}$$
⁽²⁹⁾

where ΔT_n^{ext} is the thermal contribution of exterior nanoparticles, i.e., nanoparticles other than the one being considered. Its thermal contribution can be calculated as shown below in equation 30[23]:

$$\Delta T_j^{ext} = \sum_{k=1\neq j}^{N} \frac{q}{4*\pi * \bar{k}|r_j - r_k|}$$
(30)

7.2 1D Lattice

1D Lattices consist of a continuous linear chain of N = 2x + 1 nanoparticles, with an interparticle distance p under continuous illumination[23]. In a 1D lattice, the thermal contribution of the exterior can be simply derived from equation 30, which is given as (subscript o means at the center)[23]

$$\Delta T_0^{\text{ext}} \approx \frac{q * \ln(0.89 * N)}{2 * \pi * \bar{k} * p}$$
(31)

where N is the number of nanoparticles. Equation 31 is accurate for all 1D lattice sizes even down to N=3[23]. As previously stated in equation 21, the dimensionless number ζ defines the relative contributions of ΔT_0^s and ΔT_0^{ext} , which for 1D lattices is given as[23]

$$\zeta_1 = \frac{p}{d * \ln(N)} \tag{32}$$

where p is the nanoparticle interdistance and d is the diameter. As previously stated in section 6.4, when ζ_1 is larger than 1, temperature confinement regime dominates resulting in hotspots around each nanoparticle while if ζ_1 is smaller than 1, temperature delocalized regime dominates with thermal collective effects resulting in a continuous temperature profile[2][23]. When thermal collective effects dominate, the temperature is mostly due to neighboring nanoparticles, N-1 and N+1[23]. It was showed that illumination of a single nanoparticle yielded lower temperatures than that of an array under equal illumination[60]. A temperature drop towards the edges of their sample, used for photocatalysis, far beyond the size of an individual nanoparticle was observed[60]. This indicated that the thermal contributions of distant nanoparticles in an array cannot be neglected[60]. Figure 4 shows the temperature distribution of their simulation.



Figure 4: Temperature rise ΔT of the photocatalyst sample. Reproduced with permission from Ref [60]

It can be seen that the change in temperature profile extends beyond the nanometer scale and thus thermal contributions of nanoparticles beyond the neighbouring nanoparticle need to be taken into consideration.

Figure 5 shows a 1D lattice of nanoparticles, with a temperature confinement regime (5b) and with a temperature delocalized regime (5c)[23]:



Figure 5: a) Representation of a chain of N gold nanoparticles. b) Calculated temperature distribution across an NP chain of 5 with a inter particle distance of 250[nm], radius of 15[nm], illuminated at $1.27 * 10^9 \frac{W}{m^2}$. c) Calculated temperature distribution across an NP chain of 1001 with an inter-particle distance of 100[nm], radius of 25[nm], illuminated at $1.27 * 10^8 \frac{W}{m^2}$. Reproduced with permission from Ref [23].

Figure 5b illustrates a temperature confinement regime that is characterised by hotspots with minimal thermal collective effects. Figure 5c illustrates a delocalized temperature regime that is characterised by thermal collective effects with minimal hotspots[23].

7.3 2D Lattice

For the consideration of 2D lattices, the assumption is made that they consist of a hexagonal or rectangular layout of nano particles[23]. Their respective areas are given as

$$A_{square} = p^2 \tag{33}$$

$$A_{\text{hexagon}} = \frac{\sqrt{3}p^2}{2} \tag{34}$$

where p is the particle interdistance. 2D lattices will also be distinguished based on the incoming beam, a Gaussian beam, or a circular uniform beam[23]. A circular beam yields an irradiance given as

$$I = \frac{4P}{\pi D^2}$$
(35)

where I is the intensity and D is the diameter. A Gaussian beam yields an irradiance given as

$$I(\mathbf{r}) = \frac{P}{2\pi\sigma_{abs}^2} e^{\frac{-\mathbf{r}^2}{2\sigma_{abs}^2}}$$
(36)

where I is the intensity, P is the light power absorbed, r the distance to a location and σ_{α} bs is the absorption cross area. The irradiance under Gaussian illumination at the center of the array can be simplified to $I(0) = \frac{P}{2\pi\sigma_{\alpha}^2 b_s}[23]$: As previously defined in equation 27, the self-contribution of temperature is given as:

$$\Delta T_0^s = \frac{\sigma_{abs} * I(0)}{4 * \pi * r * \bar{k}} = \frac{\sigma_{abs} * P}{8 * \pi^2 * r * \sigma^2 * \bar{k}}$$
(37)

In a similar analogy to 1D lattices, the external contribution to the temperature can be derived using equation 30[23]. However, external temperature contributions are dependent on the geometry of the array, square or hexagonal, and on the illumination, Gaussian or circular uniform[23]. Figure 6 shows the equations to calculate the external contributions to the temperature.

case 1: Gaussian illumination of an infinite array

$$\Delta T_0^{\text{ext}} \approx \frac{\sigma_{\text{abs}} P}{\bar{\kappa}} \sqrt{\frac{\ln 2}{4\pi}} \frac{1}{HA} \left(1 - \frac{4\sqrt{\ln(2)A}}{\pi H} \right)$$
case 2: Uniform and circular illumination of an infinite array

$$\Delta T_0^{\text{ext}} \approx \frac{\sigma_{\text{abs}} P}{\bar{\kappa}} \frac{1}{\pi} \frac{1}{DA} \left(1 - \frac{2\sqrt{A}}{\sqrt{\pi D}} \right)$$

$$\Delta T_0^{\text{ext}} \approx \frac{\sigma_{\text{abs}} I}{\bar{\kappa}} \frac{1}{4} \frac{D}{A} \left(1 - \frac{2\sqrt{A}}{\sqrt{\pi}D} \right)$$

case 3: Uniform illumination of a finite-size square array $\sigma = L \ln(1 + \sqrt{2}) S$

 $\Delta T_0^{\rm ext} \approx \frac{\sigma_{\rm abs} I}{\bar{\kappa}} \frac{\ln(1+\sqrt{2})}{\pi} \frac{S}{p^2}$

Figure 6: Expression giving an estimation for the external temperature contribution. Reproduced with permission from Ref [23].

As previously stated in section 6.4 using equation 21, the non-dimensional number, ζ , can be calculated for 2D arrays given as

$$\zeta = \frac{p^2}{3La} \tag{38}$$

where p is the interparticle distance, L the array size and a the nanoparticle radius. When ζ is larger than 1, temperature confinement regime dominate resulting in hotspots around each nanoparticle while if ζ_1 is smaller than 1, temperature delocalized regime dominate with thermal collective effects resulting in a continuous temperature profile[2][23]. This can be seen in figure 2 in section 6.4.

However, nondenominational numbers that define the temperature regime for 3D arrays do not exist. This is primarily due to the light intensity dropping as a function of depth within the 3D array due to absorption of the media. Nanoparticles further within the sample, relative to the light source, receive less light as some of

the incoming light has already been absorbed by the nanoparticles closest to the light source[60]. Temperature will drop within the sample as a function of depth. The absorption of the media can be calculated using the Beer-Lambert law.

8 HOT ELECTRONS

The photoelectric effect was first discovered by Heinrich Hertz in 1887. The phenomenon was later explained by Albert Einstein in 1905[61][62] when he suggested that a beam of light consists of a set of wavepacks (photons), with an energy E dependant only on the frequency and Planck's constant[63][61]. The energy of an individual photon is given as

$$\mathsf{E} = \mathsf{h}\mathsf{v} \tag{39}$$

where E is the energy of a photon, h is Planck's constant and v is the frequency. Einstein's proposal explains why below a certain frequency, it is not possible for light to cause an electron to be ejected from a metal regardless of the intensity of the given light[61]. The photoelectric effect requires a minimum photon energy higher or equal to the metals work function[61]. The excitation of an electron in a solid results in two types of carrier: an electron and a hole[61].

The first step in the excitation of an electron is the absorption of a photon from incoming light[61]. Subsequently, an electron is promoted to a higher energy level[6]. The probability of a photon being absorbed is equal to the square of the electric field inside the metal nanoparticle. This was already shown in equation 12 with regards to heat generation being proportional to the square of the electric field inside the metal nanoparticle[61]. For planar metal surfaces, most of the light is reflected resulting in poor light absorption[61]. For heat generation, plasmon resonance is very important in enhancing light absorption[61][64][65]. In metallic nanoparticles, light absorption is further enhanced at the peak plasmonic resonance wavelength[61]. This results in light collection from an area that is larger than the physical nanoparticle size[61][66][67]. This is called the antenna effect[61].

Plasmon resonances in nanoparticles can be dampened through the re-emission of a photon or the creation of a hot electron-hole pair via Landau dampening[68][61]. Landau dampening is when a plasmon quantum is transferred into a single electron-hole pair excitation[61][69] which are pure quantum mechanical processes that include direct interband transitions, photon-assisted interband transitions, and geometry-assisted transitions[15][70][71][72][73]. Landau dampening is the mechanism that contributes most to the imaginary part of the permittivity[61]. Tuning a nanoparticle to have a high imaginary permittivity allows for the possibility to maximize the hot electron generation[61]. This can be achieved through the choice of material or the geometry of the given nanoparticle[61]. Landau dampening occurs over a time frame of 1 - 100[fs][61].

Even though hot electrons are very energetic, they are unable to travel distances larger than tens of nanometers as they lose their energy via scattering[15]. Only a small fraction of the photoexcited hot electrons are able to leave the material because the ejection process competes with a very fast carrier relaxation process[61].

Following the Landau dampening, carrier relaxation occurs in which electrons that were not ejected undergo electron-electron scattering[61][74]. These scatters thermalize the hot electron bringing their energy level closer to the Fermi level of the metal[15]. The energy of the primary electron is redistributed through a cascading process to the electron gas resulting in a non-equilibrium Fermi-Dirac electron distribution[6]. Carrier relaxation allows for the redistribution of the energy from electrons of higher energy levels to those of lower energy levels[61]. Carrier relaxation occurs over a time frame of 100[fs] - 1[ps][61][75][20].

Finally, heat is generated and dissipated to the surroundings. This occurs in the time frame of 100[ps] - 10[ns][61]. The thermal contribution due to electron-electron relaxation is negligible compared to electron-phonon relaxation (Joule Heating) except for very small nanoparticles[24][76][77]. The electron-electron thermal contribution scales relative to electron-phonon interaction thermal contribution as a ratio of surface area to volume. This is due to electron-electron interaction being a sur-

face effect while electron-phonon interaction is a volume effect. The scaling is given as

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r}$$
(40)

where A is the area, V is the volume, and r is the radius. It was proven experimentally by Link and El-Sayed, and by Hartland et al. that there is no size dependence for gold nanoparticles down to 9[nm] in diameter[24][76][77]. This was established to be due to elastic scattering of electrons not contributing to any energy transfer between electrons and surface phonons[24]. Figure 7 shows the photoexcitation and subsequently relaxation process of a nanoparticle under a laser pulse illumination.



Figure 7: "Photoexcitation and subsequently relaxation process of a nanoparticle under a laser pulse illumination. a) excitation of a localized surface plasmon redirects the flow of light (Poynting vector) towards and into the nanoparticle. b) Landau damping, the athermal distribution of electron–hole pairs decays either through reemission of photons or through carrier multiplication caused by electron–electron interactions. c) Hot carriers will redistribute their energy by electron–electron scattering processes. d) heat is transferred to the surroundings of the metallic structure."[61] Reproduced with permission from Ref [61]

The Fermi level can be understood as the thermodynamic work required to add an electron to a given body[78]. Two different pathways exist for the electron transfer from the metal nanoparticle to the nearby acceptors[6]. The first, the primary electron that absorbed the photon is ejected without interacting with other electrons[6]. The second, is an incoherent process where the primary electron undergoes electron-electron interactions, where the electron transfer relies on the interaction between the athermal Fermi-Dirac electron distribution with a nearby acceptor[6]. The ejected hot electrons are transferred into available orbitals of nearby adsorbents[79][15].

This provides electrons to the surrounding material leading to an anti-bonding state of an absorbed molecule, causing either desorption or the dissociation of a bond[15][80][81]. An example of this is the generation of hot electrons and their direct transfer to O_2 forming O_2^- radicals, which results in the facilitation of the dissociation of 0_2 and the oxidation of the molecules of interest[6]. The application of hot electrons to catalysis will be further explained in section 9.2.

9 THERMO-PLASMONIC DRIVEN CATALYSIS

Nanoparticles that are dispersed into a chemical reaction medium and illuminated at their plasmonic resonance wavelength drive an increase in chemical yield of the reaction[2]. The increased chemical yield is due to at least three separate mechanics[2][6]:

- 1. Optical near field enhancement in the case of photochemical reactions
- 2. Local temperature increase due to light absorption and subsequent heat generation
- 3. Hot-electrons generation and transfer to surrounding oxidizing chemical species

Figure 8 shows the above-mentioned mechanisms.



Figure 8: A) Photo-induced temperature increase. B) Enhancement of the optical near field. C) Photo-induced hot electrons. Reproduced with permission from Ref [6].

9.1 Temperature Driven Catalysis

Chemical reactions are temperature dependent according to the Arrhenius law, given as[2]:

$$K(T) = A * e^{\frac{-L_{\alpha}}{RT}}$$
(41)

where K is the rate constant, A is the pre-exponent factor, E_{α} is the activation energy, T is the temperature and R is the universal gas constant. According to the Arrhenius law, seen in equation 41, K is proportional with T. Nanoparticle heating results in an increase in temperature leading to an increase in chemical reactions or boost in reaction kinetics[2]. Utilizing nanoparticles as opposed to a generic hot plate has several advantages[2]:

- Increased rate of thermal dynamics due to smaller scale of heating due to reduced thermal inertia
- Local superheating above the boiling point in a fluid is possible without the use of an autoclave[82]
- Nanoscale heating allows for the formation of products with a nanometer spatial resolution

Utilizing nanoparticles for purely thermally driven catalysis on a large industrial scale is not viable due to all advantages being lost[2][23][83]. A promising applications for nanoparticles within catalysis is thermo-plasmonic assisted catalysis in liquids and gases.

9.2 Hot-Electron Driven Catalysis

Electron transfer is the basis of redox reactions[6]. The plasmon-driven chemistry mechanism involves the injection of an electron originating from the nanoparticle into an anti-bonding state of an absorbed molecule, causing either desorption or the dissociation of a bond[15][80][81].

In 2011, Christopher et al.[14] proposed that metal nanoparticles illuminated at their plasmonic resonance can be the photocatalyst without the addition of metal oxides[6]. The authors observed the oxidation of molecules of NH₃, CO, and ethylene by illuminating silver nanoparticles[6]. The generation of hot electrons and their direct transfer to O_2 forming O_2^- radicals results in the facilitation of the dissociation of O_2 and the oxidation of the molecules of interest[6]. The sample was microscopically heated until 450[K] to induce the given reaction. An increase in the yield of factor 4 could be observed[6]. However, such an increase in yield corresponds to a 21[K] increase in temperature[6]. It is unclear if this increase in yield is due to the nanorods increasing the temperature of the reaction by optical absorption[6]. It is difficult to quantify the contributions of individual mechanisms due to their interlinked nature[6]. A follow up paper was published further investigating the effects of laser intensity and nanoparticle array density on the reaction [6].

Cortés et al. in 2016 set up experiments to quantify the role of hot electrons using silver nanoantennas[15]. The nanoantennas were treated to have a densely packed monolayer of 4-nitrothiophenol(4-NTP)[15]. When 4-NTP coated silver nanoantennas are illuminated at their plasmonic resonant wavelength in the presence of an acid halide media, they undergo a six-electron-mediated reduction to form 4-amino-thiophenol(4-ATP)[84]. Hot electrons, protons, and halide anions are key elements for driving the reaction[15]. Hot electrons are generated by the silver nanoantennas and transferred to the molecules adsorbed on the surface[15]. Protons serve as hydrogen sources while halide ions are required for the photorecycling of the electron-donating silver nanoantennas[15]. Halide ions(Cl⁻) fill the hot holes on the silver nanoantennas generated by the hot electrons[15]. These undergo a photodissociation reaction to regenerate the silver surface[15]. The setup of the given nanoantennas can be seen below in figure 9:



Figure 9: Single antenna used for hot electron reduction from 4-NTP to 4-ATP. Reproduced with permission from Ref [15]

Control experiments have demonstrated that these reactions are not thermal or photochemically driven[15][84]. The conversion of the monolayer from 4-NTP to 4-ATP only occurs at highly reactive regions[15]. Due to the light sensitivity of the reaction, tools such as tip-enhanced Raman spectroscopy were not used[15]. To accurately monitor this reaction gold nanorods functionalized with 11-mercaptoundecanoic acid were used[15]. The terminal carboxylic acid group of the gold nanoparticles and the terminal amino groups of the silver nanoparticles are used to form a amide bond[85] to accurately report the location of the hot electrons[15]. The gold nanoantennas were added post illumination and therefore do not contribute to the reaction and are only guided by the change in chemistry induced by the hot electrons[15]. As previously stated in Section 5.2, the optical intensity is enhanced at the extremities of a given nanoparticle. Therefore, as is to be expected, the highest rate of hot electron formation occurred at the tip of the given silver nanoantennas[15]. The hot electron flux decays as a function of distance away from the tips[15]. The tips of the nanoantennas had the highest density of gold nanorods[15]. The results can be seen below in figure 10:



Figure 10: Mapping of hot electron conversion in silver nanoantennas for different illumination times(a:1min,b:2min).Reproduced with permission from Ref [15]

The results demonstrate that a chemical reaction has taken place as otherwise, the gold nanoparticles would be unable to agglomerate on the tips as was demonstrated in a control experiment[15]. Additionally, only hot electrons were shown to be able to drive the given chemical reaction as no other mechanisms were present[15].

9.3 Thermoplasmonic-Assisted Catalysis in Gas Phase/Liquids

Gold is known to feature strong catalytic activity when coated in titanium dioxide or other oxides, due to changes in its electronic structure, catalyst-substrate interactions, and morphological features[2][86][87]. Oxidation of organic compounds such as CO, CH₃OH, HCHO has been demonstrated using gold nanoparticles on metal oxides, at moderate temperature elevation (no light involved)[2]. In 2008 Chen et al.[12] further enhanced heterogeneous catalysis by illuminating said gold nanoparticles and thus generating heat. The benefits were a global reduction in energy consumption due to the heating being able to be specifically applied to the catalytic active area rather than heating the entire system[2]. The group of Cronin' conducted further experiments that were designed to quantify such effects, and found a 2-3 orders of magnitude gain in energy consumption[2][13]. Thermoplasmonic-assisted catalysis can also be adapted for use in liquids and has already been demonstrated by Adelman et al. in 2009 through the investigation of utilizing liquid ethanol and water through thermally induced catalysis to form CO_2 , CO, and $H_2[2][83]$.

10 METHODOLOGY

The thesis is divided into two separate parts, the first is numerical, the second is experimental. The main emphasis of the thesis is numerical in nature with the study of temperature distributions of arrays and hyperclusters. Simulations are used to benchmark and predict the temperature distributions of a given nanoparticle array.

The nanoparticle array consist of a sample of $9 - 25[\text{mm}^3]$. The nanoparticle arrays consist of three different types of nanoparticles with a common architecture. All nanoparticles clusters consist of a spherical core which supports smaller satellite nanoparticles placed upon it. The larger core nanoparticles are 20 - 50[nm] in diameter. The satellite nanoparticles are approximately 1 - 5[nm] in diameter. Figure 11 shows an individual cluster, one core with its satellite nanoparticles.



Figure 11: Individual nanoparticle cluster. Orange = spherical core. Green = satellite nanoparticles

The satellite nanoparticles are used as a hot electron generator and as a heat source. The smaller satellite nanoparticles are made of either ruthenium or gold.

The spherical core are used as an optical near field enhancer providing additional light to the surrounding satellite nanoparticles as explained in section 5.2. This enhances the hot electron generation of the satellite nanoparticles. Three different core materials can be used, TiO_2 , Al_2O_3 , and gold.

10.1 Theoretical Models

Theoretical models are created to attempt to accurately simulate the temperature distribution within a complex nanoparticle array. The results are verified against results obtained using COMSOL Multiphysics.

10.1.1 Thermal Model

The thermal model uses the electric field and absorption cross area to calculate the heat generated which is given as

$$Q_{i} = \sigma_{abs} n \frac{c \epsilon_{0}}{2} |E_{i}^{ext}|^{2}$$
(42)

where Q_i is the heat generated, σ_{abs} the absorption cross area, n is the refractive index of the surrounding media, c is the speed of light, ϵ_0 is the vacuum permittivity and E_i is the electric field amplitude. The thermal model solves the Poisson equation (stationary diffusion equation 15) which is given as

$$q(\mathbf{r}) = -\mathbf{k} \bigtriangledown^2 \mathsf{T} \tag{43}$$

$$T(\mathbf{r}) = \frac{Q}{4\pi k |\mathbf{r} - \mathbf{r}_i|} \qquad \text{for } |\mathbf{r} - \mathbf{r}_i| \ge a \tag{44}$$

where T is the temperature and k is the thermal conductivity. All heat is generated within the nanoparticle. Therefore equations 43 & 44 can be further simplified down to

$$0 = \bigtriangledown^2 \mathsf{T} \tag{45}$$

where T is the temperature. A new code architecture utilizing parallel computing has been written to rapidly solve large arrays of nanoparticles.

10.1.2 Step 1: Simulating 1D, 2D, and 3D Arrays

The initial step consists in calculating the temperature profiles of 1D, 2D, and 3D arrays. Studying the temperature relation between different dimensions of arrays has allowed for further understanding into the scaling of nanoparticle arrays. Additionally, temperature profiles of 1D, and 2D arrays have allowed for benchmarking against temperature profiles published in literature.



Figure 12: Left: Isothermal temperature profile at 0.5[K] Right: Initial temperature profiles

The 1D array consists of 10 gold nanoparticles spheres with radius of 1[nm] illuminated at $1.32[\frac{GW}{m^2}]$. The isothermal plot and temperature plots show an increasing temperature towards the center of the 1D array, with a decreasing temperature towards the extremities. This can be seen in the increased volume size of the isothermal plot towards the center of the array. The temperature gradient follows a $\frac{1}{r}$ matching the gradient of published literature.

10.1.3 Step 2: Altering the Simulation Parameters

The second step consists of studying the temperature profiles of arrays while altering parameters. The parameters altered are nanoparticle radius, volume ratio and volume size. An increase in radius has yield a larger absorption cross area for the considered nanoparticle radii and thus a higher temperature. An increase in volume ratio for equal nanoparticle radius and volume results in a higher nanoparticle count resulting in higher temperature. An increase in volume ratio has yielded a higher temperature. A complete evaluation of the results is provided in section 12 and section ref13.

10.1.4 Step 3: Simulating Clusters and Hyperclusters

The third step consists in understanding how representative the temperature profile of an array is relative to that of a hyper cluster. Studies of structured arrays versus randomized nanoparticle arrangements have reported to have few differences, suggesting that temperature profiles of structured arrays are a good predictor of temperature profiles of non-structured arrays[60]. For large nanoparticle arrays, where a delocalized temperature regime dominates, the temperature profiles of hyperclusters converges towards that of structured arrays. This demonstrates that temperature profiles of structured arrays are a good predictor of temperature profiles of non-structured arrays.

10.1.5 Step 4: Benchmarking Results Against Experimental Data and Literature

The fourth step consists in benchmarking scaling laws to the results published in literature and experimental data.

10.2 Experimental Methods

The experimental part consists in measuring the temperature of nanoparticle hyperclusters under illumination. The temperature profile is measured utilizing enhanced temperature microscopy techniques as previously covered in section 6.5.2. Previous techniques were capable of determining 2D temperature profiles but were not able to obtain temperature profile as a function of depth (3D).

Innovations within the NSL lab have allowed for measuring the change in the optical path as a function of depth. This is achieved by a technique called optical diffraction tomography where the probe light is incident at the sample at multiple angles to measure phase shadows. These phase images are then recombined using the diffraction theorem to get an accurate estimate of 3D refractive index profile of the medium under heating and hence the temperature.

The setup that is used is a transmission tomography microscope, measuring changes in refractive index as explained in section 6.5.2 based on the following schematic seen below in figure 13. The setup was designed and assembled by members of the NSL lab. The setup was merely utilized to measure temperature of samples and was not developed or modified as part of this thesis.



Figure 13: Schematic setup of experimental layout

Abbreviation:	Meaning:
FS1	Fiber Splitter
CL1	Collimation Objective
WP	Wedge Prism
L4	Lens
L5&L6	Relay Imaging System
F1	IR Short Pass Filter
02	Long Working Distance Objective
S	Sample
03	Detection Objective
DM1	Long Pass Dichroic Mirror
L8	Lens
W1	Beam Sampler
SF	Spatial Filtering System
Laser4	NIR Laser Source
L7	Lens
CL3	Fiber-collimation Lens
BS1	Beam Splitter
C1	Camera

Laser4 is used as the illumination source of the nanoparticles at their plasmonic resonant wavelength leading to the generation of heat. FS1 provides two separate light sources. One that does not pass through the sample so that it can be used as a reference. The second that does pass through the sample. The two light sources have equal optical path length when the given sample is not illuminated. The difference in optical path length between the two light sources is due to temperature changes in the sample.

The schematic setup in figure 13 can be seen in figure 14(missing mirror to redirect laser light towards the sample):



Figure 14: Preliminary Setup with Annotations

The red line indicates the beam originating from the laser used to heat the sample. The green line indicates the probe beam used to measure temperature. The blue line indicates the beam used to measure the temperature that interacts with the sample.

11 THEORETICAL MODELS

11.1 Greens Function Approach

A Greens function approach is used to calculate the temperature profile of ordinary arrays and clusters. The Greens function approach is valid only for calculating temperature distributions in a uniform and homogeneous media at steady state and is given as

$$\Delta T = \sum_{i=1}^{n} Q_i G_i \tag{46}$$

$$G_{i} = \frac{I}{4\pi k(r_{j} - r_{i})}$$
(47)

where T_j is the temperature at location j, Q_i the heat generated, G_i the Greens function, k the thermal conductivity, and $r_j - r_i$ the distance between location j and the nanoparticle i. The Greens function approach allows for understanding of the temperature at any given point in space as a function of two separate factors: One based on the amplitude $\frac{Q}{4\pi k}$ and the other on geometry $\frac{1}{r}$. The splitting of the overall thermal profile into the said two factors allows for an easy understanding of the concepts that will be introduced further in the thesis. Temperature changes based on amplitude are dependent on the size of the nanoparticles, the material composition of the nanoparticles, laser intensity and the surrounding material. Changes in geometry define how heat propagates itself within a given system. Changes in factors that affect geometry will change the temperature amplitude and profile. However, the total heat generated within a given system does not change. In contrast, changes in factors that affect amplitude will not change the temperature profile, only its magnitude by altering the total heat generated within a given system.

The Greens function approach does not take into consideration the absorption of light by the surrounding media. For this the Beer-Lambert law needs to be taken into consideration.

11.2 Beer-Lambert Law

A Greens function approach assumes equal heat generated for each nanoparticle irrespective of the location of the nanoparticle. This assumption is valid for uniform irradiance for 1D and 2D arrays perpendicular to the impinging light. A scaling factor as a function of nanoparticle density and sample depth based on the Beer-Lambert law that is given as

$$\Delta T_{i} = \sum_{i=1}^{n} Q_{i} G_{i} \tag{48}$$

$$G_{i} = \frac{e^{-z_{i}/\delta_{skin}}}{4\pi k r_{i}}$$
(49)

$$\delta_{skin} = \frac{d^3}{\sigma_{abs}} \tag{50}$$

where δ_{skin} is the skin penetration depth, d is the interparticle distance, σ_{abs} is the absorption cross section and z is the sample depth[60]. The Beer-Lambert law is the change in intensity due to loss of light due to scattering / absorption in the media in which the light travels and is given as

$$I = I_0 e^{-A l} \tag{51}$$



Figure 15: Illustration of Beer-Lambert Law[1]

where I_0 is the initial intensity, l is the sample depth and A is the absorption of the media. The proposed scaling factor only has a meaningful effect on large samples or very dense samples where $\frac{\delta_{skin}}{l} > 0.1$. However, in the case of very dense samples, the Beer-Lambert law breaks down. Beer-Lambert law and the homogenization principle are only valid for low density samples.

11.3 Numerical Improvement for Rapid Computation

Solving for temperature using the Greens function approach is a simple convolution problem. It calculates the thermal contribution of each nanoparticle to a specific grid point. The simplest way to calculate temperature using the Green's formalism is to utilize four loops to be able to run through each axis (x y and z) and to run through each nanoparticle. Such 'loop' oriented methods are computationally expensive. Here we propose two alternatives for the conventional 'loop' approach. The first is to utilize the Fourier convolution theorem. The second is an approach where the the thermal contribution of each NP to the entire domain is considered through vectorization and then added up, thus requiring only one loop. This can be understood as the vectorization for the 4 looped code.

11.3.1 Fourier's convolution theorem

Fourier's convolution theorem states that the multiplication of two functions in the Fourier domain is the convolution of the same functions in the real domain. Fourier's convolution theorem offers a new approach to the calculation of temperature using the Green's function. The primary advantage being that the computational time is independent of the number of nanoparticles considered. However, utilizing Fourier's convolution theorem is computationally expensive. Fourier's convolution theorem requires 27 times more RAM as the volume being resolved is 27 times larger than the volume of the temperature profile that is calculated(3 times larger in each axis).

Mesh:	-3	-2	-1	0	1	2	3	4	5	6	7	8	9	Array Length:
Location of NP:				1	0	0	0	1					A = 5	
Distance Matrix:				2	1	0	1	2						
Contribution 1st NP:			2	1	0	1	2	0	0	0	0			2A-1
Contribution 2nd NP:			0	0	0	0	2	1	0	1	2			
New Distance Matrix: 4				3	2	1	0	1	2	3	4			
Convoluton:	4	3	2	1	4	4	4	4	4	1	2	3	4] 3A-2

Figure 16: 1D array demonstrating why 27 times larger volume for Fourier's convolution theorem is required

Figure 16 demonstrates why a 27 times larger volume is required. Consider a simple 1D array with 5 mesh locations for which the temperature is to be calculate(mesh location 1-5, labeled blue, row 1 in figure 16). Assume there are nanoparticles at the extremities, grid position 1, and 5. When superposing the distance matrix (row 3 in figure 16), we see in row four (contribution of 1^{st} NP) and five (contribution of 2^{nd} NP) that the superposed distance matrix does not provide a distance contribution for the desired area (mesh location 1-5, blue indicates provided distance values, red indicates missing distance values). This can be solved by taking a new distance matrix twice the size of the original distance matrix (figure 16 row 6). When superposing the new distance matrix, it is require to have an array 3 times larger to avoid having circular convolution induced errors. This results in a 3 times larger domain required than the domain for which the temperature is calculated. This results in a 27 times larger domain size than the domain for which the temperature is calculated for a 3D array.

For large domains, utilizing Fourier's convolution theorem is not viable. Additionally, Fourier's convolution theorem is not easily implemented for parallel computing requiring complex array splitting.

11.4 Vectorization of For Loops

The vectorization of the for loops can be achieved by calculating the thermal contribution of each nanoparticle to all grid locations instead of calculating the thermal contribution at a specific grid location from all nanoparticles. This allows for the reduction from 4 loops to a singular loop. For large domains where the required memory exceeds the computer RAM, the domain can be split into smaller domains. This allows for reduced computational load and the possibility to implement parallel computing. This can be visualized in figure 17.





11.5 Analytical vs Numerical Results

The results obtained from the Greens function approach, were benchmarked against results obtained using a numerical approach on COMSOL. The results from COM-SOL were obtained by solving the diffusion equation utilizing an iterative numerical approach.



Figure 18: Analytical solution vs COMSOL numerical solution

It can be seen that the results obtained using the analytical approach are not dependent on the simulation volume, keeping the same number of nanoparticles and excitation conditions. The numerical solution is dependent on the size of the simulated volume. The analytical solution is not dependent because the Dirichlet boundary condition is integrated within the analytical solution (assumed at $T(r = \infty) = 0$). However, this is not the case for numerical approach. The numerical approach applies the Dirichlet boundary condition at the simulation edge. This results in an artificial reduction of the temperature for smaller simulation domains. This can be seen in figure 18. An increase in simulation domain mitigates the error and therefore converges the solution of the numerical approach to that obtain in the analytical solution. Increasing the simulation size allows to reduce inaccuracy caused by the Dirichlet boundary condition.

All energy entering the system must leave the system (otherwise it violates the first law of thermodynamics, conservation of energy). This implies that the heat generated and therefore added to the system by the nanoparticles must be removed at the boundaries, so that the total heat within the system does not change. When applying the Neumann boundary condition, the temperature at the boundary will drop below its initial starting value as heat is being removed instead of flowing out. This will lead to greater deviations from the physical solution and can even lead to nonphysical solutions such as negative temperatures (which violates the third law of thermodynamics). A solution to this would be to apply a time dependent Neumann boundary condition that only starts to be applied when the boundary starts to heat up above its initial value. This, however, is a numerical fix that will not yield a physically meaningful solution.

The numerical approach offers some advantage over the analytical approach. The different thermal conductivities of the nanoparticles compared to that of the media can be taken into account. The thermal conductivity of the nanoparticles in the analytical approach is assumed to be infinite (perfect conductor) and therefore no temperature rise within the nanoparticle is present. This is however nonphysical, although the thermal conductivity of the surrounding media is significantly lower and therefore the change in temperature significantly higher, there will still be a temperature rise within the nanoparticle. Additionally, time dependent studies are not possible with the given analytical approach since steady state is a basic assumption made to obtain the given analytical approach.

11.6 Benchmarking against Experimental Results



Figure 19: Left: Experimental temperature profile of nanoparticles hypercluster Right: Simulation temperature profile of nanoparticle hypercluster

Figure 19 illustrates the temperature profile obtained through experimental measurements and those obtained through numerical simulation. It can be seen that the two temperature profiles have a similar temperature gradient. There are however differences between the two. The experimental temperature profile shows a higher minimum temperature than that of the simulation. This is due to the clusters in the surrounding media. The main temperature increase is due to a conglomeration of clusters. However, there are also clusters present in the surrounding media which contribute to heat generation. This is not the case for the simulation. The simulation assumes a hypercluster in a perfect sphere. Additionally, the experimental hypercluster is not guaranteed to be a pure sphere. All differences between the experimental and simulation results can be explained by the imperfections of the experimental sample. These imperfections are only present on the micro scale. Once increasing the domain size to a mm domain size, these differences will no longer be present.

12 TEMPERATURE SIMULATION

12.1 Nomenclature

For the following sections of the thesis the following terminology will be re-clarified and kept constant:

- \hat{n} : number of nanoparticles along one axis. A regular 3D array of $\hat{n} = 3$ will be a 3x3x3 array with 27 nanoparticles.
- Vr: volume ratio defined as the volume of nanoparticles relative to the entire volume (nanoparticles + surrounding media).
- Perfect array: nanoparticle arrays that have equally distributed and structured nanoparticles with equal interparticle distance between all nanoparticles.
- n_c: number of cluster.
- n_{ci}: number of nanoparticles on an individual cluster.
- IPDA: Average Inter Particle Distance
- IPDC: Closest Inter Particle Distance

12.2 Perfect Arrays



Figure 20: Perfect Array: $\hat{n} = 6$, r = 1[nm]

Figure 20 shows a perfect array of equally distributed nanoparticles with $\hat{n} = 6$. Hotspots of individual nanoparticles can be observed. However, thermal collective effects can be seen in the middle of the array. This indicates that the array is in a transiting state between a localized and a delocalized temperature regime.

12.2.1 Temperature as a function of Volume Ratio

Simulations were set forth to understand how an increase in volume ratio altered the temperature profile and distribution. Numerical simulations of equal volume but changing volume ratio were studied.



Figure 21: Perfect Array: V=11728027.65[nm³], r=1[nm]: Left: $\hat{n} = 2 - 16$, Right $\hat{n} = 2 - 7$,

Figure 21 left shows a linear temperature increase for the maximum, mean and minimum temperature. Given the Vr is proportional to the number of nanoparticles within the sample and all nanoparticles generate the same heat, the temperature of the sample increases in a linear manner. This can be seen in the scaling of the average inter particle distance with increasing Vr. An increase in Vr results in no change to the average interparticle distance. This indicates that the nature in which the temperature changes is one of magnitude and not of geometry. Therefore, given the increase in Q is linearly proportional to the number of nanoparticles which in turn is proportional to the Vr, an increase of Vr with equal volume results in a linear increase in temperature.

Figure 21 right shows the shift from a localized to a delocalized temperature regime. For lower volume ratios, the difference between mean and maximum temperature relative to mean and 0 is relatively large. This indicates a localized temperature regime. As the volume ratio increases, it can be seen that the difference between mean and maximum temperature relative to mean and 0 is reduced indicating a shift away from a localized to a delocalized temperature regime. As previously presented in section 7 for 2D arrays the nondimensional number ζ is given as $\frac{p^2}{3La}$ where a is the radius of the nanoparticle, L the array size, and p the interparticle distance. Although not valid for 3D arrays the trends still hold. For constant a and L, an decrease in interparticle distance should shift towards a delocalized regime. Results presented in figures 21 are in agreement with a decrease in interparticle distance shifting the temperature regime towards a delocalized temperature regime.

12.2.2 Temperature as a function of Volume Ratio and Volume

The following temperature simulations are for nanoparticles of radius 1[nm] with increasing volume size. An increase in volume size results in larger interparticle distance for equal \hat{n} as the nanoparticles are equally distributed within any given volume.



Figure 22: Perfect Array: r=1[nm]

Figure 22 shows that the temperature trends hold true across different volumes. Regardless of the volume, an increase in Vr results in a linear increase in temperature. The scaling of the maximum and minimum temperature follow the scaling of the mean temperature as a function of volume. However, it can be seen that the scaling for equal volume ratios but different volumes does not follow a linear trend. The scaling of temperature against volume follows an exponential scaling. This will be further evaluated in section 13.

12.2.3 Temperature as a function of Volume Ratio and Radius

Altering the radius has two effects on the temperature, one geometric and the other amplitude. An increase in radius changes the absorption cross area which results in a change in temperature magnitude. For equal number of nanoparticles, an increase in radius results in an increase in absorption cross area and therefor an increase in temperature, for the radii considered. However, this also results in an increase in volume ratio. For equal Vr, an increase in nanoparticle radius results in a small increase in temperature. This small increase in temperature is only valid for the nanoparticles considered, with no guarantee to hold true for other nanoparticle radii or other materials.



Figure 23: Change in temperature as a function of radius and Vr

It can be seen that altering the radius retains the linear temperature increase as a function of volume ratio observed in section 12.2.1. However, increasing the radius has an effect on the temperature regime. Although the mean temperatures are comparable, the difference between mean and maximum temperature increases with an increase in radius size for equal volume ratios. This can be seen in figure 24.



Figure 24: Maximum and mean temperature of perfect arrays with nanoparticles of increasing size

Figure 24 shows that for larger nanoparticles arrays of equal volume, the difference between mean and maximum temperature relative to mean and 0 is larger indicating a localized temperature regime. This is to be expected as for equal volume ratio, an array of smaller nanoparticles must have more nanoparticles and therefore has a higher heat source count. This is also reflected in the non dimensional number ζ given as $\frac{p^2}{3La}$ for 2D arrays. The interparticle distance, p, scales with $p = C_1 * N_t^{\frac{-1}{3}}$ where N_t is the number of nanoparticles. Given the volume of gold for equal volume ratio is the same, the number of nanoparticles scales with the N_t = $C_2 * \frac{1}{r^3}$. Thus p scales with $p = C_3 * r$. Given ζ scales with p^2 a decrease in r should result in a decrease in ζ . As stated previously, although the 2D definition of ζ does not give exact answers and is not directly applicable for 3D arrays, it does provide a general understanding of how altering factors will change the temperature regime. It can therefore be concluded that a decrease in radius for equal volume ratio will result in a shift towards a delocalized temperature regime.

The second manner in which changing the radius alters temperature is geometric in nature. The Greens function is only valid outside the nanoparticle and is not applicable inside the nanoparticle. The assumption made, is that the temperature within the nanoparticle is that of the surrounding media at the surface of the nanoparticle. Increasing the nanoparticle size will therefore increase the area of constant temperature.

12.3 Hyper Cluster Simulations

All previous simulations utilize perfect arrays. However, in practice perfect arrays do not exist. It is therefore important to understand the difference between perfect arrays and other arrays which are not structured, such as randomly distributed arrays. Such systems have already been studied and reported in literature to be in good accordance with structured arrays. Studies simulating the temperature distribution of a perfect array with interparticle distance d and arrays with interparticle distance d \pm a have been completed[60]. They found that for large arrangements of

nanoparticles there are insignificant differences between non-structured and structured arrays[60].

As our samples consisted of clusters, simulations of equal volume ratio (equal number of nanoparticles within a set volume) of perfect arrays and cluster arrangements were simulated. For each given volume, the amount of clusters simulated was increased till saturation (no more clusters can be reliably added without overlapping). For each given volume and hypercluster count, the simulations were run 6 times to be able to obtain an average value of said configuration. Figure 25 shows the temperature profile of an arrangement of 8 hyperclusters.



Figure 25: Hyperclusters under illumination (Au, r=1[nm], $n_c = 8$, $n_{ci} = 50$)



12.3.1 Benchmarking Hyperclusters against Perfect Arrays

Figure 26: Hyperclusters: $V = 11360276.99[nm^3]$, $n_c = 2 - 20$, r = 1[nm]

Figure 26 illustrates similar trends compared to those observed in perfect arrays. The linear temperature increase that was initially observed for perfect arrays can be seen in figure 26. Additionally, a clear shift from a localized temperature regime for low volume ratios to a delocalized temperature regime for higher volume ratios can be seen. Similar to perfect arrays, when both the radius and arrays size are kept constant, with an increase in volume ratio we have a decrease in interparticle distance resulting in a shift towards a delocalized temperature regime. However, the way in which the mean temperature of perfect arrays compare to a hypercluster is of great interest.



Figure 27: Mean temperature of a hypercluster versus perfect arrays Left: V = 1466003.456[nm³], Right: V = 11360276.99[nm³]

For larger volumes, the number of nanoparticles increases while keeping the volume ratio constant. Deriving from the nondimensional number for 2D arrays, it can be seen that an increase in array size results in a shift towards a localized regime. The same holds true for 3D arrays. An increase in volume for equal volume ratio shifts the temperature regime towards a delocalized temperature regime. This indicates that for very large volumes where delocalized temperature regimes dominate to the extent that local temperature peaks are insignificant, perfect arrays will be very good predictors of temperature for even heavily manipulated arrays such as a hypercluster. These results further validate and are in good alignment with those published by literature[60].



Figure 28: Max temperature of hyperclusters versus perfect arrays

As previously discussed, larger nanoparticles within a volume of equal size and volume ratio shift towards a localized temperature regime. Similarly, a hypercluster arrangement should have a more localized temperature regime compared to that of a perfect array of equal volume and volume ratio. This can be seen in figure 28. The difference between the maximum temperature of a hypercluster arrangement is higher than that of a perfect array indicating that local peaks dominate given that the mean temperatures are in good alignment. With an increase in volume ratio, and therefore a shift towards a delocalized regime, the maximum temperature of a hypercluster arrangement converges towards that of a perfect array further validating the claim that for large volumes where delocalized temperature regimes dominate, perfect arrays are good predictors of the temperature profile of non-structured arrays. It can therefore be concluded that for any arrangement of nanoparticles, as long as randomly distributed and homogeneously distributed within a sample, having equal radius and volume ratio, a perfect array will be a good predictor of the temperature profile.

Additionally, it can also be predicted that a nanoparticle arrangement following a lattice nanoparticle distribution, as seen in figure 29, will be the most optimal nanoparticle distribution, given equal size of nanoparticle and volume ratio, to reach a delocalized temperature regime.



Figure 29: Canon balls packed in a lattice arrangement[88]

Although hyperclusters with increase volume size were shown to be in good alignment with that of perfect arrays, the Beer-Lambert Law applied to perfect arrays will be a poor predictor of that of hyperclusters. This is due to the interparticle distance being heavily manipulated given the particles are clustered on a host nanoparticle. The closest nanoparticle will be significantly closer than what it would be in a perfect array of equal volume ratio. Additionally, due to the proximity of these nanoparticles, their absorption cross area will overlap. This indicates that the Beer-Lambert law will have an effect on individual clusters. To correctly apply the Beer-Lambert law for a hypercluster, one should consider the a cluster as one nanoparticle, with interparticle distance as the distance between clusters, whose absorption cross area is the total absorption cross area of all the nanoparticles inside the cluster, $\sigma_{abs-cluster}$ which is given as

$$\sigma_{abs-cluster} = \sum_{n=1}^{n_{ci}} \frac{Q_n}{I} = < n_{ci} * \sigma_{abs}$$
(52)

However, this only becomes an issue with larger nanoparticles. For smaller nanoparticles, the difference between the two will be small.

13 SCALING TEMPERATURE AS A FUNCTION OF VOLUME

It is computationally expensive to simulate large nanoparticle arrays (several days on super computers). Scaling laws that predict the temperature profile of large nanoparticle arrays allows for a significant reduction in computation time. The temperature distribution of arrays as a function of volume has been extensively studied. This has allowed for the observation of trends that define how temperature changes as a function of volume. All the following trends are dependent on geometry and not amplitude.

13.1 Scaling with Volume

Thermal simulations were completed by varying the volume size while maintaining equal volume ratios for different nanoparticle radii and different volume ratios.





Figure 30 shows that for any given volume ratio and nanoparticle radii the temperature scales with

$$\Delta \bar{\mathsf{T}} = \kappa \mathsf{V}^{\frac{2}{3}} \tag{53}$$

where \overline{T} is the mean temperature, κ is a constant and V is volume. Equation 53 is valid when a delocalized temperature regime is present. For all arrays of equal volume ratio and interparticle distance, regardless of volume, κ is a constant. κ is given as:

$$\varsigma = \frac{\Delta \bar{\Gamma}}{V^{\frac{2}{3}}} \tag{54}$$

Calculating the temperature profile of a small array ($\hat{n} = 2$, nanoscale size) with equal volume ratio and interparticle distance to that of the large volume yields κ . Once the temperature profile of the small representative array is calculated, taking the mean temperature of the entire domain and the volume ($V = (IPDC * \hat{n})^3$) yields κ as given in equation 54. Given κ and the desired volume of the larger domain are known, the mean temperature of the larger volume can be calculated with equation 53.

When taking a localized regime as reference for the calculation of κ , the value of κ is over predicted. This will be further investigated in section 13.1.1. Equation 53 has an analytical derivation to obtain the scaling law which will be further investigated in section 13.1.2.

13.1.1 Correction for Temperature Regime Change

As previously discussed in section 6.4, there are two possible temperature regimes: the localized and the delocalized temperature regimes. For a small volume where there is a localized temperature regime, κ is over predicted. Therefore, with a κ estimate from a localized temperature regime, scaling is a poor predictor of temperature of large volumes. To adjust for this, the reference simulation needs to be in the delocalized temperature regime. However, a delocalized temperature regime occurs at larger volumes and therefore higher order of \hat{n} need to be considered (to retain equal volume ratio). This results in higher computational costs. However, a factor exists which corrects for the error induced by change in temperature regime. Figure 31 illustrates how κ changes as a function of volume size.



Figure 31: Scaled kappa versus volume for different radii

It can be seen in figure 31 that the predicted value of κ drops as the volume size increases. A drop of 6% in κ can be observed. This drop will change with different Vr. When IPDC»R, the size of the nanoparticle does not greatly change the relative change in κ . Figure 32 illustrates the two different temperature regimes which cause the incorrect prediction of κ .



Figure 32: Left: localized temperature regime $\hat{n} = 3$, Scaled Kappa = 0.966, Right: delocalized temperature regime $\hat{n} = 9$, Scaled Kappa = 0.941

It can be seen in figure 32 where \hat{n} is 9, a delocalized temperature regime dominates resulting in a relative κ of 0.941. Where \hat{n} is 3, a localized regime dominates resulting in a relative κ of 0.966.

13.1.2 Analytical Solution

The scaling law presented in equation 53 also has an analytical derivative. The origin of this law is the Greens function. The Greens function dictates the temperature profile within a volume. When taking the volume integral of the Greens function, it delivers the total temperature within a volume and is given as:

$$T_{total} = \int T dV$$
(55)

$$T_{total} = \int_0^{2\pi} \int_0^{\pi} \int_0^{\bar{r}} \frac{Q}{4\pi k\bar{r}} \bar{r}^2 \sin(\theta) d\bar{r} d\theta d\phi$$
(56)

$$T_{\text{total}} = \int_0^{\pi} \int_0^{\bar{r}} \frac{Q}{2k\bar{r}} \bar{r}^2 \sin(\theta) d\bar{r} d\theta$$
(57)

$$T_{total} = \int_0^r \frac{Q}{2k\bar{r}} \bar{r}^2 (-\cos(\pi) + \cos(0)) d\bar{r}$$
(58)

$$T_{\text{total}} = \frac{Q}{k} \left[\int_{R}^{\bar{r}} \frac{1}{\bar{r}} \bar{r}^2 d\bar{r} + \int_{0}^{R} \frac{1}{R} \bar{r}^2 d\bar{r} \right]$$
(59)

$$T_{total} = \frac{Q}{k} \left[\frac{\bar{r}^2}{2} - \frac{R^2}{2} + \frac{R^2}{3} \right]$$
(60)

$$T_{total} = \frac{Q}{2k} [\bar{r}^2 - \frac{R^2}{3}]$$
(61)

where \bar{r} is average distance from all nanoparticles to the remaining of the volume (average distance temperature has to travel). This can be simplified by taking the average interparticle distance between all nanoparticles as the average distance from all nanoparticles to the remaining of the volume. Given the nanoparticles are equally spaced within the volume, nanoparticles can be understood as a course mesh. Therefore, the average interparticle distance between all nanoparticles is a discretization of the average distance from all nanoparticles to the remaining of the volume. Understanding how the average interparticle distance between all nanoparticles is calles with volume allows for the analytical derivation of the mean temperature as a function of volume.



Figure 33: Average interparticle distance between all nanoparticles scaled with volume

It can be seen in figure 33 that the average interparticle distance between all nanoparticles scales as a function of $V^{\frac{1}{3}}$. Equation 61 can be further simplified down, and is given as:

$$\bar{\mathbf{r}} = \alpha V^{\frac{1}{3}} \tag{62}$$

$$\bar{T} \propto T_{\text{total}} = \beta [\alpha^2 V^{\frac{2}{3}} - \frac{R^2}{3}]$$
(63)

The exact scaling law is given in equation 63 where R is the radius and V the volume. Given the volume is significantly larger than the radius, the scaling law can be further simplified down leading the original proposed scaling law, equation 53:

$$\overline{T} \propto \kappa V^{\frac{2}{3}}$$
 for $\alpha^2 V^{\frac{2}{3}} >> \frac{R^2}{3}$ (64)

13.2 Scaling in Z

The previous scaling law only applies for scaling from a small cube to a larger cube. It however does not allow for scaling to other geometries. Here we propose a scaling law to change the size of one axis of the cube. Figure 34 shows how the mean temperature of a cube changes as a function of the length of one axis of the cube.



Figure 34: Scaled temperature versus volume for increase Vr and Volume

The scaling displayed above in figure 34 is a geometric scaling law and holds true for different volume ratios and volumes. The relative temperature drop can simply be calculated with the following relationship:

$$T_{\rm r} = 0.9265e^{0.2858V_{\rm r}} - 0.9229e^{-1.378V_{\rm r}}$$
(65)

where V_r is the relative volume change and T_r is the relative temperature change.

13.3 Benchmarking Scaling Laws with Literature

Ieng Wai Un et al. published a temperature plot of a 3D array providing sufficient information to replicate the results. The authors utilized the Greens function to solve the temperature profile of the entire domain using a supercomputer. They reported it taking over two weeks. The geometry at hand consists of a cylinder with radius 5.65[mm], thickness of 1[mm], intensity of $800[\frac{W}{m^2}]$, thermal conductivity $0.0503[\frac{W}{mK}]$ and refractive index 1.2 with gold nanospheres of radius equal to 6[nm] and a interparticle distance of 225[nm]. The temperature plots are provided allowing for the validation of the above mentioned scaling laws.

Initial step consists in determining the scaling factor κ . This is achieved by simulating a $\hat{n} = 2$ array with, r = 6[nm], IPDC = 225[nm] and total volume of IPDCx $\hat{n} = 450^3[nm^3]$. The calculated temperature profile can be seen in figure 35.



Figure 35: Temperature profile of $\hat{n} = 2$, r=6[nm], $T_{max} = 1.0968 * 10^{-5}$, $T_{mean} = 2.0381 * 10^{-6}$, $T_{min} = 1.1967 * 10^{-6}$

The simulation yielded a mean temperature of $2.0381 * 10^{-6}$ [K]. Due to the localized temperature regime, the value of κ is over predicted by 6% as explained in section 13.1.1. Using equation 53, kappa is calculated as follows with the correction for the temperature regime induced error:

$$\kappa = \frac{0.96 * T}{V_3^2} = \frac{0.96 * 2.0381 * 10^{-6}}{91125000^{\frac{2}{3}}} = 9.461 * 10^{-12}$$
(66)

Given kappa, it is now possible to predict the mean temperature for a larger volume. However, the given example consists of a cylinder and not a cube. Therefore, a cube with edges the length of the diameter of the cylinder is taken. This means the cube will have equal length in two axis to that of the cylinder. The third axis can then be obtained by altering the length of the last axis and scaling the temperature with the scaling law presented in section 13.2. The mean temperature of a the larger volume is calculated as follows:

$$T_{Large} = \kappa * V^{\frac{2}{3}} = 9.461 * 10^{-12} * (2 * 5.64 * 10^6)^{3 * \frac{2}{3}} = 1203.8025[K]$$
(67)

As stated previously, the Z axis will be scaled down to obtain a rectangle of equal height to that of the cylinder. The volume of the cube is $(2 * 5.64 * 10^6)^3$ while the desired rectangle is $(2 * 5.64 * 10^6)^2 * 10^6$. The relative volume can therefore be calculated as follows:

$$V_{\rm r} = \frac{(2*5.64*10^6)^2*10^6}{(2*5.64*10^6)^3} = 0.088652$$
(68)

With the relative volume known, the relative temperature can be calculated using equation 65 as follows:

$$T_{\rm r} = 0.9265e^{0.2858*0.088652} - 0.9229e^{-1.378*0.088652} = 0.1335 \tag{69}$$

$$\Gamma_{rectangle} = T_r * T_{large} = 0.1335 * 1203.8025[K] = 160.71[K]$$
(70)

It follows that for a rectangular volume 8.8652% smaller than a cube, the temperature of the rectangle is 13.35% of the original temperature of the cube. The rectangle is of equal height, width and length to the desired cylinder. The geometry of a rectangle is not the same than that of a cylinder and therefore nor is the temperature. The temperature of a cylinder is lower given the rectangle has additional thermal contributions from the corners. This can be seen in figure <u>36</u>.



Figure 36: Thermal Contribution of a Cylinder (corners missing relative to a rectangular heating, dark blue)

To predict the effect that changing the morphology of a given fixed volume and volume ratio has on the temperature, one must simply look at the surface area of a given shape. Two morphologies of equal volume but different surface areas, the one with the largest surface area has the lowest mean temperature. A simple example of this would be comparing a 1D line of nanoparticles versus a sphere both of equal volume. The sphere has the lowest surface area and therefore must have the highest temperature. The 1D line of nanoparticles has the higher surface area and therefore lower temperature. With equal volume and volume ratio, the given geometries have equal amount of heat sources. The geometry with the larger surface area has more possibilities for heat to leave the system and heat must travel further given the average interparticle distance of a geometry with larger surface area is longer.

However, for the given considered case, volume is not preserved. The geometry of the cylinder can be placed within that of the rectangle. Therefore, the temperature of the cylinder must be less than that of the rectangle. When removing the thermal contributions of the corners of the rectangle, a temperature drop of 19% is observed. This is a geometrical relation that will hold true for rectangles and cylinders of equal aspect ratio but different volume. This reduces the predictive temperature from 160.71[K] to 131.72[K].

However, the Beer-Lambert law has not been taken into consideration until now. When applying the Beer-Lambert law the mean temperature drops from 131.72[K]



to 33.873[K]. Figure 37 shows two different temperature plots, one with and one without the Beer-Lambert law.

Figure 37: Top: Temperature profile of cylinder without Beer-Lambert Bottom: Temperature profile of cylinder with Beer-Lambert

It can be seen in the bottom figure of figure 37 that the thermal contribution at the bottom of the cylinder is more significant than at the top. This is due to the light entering the cylinder from the bottom. The light is absorbed at the bottom surface resulting in reduced intensity for nanoparticles further up within the sample. This absorption has a significant impact on the temperature as the mean temperature drops from 131.72[K] to 33.873[K].

The obtained results through scaling overpredict the published results by approximately 1[K]. Additionally, a stronger temperature drop at the extremities of the cylinder can be observed. Both these trends are reduced when decreasing the mesh size. When changing the mesh size from 0.1[mm] to 0.07[mm] to 0.049[mm] to 0.04[mm], the mean temperature changes from 35.9691[K] to 35.6107[K] to 34.8747[K] to 33.873[K]. This drop in temperature can be seen in figure 38.



Figure 38: Left: Temperature profile of cylinder as a function of depth with mesh size = 0.04[mm]

Right: Temperature profile of cylinder as a function of depth with mesh size = 0.1[mm]

The origin of the error comes from the application of the Beer-Lambert law. The Beer-Lambert law, equation 49, $e^{-z_i/\delta_{skin}}$ where z is the depth and therefore is mesh dependent. Varying the mesh size induces a change in the average energy drop (average value of $e^{-z_i/\delta_{skin}}$). Decreasing the mesh size, and therefore increasing the number of mesh elements (finer mesh), results in an increase in energy drop (less energy being absorbed and thus lower temperature). This can be seen in figure 39.



Figure 39: Energy absorbed versus mesh points along the z axis

As seen in figure 39, the energy absorbed converges towards a fixed value when increasing the number of mesh points. This is due to the Beer-Lambert law being an exponential function. Increasing the points considered is a linear scaling but the values of the points are exponential. As an example to illustrate this, lets consider a mesh size of 10, for which the values in the middle is x_5 . When halving the mesh size, the points considered are now at 7.5 and 2.5 with values $x_{7.5}$ and $x_{2.5}$ respectively. If the function considered were linear, $x_5 = \frac{x_{7.5} + x_{2.5}}{2}$ would hold true. However, given the function is not linear, this is not the case. Therefore having a finer mesh is important to accurately simulate the Beer-Lambert law.

The nature of the error is dependent on the mesh location and is therefore geometrical and not one of amplitude. The solution is to increase the resolution of the mesh but this is not possible due to computational limitations. Another approach would be to correct the geometrical error by altering the amplitude of the temperature. Although this is physically not the correct approach, since the error is small, it is possible to correct the error by changing the amplitude of the temperature as a function of the relative energy absorbed. Figure 40 & figure 41 show the results obtained when correcting for the error induced by the coarse mesh benchmarked against the results published in literature.



Figure 40: Left: Temperature profile along the top of the cylinder published in literature. Reproduced with permission from Ref [[60]]Right: Temperature profile along the top of the cylinder resulting from scaled simulations with correction for mesh induced error of Beer-Lambert law





Right: Temperature profile of cylinder as a function of depth resulting from scaled simulations with correction for mesh induced error of Beer-Lambert law

Figures 40 & 41, once the error induced by the coarse mesh is corrected, the temperature predictions are remarkably accurate. The maximum temperature and temperature profile of both surface and depth plots are visually not distinguishable. The reported peak temperature is approximately 43[K] while our predicted peak temperature is 43.3549[K]

There is no guarantee that the obtained results exactly match those published in literature. Additional parameters that are not provided can account for discrepancies within the temperature prediction, e.g., the inter particle distance and the absorption cross area. Additional assumptions such as boundary conditions and other parameters may also slightly vary.

Utilizing the above mentioned scaling laws, the temperature profile of large arrays can be calculated with minimal computational cost. When neglecting the coarse mesh induced errors, the temperature predictions are only off by a few percent allowing for an understanding of the potential temperature that can be expected. This will facilitate calculation and prediction of large nanoparticle arrays with minimal computation cost. Additionally, when correcting errors as explained and proposed, extremely accurate temperature profiles can be predicted without running a complete simulation.

14 CONCLUSION

Thermal profiles of perfect arrays were studied allowing for the discovery of two scaling laws and an enhanced understanding of how heat is diffused within nanoparticle constellations.

Nanoparticle arrays were found to be good predictors of temperature profiles of non-structured arrays when in the delocalized temperature regime. The delocalized temperature regime was found to be more dominant with an increase in volume and volume ratio. It can therefore be concluded that an increase in heat sources results in a more significant bulk temperature contribution and thus, a further shift to the delocalized temperature regime. When increasing volume size and nanoparticle count, resulting in a shift towards a delocalized temperature regime, the temperature profile of hyperclusters converges towards that of perfect arrays.

The temperature for both perfect arrays and hyperclusters was found to scale linearly with volume ratio. An increase in volume ratio resulted in a linear increase in temperature. Additionally, a clear shift from a delocalized temperature regime to a localized temperature regime was found following the trends of the nondimensional number ζ for both perfect arrays and hyperclusters. Changes in nanoparticle radius were shown to result in a change in temperature magnitude relative to the change in absorption cross area. Changes in volume were shown to result in a change in temperature magnitude relative to the change in temperature magnitude relative to the volume.

Scaling laws were found to scale temperature as a function of volume and change in length of one axis of a cube. These scaling laws allow for the rapid and easy calculation of large temperature profiles. The application of the scaling laws was demonstrated compared to results reported in the literature. The predicted temperature profiles are in excellent alignment with those published, demonstrating the validity of the scaling laws.

14.1 Further Improvements

The Greens function is not without limitations. It assumes a stationary system with a homogeneous thermal conductivity. These assumptions limit the accuracy of simulations. In order to address this, one could utilize an iterative code which uses the discovered scaling laws to predict the temperature profiles while altering the thermal conductivity per iteration. An initial step would be to utilize the Maxwell Garnett relation, effective medium approximation, to find an average thermal conductivity of the media as a function of volume ratio of the individual components. This would be an improvement over current simulations, albeit not a perfect solution.

Natural convection due to buoyancy has two origins: changes in density due to temperature changes, and changes in density due to changes in media composition. Natural convection can be studied by running CFD simulations. Once the bulk temperature distribution is calculated, the temperature profile can be used to simulate natural convection due to temperature changes in density. Due to the small time scale of plasmonic heating (nanoseconds) relative to natural convection (seconds) the two effects can be separated. The bulk temperature can be assumed to be stationary due to the difference in time scale. This assumption holds true for nanoscale systems. However, this is no longer the case when considering larger systems (mm scale and larger). Although the temperature generated at the individual nanoparticle is at the nano second time scale, this will not hold true for bulk heating (delocalized regime). The kinetics of bulk heating are of a significantly higher order of magnitude than those of individual nanoparticles. A time scale study evaluating fluid flow relative to bulk heat generation will be necessary to evaluate natural convection. Changes in density due to changes in chemical composition of the media will also be of great importance when evaluating natural convection.

Light interaction between nanoparticles has not been taken into consideration. Expanding the scope of the studies to investigate electromagnetic interactions between nanoparticles will allow for a more accurate and complete picture of heat generation. Inter particle scattering, although low for small nanoparticles, will play an increasing role as nanoparticles increase in size, volume increases in size and when nanoparticles are no longer arranged in a perfect array. Understanding how scattering takes place in a cluster and in between clusters will allow for more accurate temperature predictions. Additionally, light scattering directly contributes to the generation of hot electrons, allowing for a better understanding of how hot electrons drive catalysis.

A current limitation in the scaling laws is the lack of understanding of the transition between the different temperature regimes. A nondimensional number for 3D arrays will allow for further understanding of temperature profiles and reduce complexity of predicting and understanding κ .

Further experiments should be completed to validate the scaling laws. Two experiments can be set forth to validate the above mentioned theories: the first is changing the volume ratio, the second is changing the volume size. Changing the volume ratio requires different samples which is time consuming and expensive to produce. Changing the volume size can be achieved by altering the beam size while keeping intensity constant.

Changing volume ratio requires different samples. It is time consuming and expensive to produce different samples relative to experiments requiring only a singular sample. Changing the volume ratio should results in a linear scaling of temperature. This becomes more complex when utilizing larger samples where the Beer-Lambert law is in effect. For smaller samples the effects of the Beer-Lambert law are less pronounced. However, measuring temperature of small samples is difficult. Measuring temperature of large samples is easier but requires post processing to account for the Beer-Lambert law.

Changing the volume size is achieved by altering the laser beam width and keeping intensity of the laser constant. Similar to before, for small and low volume ratio samples, the effects of the Beer-Lambert law are less pronounced. However, measuring temperature of small samples is difficult. Additionally, small and low volume ratio samples, could be in the delocalized temperature regime resulting in an incorrect scaling due to the changes in κ . Similar to before, measuring temperature of large samples is easier but requires post processing to account for the Beer-Lambert law.

Validating the second scaling law where temperature is scaled as a function of altering the length of one axis, will be more complex. Altering the depth axis would require producing new samples for each different iteration. This is time consuming and expensive. Additionally, changes due to the Beer-Lambert law would need to be considered. A simpler approach is to keep the depth axis constant and alter one of the two surface axis (x or y) instead. This would allow all experiments to be completed on the same sample. Additionally, the Beer-Lambert law can be neglected when altering a surface axis.

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