Hot Nanoparticles

Jollans, T.G.W.

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Author: Jollans, T.G.W.
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1 Introduction

In the mid-19th century, when the ether was still widely thought to exist, and years before James Clerk Maxwell's seminal paper on his theory of electromagnetism [1], Michael Faraday was performing experiments with very fine gold-leaf[1] in an effort to learn something about the nature of light and its interaction with objects of a size comparable to the wavelength. He discovered that, when a gold film on a glass plate is heated, it appears to vanish, and the surface of the glass acquires a reddish hue (very different from the green tint of the gold-leaf).

After establishing through chemical means that the gold, though invisible even under his microscope, was still present on the glass plate, Faraday postulated that the gold film had somehow run into separate particles so small as to be invisible, and that the distinctive red colour of the invisible gold was due to the small size of these particles. [2]

This suggestion would turn out to be remarkably prescient.

1.1 Gold nanoparticles

Today, we have no doubt of the existence of the gold nanoparticles Faraday postulated. A veritable zoo of nanoparticles of different materials and shapes can now readily be synthesized and studied either collectively or individually using optical methods (as we shall do in this thesis), and also examined using electron microscopy for detailed information about their structure. [3–6]

Nevertheless, the optical properties of nanoparticles of gold (or other metals, for that matter) are no less intriguing today than they were 162 years ago: the yellow colour of bulk gold is so distinctive and familiar that the entire field of heraldy refers to the colour yellow, when it appears on arms and flags, as 'gold', or, more properly, 'or' [7], and it is easily explained by reference to the band structure of atomic Au. The colour of gold nanoparticles (in solution,

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[1] Today, we would presumably speak of a 'thin film'.

this is typically a shade of red, though it depends on the shape and size), on the other hand, evidences behaviour of gold at the nanoscale that is different both from the behaviour at macroscopic scales and at the atomic scale.

If ‘more is different’[2] is the unofficial motto of condensed matter physics, we might think along the same lines and use ‘smaller is different’ as a motto for nanoscale optics (and nanoscale physics more broadly). Just as (e.g.) the discrete translational symmetries in crystals and the breaking of these symmetries due to defects can produce incredibly rich physics in the macroscopic solid state, breaking material symmetries by introducing a surface at subwavelength scales can lead to equally rich optical properties that are not found at other scales.

This principle, that ‘very small’ objects — where, for the purposes of optics, ‘very small’ effectively means ‘sub-wavelength’ — are prone to show behaviour unknown at larger (bulk) or smaller (atomic) scales, applies not only to metal nanoparticles, but to a wide variety of structures, including molecules, nanotubes, dielectric nanoparticles, and semiconductor nanostructures (such as quantum dots). Gold nanoparticles, however, are the specific context of this thesis.

1.1.1 Optical properties of gold nanoparticles

Most of the optical properties of metal nanoparticles can be understood using a fully classical treatment, applying Maxwell’s equations to a plane wave incident on an object of the right nanoscale size and shape and the bulk (complex) permittivity $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ and calculating how light is scattered and absorbed by the object. In other words, most optical properties of a ~10 nm sphere would be reproduced by a ~1 m sphere investigated using shortwave radio, as long as it had the same permittivity in that frequency range (which a 1 m gold sphere certainly wouldn’t).

There are exact solutions to the problem for several simple geometries, of which the most relevant for this thesis are the sphere and the layered sphere. Collectively, these are generally (especially for spherical geometries) known as ‘Mie theory’, after Gustav Mie, who was one of a number of people, also

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[2] The phrase ‘more is different’ refers to emergent behaviour that appears when many atoms (or molecules, birds, commuters, ...) interact, and is the title of an influential article by Philip W. Anderson [8], the later Nobel laureate who is credited with coining the term ‘condensed matter physics’ [9].

including Peter Debye and Ludvig Lorenz, who solved the problem of light scattering by a dielectric sphere around the turn of the 19th century [10–14]. To lowest order — i.e. in the electrostatic approximation, which is valid for small spheres with a radius $R \ll \lambda_0$ — the Mie result for a sphere (equivalent to Rayleigh scattering) can be written as

$$\sigma_{\text{sca}} = \frac{k^4}{6\pi}|\alpha|^2 \quad \text{and} \quad \sigma_{\text{abs}} = k\,\text{Im}(\alpha) \quad \text{where} \quad \alpha = 4\pi R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}, \tag{1.1}$$

α being the polarizability volume, $k = 2\pi n_m/\lambda_0$ is the wavenumber in the surrounding medium, and ε_m is the permittivity of the medium surrounding the sphere. σ_{abs} and σ_{sca} are the absorption and (integrated) scattering cross sections, respectively [14].

The essential physics can already be extracted from eq. (1.1): Firstly, the sphere has a resonance at $\text{Re}(\varepsilon + 2\varepsilon_m) = 0$. This is known as the plasmon resonance, and is the main way to address gold nanoparticles optically. (It is also responsible for the red colour Faraday observed.) Secondly, we can make note of the fact that the optical properties depend on size, wavenumber and the material's permittivity $\varepsilon(\omega)$, but also on the permittivity of the medium, ε_m. Thirdly, scattering and absorption have different dependences on size ($\sigma_{\text{sca}} \propto R^6$ and $\sigma_{\text{abs}} \propto R^3$); we should expect absorption to dominate in the limit $R \longrightarrow 0$, and scattering to dominate at some larger size. What this size is will of course depend on the permittivities. Fig. 1.1a shows that for the sizes used in this thesis (viz. 50 nm to 100 nm)[3] absorption and scattering are comparable, and use of the electrostatic approximation is not justified; fig. 1.1b shows illustrative calculated spectra for an 80 nm sphere, showing the plasmon resonance in the visible.

As we work with sizes for which scattering is significant, it is important to introduce a third quantity next to scattering and absorption: the *extinction* cross section is defined as $\sigma_{\text{ext}} = \sigma_{abs} + \sigma_{sca}$; it corresponds to the amount of light that is not transmitted through a sample. When scattering is negligible, e.g. for most molecules, the distinction between extinction and absorption is often neglected since, in that case, $\sigma_{\text{ext}} \simeq \sigma_{\text{abs}}$. We cannot make that approximation.

While the wavenumber k does feature in eq. (1.1), the optical properties of a nanoparticle cannot be understood without reference to the bulk permittivity;

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[3] Without further qualification, the 'size' of a nanoparticle refers to its diameter, not its radius.

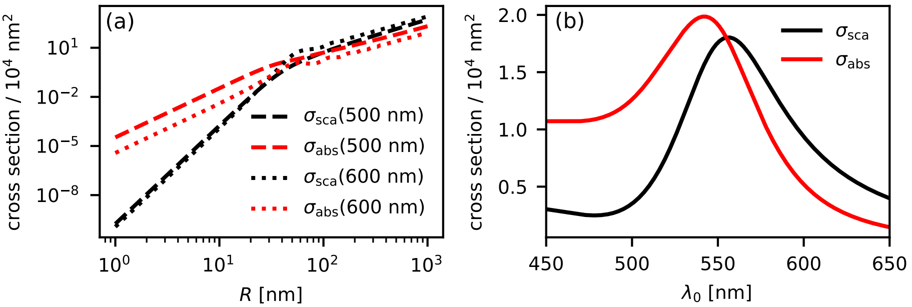

Figure 1.1: Mie theory calculations (using the implementation by Peña and Pal [15]) of the scattering and absorption cross sections of a gold sphere in a medium with $n_m = 1.33$ (e.g. water). **(a)** dependence of the cross sections on radius for two example wavelengths, which agrees with the approximation in eq. (1.1) for $R \lesssim 20\,\text{nm}$. **(b)** cross sections for $R = 40\,\text{nm}$ as a function of vacuum wavelength λ_0.

that of gold is reproduced in fig. 1.2. At low energies, it is well reproduced by a free electron (Drude–Sommerfeld) model; around and to the blue of ~500 nm, the permittivity is characterized by interband transitions in gold. These are responsible for the large absorption seen in this region in fig. 1.1b.

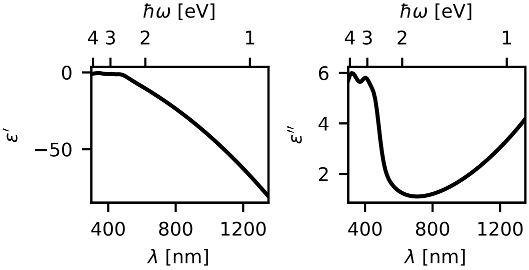

Figure 1.2: The permittivity $\varepsilon(\omega) = \varepsilon' + i\varepsilon''$ of gold as measured by Olmon et al. [16].

While the classical model can give us a good understanding of elastic scattering and absorption, it does not consider higher-order effects, some of which have proved to be extremely useful. Among the most important are near-field processes [17, 18], inelastic (Raman) scattering, and nanoparticle photoluminescence. The latter two go hand-in-hand and are introduced in some more detail in § 5.1.2.

1.1.2 Single gold nanoparticles

As discussed, the optical properties of gold nanoparticles are sensitive to the environment of the particles and, to a lesser extent, to their size. This has experimental implications: Gold nanoparticles, including the nanospheres used in the work presented in this thesis, are typically grown chemically. Whatever the method of production, there will be some random variation in the size of the particles, and thus of their optical properties. More importantly for our purposes, in a complex medium, the particles may see a variety of different environments depending on their location in space, or, in a dynamic environment, as a function of time.

Furthermore, the optical properties of gold nanoparticles are known to depend strongly on particle shape, and even the permittivity is not necessarily constant: ε depends, beyond the frequency, on the thermodynamic variables of state (temperature, density, etc.) [19, 20], on the crystal structure [21], and, for ~30 nm and smaller particles, even on the size [22].

These sources of inhomogeneous broadening, alongside the plain technical challenge, motivate the study of *single* nanoparticles and their optics: by monitoring a single nanoparticle optically, we get not only an unencumbered view of the properties of *that* particle, but also an indirect measure of the current environment of the particle — a sensor reading out properties of an attolitre volume, potentially in real time with nanosecond resolution (chapter 2), or, using pump-probe spectroscopy, with much higher time resolution (chapters 4 and 5).

This style of highly localized and very fast measurement lends itself to the study of dynamic processes at the nanoscale. A central theme of this thesis is applying this idea to heat transfer.

1.2 Hot nanoparticles

We have already established that gold nanoparticles absorb light. The absorbed energy, apart from the tiny fraction that is later reemitted as light, is dissipated as heat. For many purposes, this is a problem: a resonantly illuminated gold (or other metal) nanoparticle will heat up its surroundings, which may have unintended side-effects. Further, if the metal gets hot enough, it may melt, reshape (particularly if it was not spherical to begin with), and even fragment [23].

However, we can also make use of the fact that a gold nanoparticle becomes a nanoscale heat source which we, by varying the illumination, can control. As alluded to in the previous section, we can use it to study heat transfer at the nanoscale, or we could make use of the heat in one way or another [24].

Briefly, nanoparticles as nanoscale heat sources have found biomedical applications: biological tissue is sensitive to temperature, and localized hyper- or hypothermia has long been used for medical purposes — most crudely with contraptions like hot water bottles and ice packs. Localized hyperthermia is now being explored as a way to fight tumours, and metal nanoparticles have proven to be a promising way to introduce a highly localized heat source into the body. This idea is known as plasmonic photothermal therapy [25–28].

Beyond the temperature increase around a heated nanoparticle as such, we may also make use of secondary effects of the increased temperature: depending on the material properties of the medium, a change in temperature will lead to a change in density and, with it, to a change in refractive index. By illuminating a nanoparticle or an array of nanoparticles, then, we can exert influence on the temperature and refractive index distribution in space, and, to a certain extent, control it [29, 30]. If we control the refractive index distribution in a certain volume, we control the path light takes through that volume.

1.2.1 Photothermal microscopy[4]

If optically heating a particle changes the refractive index around it, and the optical properties of that same particle depend on the surrounding refractive index, then by illuminating an absorbing particle, we are changing its optical properties. While this nonlinear effect is naturally quite small, it has turned out to be very useful: To first approximation, the change in scattering due to optical heating $\partial\sigma_{\mathrm{sca}}/\partial P_{\mathrm{heat}}$ is proportional to the change in refractive index $\partial n/\partial P_{\mathrm{heat}}$, which, in turn, is proportional to the absorption cross section σ_{abs}, the change in refractive index with temperature $\partial n/\partial T$, and further thermal properties of the medium. [32–34]

Since the change in scattering depends only on a broadband refractive index change (typically referred to as a ‘thermal lens’), we can apply a two-

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[4] This section is partly based on the corresponding section in the publication: T. Jollans et al., ‘Nonfluorescent Optical Probing of Single Molecules and Nanoparticles’, J. Phys. Chem. C **123**, 14107–14117 (2019).

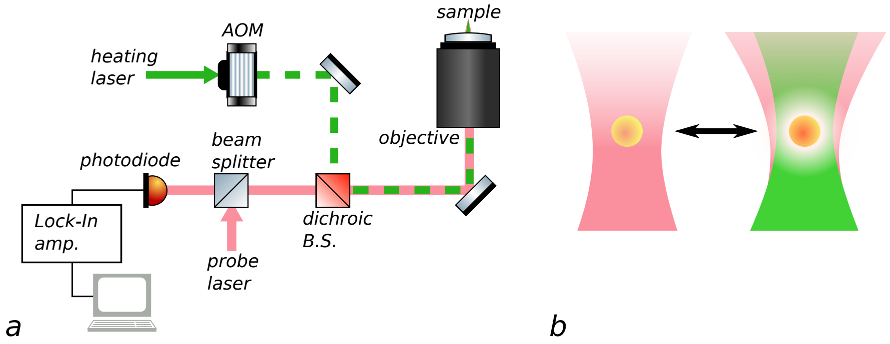

Figure 1.3: (a) simplified scheme of a photothermal microscope. (b) cartoon representation of thermal lens creation in a photothermal microscope's focus.

colour technique with a heating beam near the absorption resonance of the nanoabsorber and a probe beam of a different colour. The probe wavelength can then be judiciously chosen to lie far from the resonance in order to minimize damage and saturation due to the probe, thereby allowing for high probe intensities and accordingly low photon noise. [33]

What remains is extracting the *change* in scattering from the scattered light. To this end, the intensity of the heating beam is modulated at a certain frequency, generally in excess of 100 kHz, and the corresponding oscillating component of the scattered probe beam is extracted to recover the actual signal — generally with a lock-in amplifier. [32]

Fig. 1.3 shows a sketch of the technique, known as photothermal microscopy. For gold nanoparticles, we use a heating beam near the plasmon resonance (532 nm), and a probe beam far enough to the red that its absorption is negligible by comparison (815 nm in chapters 2 and 3, 785 nm in chapters 4 and 5). The heating beam intensity is modulated using an acousto-optic modulator (AOM).

Since the signal depends on the heating beam causing a temperature gradient, it is only sensitive to objects that absorb light of the chosen heating wavelength. The technique can therefore have extremely low background in a weakly-absorbing environment. With a suitable contrast agent, such as gold nanoparticles, it can be used in noisy biological environments [35, 36], and it can, under the right conditions, be used to detect even very weakly absorbing objects, down to single molecules [33, 37, 38].

Since the photothermal signal is dependent on the amount of energy absorbed by whatever is illuminated, we can, with a suitable calibration, use it to measure the absorption cross section of a single nano-object. Even without a calibration, we can discriminate different nano-objects based on their absorption; in particular, this technique is used in all the following chapters to identify single gold nanoparticles and distinguish them from clusters or aggregates of nanoparticles.

1.2.2 Plasmonic vapour nanobubbles

With a sufficient heating power, the liquid environment of a heated nanoparticle can reach temperatures of potentially hundreds of kelvin above the bulk boiling point while remaining in the liquid state [39]. Only as the medium is heated up so far as to cross the spinodal — the point, near the critical point, where the liquid phase ceases to be stable — does it decompose into a vapour bubble at the hot metal surface, and the remaining liquid phase further outside [40]. The vapour bubble expands rapidly outward before collapsing while the particle and its surroundings cool down.

This much, at least, theory and experiment have established for *pulsed* illumination, in which superheating of the medium is in any case confined to a short period of time, and in which a vapour nanobubble is, by the very nature of the excitation, a *transient* vapour nanobubble. Whether the spinodal picture applies under continuous-wave illumination, where transient vapour nanobubbles can form around a plasmonic nanoparticle and rapidly collapse despite the system having time to equilibrate [41], is as yet unclear.

Transient plasmonic vapour nanobubbles have been observed under both pulsed and continuous-wave illumination [41–44], and provide a fascinating test case for nanoscale heat transfer at nanosecond time scales [40, 45]. Chapter 2 explores transient and long-lived vapour nanobubbles in that context.

It has been suggested that bubble formation around heated nanoparticles is helpful in plasmonic photothermal therapy of cancer (see p. 6) [46–49]. This suggestion is primarily based on promising results published by Dmitri Lapotko, Ekaterina Lukianova-Hleb, and co-workers. However, the retraction and/or correction of several (but not all) of their papers on the subject [50–53] and the apparent subsequent departure of Lukianova-Hleb and Lapotko from academia cast considerable doubt on the idea.

1.3 Outline of this thesis

This thesis examines the processes surrounding laser-heated nanoparticles under a number of different conditions, and from a number of different angles. The following few paragraphs give a brief outline of its contents:

In **chapter 2**, we heat gold nanoparticles to the point at which vapour nanobubbles can form around them and beyond. We investigate how the dynamics vary with heating power and identify three distinct boiling régimes at the nanoscale: explosive boiling, semi-stable transition boiling, and nanoscale film boiling. We discuss how these relate to the well-known boiling régimes at macroscopic scales and draw parallels to the macroscopic boiling crisis. In the semi-stable transition régime, we observe remarkably stable nanobubble oscillations and discuss their properties in context.

Chapter 3 proposes an extension of photothermal microscopy to measure the chirality of or around single nanoparticles or nanostructures. After introducing chirality in general terms, we discuss the requirements on the symmetries of the experimental setup with reference to preliminary measurement results. We then apply the theory of tightly focussed beams to examine the consequences of different asymmetries for the experiment.

Chapter 4 uses pump-probe spectroscopy to probe the dynamics of already hot gold nanoparticles subjected to additional pulsed heating on picosecond-to-nanosecond timescales. The chapter looks in particular at heat transfer from the particle to its surroundings and discusses the idea of studying vapour nanobubble formation at a picosecond timescale.

Finally, in **chapter 5**, we turn our attention to the photoluminescence of hot gold nanoparticles. Anti-Stokes luminescence, in which photons extract energy from the thermal bath in the nanoparticle, is an indicator of the temperature within the nanoparticle. We use this to measure the electron temperature prevalent in a nanoparticle under pulsed laser illumination, which is of order 10^3 K. Using a two-colour pump-probe technique, we then measure how the temperature of a pulse-excited electron population in a single nanoparticle first grows and then decays within picoseconds.