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# Photothermal circular dichroism studies of single nanoparticles

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# 1

# Introduction

*The polarization of light has fascinated scientists for more than three centuries. Light polarization is utilized in many fields of science and has found various technical applications in the stress analysis of solids, ellipsometry, photography, display technology and polarized-light microscopy, just to name a few. Also in nature polarization effects are exploited, some animals have developed sophisticated polarization-sensitive eyesight making them able to see and communicate among channels others cannot and therefore puts them in advantage. From a historical perspective it was the study of optical activity, the difference in propagation speed between two perpendicular circular polarization states, that has led to a better understanding of the interaction of polarized light and matter. Circular dichroism (CD), the absorbtive manifestation of optical activity, is the differential absorption of an object with light of opposite handedness. In biochemistry it provides valuable information that cannot be extracted from ordinary absorption measurements alone and it is widely used in the study of the optical properties of crystals, along with linear birefringence and linear dichroism. In the realm of nano-optics and plasmonics, circular dichroism is of special interest as the shape affects the optical properties of a nano-object and it also affects its interaction with polarized light. Although highly sophisticated CD-sensitive techniques exist, they are, to date, mostly limited to measurements of ensembles of molecules or nanoparticles. Moreover, most CD techniques measure in transmission and therefore scattering is also playing a role when studying nanoparticles, in addition to absorption. The ensemble properties of such nanoparticles can often differ strongly from the single-particle properties, because in general the particles in an ensemble are not identical. In addition, when performing ensemble measurements one takes the average signal over all particle orientations. Therefore single-particle CD techniques are necessary to get a better understanding of the optical properties. In this work we investigate how photothermal imaging can be used to study the circular dichroism of individual (gold) nanoparticles and of superparamagnetic magnetite particles.*

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## 1.1. Optical properties of gold nanoparticles

Throughout this thesis we will mostly perform investigations on gold nanoparticles. Although other materials exhibit similar optical properties the choice often falls on gold due its chemical inertness. The optical properties of gold nanoparticles in the visible and near infrared can be well understood by the collective response of their quasi-free conduction electrons. An external electromagnetic plane wave with frequency $\omega$ causes the conduction electrons of a metal to oscillate. Their response is captured in the dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, which is related to the complex refractive index via $n^2 = \epsilon(\omega)$. Gustav Mie derived an analytical solution for the scattering problem of an electromagnetic wave incident on a spherical object. Mie's solution of Maxwell's equation is, in principle, valid for arbitrary sizes of the object. When dealing with small nanoparticles we often employ a dipolar approximation where we can neglect retardation effects. This holds true for particles much smaller than the wavelength. In this limit we can write the polarizability of a spherical nanoparticle as:

$$\alpha = 3V \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}, \tag{1.1}$$

where *V* is the particle's volume and $\epsilon$ and $\epsilon_m$ are the respective permeabilities of gold and of the surrounding medium [1]. The scattering and the absorption cross sections can be expressed as

$$\sigma_{sc} = \frac{k^4}{6\pi}|\alpha|^2 \quad and \quad \sigma_{abs} = k\,\mathrm{Im}(\alpha), \tag{1.2}$$

respectively [2], and $k = \omega n_m/c$ is the wavevector of the light in the surrounding medium. Equations 1.1 and 1.2 allow us to extract the most important optical properties of metal nanoparticles. Firstly, we find a resonance condition when the real part of $\epsilon + 2\epsilon_m$ approaches 0 - this is also known as plasmon resonance [3]. Another important quantity that can directly be extracted from equation 1.2, by invoking the optical theorem, is the extinction cross section, which writes: $\sigma_{ext} = \sigma_{abs} + \sigma_{sc}$. Furthermore, we find that the scattering term scales with the square of $\alpha$ whereas the extinction term scales linearly. This has important physical implications, namely, that at small sizes scattering can be neglected and the extinction becomes equivalent to the absorption, whereas for larger sizes the scattering term dominates. In a spherical nanoparticle we have three degenerate plasmon resonances due to the spherical symmetry. If the particle has other shapes e.g. a rod-like shape, one of these plasmon resonances is shifted to longer wavelengths [1, 4]. By tuning the length-to-diameter ratio of a nanorod one can tune its resonance. The resonance along the long axis is typically called *longitudinal plasmon* and the two-fold degenerate plasmon along the short axes is called *transverse plasmon*. Notably, the longitudinal plasmon can be shifted to far longer wavelength whereas the transverse plasmon usually does not shift much. One important implication of this lifted degeneracy is that the response of the nanorod not only depends on the size but also on the direction along we excite it and therefore on the polarization of light.

## 1.2. Chirality

Chirality - the absence of mirror symmetry of an object is a property found in a broad length scale ranging from nanosized objects like single molecules to macroscopic objects like our

hands. The basic building blocks of life are chiral and therefore the biochemistry that takes place in our bodies is strongly dependent on the specific interactions between those chiral objects and usually on their *handedness*. This strong interplay between form and function has led to a great importance of chirality in biochemistry. For drug molecules one particular handedness can be the cure while the other one is harmful [5]. CD has proven to be particularly useful in the study of the secondary structure of biomolecules [6–8]. However, chirality is not only relevant for chemical or biological considerations. Throughout this dissertation, in fact, we will mainly focus on the chirality of metal nanoparticles, which are usually much larger than most biomolecules. By the emergence of sophisticated chemical synthesis and nanofabrication methods, chiral nano-sized particles and structures can now be crafted with various unique optical properties which are related to their chiral geometry [7, 9–13].

### 1.2.1. Optical manifestation of chirality

The handedness of a chiral object affects how it interacts with other chiral objects. When we shake hands for example we will immediately know whether we shake a left or a right hand, likewise a right-handed screw requires opposite turning than a left-handed one to drive it into wood. On the nanoscale such distinctions turn out to be more difficult. Although modern microscopy methods such as AFM imaging or electron microscopy have superb spatial resolution, so far they have limited application for the study of chiral nanoparticles (with some exceptions [9, 14]). Far-field optical microscopy is limited by diffraction to $\sim 200\,\mathrm{nm}$ (depending on the wavelength) and therefore cannot resolve the geometry of a nanoparticle, and yet it can discriminate the two enantiomers of chiral nanoparticles or even enantiopure ensembles of molecules. Polarized light can be chiral - with left and right circularly polarized light being of opposite handedness. Chiral objects have an important quality, they interact differently with light of opposite handedness [15]. This property is called circular dichroism for absorption and circular birefringence for retardation (complex and real part of the polarizability) and can be exploited to discriminate and study chiral objects.[1] In general for an object to exhibit circular dichroism it requires two ingredients. First, it requires a geometry that breaks mirror symmetry, a simple example would be a helix, and second, the object's size should be large enough compared to the wavelength of light so that retardation effects become relevant. The reason why many biomolecules often exhibit weak CD in the visible range, is because their "helical pitch" is much smaller than the pitch of the electric field of circularly polarized light [15].

A typical circular dichroism spectrometer is based on a transmission geometry and probes the differential extinction, containing an absorption and a scattering contribution, of left and right handed circularly polarized light of an analyte. When light of opposite handedness is transmitted through a cuvette containing a chiral analyte and if the analyte absorbs or scatters at the light wavelength, its transmission will depend on the handedness of polarization. Small changes in transmission can be translated into differential extinction, which can be detected with high accuracy via lock-in amplification. Modern spectropolarimeters are based on the design developed by Jellison [16] and can measure differences in extinction down to $10^{-5}$ [8, 17], however, this accuracy can only be achieved in an en-

[1] Circular birefringence is considered less often although it carries the same physical information as it is linked to circular dichroism via a Kramers-Kroning relationship [5].

semble measurement, thereby averaging the response of many molecules or particles.

### 1.2.2. Linear dichroism and circular dichroism

We have just established that CD is the difference of absorption between left and right circularly polarized light. CD appears when an object has a broken symmetry (lack of mirror symmetry) and requires a true 3D spatial arrangement. A related effect to CD is linear dichroism (LD), the difference in absorption of two orthogonal *linear* polarization states. We have discussed in paragraph 1.1 that a nanorod's resonance wavelength depends on the axis we excite it at. If we compare the nanorod's absorption with linearly polarized light at the longitudinal plasmon resonance wavelength, we find a strong absorption along the long axis but weak absorption along the short axis. The two different plasmon conditions lead to LD. However, if we perform the same measurement in a 45° rotated axis, for example, we find zero difference in absorption, as in both cases the driving field causes the same excitation in the nanorod.

Although throughout this thesis we are mainly interested in the measurement of the CD of a given object, we must also take into account its LD, for the simple reason that a real measurement never is perfect. An ideal way to measure CD is to measure the differential absorption of two orthogonal circular polarization states by performing a square-wave modulation of the polarization. In a real experiment such a square-wave modulation is not feasible and therefore elliptic polarization states will be involved that can give rise to leakage of an LD signal into the CD signal.

LD is often magnitudes stronger than CD and therefore, when not carefully subtracting LD components from our CD signal, we might draw the wrong conclusions. In chapter 3 we will see in detail how to subtract LD components to leak into the CD signal.

### 1.2.3. Magnetic circular dichroism

In 1846 Michael Faraday discovered that heavy glass, when subject to a strong magnetic field, can rotate the plane of polarization of linearly polarized light [18]. This effect, also known as Faraday rotation, showed the interaction of light with (electro) magnetic fields inside matter. Shortly after Faraday, John Kerr found, by reflecting polarized light from a polished and strongly magnetized iron surface, that the plane of polarization of the reflected beam was rotated with respect to that of the incoming beam [19]. Faraday's and Kerr's experiments have marked the advent of magneto-optics which is still a vivid field of research and led to important technological developments as for example magnetic data storage or optical isolators (Faraday rotator). Both experiments measured a birefringence effect, which is related to the real part of the refractive index. The absorptive counterpart of this effect is called magnetic circular dichroism (MCD). Magnetic circular dichroism, like geometric circular dichroism (circular dichroism due to a lack of mirror symmetry) is the difference of absorption of left and right circularly polarized light. The most important difference between geometric CD (chirality) and MCD is that the former requires geometric features in a spatial arrangement that have helical handedness. In contrast, MCD can be found in all (magnetic) matter, independently of the spatial arrangement as long as a net magnetization is present [20]. It results from a magnetic perturbation of the electronic states involved in

optical transitions in absorption bands [21]. In the case if the magneto-optic Kerr effect it is the interplay of magnetic moments and spin-orbit coupling that leads to a differential absorption of left and right circularly polarizer light [22]. A detailed mathematical treatment of the effect is presented in the works of Oppeneer [23] and Argyres [24].

## 1.3. Photothermal effect

We have introduced circular dichroism as an optically measurable quantity of chirality. We have also seen that CD is typically probed in a transmission geometry where a cuvette contains a solution of the sample of interest. Measurements in a transmission geometry probe extinction and therefore entail not only an absorption but also a scattering contribution of the sample. Although the scattering component can be often neglected, when for example studying molecules (due to their small size), if one wants to study the circular dichroism of objects such as plasmonic nanoparticles, one can no longer neglect the scattering contributions to the CD signal [6, 25]. The study of the "true" circular dichroism of such particles therefore requires an optical technique that is only sensitive to absorption. Additionally, ensemble measurements averages the CD signal over all possible particle orientations, whereas single particle measurements measures the CD of a single orientation. In this section we introduce photothermal microscopy as an optical technique that is exclusively sensitive to absorption and therefore is well-suited to study the circular dichroism of individual nanoparticles.

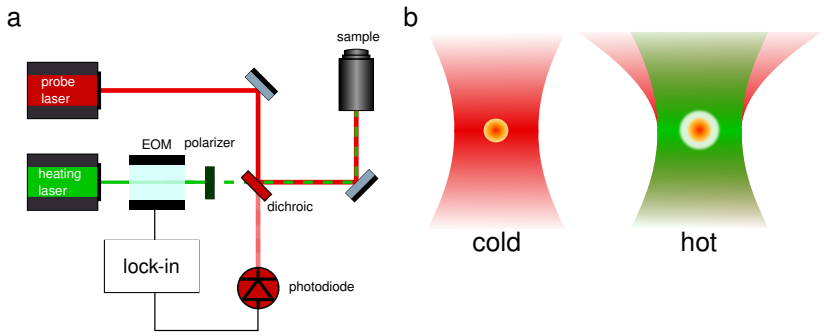


Figure 1.1: (a) Schematic photothermal setup in a reflective geometry. A red probe laser is combined with a green heating laser by means of a dichroic element. The dichroic also serves to filter out the green light on the detection path. The intensity of the heating laser is modulated via a combination of EOM and polarizer. (b) Photothermal effect of a nanoparticle immersed in a liquid. When a heating beam heats the particle a thermal lens forms that changes the probe beam's propagation. This causes a small difference in light collection. Those small differences can be detected by means of lock-in amplification with high sensitivity. The deviation of the probe beam upon thermal lens formation is exaggerated.

We have established in section 1.1 that small gold nanoparticles strongly absorb light. The absorbed energy decays mostly nonradiatively and, as a consequence, heat is produced. The heat is subsequently released into the surrounding environment, thereby changing its refractive index close to the particle. We call this local refractive index gradient a *thermal lens* [26]. The thermal lens can be probed by a second laser, that we shall name probe beam and whose wavelength is chosen far away from the absorption resonance of the particle to prevent further heating. In PT microscopy we measure the change in scattering of the *probe*

*beam* upon the formation of a thermal lens $\partial\sigma_{sc}/\partial P_{heat}$ that is created by the absorption of a *heating beam*. Therefore, we separate the residual heating photons from the collected probe photons by means of a long pass filter. In first approximation and for small particles, the change of collected probe photons upon heating depends linearly on the thermorefractive coefficient $\partial n/\partial T$ [27] of the surrounding medium. In general, the effect of the thermal lens is quite small as the heat-induced refractive index change is typically on the order of $10^{-4}$/K for most liquids [28]. To make up for this small change, in PT imaging we do not employ a CW heating scheme, but we modulate the heating beam intensity, typically at frequencies between $50\,\mathrm{kHz}$ and $1\,\mathrm{MHz}$. This leads to a periodic variation of the thermal lens at the modulation frequency. If we employ lock-in amplification, we can extract the signal at that heating beam modulation frequency, thereby removing most of the 1/*f* noise and achieve shot-noise-limited detection [29]. A simple version of such a PT setup, in a reflection geometry, is depicted in figure 1.1(a). The heating beam is intensity-modulated by a electro-optic modulator and a subsequent polarizer. The probe beam and the heating beam are combined by a dichroic mirror and sent to the objective. A gold particle is residing close to the focus of the probe beam. When the particle is illuminated by the heating beam, heat is created and a thermal lens forms which affects the probe beam propagation and therefore the probe beam collection. The collected probe beam is separated from the heating beam by a dichroic mirror (or long pass filter) and sent to a photodiode. A lock-in amplifier referenced to the driving frequency of the EOM extracts the minute changes of the scattered probe beam. The choice of the probe wavelength far away from the absorption resonance allows for using large probe powers and accordingly for lowering photon noise. When measuring the absorption of gold nanoparticles we typically use $532\,\mathrm{nm}$ for the heating beam, as it is close to the plasmon resonance of gold nanoparticles [30], and a probe beam far enough red-shifted to neglect absorption effects (typically $\sim$780 nm). This leads to a very low background and allows for detecting gold particles down to $1.4\,\mathrm{nm}$ in size [31] or even single molecules [32]. The strength of PT imaging for studying circular dichroism is that, in first approximation, it depends on the absorbed heating beam causing a temperature gradient and therefore is only sensitive to absorption. We will see in chapter 2 how we can exploit photothermal microscopy, combined with polarization modulation, to study and measure circular dichroism.

## 1.4. Outline of this thesis

The first two chapters of this thesis (chapters 2 and 3), focus on the development of a technique that is sensitive to differential absorption of light of opposite handedness. The technique has been developed in two steps.

In **chapter 2** we examine how PT microscopy paired with polarization modulation can be employed to perform diffraction-limited circular dichroism measurements at the single-particle level. We discuss how to build a setup geometry in reflective mode and how to avoid polarization artefacts induced by optical components and strongly focused light.

**Chapter 3** presents a refined version of the technique introduced in chapter 2; we further discuss artefacts inherent to the technique and how dual modulation of polarization is a viable remedy. Furthermore we show that we can measure all absorptive properties of a nanoparticle and that the technique can be extended to perform spectral analysis.

In **chapter 4** we investigate, by correlated TEM and optical absorption imaging, on geometric features responsible for the circular dichroism of two nanoparticle systems. We investigated quasi achiral spherical nanoparticles and tailor-made "superchiral" plasmonic nanoparticles.

Finally, we will see in **chapter 5** that circular dichroism does not necessarily requires chiral geometry as soon as magnetic moments are involved. By studying superparamagnetic magnetite particles under a variable external magnetic field we show that PT CD can be used to study the magnetic moments of nanoparticles.

## 1.5. Contribution

Part of the experimental work and data analysis, shown in this manuscript, has been obtained in collaboration with colleagues in Leiden and research groups in Delft and Antwerpen. Therefore it is befitting to clarify the author's contribution to each chapter: In **chapter 2** the author designed and built the setup and performed the optical measurements. The measurements, simulations and data analysis in **chapter 3** have been entirely performed by the author, with exception of the measurements in figure S3.7 and figure S3.5. In **chapter 4** the author has performed the optical measurements. In **chapter 5** the measurements and data analysis have been entirely done by the author, with exception of the measurements in figure S5.2 and figure S5.1.

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