# An introduction to the Optical Properties of the Solid State

alexandre.baron@u-bordeaux.fr

April 26, 2023

# Contents

# Chapter 1

# Electromagnetism in matter

To understand how light interacts with matter it is first important to understand how electromagnetic waves interact with matter. This is because light itself is an electromagnetic wave that oscillates at frequencies that are not too far from the visible. We owe so much of our current understanding of how electromagnetic waves behave to James Clerk Maxwell who was a Scottish Physicist and mathematician who, towards the second half of the nineteenth century was able to beautifully unify all the laws of electricity and magnetism into a small set of equations. Today they count as four equations and many Physicists consider his contribution to science to be comparable in significance to those of Isaac Newton and Albert Einstein. Thanks to Maxwell, we know how moving charges generate electromagnetic waves as well as how electromagnetic waves create charge displacement. It is with his model, that he realized that electromagnetic waves actually travel at the speed of light. This made him suggest that light was actually nothing more than an electromagnetic wave.

Figure 1.1: James Clerk Maxwell

This chapter is not a rigorous course on electromagnetism, but an introduction to basic tools of electromagnetism that are useful to understand how light and matter interact and what observables can be used to characterize the solid state.

## 1.1 Maxwell's equations in matter

When an electromagnetic field impinges on an area of space containing charges, the Lorentz force sets these charges into motion. The Lorentz force simply reads

$$\mathbf{F} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right) \tag{1.1}$$

where $q$ is the electric charge, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field and $\mathbf{v}$ is the velocity of the charge moving through the fields.

Maxwell's equations describe the spatial and time variations of the electric and magnetic fields as well as how they generate one another. They also describe how they relate to the position and motion of charges. They are the following differential set of coupled equations

$$\begin{aligned}
\nabla \times \mathbf{E}(\mathbf{r},t) &= -\frac{\partial \mathbf{B}(\mathbf{r},t)}{\partial t} && (1.2)\\
\nabla \times \mathbf{H}(\mathbf{r},t) &= \frac{\partial \mathbf{D}(\mathbf{r},t)}{\partial t} + \mathbf{J}(\mathbf{r},t) && (1.3)\\
\nabla . \mathbf{D}(\mathbf{r},t) &= \rho(\mathbf{r},t) && (1.4)\\
\nabla . \mathbf{B} &= 0 && (1.5)
\end{aligned}$$

where we can list the following physical vector and scalar fields (and their units)

- $\mathbf{E}$ is the electric field (in V/m)
- $\mathbf{H}$ is the magnetic field (in A/m).
- $\mathbf{B}$ is the magnetic flux density (in T). In the simple cases we shall be interested with in this course, this vector field may be viewed as the magnetic response of the material to the magnetic field present in the material.
- $\mathbf{D}$ is the electric displacement (in C/m$^2$). Similarly, this field may be viewed as the electric response of the material to the electric field in the material.
- $\mathbf{J}$ is the electric current density (in A/m$^2$).
- $\rho$ is the electric charge density (in C/m$^3$). In most definitions of Maxwell's equations in matter, the charges considered in this density

are free charges[1]. This is because the charge density that accounts for bound charges is hidden in the definition of **D**, but this will become clear a little later. And as a matter of fact, the free-charge density can also be hidden into the definition of **D** such that for the rest of the course, we shall consider $\rho = 0$.

The sources of the electromagnetic field in the previous equations are both **J** and $\rho$. This means that the distribution of charges and currents is what generates an electromagnetic field. The $\nabla\times$ term is the *curl* operator, which characterizes the rotation of vector fields. According to the Stokes theorem (also known as the curl theorem), whenever the curl of a vector **U** is equal to some other vector field **V**, we can equivalently formulate that the circulation of **U** along a closed line $\Gamma$ around any surface $\Sigma$ is equal to the flux of **V** across that surface (see Fig. 1.2 for a typical reprensentation of $\Gamma$ and $\Sigma$). So for instance, eqs. 1.2 and 1.3 can be re-written as

$$\oint_\Gamma \mathbf{E}.d\mathbf{l} = -\iint_\Sigma \frac{\partial \mathbf{B}}{\partial t}.d\mathbf{S} \tag{1.6}$$

$$\oint_\Gamma \mathbf{H}.d\mathbf{l} = \iint_\Sigma \left(\frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}\right).d\mathbf{S} \tag{1.7}$$

where $d\mathbf{l}$ is an infinitesimal curvilinear abscissa along the $\Gamma$ contour and $d\mathbf{S}$ is an infinitesimal surface element normal to the surface and pointing towards the exterior of the surface. The directions of $d\mathbf{l}$ and $d\mathbf{S}$ are set such that they respect the cork screw rule, that is that if the cork screw were to rotate along the direction set by $d\mathbf{l}$, then it would move in the direction of $d\mathbf{S}$ (see Fig. 1.2 for a typical reprensentation of $S$ and $V$). So interpreting these last two equations, we can first say that a time varying magnetic flux density **B** will generate an electric field **E** that rotates around it. Similarly, a time-varying electric displacement field **D** and an electric current density field **J** both generate a rotating magnetic field around them.

The $\nabla.$ term is the *divergence* operator, which characterizes how vector fields *leave* closed surfaces. According to the Green-Ostrogradski theorem (also known as the divergence theorem), whenever some vector field **W** is equal to some scalar field $\psi$, then the flux of **W** across a closed surface $S$ surrounding a volume medium $V$, is equal to the volume integral of $\psi$ in $V$.

---

[1] Free charges are charges that are free to move inside a material. For instance, when an electric potential is applied between the two extremities of a metallic wire, an electric current flows through it. This current is composed of a flow of free charges. Alternatively, there are bound charges in matter. These are electrons bound to an atomic nucleus or to a molecule for instance. When a field is applied to bound charges, they are put into motion by the field but the atomic nucleus casts a restoring force that pulls the charge back towards it.

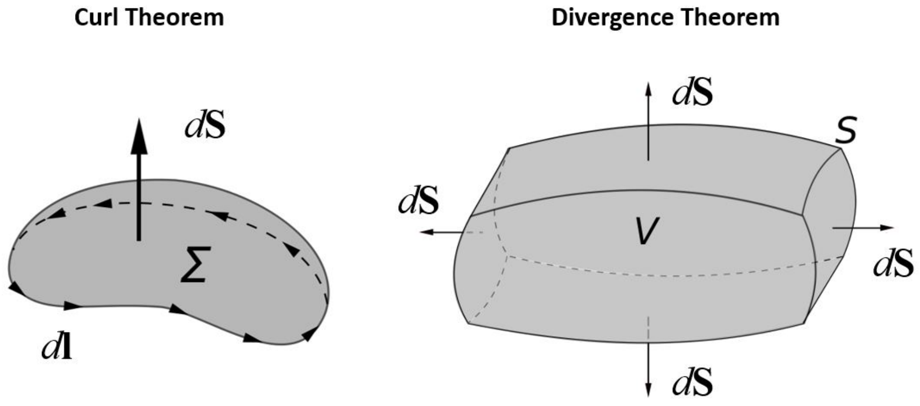

Figure 1.2: An illustration of the contours, surfaces and volumes involved in the integral theorems.

So, applying this to eqs. 1.4 and 1.5, we get

$$\oiint_S \mathbf{D}.d\mathbf{S} = \iiint_V \rho dV \tag{1.8}$$

$$\oiint_S \mathbf{B}.d\mathbf{S} = 0 \tag{1.9}$$

Here the first equation states that the electric displacement field diverges from regions of space with positive charge densities and converges to regions of space with negative charge densities. The second equation is an interesting and very strong statement. It states that magnetic flux densities cannot diverge from any point of space. Another way of saying this is to say that there are no magnetic monopoles[2].

For the rest of this course, we shall only consider time harmonic solutions to Maxwell's equations. In practice, this means that the solutions have a time-variation that is sinusoidal. The introduction of time-harmonic fields is quite convenient here as it enables us to describe the fields in terms of the frequency at which they oscillate rather than as a function of time. To do this we use the Fourier transform of each field. For instance, the Fourier transform of the electric field is

$$\hat{\mathbf{E}}(\omega) = \int_{-\infty}^{+\infty} \mathbf{E}(t) e^{i\omega t} dt \tag{1.10}$$

Using the Fourier transformed field greatly simplifies the problem as every partial derivative with respect to time is simply replaced by a multiplication

---

[2] If the reader were to produce magnetic monopoles, that is, if she were to disprove eq. 1.5, she would be rewarded with the Nobel prize in Physics.

by $(-i\omega)$ in the frequency domain[3]. In what follows, we shall only be interested in the Fourier transformed fields and drop the *hat* notation on top of the fields. So Maxwell's equations become

$$\begin{aligned} \nabla \times \mathbf{E}(\mathbf{r},\omega) &= i\omega\mathbf{B}(\mathbf{r},\omega) && (1.12)\\ \nabla \times \mathbf{H}(\mathbf{r},\omega) &= -i\omega\mathbf{D}(\mathbf{r},\omega) + \mathbf{J}(\mathbf{r},\omega) && (1.13)\\ \nabla.\mathbf{D}(\mathbf{r},\omega) &= 0 && (1.14)\\ \nabla.\mathbf{B} &= 0 && (1.15) \end{aligned}$$

To find electromagnetic waves that satisfy Maxwell's equations, we need additional relations that specify how **D** relates to **E** and how **B** relates to **H**. These are called *constitutive relations* and without them, there would be too many variables to uniquely solve the system. These constitutive relations arise from physical considerations on matter. In this course we shall only be interested in linear isotropic media fro which

$$\begin{aligned} \mathbf{D} &= \varepsilon_0\varepsilon\mathbf{E} && (1.16)\\ \mathbf{B} &= \mu_0\mu\mathbf{H} && (1.17)\\ \mathbf{J} &= \sigma\mathbf{E} && (1.18) \end{aligned}$$

where we have introduced the following quantities

- $\varepsilon_0$ is the electric permittivity of vacuum (in F/m).
- $\varepsilon$ is the relative electric permittivity of the material and has no units. It is often referred to as the dielectric constant of the material. The higher this quantity is the larger the electric response of the medium. It may be thought of a measure of how well a material stores electric energy.
- $\mu_0$ is the magnetic permeability of vacuum (in H/m).
- $\mu$ is the reduced magnetic permeability of the material and has no units. It may be thought of a measure of how well a material stores magnetic energy. Magnetism in matter is usually very weak and at optical frequencies, it is actually vanishingly weak, such that for all practical purposes, we can assume $\mu = 1$.
- $\sigma$ is the electric conductivity of the material (in $S/m$ or $\Omega^{-1}m^{-1}$). It describes the degree to which a material conducts electricity.

---

[3] To get back to the time domain, one simply uses the inverse Fourier transform of the field

$$\mathbf{E}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \hat{\mathbf{E}}(\omega)e^{-i\omega t} \qquad (1.11)$$

It is straightforward from this expression that differentiating with respect to time is equivalent to a multiplication by $(-i\omega)$ in the frequency domain.

Equation 1.18 is also called *Ohm's law* and is none other than another formulation of Ohm's law as we learn it in electricity. It states that current density is proportional to the electric field and the proportionality constant is the conductivity which is none other than the inverse of resistivity. In electricity, we would say that current $I$ is proportional to voltage $U$ according to Ohm's law : $I = U/R$, where $R$ is resistance.

The constitutive relations presented here are a macroscopic description of the solid state. The material parameters listed are ensemble properties that originate in the microscopic constituents of matter.

## 1.2 From the miscoscopic to the macroscopic

The solid state is made of ensembles of atoms (or molecules[4]). These atoms respond to impinging electromagnetic radiation. The superposition of all these responses gives an average material response which is used in the constitutive relations given in the previous section.

### 1.2.1 Dipole moment and polarizability of atoms

Figure 1.3 shows what happens in a material typically when an electromagnetic field is present. Each atom sees their charged displaced with respect to their rest position by an amount $\mathbf{r}$ and acquire a dipole moment

$$\mathbf{p} = q\mathbf{r} \tag{1.19}$$

where q is the charge that has been displaced. That dipole moment will then radiate another electric field which will interfere with the external electric field to produce a different field. Usually the resulting total field propagates at a speed that is slightly smaller than the speed of light, which gives the material an apparent *refractive index.* We shall see in the next section how this refractive index is related to the constitutive relations. But before that, we need a theory of how each atom responds to an external electric field. If we assume the material to be linear, then the dipole moment can be assumed to be proportional to the local exciting electric field $\mathbf{E_{loc}}$ and the major term in the proportionality constant is called the electric polarizability and is usually noted $\alpha$, which has the units of a volume

$$\mathbf{p} = \varepsilon_0 \alpha \mathbf{E}_{\text{loc}} \tag{1.20}$$

In this last relation, $\mathbf{E}_{\text{loc}}$ is the electric field *near* the atom and is different to the average electric field (usually noted $\mathbf{E}$), which is the field used in the constitutive relations of the previous section.

---

[4] From the point of view of of electromagnetism or optics of the solid state, it does not matter whether matter is made of molecules or atoms, all that matters is that they represent an object that exhibits some electromagnetic response. We call these polarizable units and we shall use the term *atom* for all polarizable units.

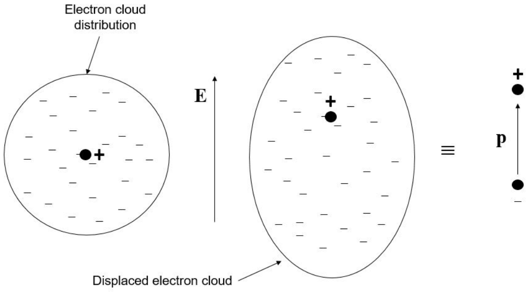

Figure 1.3: An illustration of how atoms respond to an electric field in a material. The left-hand sketch represents an atom at rest with an electron cloud distribution of negative charge around a positive charge nucleus. Under excitation by an external electric field **E**, the atom acquires a dipole moment due to the displacement of negative charges with respect to positive charges. As a matter of fact, both positive and negative charges are set into motion, but the electron cloud mass is so small compared to that of the nucleus, that is mostly the cloud that is put into motion. The atom can be equivalently described by displaced barycenters of positive and negative charges separated by some distance. The product of charge by the separation distance is the dipole moment **p**.

### 1.2.2 Polarization and the Claussius-Mossoti relation

IF we are to describe the material containing an ensemble of identical atoms with an average density $N$ (that is, the number of atoms per unit volume), we should introduce the dipole moment per unit volume, which is none other than the polarization field

$$\mathbf{P} = N\mathbf{p} = N\varepsilon_0\alpha\mathbf{E}_{\mathrm{loc}} \tag{1.21}$$

When considering the response of a material, we are rarely concerned with the local field and polarizability of the atoms that constitute the material, and we usually reason on the average external field **E**. It can be shown that the local electric field sufficiently near the atom is[5]

$$\mathbf{E}_{\mathrm{loc}} = \mathbf{E} + \frac{\mathbf{P}}{3\varepsilon_0} \tag{1.22}$$

This means that the electric field experienced by the atoms is larger than the average field in the material and is often called the Lorentz field[6]. Injecting

---

[5] This is true only for cristalline structures for which the local Lorentz field correction applies.

[6] In reference to the Dutch theoretical physicist Hendrik Lorentz (1853-1928) who was awarded the Nobel prize in 1902 for his work on the nature of light and the constituents of matter.

the local field in eq. 1.21 and solving for $\mathbf{P}$, we find

$$\mathbf{P} = \varepsilon_0 \frac{N\alpha}{1 - \frac{N\alpha}{3}} \mathbf{E} = \varepsilon_0 \chi \mathbf{E} \tag{1.23}$$

where we have introduced the electric susceptibility $\chi$ of the material, which is a macroscopic quantity.

### 1.2.3 The complex dielectric constant

Now that we have a macroscopic description of the response of the material, we can express the displacement field $\mathbf{D}$ of the previous section

$$\begin{aligned} \mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P} && (1.24) \\ &= \varepsilon_0 (1 + \chi) \mathbf{E} && (1.25) \\ &= \varepsilon_0 \varepsilon \mathbf{E} && (1.26) \end{aligned}$$

So now we now that we have related the dielectric constant of the material to its electric susceptibility ( $\varepsilon = 1 + \chi$), we can relate $\varepsilon$ to the polarizability

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\alpha}{3} \tag{1.27}$$

This last equation is the famous Clausius-Mossotti relation.

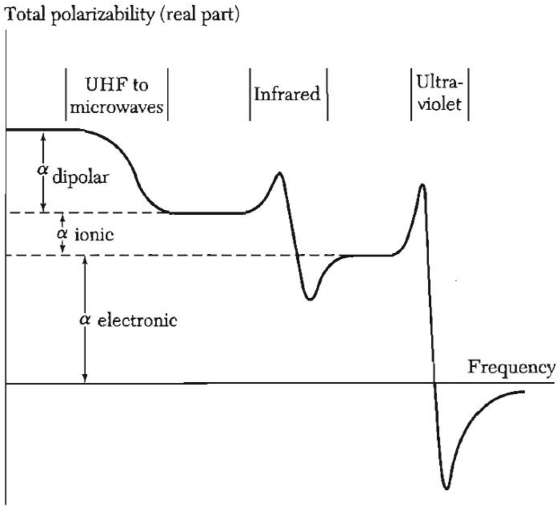

Figure 1.4: Frequency dependence of different contributions to the electric polarizability in a material. This graph was taken from [1]

The total polarizability (and the dielectric constant) can be decomposed according to its three major contributions : an electronic, and ionic and a dipolar contribution (see Fig. 1.4). The electronic contribution comes from the electronic dispacement of the electron cloud with respect to the atomic nucleus. The ionic contribution is due to the motion of an ion with respect to any other ion. The dipolar contribution arises due to molecules that exhibit a permanent electric dipole moment that may change its orientation when an electric field is applied. As can be seen, at optical frequencies, contributions to the dielectric constant are exclusively of electronic origin.

We know that $\mu = 1$ for most materials at optical frequencies and that $\varepsilon$ describes the electric response due to the polarizability of atoms. We still have to account for the electric conduction of materials. This information is carried by the constitutive relation for the current density : $\mathbf{J} = \sigma\mathbf{E}$. We can simplify the problem by noticing that this proportionality between current and electric field is somewhat similar to the proportionality between electric displacement and electric field : $\mathbf{D} = \varepsilon_0\varepsilon\mathbf{E}$, so eq. 1.13 can be re-written as

$$\begin{aligned}\nabla \times \mathbf{H} &= -i\omega\mathbf{D} + \mathbf{J} && (1.28)\\ &= -i\omega\varepsilon_0\varepsilon\mathbf{E} + \sigma\mathbf{E} && (1.29)\\ &= -i\omega\varepsilon_0\left(\varepsilon + i\frac{\sigma}{\varepsilon_0\omega}\right)\mathbf{E} && (1.30)\\ &= -i\omega\varepsilon_0\tilde{\varepsilon}\mathbf{E} && (1.31)\end{aligned}$$

where we have introduced a complex dielectric constant $\tilde{\varepsilon}$ with a real part equal to the dielectric constant considered thus far and an imaginary part proportional to the conductivity. The *tilde* notation is there just to distinguish it from the real quantity $\varepsilon$. For the rest of this course, we shall omit the tilde and note $\varepsilon$ the complex dielectric constant and $\varepsilon'$ its real part and $\varepsilon''$ its imaginary part

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon' + i\frac{\sigma}{\varepsilon_0\omega} \qquad (1.32)$$

Since the imaginary part of the dielectric constant is related to conductivity, this means that it is actually associated with transfer of energy to free electrons. These free electrons thus absorb electromagnetic energy to acquire kinetic energy and eventually dissipate it in the form of heat through collisions (Ohm's law). Since all materials necessarily have a positive conductivity, meaning that they dissipate (and do not create) energy, the imaginary part of the dielectric constant is necessarily positive in the convention we have used[7]. As a matter of fact, the imaginary part describes any and all types of absorption of photons.

### 1.2.4 Basic optical properties of the solid state

Before moving further, we should introduce five important material properties that characterize how a material behaves. We shall focus the definition

---

[7] The convention we have used is to assume time-harmonic fields assuming a phasor $e^{-i\omega t}$. Had we chosen $e^{i\omega t}$, we would have had the result that dissipative materials exhibit a negative imaginary part of the dielectric constant. This is just a matter of convention.

of these properties on the description of $\varepsilon$, but it could equivalently have been made by considering $\alpha$ or $\chi$.

### Dispersion

We see from Fig. 1.4, that polarizability actually depends on the frequency of the electromagnetic field and that the same is true for the dielectric constant. This phenomenon is called dispersion and is due to the fact that atoms have their own resonance frequency and they cannot always follow the field that is driving them. They take some time to respond to an excitation. So under excitation by a driving field, the material response is due to the instantaneous field at some time $t$ as well as a continuous sum of all prior fields. As a result, we should always bare in mind that whenever we write $\alpha$ or $\varepsilon$, we actually mean $\alpha(\omega)$ and $\varepsilon(\omega)$. We shall see a little further on, what models can be derived to describe the frequency dependence of $\alpha$ and $\varepsilon$. So a material that exhibits dispersion is said to be dispersive.

### Homogeneity

A material is said to be homogenous if its properties are independent of the point considered within the material. So this means that $\varepsilon$ is independent of the position vector $\mathbf{r}$.

### Isotropy

A material is said to be isotropic if its properties are independent of the orientation of the electric field $\mathbf{E}$. Mathematically, the consequence of this property is that $\varepsilon$ is a scalar. A material that is not isotropic is called anisotropic and the dielectric constant becomes a tensor

$$\mathbf{D} = \varepsilon_0 \, [\varepsilon] \, \mathbf{E} \tag{1.33}$$

This means that each component of $\mathbf{D}$ is expressed as a superposition of every component of $\mathbf{E}$

$$D_i = \varepsilon_0 \sum_{j=x,y,z} \varepsilon_{ij} E_j \tag{1.34}$$

### Linearity

A material is said to be linear if the relation between the polarization of the material and electric field is linear

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \tag{1.35}$$

In practice, this is only true for small enough fields. As soon as the amplitude of the field becomes large, the response of the atoms become nonlinear and can be (sometimes) descried as power expansions of the electric field. The field dedicated to the study of theses processes is called nonlinear optics and emerged with the invention of lasers that produce intense fields. These processes are very much outside the scope of this lecture, but we shall just say that they enable (among many applications) the generation of frequency doubling which is the process by which a green laser pointer can be obtained since green light does not correspond to any known natural laser transition in matter.

#### Locality

A material is said to be local if its response only depends on the point at which it is excited. In real life, this is not true. The response of a material is always dependent on the field at other points in the material and as a result, materials are intrinsically non-local (we also say that they are spatially dispersive[8])

## 1.3 The propagation equation

In this section, we shall show how light can travel (propagate) through matter according to Maxwell's equations

### 1.3.1 Establishing the propagation equation

Starting with eq. 1.12, and eq. 1.13 as well as the consitutive relation for **B** and the complex dielectric constant, we can write

$$\begin{aligned}
\nabla\times\nabla\times\mathbf{E} &= i\omega\,(\nabla\times\mathbf{B}) && (1.36)\\
&= i\mu_0\omega\,(\nabla\times\mathbf{H}) && (1.37)\\
&= \mu_0\omega^2\mathbf{D} && (1.38)\\
&= \varepsilon_0\mu_0\varepsilon\omega^2\mathbf{E} && (1.39)
\end{aligned}$$

According to the regular vectorial operations, we have that $\nabla\times\nabla\times\mathbf{E} = \nabla(\nabla.\mathbf{E}) - \Delta\mathbf{E}$, where $\Delta$ represents the Laplacian operator. Also, we know that $\varepsilon_0\mu_0 = 1/c^2$ and since the material is linear, isotropic and local, we have that $\nabla.\mathbf{E} = \nabla.\mathbf{D}/(\varepsilon_0\varepsilon) = 0$ (according to eq.1.14). As a result, we may write

$$\Delta\mathbf{E} + \varepsilon(\omega)\frac{\omega^2}{c^2}\mathbf{E} = 0 \qquad (1.40)$$

We recognize this equation as being the Helmoltz equation for which there are known solutions that are the so-called plane wave solutions. This equation is also known as the propagation equation for electromagnetic waves.

---

[8] As opposed to temporally dispersive when we spoke of dispersion.

### 1.3.2 Plane Wave solutions

The Helmoltz equation admits plane wave solutions that are typically written as[9]

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}_0 \exp\left(i\mathbf{k}.\mathbf{r} - i\omega t\right) \tag{1.42}$$

where $\mathbf{k}$ is called the wave vector. With such solutions, any time the $\nabla$ operator is used, it can be replaced by $i\mathbf{k}$ and the $\Delta$ is the same as a multiplication by $-k^2 = -|\mathbf{k}|^2$. So introducing this fact into eq. 1.40, we find the elegant dispersion relation of the material

$$k(\omega) = \sqrt{\varepsilon(\omega)}\frac{\omega}{c} = \sqrt{\varepsilon(\omega)}k_0 = \sqrt{\varepsilon(\omega)}\frac{2\pi}{\lambda} \tag{1.43}$$

where we have introduced the vacuum wavevector $k_0$ and where $\lambda$ is the wavelength of the plane wave. So plane waves are sinusoidal waves that propagate in the direction set by $\mathbf{k}$. The electric field oscillates perpendicularly to $\mathbf{k}$ along the direction set by $\mathbf{E}_0$ inside the material[10]. The direction of $\mathbf{E}$ is called the polarization of $\mathbf{E}$, which might be confusing, since we have called polarization the average polarizability per unit volume, but usually the context in which these terms are used enables one to understand which polarization we are talking about. The typical structure of a plane wave is shown on Fig. 1.5 and it travels with a phase velocity

$$v_\phi = \frac{c}{\sqrt{\varepsilon(\omega)}} = \frac{c}{n(\omega)} \tag{1.45}$$

where we have introduced the complex index of refraction $n(\omega) = \sqrt{\varepsilon(\omega)}$.

Before we move further into the interpretation of the complex refractive index, we should notice that applying the $\nabla$ operator to a plane wave field amounts to using the $i\mathbf{k}$ operator. In other words

$$\begin{aligned} \nabla \times \mathbf{E} &= i\mathbf{k} \times \mathbf{E} && (1.46)\\ \nabla.\mathbf{E} &= i\mathbf{k}.\mathbf{E} && (1.47) \end{aligned}$$

This simplification will prove useful when we shall look at energy balances inside the solid state.

---

[9] Here we are using the complex electric field, which considerably simplifies calculations. The real electric field can be be obtained simply by taking the real part of the complex field. So here, it would simply be

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}_0 \cos\left(i\mathbf{k}.\mathbf{r} - i\omega t\right) \tag{1.41}$$

[10] The fact that $\mathbf{E}$ and $\mathbf{k}$ are orthogonal is an immediate consequence of eq. 1.14 of Maxwell's equations. Indeed, we have that $\nabla.\mathbf{D} = 0$, which means that $i\varepsilon_0\varepsilon\mathbf{k}.\mathbf{E} = 0$. In the end

$$\mathbf{k}.\mathbf{E} = 0 \tag{1.44}$$

and as a result, $\mathbf{k} \perp \mathbf{E}$.

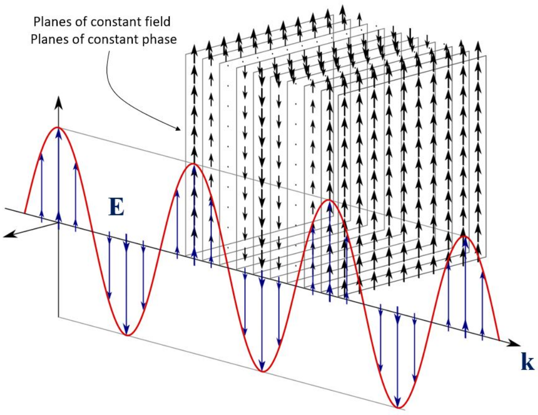

Figure 1.5: Spatial profile of a plane wave. The electric field oscillates perpendicularly to the direction of propagation set by **k**. They are called plane waves because any plane that cuts the wave perpendicularly to **k** is a plane of constant field. We also call them planes of constant phase, because **k**.**r** is constant across the plane. [1]

**Exercise**

1. Assuming a plane wave for the electric field **E**, demonstrate eqs. 1.46 and 1.47.
2. Assuming a plane wave for the magnetic field **H** as well, rewrite all of Maxwell's equations using **k** instead of $\nabla$. Deduce that $\mathbf{k} \perp \mathbf{E} \perp \mathbf{H}$ and that $(\mathbf{k}, \mathbf{E}, \mathbf{H})$ form a right-hand set.
3. Re-write the propagation equation and establish the dispersion relation (eq. 1.43).

### 1.3.3 The complex index of refraction

At this stage, we ought to specify what it means to have a complex index of refraction. Let us consider a direction **r** that is parallel to the wavevector $\mathbf{k} = k\mathbf{u} = n\frac{\omega}{c}\mathbf{u}$, where **u** is a unitary vector[11]. For simplicity, let us assume that $\mathbf{r} = x\mathbf{u}$ is along the $x$-axis. In that case, the plane wave solution of eq. 1.42 becomes

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0 \exp\left(in\frac{\omega}{c}x\right) \tag{1.49}$$

---

[11] To obtain such a unitary vector, one just has to divide the wavevector by its norm

$$\mathbf{u} = \frac{\mathbf{k}}{|\mathbf{k}|} \tag{1.48}$$

.

Now let us introduce the fact that $n = n' + in''$, where a single prime denotes the real part, while a double prime denotes the imaginary part. Injecting this complex expression of $n$ into our plane wave solution, we find

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}_0 \exp\left(in'\frac{\omega}{c}x\right) \exp\left(-n''\frac{\omega}{c}x\right) \tag{1.50}$$

So we see that we have a propagation term ($e^{in'\omega/c}$) that simply adds phase to the field and an exponentially decaying term ($e^{-n''\omega/c}$) and thus the imaginary part actually accounts for a decaying field. Fields decay due to absorption. For this reason, the imaginary part of the refractive index is always associated to the absorption of the material. While the real part is associated with refraction at an interface and phase accumulation through propagation in the bulk of a material.

We often use the absorption coefficent $\alpha$, that is defined such that the exponential decay of the field is simply $e^{-\alpha x/2}$. The reason that the term inside the exponential is divided by 2 comes from the fact that the absorption coefficient is actually suited to measurements of decaying intensity. For reasons that will become clear, a little later on in the course, the intensity of the light $I(x,\omega)$ (expressed in W/m$^2$) is proportional to the norm squared[12] of the field ($I(x,\omega) \propto |\mathbf{E}|^2$). So eq. 1.50 becomes

$$I(x,\omega) = I_0 e^{-\alpha(\omega)x} \tag{1.51}$$

Here, you might recognize Beer-Lambert's law of exponential attenuation of light propagating through a medium. Chemistry students often learn about this law for light propagating through a solution. As it turns out, this is also true for light propagating through a solid. In both cases, characterizing $\alpha(\omega)$ (by absorption spectroscopy basically) actually provides us with important information on a solid. So identifying this absorption coefficient with the term inside the exponential in eq. 1.50, we find

$$\alpha = 2n''\frac{\omega}{c} = 4\pi\frac{n''}{\lambda} \tag{1.52}$$

where we have used the fact that $\omega = 2\pi\frac{c}{\lambda}$. We see that $\alpha$ has units of inverse length, so another quantity that is often used in experiments is the penetration depth, also call the attenuation length or extinction length

$$l_e = \frac{1}{\alpha} = \frac{\lambda}{4\pi n''} \tag{1.53}$$

This length characterizes the distance after which, the intensity has decreased $e^{-1} \approx 37\%$ of what it was.

---

[12] We also say the magnitude squared.

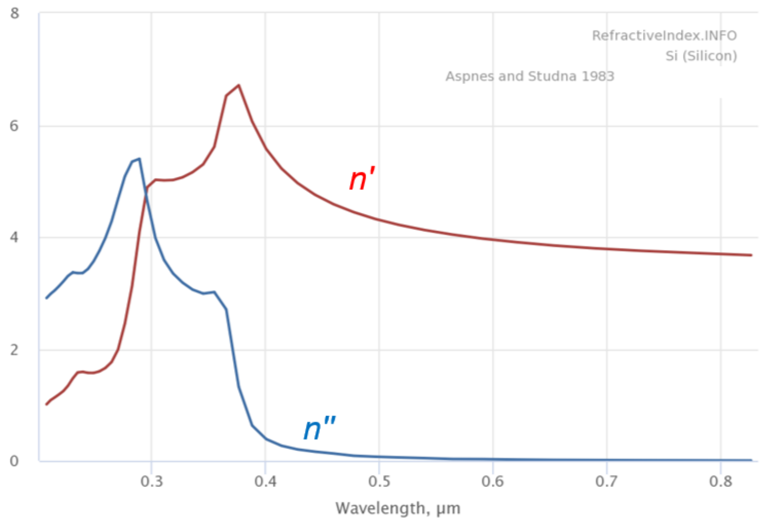

Figure 1.6: Spectrum of real (red) and imaginary (blue) parts of the refractive index of crystalline silicon.

**Exercice**

Figure 1.6 provides the spectrum of the real and imaginary parts of crystalline silicon.

1. Determine the extinction length of silicon at $\lambda = 400$ nm.
2. At that wavelength, would it be possible to detect a beam of light that has gone through a 275 $\mu$m thick silicon wafer ?
3. What is the attenuation after propagation through 100 nm of silicon?
4. Still at $\lambda = 400$ nm, determine the real and imaginary parts of the dielectric constant $\varepsilon$ of silicon.
5. What are the expressions of the real and imaginary parts of the complex index of refraction as a function of the real and imaginary parts of the dielectric constant.

## 1.4 Reflectance, Transmittance and absorption

The complex refractive index is a powerful material property since it governs a certain number of physical observables such as reflectance, transmittance and absorption. But perhaps the most famous phenomenon is the phenomenon of refraction, which is the first property to have been observed in the solid state that required introducing a refractive index and actually gave its name to it. The problem is as described on Fig. 1.7. We shall consider a

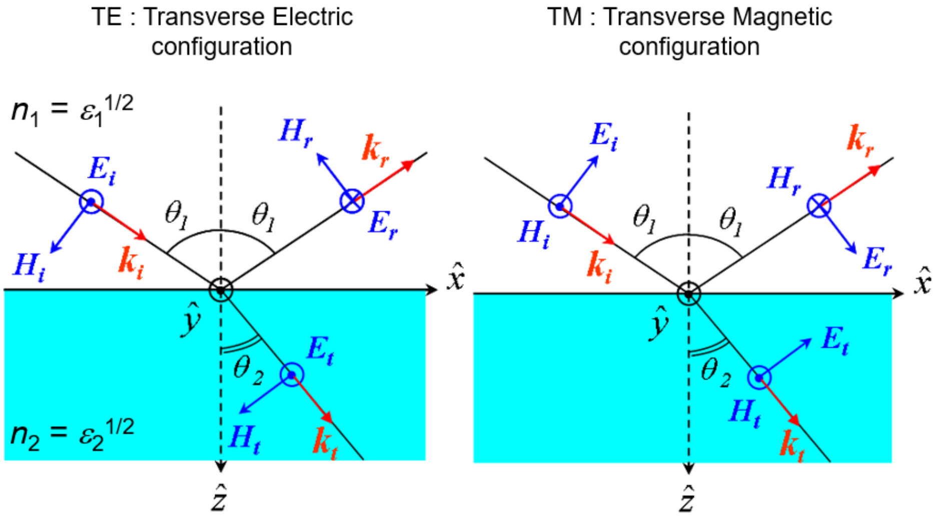

Figure 1.7: Situation of an impinging electromagnetic plane wave (of wavevector $\mathbf{k}_i$) on an interface between two media of index $n_1$ and $n_2$ for two polarization configurations (Transverse Electric and Transverse Magnetic). The transverse electric (resp. transverse magnetic) configuration is that in which the electric (resp. magnetic) field is polarized perpendicularly to the incidence plane. There is a transmitted wave (of wavevector $\mathbf{k}_t$) that undergoes refraction and a reflected wave (of wavevector $\mathbf{k}_r$). Adapated from wikipedia.

plane wave impinging on the interface between two media. The top medium is assumed to have an index $n_1$ and the bottom medium is assumed to have an index $n_2$ for that wave[13]. A plane wave of wavevector $\mathbf{k}_i$ is incident on an interface at an angle $\theta_1$ with the normal to the interface. It will transfer part of its energy to a transmitted wave (of wavevector $\mathbf{k}_t$) that will undergo refraction and part to a reflected wave (of wavevector $\mathbf{k}_r$). Refraction means that the outgoing transmitted wave will leave with and angle $\theta_2$ that is different to $\theta_1$. The following section will provide the reflection and transmission coefficients as a function of the refractive indices of both the top and bottom media and the angles involved.

### 1.4.1 The Fresnel coefficients

The Fresnel coefficients give the expressions of the reflection $r$ (and transmission $t$) coefficients that are defined as the ratio between the reflected (resp. transmitted) and incident electric field. There are two possible illumination

---

[13] It is important to specify that it is for that wave as we are assuming a plane wave that oscillates at a specific frequency $\omega$. This means that the refractive index is only valid for a plane wave at that frequency

configurations (we sometimes refer to these as *modes*). The transverse electric (TE) configuration (see Fig. 1.7) is a situation in which the electric field is polarized perpendicularly to the plane of incidence. The plane of incidence is the plane containing $\mathbf{k}_i$ and the interface ($\hat{x}$ axis on Fig. 1.7). The transverse magnetic (TM) configuration is a situation in which the magnetic field is polarized perpendicularly to the plane of incidence. Each configuration exhibits different reflection and transmission coefficients

$$r_{\mathrm{TE}} = \frac{E_r^{\mathrm{TE}}}{E_i^{\mathrm{TE}}} = \frac{n_1 \cos\theta_1 - n_2 \cos\theta_2}{n_1 \cos\theta_1 + n_2 \cos\theta_2} \tag{1.54}$$

$$t_{\mathrm{TE}} = \frac{E_t^{\mathrm{TE}}}{E_i^{\mathrm{TE}}} = \frac{2n_1 \cos\theta_1}{n_1 \cos\theta_1 + n_2 \cos\theta_2} \tag{1.55}$$

$$r_{\mathrm{TM}} = \frac{E_r^{\mathrm{TM}}}{E_i^{\mathrm{TM}}} = \frac{n_2 \cos\theta_1 - n_1 \cos\theta_2}{n_1 \cos\theta_2 + n_2 \cos\theta_1} \tag{1.56}$$

$$t_{\mathrm{TM}} = \frac{E_t^{\mathrm{TM}}}{E_i^{\mathrm{TM}}} = \frac{2n_1 \cos\theta_1}{n_1 \cos\theta_2 + n_2 \cos\theta_1} \tag{1.57}$$

where $\theta_2$ is given by the Snell-Descartes law which simply expresses the continuity of the tangential component of the wavevector

$$n_1 \sin\theta_1 = n_2 \sin\theta_2 \tag{1.58}$$

All these reflection and transmission coefficients are complex numbers. In particular this means they can all be written in the form of a magnitude times a phasor ($e^{i\phi}$), so for the reflection and transmission coefficients for instance, this means $r = |r|e^{i\phi_r}$ and $r = |t|e^{i\phi_t}$.

### 1.4.2 Energy Balances

The Poynting vector is a vector field that describes the energy flux of an electromagnetic field and is defined by

$$\mathbf{S} = \mathbf{E} \times \mathbf{H} \tag{1.59}$$

It has the same direction as the wavevector $\mathbf{k}$ and as a result, it points toward the propagation direction. It has units of watts per square meter : W/m$^2$. It represents the instantaneous power flow. Taking the time-average of the Poynting vector gives the average power flow

$$\langle \mathbf{S} \rangle = \frac{1}{2}\mathrm{Re}\left(\mathbf{E} \times \mathbf{H}^*\right) \tag{1.60}$$

where the star superscript denotes complex conjugation. The average intensity of the light is given by the norm of the previous time-averaged vector and we can show

$$I = |\langle \mathbf{S} \rangle| = \frac{\varepsilon_0 c n'}{2}|\mathbf{E}|^2 \tag{1.61}$$

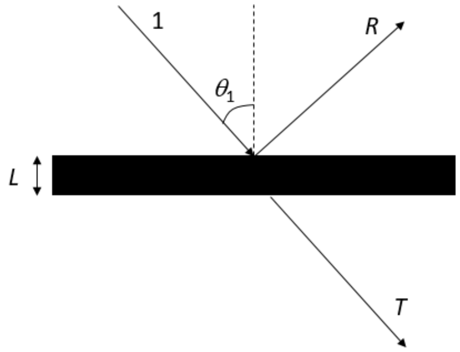

Figure 1.8: Illumination configuration of slab of material of length $L$ defining Reflectance ($R$) and Transmittance ($T$).

So we see as was suggested previously that the intensity is proportional to the squared magnitude of the electric field. Retrieving the complex reflection $r$ and transmission $t$ coefficients presented in the previous section is quite difficult and requires special experimental techniques that involve interferometry. Most basic experiments usually measure the intensity of light reflected ($I_r$) and/or transmitted ($I_t$) by a slab of material of height $h$ when illuminated by a beam of intensity $I_0$ (see Fig. 1.8). Since intensity is proportional to $|\mathbf{E}|^2$, the measure quantities are actually

$$R = \tfrac{I_r}{I_0} = |r|^2 \tag{1.62}$$

$$T = \tfrac{I_t}{I_0} = |t|^2 e^{-\alpha L} \tag{1.63}$$

where $R$ is referred to as the *reflectance* of the material, $T$ is the *transmittance*, $\alpha$ is the absorption coefficient and $L$ is the distance over which light has propagated inside the material. Of course, depending on the illumination configuration (TE or TM), we should use the corresponding coefficient. Without any loss of generality, these observables depend on wavelength (or frequency), the angle of incidence ($\theta_1$) and of course the index of refraction of the material. $R$ and $T$ can both respectively be interpreted as the fractions of incident power that are reflected and transmitted by the material. As a result, energy conservation imposes that the rest of the energy is dissipated in the material (usually in the form of heat) corresponding to absorbed power. So knowing $R$ and $T$ enables the determination of absorption[14]

$$A = 1 - R - T \tag{1.64}$$

---

[14] This line of reasoning is valid only in the case of weakly scattering materials. If the material scatters a lot (at its surface or its volume), then $1 - R - T$ is actually called extinction and is the sum of absorption and scattering.

Absorption should not be confused with absorbance which is often used in Chemistry. Indeed absorbance is

$$A' = -\ln T = \alpha L = \frac{L}{l_e} \tag{1.65}$$

where we have re-introduced the extinction length $l_e$.

**Exercise**

1. Demonstrate eq. 1.61.
2. Using the graph on Fig. 1.6, determine the reflectance and transmittance under normal incidence of a silicon thin film that is 500 nm thick at a wavelength of 400 nm. Calculate the absorption ?
3. At an incidence angle of 45 deg, what is the distance $L$ over which light will propagate inside the material? Determine the reflectance and transmittance for a TM-polarized wave.
4. Find the brewster angle $\theta_B$ which is defined as the angle of incidence at which the reflected TM-polarized light is canceled. At that angle, what is the propagation length inside the silicon film.

## 1.5 Models for the dielectric constant

Now that we have the dielectric constant (or equivalently the refractive index), we have a material parameter to describe almost every type of material. We can be a little more thorough however by relating the different kinds of microscopic charge interactions and deduce different models for the dielectric constant. There are two major models that are based on whether the electron is free to move in the solid state or bound to atomic nuclei.

### 1.5.1 The free electron model : Drude model

The Drude model is the model that is concerned with describing free electrons. Is is suited to the description of metals for instance. Under excitation by an electromagnetic field $\mathbf{E}$ in the material, a free electron is exposed to the Lorentz force (eq. 1.1) and following Newton's second law, we have

$$m\frac{d^2\mathbf{r}}{dt^2} = -e\mathbf{E} - m\Gamma\frac{d\mathbf{r}}{dt} \tag{1.66}$$

where $\mathbf{r}$ is the position vector, $m$ is the mass of the electron, $e$ is the electron charge and $\Gamma$ is the free electron collision frequency that accounts for dissipation of the kinetic energy of electrons. We have neglected the magnetic field force. Assuming a time-harmonic solution and the Fourier transform of the fields, we may rewrite the previous differential equation and solving for $\mathbf{r}$, we find

$$\mathbf{r} = \frac{e}{m}\frac{1}{\omega^2 + i\omega\Gamma}\mathbf{E} \tag{1.67}$$

This model basically describes the fact that energy oscillates between the kinetic energy of electrons and the oscillating electric field in the metal and collisions between electrons will dissipate the energy. To relate this to the dielectric constant, we can use the expression of the polarization $\mathbf{P}$, which is nothing more that the dipole moment density[15]

$$\mathbf{P} = \varepsilon_0(\varepsilon - 1)\mathbf{E} = -Ne\mathbf{r} \tag{1.68}$$

where $N$ is the free electron density in the material. Substituting $\mathbf{r}$ with its expression from eq. 1.67, we get

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \tag{1.69}$$

where we have introduced the plasma frequency

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}} \tag{1.70}$$

Equation 1.69 is a very important formula that is often used for metals and to describe semiconductors above the bandgap. A word of caution though,we should keep in mind that in establishing it, we have only considered free electrons, but materials may have many other types of resonances that occur at frequencies that are much larger than the plasma frequency (in the limit $\omega \to \infty$). Instead of going too much into the details of these particular charge resonances, we simply assume that they will contribute with a constant background dielectric constant, which of course will not be equal to 1 contrary to what eq. 1.69 might suggest. So instead, we shall simply remember that the Drude model for the dielectric constant is as follows

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \tag{1.71}$$

Figure 1.9 shows the typical variations of the real and imaginary parts of both the dielectric constant and the complex refractive index following the Drude model. Gold and Silver are typically described with this model at frequencies far enough from the plasma frequency. Figure 1.10 compares the Drude model to empirical values of the real and imaginary parts of the dielectric constant of gold.

---

[15] Remember that $\mathbf{P} = \varepsilon_0\chi\mathbf{E}$ and that $\varepsilon = 1 + \chi$.

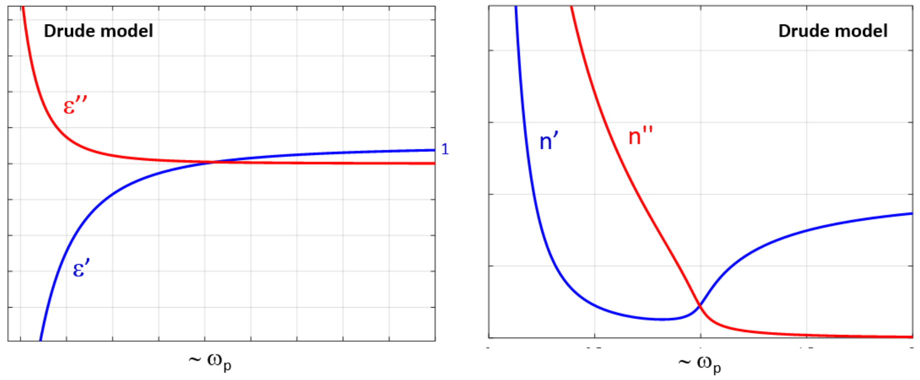

Figure 1.9: Graph showing the real and imaginary parts of the dielectric constant and the refractive index following the Drude model.

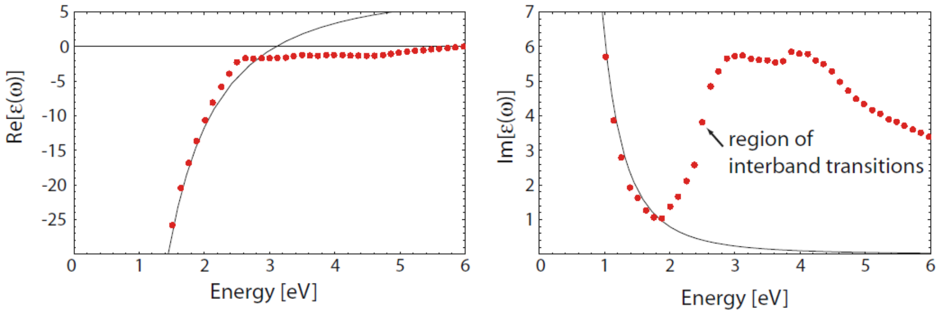

Figure 1.10: Dielectric constant $\varepsilon(\omega)$ following the Drude model (continuous line) fitted to experimental data (red dots) from Johnson and Christy [2]. These graphs were taken from [3]. Interband transitions make the Drude model inaccurate at higher frequencies.

**Exercise**

1. Compute the real and imaginary parts of the dielectric constant assuming a Drude Model. What can be said about the real part $\varepsilon'$. Draw a graph of the variations of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$
2. Assuming $\Gamma \ll \omega_p$, what can be said of the complex index of refraction of the Drude material?

### 1.5.2 The bound electron model : the Lorentz model

In a canonical dielectric material, there are no free charges. The polarization of the material is completely determined by the atoms that constitute the material that can essentially be viewed as electrons bound to an atomic nucleus. We can use the Lorentz oscillator model (in analogy to a mass on a spring). In that case, the equation of motion is

$$m\frac{d^2\mathbf{r}}{dt^2} = -e\mathbf{E} - m\omega_0^2\mathbf{r} - m\gamma\frac{d\mathbf{r}}{dt} \tag{1.72}$$

where $\omega_0$ is the resonance frequency of the bound oscillation and where we have used $\gamma$ as a damping frequency to distinguish it from the collision frequency of the Drude model. In this case, we find the following relation for the motion of the electron

$$\mathbf{r} = \frac{e}{m}\frac{1}{(\omega^2 - \omega_0^2) + i\omega\gamma}\mathbf{E} \tag{1.73}$$

Then using the same sort of identification as was done in the previous section with the polarization, we find the following relation for the dielectric constant

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - i\omega\gamma} \tag{1.74}$$

This model of the dielectric constant is particularly well suited to the description of dielectric materials. Figure 1.11 shows the typical dispersion of the Lorentz model.

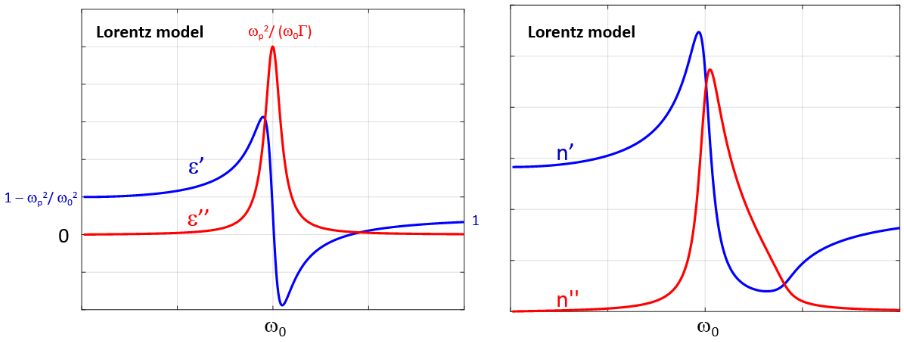

Figure 1.11: Graph showing the real and imaginary parts of the dielectric constant and the refractive index following the Lorentz model.

The Lorentz model is so powerful, it can be generalized to many types of electrons by introducing a summation

$$\varepsilon = 1 + \sum_i \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\omega\gamma_i} \tag{1.75}$$

where $\omega_{p,i}$, $\omega_{0,i}$ and $\gamma_i$ are the plasma, resonant and damping frequencies respectively for the $i^{\text{th}}$ type of electron. And as a matter of fact, it may be used to describe any type of photon interaction with an oscillating particle. So it can be used to describe phonon-photon interaction as well.

Looking at frequencies above $\omega_0$, we see that the Lorentz model behaves somewhat like the Drude model. This means that certain dielectrics (semiconductors in particular), can sometimes be described as metals in certain frequency ranges.

# Chapter 2

# Optical Properties of metals

As we have seen in the previous chapter, the dielectric constant of metals is best described by the Drude model. This has important consequences on the optical properties of solids. For one thing, it tells us how Fermi electrons are collectively excited and how they interact with light.This chapter is a brief introduction to plasmons, that are a plasma oscillation that can be directly calculated from Maxwell's equations.

## 2.1 Volume plasmons and transverse optical plasma modes

### Volume plasmons

Metals are made of arrays of atoms that have electrons that are easily lost. When these electrons are lost, they leave positive ions behind. As they are freed, they form a sort of sea of free charges. When an electric field is present, the sea of electrons shifts, which creates regions of positive charge composed of the atoms from which the electrons have left and regions of negative charge where the electrons have shifted. These accumulations of charge are themselves going to create an electric field which will pull the electrons back towards their initial position, but since they have mass, they will overshoot their position and reverse the electric field. As time goes by, the back and forth sloshing of electrons oscillates and these oscillations can be sustained at the plasma frequency $\omega_p$. This oscillation is what is called a (volume) plasmon. Going back to the Drude model of the dielectric constant of a metal (and neglecting the collision frequency), we have

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{2.1}$$

where we recall the expression of the plasma frequency

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}} \tag{2.2}$$

We see that $\varepsilon(\omega_p) = 0$. This means that the electric displacement is null and following Maxwell's equation we can have $\nabla.\mathbf{D} = 0$ with $\nabla.\mathbf{E} \neq 0$. In the end, this means

$$\mathbf{k}.\mathbf{E} \neq 0 \tag{2.3}$$

and these correspond to longitudinal optical modes of oscillation. So a plasmon propagates through a plasma much like a sound wave. The following table shows typical values of the plasma frequency and we see that these are generally in the ultra-violet. Certain classes of semiconductors may sometimes be described as metals at very high frequencies. Silicon for instance has a plasma frequency of $\hbar\omega_p = 16.0$ eV, which corresponds to a wavelength of $\sim 77$ nm.

| Metal | Symbol | Plasma Frequency (THz) | Wavelength (nm) |
|---|---|---|---|
| Aluminum | Al | 3624 | 82.78 |
| Chromium | Cr | 2601 | 115.35 |
| Copper | Cu | 2620 | 114.50 |
| Gold | Au | 2185 | 137.32 |
| Nickel | Ni | 3852 | 77.89 |
| Silver | Ag | 2180 | 137.62 |

Due to the longitudinal nature of these charge oscillations, volume plasmons do not couple to transverse electromagnetic waves and thus cannot be excited by a light field. They require particle impact in general.

It should be mentioned for completeness, that longitudinal oscillations can also be excited in dielectrics. This happens because valence electrons oscillate collectively with respect to ion cores.

### Transverse optical plasma modes

In the previous chapter, we had established the following dispersion relation in an linear, isortopic and homogenous material

$$k = \sqrt{\varepsilon(\omega)}\frac{\omega}{c} \tag{2.4}$$

Injecting the Drude model for the dielectric constant into this dispersion relation and re-arranging the terms so as to express frequency as a function of wavevector, we find

$$\frac{\omega}{\omega_p} = \sqrt{1 + \frac{c^2k^2}{\omega_p^2}} \tag{2.5}$$

So already, we see that for $\omega < \omega_p$, $k$ becomes a purely imaginary quantity, and the waves will decay exponentially and accumulate no phase. For these frequencies, light will be completely reflected and will not penetrate the metal at more than the penetration depth. This is consistent with what we know of the refractive index of metals, namely that for such frequencies $n'' \gg n'$ and $n'' \gg 1$ and as a result, reflectance (under normal incidence here) is

$$R = \left| \frac{n' + in'' - 1}{n' + in'' + 1} \right|^2 \approx 1 \tag{2.6}$$

However, for $\omega > \omega_p$, we see that these optical modes exist and are free to propagate (see Fig. 2.1). In the high frequency limit, they tend towards free-space propagation ($\omega \approx ck$).

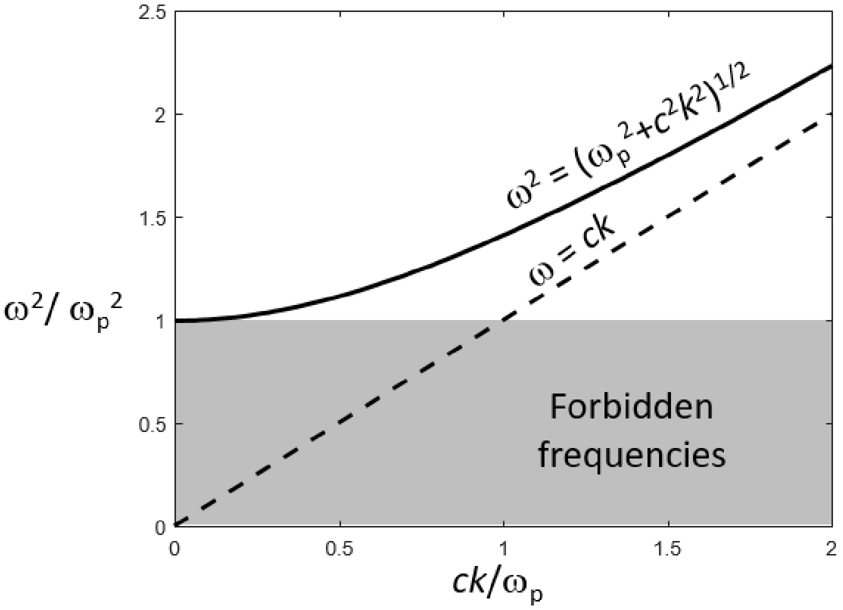

Figure 2.1: Dispersion relation for transverse optical modes in metals.

The group velocity is defined as

$$v_g = \frac{\partial \omega}{\partial k} \tag{2.7}$$

which is the slope of the dispersion curve. We see that as the plasma frequency is approached, $v_g \to 0$, which is sometimes referred to as a slow optical mode.

## 2.2 Surface plasmons

Surface plasmons are coherent delocaliazed electron oscillations that exist at the interface between a material of negative dielectric constant (a metal typically) and a material of positive dielectric constant (a dielectric). They are surface waves that are guided along the interface and are transverse magnetic[1] and have the following form

$$\mathbf{H} = H_0 e^{i\beta z} e^{ik_{d,m}x} \hat{\mathbf{y}} \tag{2.8}$$

where we have used the frame defined in Fig. 2.2. $\beta$ is called the propagation constant and governs the propagation of the surface plasmon along the $z$-direction, while $k_{d,m}$ is simply the transverse component of the wavevector associated with the surface plasmon field, which depends on whether we are considering the field in the metal or in the dielectric. So $k_d = \varepsilon_d \omega / c$ in the dielectric (where the dielectric constant is $\varepsilon_d$) and $k_m = \varepsilon_m \omega / c$ in the metal (where the dielectric constant is $\varepsilon_m$). These guided waves are often referred to as Surface Plasmon Polaritons (SPP). The electric field of the surface plasmon can be deduced from the magnetic field, using Maxwell's

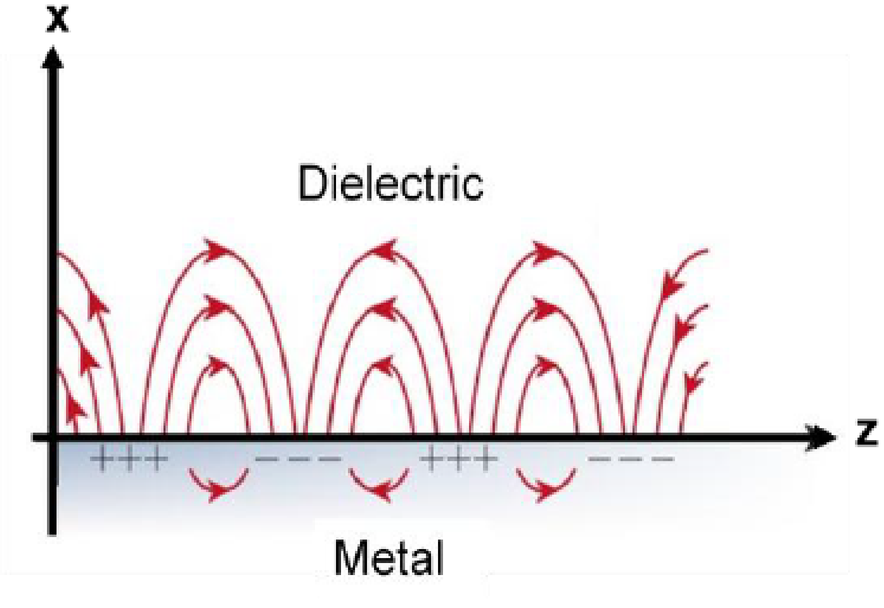

Figure 2.2: Illustration of surface plasmon polaritons. They are localized electromagnetic modes coupled to charge density oscillations bounded to a metal/dielectric interface.

---

[1] Here, this means that the magnetic field **H** is polarized parallel to the interface.

equations. It has two components

$$E_x = -i\frac{H_0}{\omega\varepsilon_0\varepsilon_{d,m}}k_{d,m}e^{i\beta z}e^{ik_{d,m}x} \tag{2.9}$$

$$E_y = -\frac{H_0}{\omega\varepsilon_0\varepsilon_{d,m}}\beta e^{i\beta z}e^{ik_{d,m}x} \tag{2.10}$$

The propagation constant is given by

$$\beta = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d\varepsilon_m}{\varepsilon_d+\varepsilon_m}} \tag{2.11}$$

This dispersion relation is shown on Fig. 2.3, where we have used a Drude model for $\varepsilon_m$ with negligeable damping. Because SPPs are bound to an interface, these excitations are located to the right of the light lines for the corresponding dielectric (of dispersion relation $\omega = ck_d$). Since they have higher wavevectors than those of light in the dielectric, they cannot be excited simply by shining light from the dielectric side[2]. They require a special kind of phase matching that resorts to grating or prism coupling. For small wavevectors, the SPP propagation constant is very close to $k_d$ and almost follows the light line. In such cases, the SPP field extends over many wavelengths into the dielectric and are also referred to as *Sommerfeld-Zenneck* waves. As in the transverse optical modes in the bulk above the plasma frequency, we see that near the frequency $\omega_{sp}$, there is a horizontal asymptote meaning that the group velocity is tending towards vanishingly small quantities. Of course, this is an idealized version of the dispersion diagram as we have neglected the collision frequency in the metal.

### Exercise

1. Using the Drude model and neglecting the collision frequency, give the relation of $\beta$ as a function of $\omega/\omega_p$ and sketch the dispersion diagram. In the case of air, what is the value of $\omega/\omega_p$ for which $v_g \to 0$.

2. Using a configuration (see Fig. 2.4) in which a thin film of metal is evaporated on a slab of dielectric of dielectric constant $\varepsilon_d$, how can light incident from the dielectric side couple to an SPP on the air side ? At what angle of incidence will the coupling be resonant ?

---

[2] We sometimes say, that light in the dielectric does not have enought momentum to couple to the SPP. This is because the momentum of a quantum of SPP is $\hbar\beta$ and the momentum of a quantum of light in the dielectric is $\hbar k_d$.

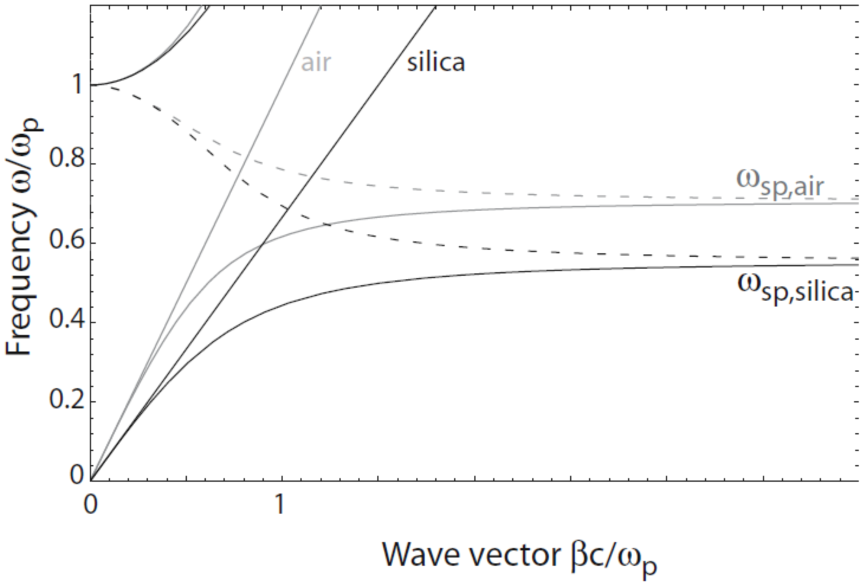

Figure 2.3: Dispersion relation of SPPs at the interface between a Drude metal with negligible collision frequency and air (gray curves) and silica (black curves). Graph was taken from [3]

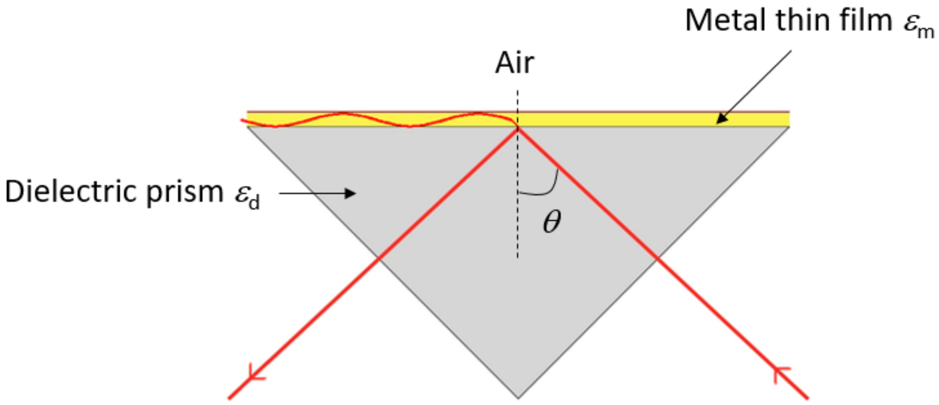

Figure 2.4: Sketch of the Kretschmann configuration for the excitation of surface plasmon polaritons on the air side by using a dielectric prism.

# Chapter 3

# Optical properties of nanoparticles

## 3.1 Brief reminder of crucial physical concepts

As we have seen in the first Chapter, light is an electromagnetic wave. Here we shall start by producing a brief reminder of key physical concepts that will enable us to move forward with the description of nanoparticles. This means that it is the joint oscillation of an electric wave **E** and a magnetic wave **B**, both of which are vector fields. Most of the time in optics, we are only interested in representing the electric field. As all waves in physics, it is characterized by its wavelength $\lambda$, which is the distance between two consecutive crests. Another important parameter is a vectorial quantity called the wavevector **k**. Its norm is $2\pi/\lambda$ and it is directed in such a manner that the trihedron formed by $(\mathbf{k}, \mathbf{E}, \mathbf{H})$ is right-handed.

Figure 3.1 is an illustration of one such wave, which is a sinusoidal function of $x$. The wavector points in the direction of propagation of light and governs how it accumulates phase. We may write

$$\mathbf{k} = \frac{2\pi}{\lambda}\mathbf{u}_x = k\mathbf{u}_x \tag{3.1}$$

where $\mathbf{u}_x$ is the normal vector in the $x$-direction, which we set as the direction of propagation. So the electric field writes

$$\mathbf{E} = E_0 \cos\left(\frac{2\pi}{\lambda}x + \phi_0\right)\mathbf{u}_x \tag{3.2}$$

where $E_0$ is the electric field amplitude, the first term in the cosine function is called a propagator and is equal to $k \times x$ and $\phi_0$ is called the phase. The phase governs the value that the electric field norm will take at the coordinate orgin $x = 0$.

It should be noted first that the propagator is sometimes included in the phase, such that we refer to the phase $\phi$ of the wave as being the sum of the

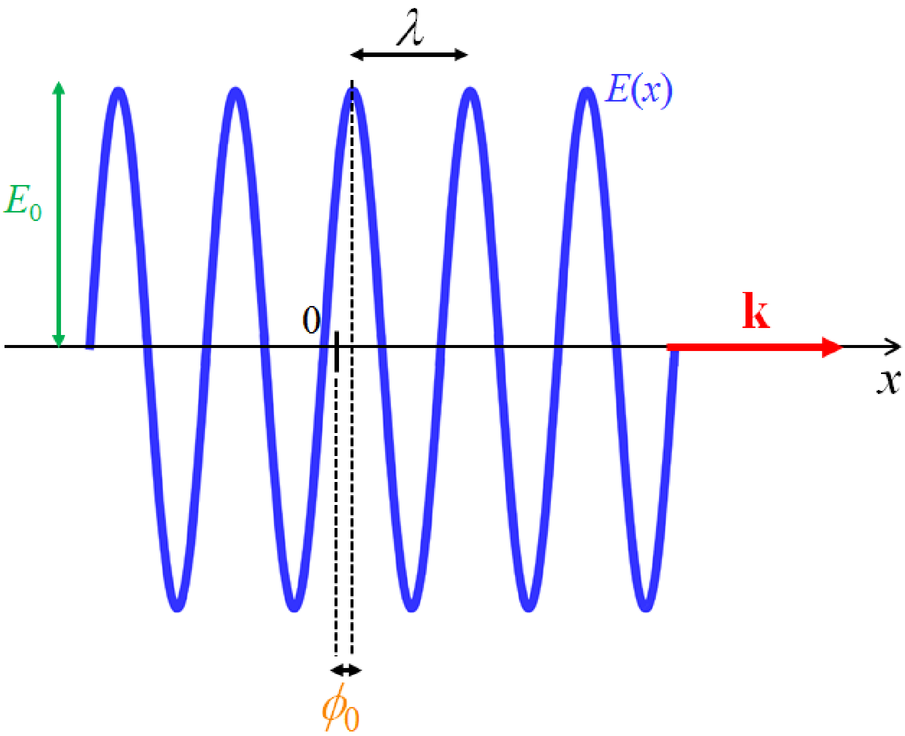

Figure 3.1: Illustration of a wave with key quantitites that characterize de wave. The wave is taken to be a sinusoidal function of $x$ (E(x)). $E_0$ is the amplitude of the wave, $\lambda$ is the wavelength, $\mathbf{k}$ is the wavenumber and $\phi_0$ is the phase.

propagator and $\phi_0$. Second, we often use complex notation to represent the electric field as it considerably simplifies algebra and analysis

$$\mathbf{E} = E_0 e^{i\phi} \mathbf{u}_x \tag{3.3}$$

Of course, the norm of the field given in eq. 3.2 is simply the real part of this complex notation.

### 3.1.1 Plane Wave and intensity

A concept that is often used is that of the *plane wave*. If we superimpose several sinusoidal fields as the one represented in Fig. 3.1 in a direction orthogonal to the plane of the page, we get what we call a plane wave (see Fig. 3.1(a)). This is a just a generalization of the sinusoidal wave to a plane. The lines that are in the same phase state are called *wavefronts*. For instance, we may consider the wavefront by connecting the crests of all waves (see dashed lines on Fig. 3.2(a)). In free-space, the propagation of the energy carried by the plane wave is directed along what is called the

Poynting vector. Its field lines are represented by the black arrows parallel to the $x$-axis in Fig. 3.2(a). So a plane wave can either be represented by its wavefront or by its field lines.

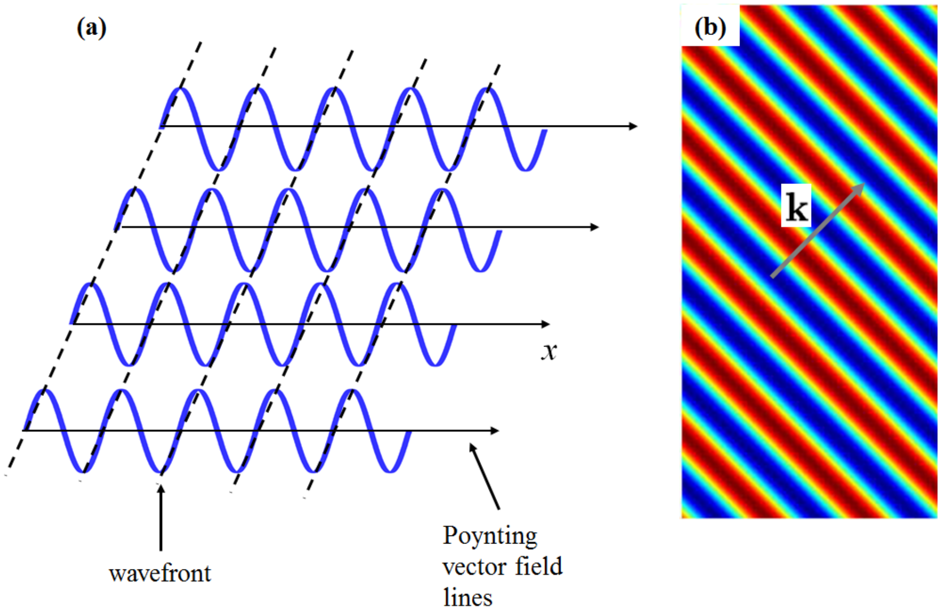

Figure 3.2: Illustration of a plane wave. (a) Simple sketch of how a plane wave is generated from the simple sinusoidal wave. (b) Color map representation of the electric field oscillation of a plane wave propagating in the direction of **k**.

Light is composed of photons. So the total energy carried by light is the number of photons $N$ multiplied by the energy of a single photon

$$\mathcal{E} = N\frac{hc}{\lambda} \tag{3.4}$$

where $h$ is Planck's constant and $c$ is the speed of light in vacuum. Knowing the energy, we can define *fluence* $\mathcal{F}$, which is the flow of energy through a flat surface of area $S$ (see Fig. 3.3). In other words, it represents (in energy), the amount of photons passing per unit area. Fluence is expressed in $\mathrm{J/m^2}$.

$$\mathcal{F} = \frac{\mathcal{E}}{S} \tag{3.5}$$

In this last equation, the energy has to be taken as the energy passing through the surface of area $S$. This is equivalent to counting the amount of photons going through $S$ and multiplying it by the energy of a single photon.

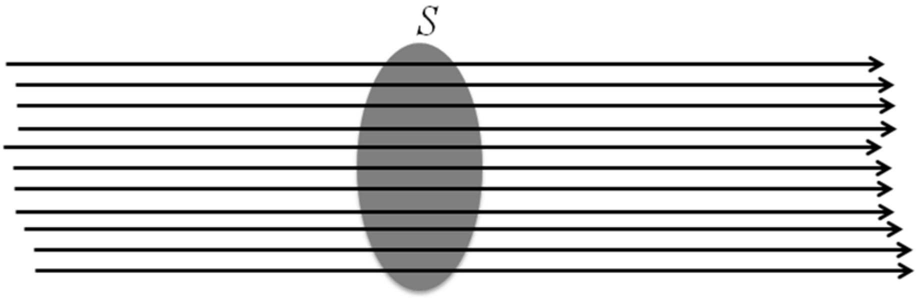

Figure 3.3: Illustration of light flowing through a fictitious surface of area $S$. The black arrows represent the Poynting vector field lines.

The *intensity* is the power $\mathcal{P}$ flow per unit area. This means that it is the amount of energy per unit second flowing through $S$, so it is simply the time derivative of the fluence[1]. From Maxwell's equations, it can be shown that in free-space the intensity is proportional to the magnitude square of the electric field

$$\mathcal{I} = \frac{\mathcal{P}}{S} = \frac{d\mathcal{F}}{dt} = \frac{1}{2Z_0}|E|^2 \tag{3.6}$$

where $Z_0 = \sqrt{\varepsilon_0/\mu_0}$ is the impedence of free-space. The intensity of light, as is defined here, is expressed in $\mathrm{W/m^2}$.

### 3.1.2 Scattering formalism and the optical theorem

Let us consider a particle under uniform illumination by a plane wave (see Fig. 3.4). This means that the intensity is the same at every point in space and is proportional to the magnitude square of the incoming field $E_{\text{in}}$

$$\mathcal{I} \propto |E_{\text{in}}|^2 \tag{3.7}$$

Under this constant illumination, the object polarizes and its polarization $\mathbf{P}$ will radiate a field, which we may call the scattered field and the induced polarization currents in the particle will cause some dissipation of energy through ohmic losses. The power absorbed is written $\mathcal{P}_{\text{abs}}$ and is due to the fact that induced current densities within the particle will generate losses through charge collisions[2]. The total electric field is the superposition of the

---

[1] We should stress at this point that, for pedagogical purposes, the way we define energy, fluence and intensity is a simplification of the rigorous definitions. Rigorously, intensity is the norm of the Poynting vector $\mathbf{\Pi} = \frac{1}{\mu_0}\mathbf{E} \times \mathbf{B}$. Fluence is the time integral of intensity: $\mathcal{P} = \int \mathcal{I} dt$ and the power flowing through any surface $\Sigma$ (open or closed) is $\mathcal{P}_\Sigma = \iint_\Sigma \mathbf{\Pi}.d\mathbf{S}$, where $d\mathbf{S}$ is an infinitesimal area vector orthogonally oriented with respect to the surface.

[2] The total absorbed power is obtained by integrating over the entire volume contained within a closed surface $\Sigma$ encapsulating the particle, the density of power absorbed: $\mathcal{P}_{\text{abs}} =$

incoming ($E_{\text{in}}$) and scattered field ($E_{\text{scatt}}$)

$$\mathbf{E}_{\text{T}} = \mathbf{E}_{\text{in}} + \mathbf{E}_{\text{scatt}} \tag{3.8}$$

A corresponding scattered intensity may be defined which is proportional to the magnitude squared of the scattered field $\mathcal{I}_{\text{scatt}} \propto |\mathbf{E}_{\text{scatt}}|^2$. The scattered power is the flux of the scattered intensity across a closed surface $\Sigma$ enclosing the particle[3]

$$\mathcal{P}_{\text{scatt}} = \oiint \mathcal{I}_{\text{scatt}} dS \tag{3.9}$$

The scattering cross-section is the proportionality constant between the scattered power and the incoming intensity[4]

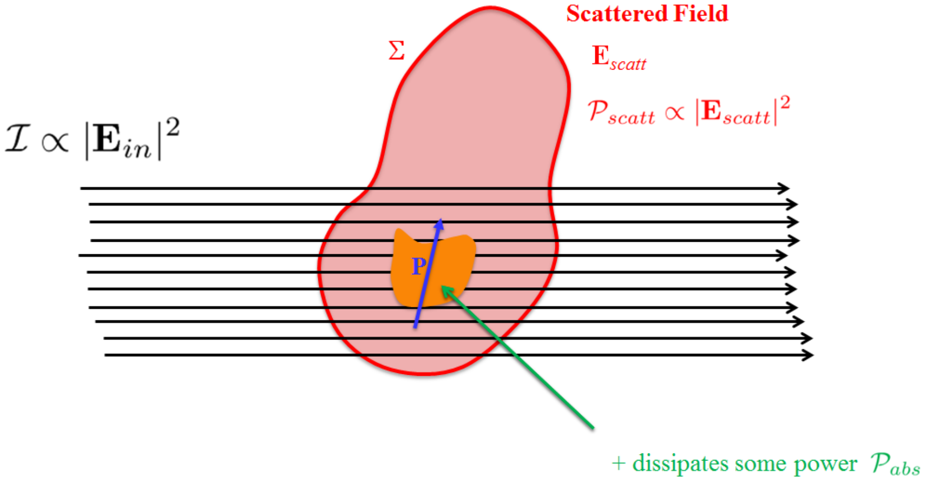

Figure 3.4: Illustration of the scattering formalism for a single particle.

$$\sigma_{\text{scatt}} = \frac{\mathcal{P}_{\text{scatt}}}{\mathcal{I}} \tag{3.10}$$

Similarly, an absorption cross-section may be defined

$$\sigma_{\text{abs}} = \frac{\mathcal{P}_{\text{abs}}}{\mathcal{I}} \tag{3.11}$$

---

$\iiint \mathbf{J}.\mathbf{E}_{\text{T}} dV$, where $\mathbf{J}$ is the current density and $dV$ is an infinitesimal volume element within $\Sigma$.

[3] Here also, the rigourous definition of the power scattered by the particle requires using the Poynting vector field of the scattered field: $\mathbf{\Pi} = \frac{1}{\mu_0}\mathbf{E}_{\text{scatt}} \times \mathbf{B}_{\text{scatt}}$ and then calculating its flux across a closed surface $\Sigma$ ecompassing the particle: $\mathcal{P}_{\text{scatt}} = \oiint_{\Sigma} \mathbf{\Pi}_{\text{scatt}}.d\mathbf{S}$. In eq. 3.9, the double integral is necessary because the intensity distribution is not constant over all perpendicular direction to $\Sigma$.

The cross-sections may also be viewed as the probability per unit area of an event (absorption or scattering) occuring on a particle.

At this point, we need to keep track of energy and make sure that the definitions of the scattering cross-sections do not violate energy conservation. Simply expressed in terms of power, energy conservation imposes that

$$\mathcal{P}_{\mathrm{in}} = \mathcal{P}_{\mathrm{T}} + \mathcal{P}_{\mathrm{abs}} \tag{3.12}$$

where $\mathcal{P}_{\mathrm{in}} \propto |\mathbf{E}_{\mathrm{in}}|^2$ is the impinging power and $\mathcal{P}_{\mathrm{T}}$ is the power carried by the total elecric field. Since the total electric field is the interference between the incoming electric field and the scattered electric field, it will be proportional to the sum of the scattered and incoming fields and as a result this interference term will impact the total power as follows

$$\begin{aligned}
\mathcal{P}_{\mathrm{T}} &\propto |\mathbf{E}_{\mathrm{in}} + \mathbf{E}_{\mathrm{scatt}}|^2 && (3.13)\\
&\propto |\mathbf{E}_{\mathrm{scatt}}|^2 + |\mathbf{E}_{\mathrm{in}}|^2 + 2\Re[\mathbf{E}_{\mathrm{scatt}}.\mathbf{E}_{\mathrm{in}}] && (3.14)\\
&\propto \mathcal{P}_{\mathrm{scatt}} + \mathcal{P}_{\mathrm{in}} - \mathcal{P}_{\mathrm{ext}} && (3.15)
\end{aligned}$$

In this last equation, we see that the total power may actually be expressed as the sum of three terms. Perhaps, the most peculiar term is actually the last term which is the extinction power and corresponds to a dot product term between the scattered field and the incoming field. Of course these two fields are orthogonal most of the time except in the forward scattering direction, i.e. ahead of the particle on Fig. 3.4. This power is taken into account negatively so as to make sure that the total power does not exceed the incoming power.

Next, by injecting eq. 3.15 into eq. 3.12, and express the powers in terms of scattering cross-sections instead of powers, we get the famous light scattering property for an object, known as the *optical therem*

$$\sigma_{\mathrm{ext}} = \sigma_{\mathrm{scatt}} + \sigma_{\mathrm{abs}} \tag{3.16}$$

In other words, extinction is equal to scattering plus absorption. At first glance, it may seem strange that the power carried by some interference term between the scattered and incoming light be equal to the power carried by the scattered light plus some additional losses, but we should keep in mind that this interference term is only the amount of power that does not go trough in the forward direction. It is a "lack" of power so to speak. The optical theorem just specifies that this absence is equal to what has been scattered in all directions and what has been absorbed[4].

---

[4] Most experimentalists who are not opticial scientists and use absorption spectroscpy to measure the optical properties of a solution – say of nanoparticles – will plot the absorption as a function of wavelength. But for an optical scientists, this plot is actually wrong, since the quantity measured is actually the intensity of light in the forward direction, which as we have pointed is actually the interference between incoming light and light scattered in the forward direction. As a result, it is extinction that is actually measured. The information contained in these experiments is the sum of light absorbed by the nanoparticles contained in the solvent and light scattered by the nanoparticles in every direction.

### 3.1.3 Scattering efficiency

It is important to know that for sub-wavelength – or close to wavelength – objects, cross-sections may be larger than the geometric cross-section the object. This is a rather strange property compared to what we usually observe when we look at macroscopic objects in every day life[5]. This means that the particle "affects" the field lines in regions where the particle is not located as can be seen on Fig. 3.5.

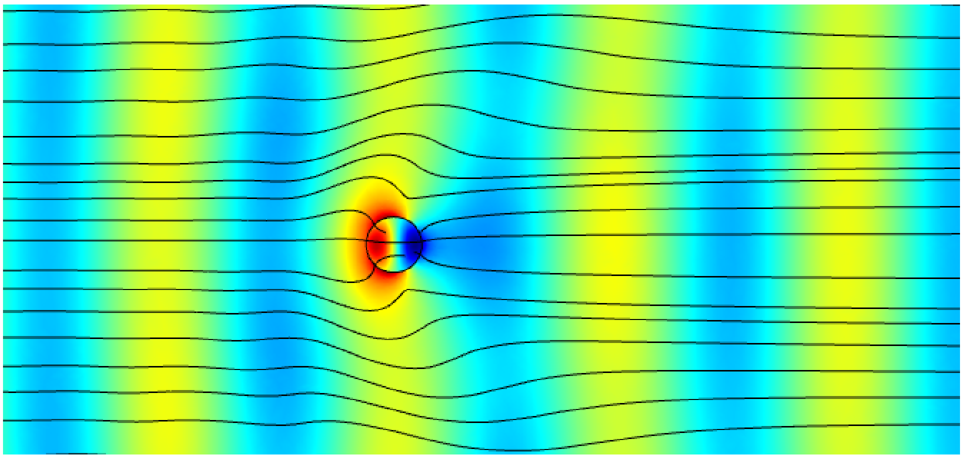

Figure 3.5: Illustration of total field around a nanoparticle under plane wave illumination. In this figure, the plane wave is incoming from the left-hand side. We see from that the field lines bend around the nanoparticle, which indicates that the particle has a scattering cross-section that is larger that its geometric cross-section.

For this reason – and in order to avoid carrying very small quantities – we often normalize the cross-sections by the geometric cross-section. For a spherical particle, this quantity is $\pi a^2$, where $a$ is the radius of the particle[6]. So normalizing eq. 3.16 by $\pi a^2$ gives us the optical theorem in terms of efficiency

$$Q_{\text{ext}} = Q_{\text{scatt}} + Q_{\text{abs}} \tag{3.17}$$

### 3.1.4 Dipoles and multipoles

In the context of light scattered by nanoparticles, a dipole is simply a particle that may be "seen" as a dipole. In physics, an electric dipole is a distribution of at least two different charges that generates an electric dipolar moment. A

---

[5] If we were to stand straight in front of a wall, with a plane wave – or normally incident sunlight – shone at us, the area of shadow we would cast would be exactly equal the area of contained within our silhouette.

[6] Some authors like to normalize by $a^2$ instead of $\pi a^2$. This effectively increases the efficiency, but we should keep in mind, that the cross-sections of the particle are identical.

magnetic dipole is a distribution of at least one current loop that produces a magnetic dipolar moment. These dipolar moments produce in turn a distribution of field lines. An example of a dipole produced by a nanoparticle is represented on Fig. 3.6, along with the associated dipole moment **p**.

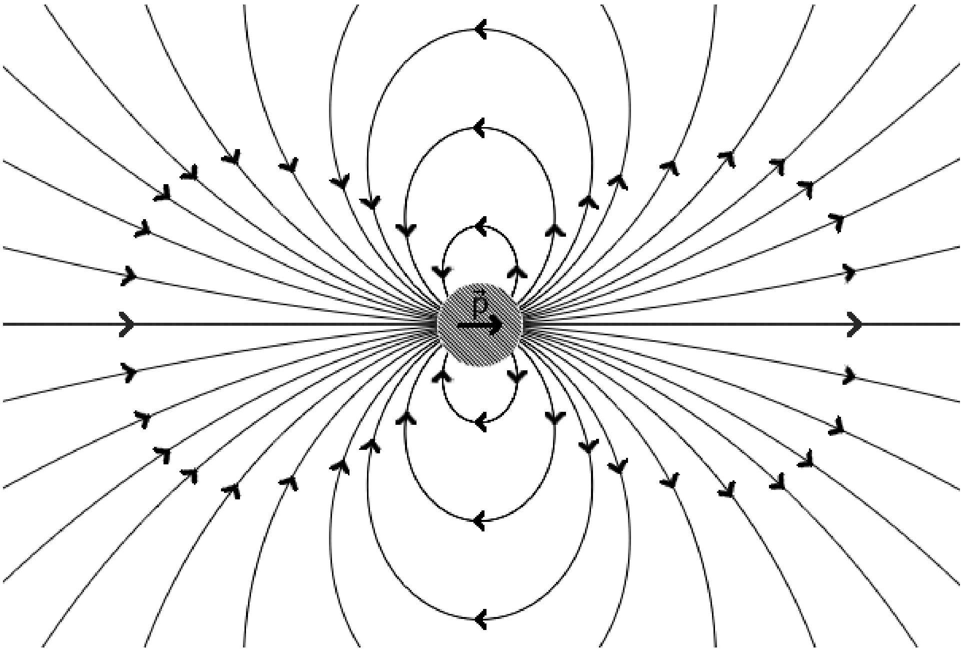

Figure 3.6: Illustration of the electric (or magnetic) field lines generated by and electric (or magnetic) dipole of dipole moment **p**.

The field lines emerge in the direction of the dipole moment and curve back at the back-end of the dipole moment vector. The field lines are electric or magnetic field lines and not Poynting vector field lines, contrary to those shown in Fig. 3.5. So the power radiated by this dipole – given by the Poynting field lines – is actually orthogonal to the field lines represented here and to the dipole moment.

The dipole may be an electric dipole if the dipole moment is responsive to an electric field and generates electric fields. It may also be a magnetic dipole if the dipole moment is responsive to a magnetic field and is responsive to magnetic fields. We usually distinguish between the two kinds of dipoles by including a subscript $e$ or $m$ depending on whether it is an electric or magnetic dipole moment

$$\mathbf{p}_e = \varepsilon_0 \alpha_e \mathbf{E}_{\text{in}} \tag{3.18}$$

$$\mathbf{p}_m = \varepsilon_0 \alpha_m \mathbf{H}_{\text{in}} \tag{3.19}$$

These two equations express the electric and magnetic dipole moments produced by an incoming electric field. The proportionality constant is called the *polarizability*[7].

Multipoles are the moments that are generated when more than two poles exist. Figure 3.7 is a chart that represents dipoles, quadrupoles and octupoles of electric and magnetic nature along with the associated radiation diagram. Electric (magnetic) dipoles are produced by two charges (one current loop), quadrupoles by four charges (four current loops) and octupoles by eight charges (eight current loops).

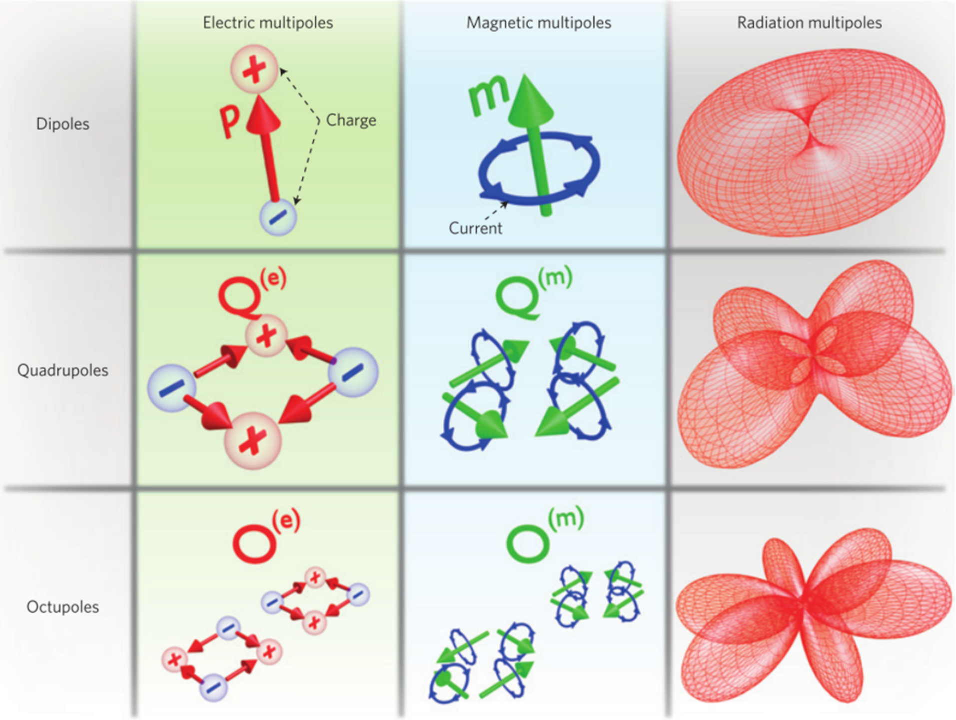

Figure 3.7: Illustration of the electric and magnetic multipoles up to the octupole, along with the associated radiation diagrams. This figure is adapated from Papasimakis *et al.* [5].

In strict analogy to atomic systems studied in quantum chemistry, the electric field of the multipoles – when considering a spherical system – can be decomposed on the set of spherical harmonics $Y_l^m$. The $l$-number is the azimuthal quantum number in quantum chemistry and is the number that lists the multipoles:

---

[7] Here we have made the assumption that the polarizability is a scalar quantity. This means that the incoming electric (magnetic) field and the induced electric (magnetic) dipole moment are colinear. But without loss of generality, the dipolar moments and fields are not necessarily colinear. For instance, the $x$-component of the electric dipole moment may be expressed as a linear combination of all components of the electric field. So, in general, the concept of polarizability is expressed in a $3 \times 3$ tensor.

- $l = 0$, monopole
- $l = 1$, dipole
- $l = 2$, quadrupole
- $l = 3$, hexapole
- $l = 4$, octupole

### 3.1.5 Resonator

It is important to realize that nanoparticles that scatter or absorb light may be considered as resonators. Indeed, the scattering process is actually a process by which the incoming light excites the nanoparticle and produces a response that is driven at the excitation frequency and is sustained over a characteristic lifetime $\tau$, which we may refer to as the nanoparticle-cavity lifetime. The light eventually exists the particle during this lifetime and is scattered. The absorption may occur, because some energy is dissipated in the material composing the nanoparticle. So, if one were to represent the response of the particle – say the electric field inside the particle – as a function of time when excited by a very short pulse of light, one would observe something similar to what is represented on Fig. 3.8. By very short pulse, we mean a pulse with a duration that is very small compared to the oscillation period of the response.

This situation is very similar to that of classical resonators we may experience in everyday life, such as a tuning fork. The equivalent experiment would consist in hitting the tuning fork very abruptly on a table – equivalent to the excitation pulse – and letting it ring. The ringing sound would have a characteristic period – or equivalently a frequency equal to the inverse of the period –, which defines the note of the fork and a typical decay time, which defines the time over which the note may be heard. If we were to hold a microphone near a tuning fork after hitting it in such a manner, the recorded signal as a function of time would show a function that is very similar to the field represented on Fig. 3.8.

We see in Fig.3.8 that the response function is the product of an sinusoidal wave and a time-decaying function, so it may be written in the following form[8]

$$\mathcal{R}(t) \propto \cos(\omega_0 t) \times e^{-t/\tau} \tag{3.21}$$

The oscillation frequency $\omega_0$ is the central cavity frequency of the resonator and corresponds to the wave that best resonates with the particle. That

---

[8] Or else, as stated before, we like to use the complex notation:

$$\mathcal{R}(t) \propto e^{i\omega_0 t} \times e^{-t/\tau} \tag{3.20}$$

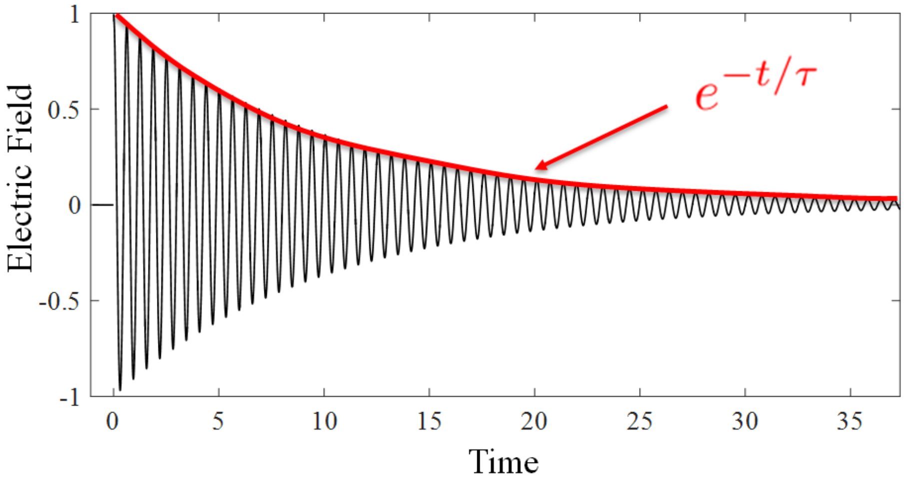

Figure 3.8: Illustration of the elecric field inside a nanoparticle under excitation by a very short pulse.

being said, since the response is actually decaying in time, it carries a finite amount of energy, contrary to a perfectly sinusoidal wave which would oscillate forever. This fact also implies that the response cannot fully be described as we just did in eq. 3.21. Indeed, it is only an approximation. This *wave packet* could only be correctly described mathematically as a continuous superposition of waves. Practically speaking, this means that the signal actually contains a distribution of waves with frequencies very close to $\omega_0$. The "$\omega_0$" wave is the one that carries the most energy and the farther the waves are from this central frequency, the less energy they carry. This is the reason, we like to use the Fourier transform to describe such responses[9]. The process of Fourier transforming consists in summing all the components in time and projecting them on a frequency basis, so as to see how the response is distributed in frequency.

For the response function considered here, we would find that the magnitude square of the Fourier transform has a Lorentzian shape centered around the frequency $\omega_0$ (see Fig. 3.9). To a physicist, this is expected from a resonator. The physicist is interested in two quantities when he/she looks at this distribution. The first is the frequency at which this lorentzian shape peaks, which gives the resonance frequency $\omega_0$. The second quantity is the linewidth $\Delta\omega$, which is basically the width of the shape and is proportional

---

[9] We recall that the Fourier transform of the response function would be

$$\tilde{\mathcal{R}}(\omega) = \int \mathcal{R}(t)e^{-i\omega t}dt \tag{3.22}$$

to the inverse of the decay time $\tau$[10].

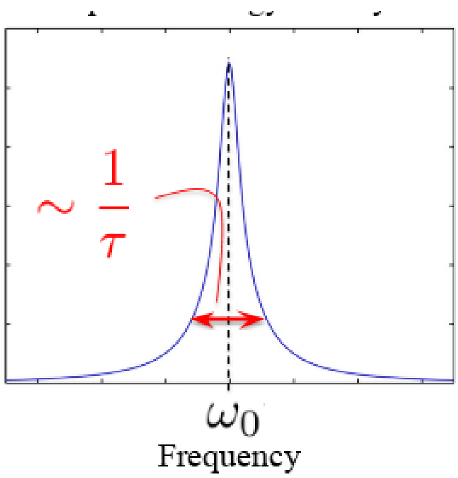

Figure 3.9: Graph showing a typical Lorentzian frequency distribution of spectral energy density that is proportional to the magnitude square of the Fourier transform of the response function of a resonator.

The linewidth of the resonance is a very important quantity because it is closely related to the losses of the cavity, namely to the amount of energy lost to scattering and ohmic dissipation.

## 3.2 Historical Intermezzo

Studying light scattering actually starts with trying to understand why the sky is blue. Hasan Ibn al-Haytham also known as Alhazen was a medieval arab scientist, sometimes thought of as the *first* scientist, because he was a mathematician as well as a strong promoter of empiricism to understand natural phenomena. He is notably famous for his work in optics. He is believed to have come up with a theory of why the sky is blue:

> The sky is blue because something in the air is blue in color. Sunlight travels through more air at sunset, so light is weakened by its long travel and therefore appears red.

**Hasan Ibn al-Haytham, ca 1000**

Of course, it is easy for the modern scientist to smile at this sentence and see that it is wrong, since Alhazen believes the sky is blue because it is somehow composed of a substance that is blue in color. However, he already suggests

---

[10] The decay time and linewidth are mathematically related through the Fourier transform and this provides us with the *time-bandwidth product* $\tau \times \Delta\omega \sim 1$

Figure 3.10: Alhazen is shown on the left-hand side of this figure. Leonardo Da Vinci is on the right-hand-side. The central panel wshow a picture of the sky at sunset where colors ranging from red to dark blue can be observed due to scattering of light in the atmosphere.

that the reason why the sky appears redder at sunset is because light travels a longer path. We now know that the path light travels does indeed play an important role in explaining the red color at sunset. So we at least have part of the story already around the eleventh century.

Later, Leonardo Da Vinci realized something quite interesting: smoke on which light rays fall will make a black piece of velvet, on which the rays do not fall, appear blue. This is already a scattering experiment and this leads Da Vinci to hypothesize that the atmosphere is composed of particles of moisture that produce the blue color.

> "I say that the blueness we see in the atmosphere is not intrinsic color, but is caused by the warm vapor evaporated in minute and insensible atoms on which the solar rays fall, rendering them luminous against the infinite darkness of the fiery sphere which lies beyond and includes it... If you produce a small quantity of smoke from dry wood and the rays of the sun fall on this smoke and if you place (behind it) a piece of black velvet on which the sun does not fall, you will see that the black stuff will appear of beautiful blue color... Water violently ejected in a fine spray and in a dark chamber where the sunbeams are admitted produces then blue rays... Hence it follows, as I say, that the atmosphere assumes this azure hue by reason of the particles of moisture which catch the rays of the sun."

**Leonardo Da Vinci, ca 1500**

In the second half of the nineteenth century, an Irish scientist called John Tyndall discovered what is now known as the *Tyndall effect*. He realized that the light passing through a transparent substance such as water becomes rather turbid when colloids are added to it and scatters light sufficiently that the beams of light can be seen when looking away from the direction of the source.

> ”The blue color of the sky, and the polarization of skylight... constitute, in the opinion of our most eminent authorities, the two great standing enigmas of meteorology. Indeed it was the interest manifested in them by Sir John Herschel, in a letter of singular speculative power, that caused me to enter upon the consideration of theses questions so soon.”

**John Tyndall, 1869**

As a matter of fact, we learn with Tyndall that small particles scatter blue light and that the light is scattered at right angles with respect to the incident beam and is linearly polarized. The scattered intensity only depends on the particles being small enough. Towards the second half of the nineteenth century, Lord Rayleigh explains why light from the sky is blue and why light. His reasoning is surprisingly simple and almost entirely based on dimensional analysis, which is quite beautiful when you come to think of it. Basically considering the scattering problem illustrated on Fig. 3.12. Rayleigh makes the simple hypothesis that the scattered intensity should be proportional to the incoming intensity $I_0$ and that the proportionality constant is a function $f$ of a number of paramaters to be listed. We know from Tyndall that it should depend on the size of the particle, so it is reasonable

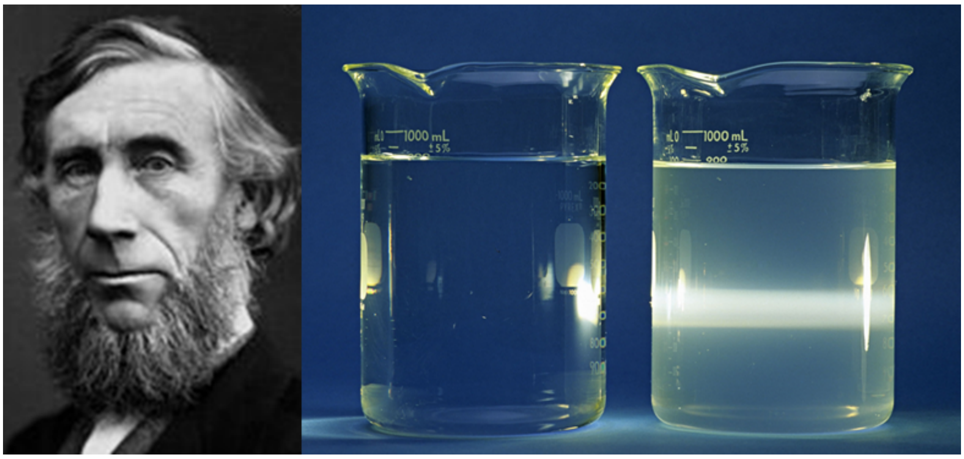

Figure 3.11: The left-hand side picture is a photograph of John Tyndall. On the right-hand side are two beakers: one without any colloids on the left and one with colloids suspended on the right. A light source is placed on the left of the two beakers. We see that light passes through the first beaker without any scattering, while the beam of light leaves a trace in the second beaker due to scattering.

to say that $f$ should be a function of the volume $V$ of the particle. Furthermore, it should of course depend on the distance $r$ at which the scattered intensity is observed since se expect the intensity to decrease with distance. Then it should depend on wavelength because we know – again from Tyndall – that blue seems to scatter more. Finally, $f$ should also be a function of the index of refraction of the particle $n_1$ and of the environment in which the particle is located – the atmosphere – $n_2$:

$$I = f(V, r, \lambda, n_1, n_2) I_0 \tag{3.23}$$

We already know since Maxwell that the intensity of light is proportional to magnitude square of the dipole moment, which itself is proportional to the volume of matter producing the dipole. So the scattered intensity should be proportional to $V^2$. Since light is scattered at 90°, this means that all scattered rays are contained in a disk perpendicular to the incoming direction. Because energy has to be conserved, this means that the larger the disk considered, the smaller the intensity should be in a given direction. The energy fall should be proportional to the disk area and as a result $I$ is proportional to $1/r^2$. So we get that $I$ should be proportional to $V^2/r^2$ which is has dimensions of length to the power four. But the term in front of $I_0$ should be dimensionless, so we are to conclude that the final proprtionality term concerning the wavelength must be $1/\lambda^4$. In the end, we have

$$I = g(n_1, n_2) \left( \frac{V^2}{r^2 \lambda^4} \right) I_0 \tag{3.24}$$

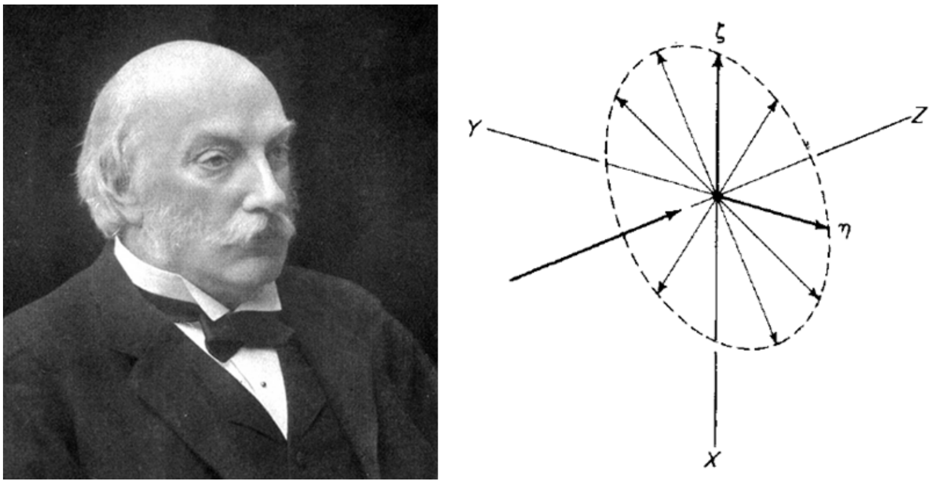

Figure 3.12: A photograph of Lord Rayleigh (left-hand side). The right-hand side is a representation of the scattering problem. The solar radiation is impinging along the Z-axis. The disk represented in the XY-plane is the direction of scattering of light.

where, a function $g$ is left to account for the complicated dependence of scattering with the refractive indices. So by the simple reasoning, Rayleigh demonstrates that the scattered intensity must be proportional to the inverse fourth power of wavelength, which explains why blue scatters more than any other wavelength and why red may be observed at sunset: light travels through more atmosphere as already noticed by Alhazen. The important result is of course that smaller wavelengths are more scattered.

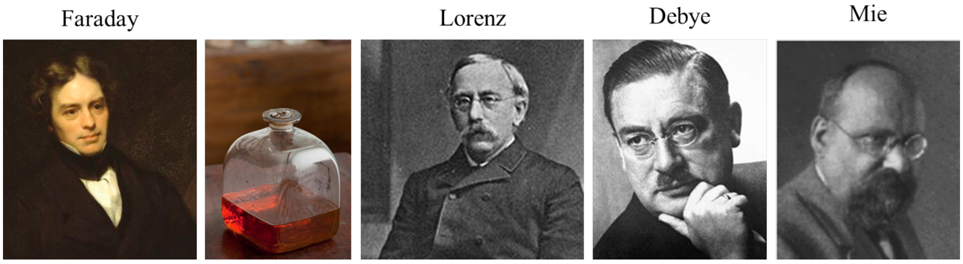

Figure 3.13: Images of the main people involved in the developement of Mie theory. The second picture from the left is a photograph of a vask containing a suspension of gold nanocolloids which scatter this ruby color.

At the turn of the twentieth century, people were trying to move towards larger and larger scatterers, which eventually led to the developpement of what we now call Mie theory. But prior to that we have to mention Michael Faraday's work because the first physicists to have ventured into the developement of a theory were actually trying to explain his observations. In 1857, the british chemist, who had already established himself as a well-known empirist created gold colloidal suspensions by accident and realized that they had a a vivid ruby color. He even realized that for this color to appear, these colloids needed to be small enough or else the color disappeared[11].

Ludvig Lorenz in the 1890s actually developed a prototype of what we may call Mie theory today, however he wrote in Danish and used his own version of electromagnetism that overlooked and even ignored Maxwell's work, so he ended up being overlooked himself. In 1908, Peter Debye defended his thesis in which he was trying to understand the pressure light exerts on a spherical particle. This problem is very much linked to the problem of scattering by a particle and his theory was mathematically predictive. Finally, later that same year, Gustav Mie got interested in trying to explain Faraday's color in suspensions of gold colloids. So he developped a thoery to explain the scattering of these peculiar particles and came up with a scaling theory of light scattered by a sphere of arbitrary size and arbitrary refractive

---

[11] Those who are familiar with the concept might recognize here that Faraday had actually fabricated the first plasmonic nanoparticles. We might say that this was the beginning of plasmonics.

index. This theory is what we now call Mie theory, in spite of the fact, he was not the first to have provided one.

## 3.3 Mie Theory

Two very good books exist on the topic of light scattering by particles that researches and professors like to refer to. The first one is by far the most-read book on the subject and is the book by Craig F. Bohren and Donald R. Huffman[4]. The second book is the one written by Milton Kerker[6].

### 3.3.1 Multipolar coefficients

In section 3.1.4, we defined what multipoles were. Mie theory provides us with the mathematical means to compute the so-called multipolar coefficients of a spherical particle with an arbitrary refractive index immersed in a matrix with an equally arbitrary index. These coeffcients are proportional to the polarizability of the multipoles and are what enable one to calculate the scattering properties of a particle including the scattering, absorption and extinction cross-sections. They are indexes by $n$ which is the pole order and are labeled $a_n$ ($b_n$) for *electric-type* (*magnetic-type*) poles. By electric-type, we mean that the fields scattered by the particle will be those of a corresponding electric multipole

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \mu\psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \mu\xi_n(x)\psi_n'(mx)} \tag{3.25}$$

$$b_n = \frac{\mu\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\mu\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)} \tag{3.26}$$

In these two equations, the Mie coefficients are expressed as functions of $\psi_n$, $\psi_n'$ (the derivative of $\psi_n$) $\xi_n$ and $\xi_n'$ (the derivative of $\xi_n$). $\psi_n$ and $\xi_n$ are respectively the $n^{th}$ order Ricatti-Bessel and Hankel functions. The important thing to notice in these complicated formulas is that they can be functions of the argument $x$ or of the product $m \times x$, which are the two important parameters to define. The quantity $m$ also appears elsewhere as a prefactor of the functions as well as $\mu$. $\mu$ is the magnetic permeability and we can straight away set this number to one, which characterises the absence of a magnetic response in matter. Since most materials at optical frequencies actually exhibit no magnectic behavior, we may rewrite the two previous equations without $\mu$. So in the end $x$ and $m$ are the only two parameters that govern the Mie coefficients.

The first parameter $x$ is dimensionless : $x = n_h ka$, where $n_h$ is the refractive index of the host material, $k$ is the wavevector of light in free-space and $a$ is the radius of the particle. Therefore, this quantity is a normalized number that is proportional to the size-to-wavelength ratio. The scalability of Mie theory comes from the fact that this parameter is dimensionless. This means that we may consider a very large or else very small object and the predictions will be the same as long as the wavelength is scalled accordingly. We may refer to $x$ as the *reduced frequency* or else *frequency* for simplicity.

The second parameter $m$ is simply the refractive index contrast between the particle and the host material $m = n/n_h$. It is instructive to understand how $a_n$ and $b_n$ depend on these two parameters. For this reason we look at $|a_1|$ for two values of $m$ just to get and intuition as well as compare $|a_1|$ (in blue on 3.14) to $|a_2|$ (in red on Fig. 3.14). We learn empirically here that

> Increasing the refractive index contrast ($m$) narrows the distribution of polarizability and increases the resonance wavelength (i.e. decreases the resonance frequency). We also learn that higher order ($n$) multipoles appear at smaller wavelengths (higher frequencies) compared to lower order multipoles.

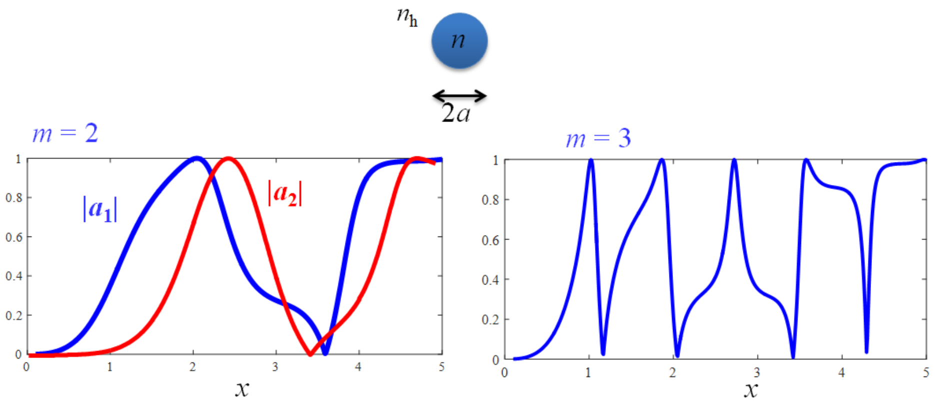

Figure 3.14: The top sketch is an illustration of a nanoparticle of refractive index $n$ immersed in a host medium of refractive index $n_h$. The bottom-left graph plots $|a_1|$ and $|a_2|$ as a function of $x$ for $m = 2$. The bottom-right graph $|a_1|$ for $m = 3$.

### 3.3.2 Cross-section efficiencies

Next, the scattering and extinction cros-section efficiencies $Q_{\text{scatt}}$ and $Q_{\text{ext}}$ can be calculated directly from these coefficients using the following expressions

$$Q_{\text{scatt}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \left[ |a_n|^2 + |b_n|^2 \right] \tag{3.27}$$

$$Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \Re[a_n + b_n] \tag{3.28}$$

From this last equation, we see that the basic properties of the Mie coefficients will be transferred to the cross-section efficiencies and we may provide the general rule of thumb

> A good scatter is a particle made of a material with a large refractive index.

This property directly comes from the fact that a large refractive index, produces a narrower value resonance as noticed in Fig. 3.14. This in turn means that the resonator is of better quality (with a larger quality factor) as it is capable of storing energy over a longer period as we saw in section 3.1.5.

The optical theorem enables one to compute the absorption cross-section efficiency directly from the knowledge of the scattering and extinction cross-section efficiencies

$$Q_{\text{abs}} = Q_{\text{ext}} - Q_{\text{scatt}} \tag{3.29}$$

## 3.4 Particles small compared with the wavelength

The previous section is a complete theory of the scattering, absorption and extinction of spherical particles, however big they are. We can make mathematical expansions of eqs. 3.25 and 3.26 for instance in cases when the particles are small compared to wavelength, which considerably simplify the mathematical expressions and provide much better physical insight into the optical behavior of nanoparticles.

Considering particles that are small compared to wavelength translates mathematically into the fact that the reduced frequency parameter $x$ is very small compared to 1 ($x \ll 1$). If this holds we are justified in making the following expansions up to order $x^5$

$$\begin{aligned} a_1 &\approx -\frac{i2x^3}{3}\frac{m^2-1}{m^2+1} - \frac{i2x^5}{5}\frac{(m^2-2)(m^2-1)}{(m^2+2)^2} && (3.30) \\ b_1 &\approx -\frac{ix^5}{45}(m^2-1) && (3.31) \end{aligned}$$

If $x \ll 1$, then we can even push our luck further and be justified in retaining only the firs term (the one proportional to $x^3$) in the expression of $a_1$ and since the scattering efficiency will be proportional to the magnitude squared of that quantity (see eq. 3.27), such that we have

$$Q_{\text{scatt}} = \frac{8x^4}{3}\left|\frac{m^2-1}{m^2+1}\right|^2 \tag{3.32}$$

So scattering is proportional to $x^4$ and since $x = \frac{2\pi}{\lambda}n_h a$, where $a$ is the size of the radius of the particle, $n_h$ is the host refractive index and $\lambda$ is wavelength, we find the following important dependence

$$\sigma_{\mathrm{scatt}} \propto \frac{a^6}{\lambda^4} \propto \frac{V^2}{\lambda^4} \tag{3.33}$$

which is the exact proportionality relation found by Lord Rayleigh (see eq. 3.24).

This approximation is sometimes referred to as the *electrostatic approximation* since it essentially implies that the electromagnetic field is constant over the typical size of the nanoparticle. The absorption efficiency may be approximated by the following formula[12]

$$Q_{\mathrm{abs}} = 4x\mathrm{Im}\left(\frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h}\right) \tag{3.34}$$

where $\varepsilon_h$ is the dielectric constant of the host medium and $\varepsilon$ is that of the particle.

**Exercise**

1. Following eqs. 3.32 and 3.34, give the dependence of scattering and absorption with respect to the nanoparticle size $a$ in the electrostatic approximation. In the limiting cases, what regimes dominate? Sketch a log-plot of the dependence of absorption and scattering with particle size.
2. Considering a constant positive value of $\varepsilon_h$ and using a Drude model without collisions ($\Gamma = 0$) for $\varepsilon$ (dielectric constant of a metal), derive the typical behavior of the absorption efficiency. Determine the frequency $\omega_{\mathrm{sp}}$ at which the idealized localized surface plasmon resonance occurs.
3. Same question when the collision frequency $\Gamma$ is considered.
4. Sketch the two situations on a graph.

## 3.5 Thermal radiation

For temperatures $T \neq 0$ K, the solid state can emit light, as well as absorb and scatter light. The emission process resorts to the concept of blackbody radiation. A blackbody is an idealized opaque and non-reflective body that emits light. The emission properties depend on the temperature of the blackbody.

Consider a region of space enclosed by a surface. the dimensions of this regions of space should be large compared to wavelength but it's shape can

---

[12] This actually follows from the same expansions.

be completely arbitrary and made of virtually any material, it does not matter. All that matters really is that a definite equilibrium temperature $T$ can be assigned to that region of space. The equilibrium radiation field that will emanate from that region of space will be isotropic, homogenous and unpolarized. At any point, the power radiated per unit frequency interval and per unit solid angle in any direction, which crosses a unit area normal to this direction is given by the Planck function[13]

$$I_e(\omega, T) = \frac{\hbar\omega^3}{4\pi^3 c^2} \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} \tag{3.35}$$

where $k$ is Boltzmann's constant. So this function has units of W/m$^2$/sr. Figure 3.15 shows the different spectral regions where a blackbody emits as a function of its temperature. Of course, the blackbody radiation distribution function is idealized for a blackbody.

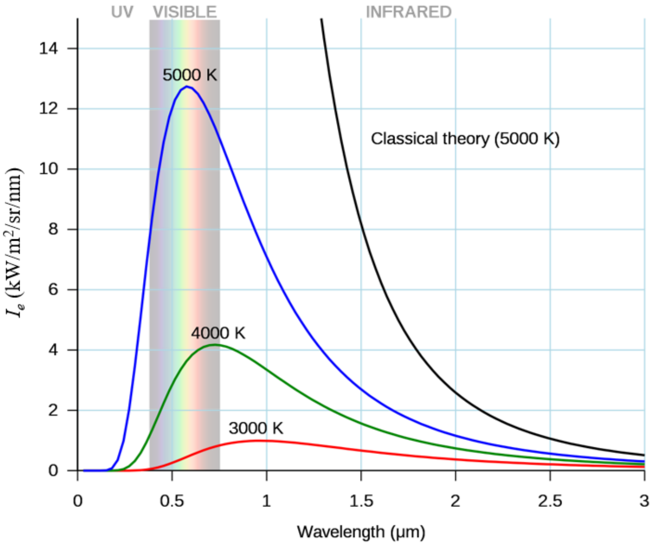

Figure 3.15: Graph of the Planck Blackbody ditribution as a function of wavelength for different temperatues of the Blackbody. Adapted from Wikipedia.

Let us consider a spherical particle of radius $a$ made of any material and let us place it in the region of space we have been considering. If the spherical particle is in equilibrium with that region of space, the distribution of radiation is unchanged in principle and should follow Planck's law. Considering a spherical surface of radius $R \gg a$, such that every infinitesimal portion of surface $dS$ at its surface is the source of a near plane-wave illuminating the particle with an irradiance $I_e \times d\Omega$ (see Fig. 3.16), where

---

[13] Also referred to as the *blackbody radiation distribution function.*

$d\Omega$ is the unit solide angle ($dS/R^2$). As a result the total power absorbed per unit time by the particle is simply

$$\int_0^{+\infty}\int_\Omega \sigma_{\text{abs}} I_e d\Omega d\omega = 4\pi \int_0^{+\infty} \sigma_{\text{abs}} I_e d\omega \tag{3.36}$$

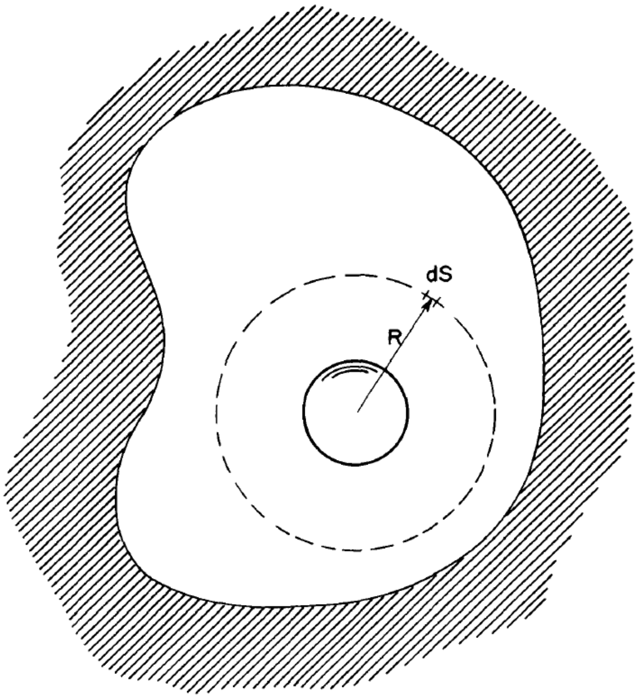

Figure 3.16: A region of space at temperature $T$ containing a spherical particle, and a radiation field in thermodynamic equilibrium. Sketch was taken from [4].

where $\sigma_{\text{abs}}$ is the absorption scattering cross-section of the particle. In equilibrium the total power emitted by the particle should equal that absorbed b it, such that

$$\int_0^{+\infty} W_e d\omega = 4\pi \int_0^{+\infty} \sigma_{\text{abs}} I_e d\omega \tag{3.37}$$

where $W_e$ is the power per unit frequency which, for symmetry reasons, is emitted uniformely in all directions. If we define emissivity $\mathcal{E}$ in the following fashion (i.e. the ratio of the power emitted by the particle to the power emitted by a particle that emits according to the blackbody distribution function)

$$\mathcal{E} = \frac{W_e}{4\pi^2 a^2 I_e} \tag{3.38}$$

then, we can deduce from eq.3.37

$$\int_0^{+\infty} (Q_{\text{abs}} - \mathcal{E}) I_e d\omega = 0 \tag{3.39}$$

And a suffciant condition for this to be valid is

$$Q_{\text{abs}} = \mathcal{E} \tag{3.40}$$

This last equation is also known as Kirshoff's law of thermal radiation which, in simple terms states that absorption is equal to emission for a body in thermal equilibrium.

As should be clear by now, the absorption efficiency of a subwavelength particle can be larger than 1. So following eq. 3.40, this means that the emissivity of the body is actually larger than 1. On that matter, we shall cite Bohren and Huffman [4], who say

> We shall occasionally encounter spherical particles with absorption efficiencies greater than 1, sometimes much greater [...]. But if $Q_{\text{abs}}$ can be greater than 1, the emissivity can be greater than 1, which treads heavily on deep-seated prejudices about the upper limit a proper emissivity can assume; at first glance; an emissivity greater than 1 implies that the particle emits more than a *perfectly black particle.* But what is a perfectly black particle? The standard definition of a perfect blackbody is that it absorbs all the light that is *incident on it.* The key phrase is italicized the notion of light geometrically incident on a body is a concept from geometrical optics, which fails to be valid for particles with dimensions comparable to or less than the wavelength. This was recognized by Planck (1913), who stated that "throughout the following discussion it will be assumed that the ... radii of curvature of all surfaces under consideration are large compared with the wavelengths of the rays considered." According to Baltes (1976), Kirchhoff was also well aware of the restrictions on his derivations. Unfortunately, as so often happens in physics, each successive author in a chain extending from the sources of a theory tends to omit more of the fine print underlying its validity. When a "paradox" is inevitably uncovered, brickbats are unfairly hurled at the theory when their proper target is those who uncritically use it in a state of blissful ignorance about its limitations.

# Appendix

## Complex Numbers

### Cartesian/polar form

For the entire appendix, we shall consider a complex number $z$ of the form

$$z = z' + iz'' \tag{3.41}$$

$$z = |z|e^{i\theta} = |z|\left(\cos\theta + i\sin\theta\right) \tag{3.42}$$

where the first line is the cartesian form and the second line is called the polar form

- $z \in \mathbb{C}$
- $z' \in \mathbb{R}$ is the real part of $z$
- $z'' \in \mathbb{R}$ is the imaginary part of $z$
- $|z|$ is the modulus of $z$ and is equal to

  $$|z| = \sqrt{z'^2 + z''^2}$$

- $\theta$ is the angle or the argument of $z$ and is such that

  $$\tan\theta = \frac{z''}{z'}$$

### Complex conjugate

The complex conjugate of $z$ is simply

$$z^* = z' - iz'' \tag{3.43}$$

and has the following properties

$$z + z^* = 2z' \tag{3.44}$$

$$z - z^* = 2iz'' \tag{3.45}$$

$$|z|^2 = zz^* \tag{3.46}$$

$$\tag{3.47}$$

### Modulus properties

$$\begin{aligned} |z_1 z_2| &= |z_1||z_2| && (3.48) \\ z_2 \neq 0, \left|\frac{z_1}{z_2}\right| &= \frac{|z_1|}{|z_2|} && (3.49) \\ |z_1 + z_2| &\leq |z_1| + |z_2| && (3.50) \end{aligned}$$

### Moivre formula

$$(\cos\theta + i\sin\theta) = \cos(n\theta) + i\sin(n\theta) \qquad (3.51)$$

where $\theta \in \mathbb{R}$ and $n \in \mathbb{Z}$

### Euler formula

$$\begin{aligned} \cos x &= \frac{e^{ix} + e^{-ix}}{2} && (3.52) \\ \sin x &= \frac{e^{ix} - e^{-ix}}{2i} && (3.53) \end{aligned}$$

where $x \in \mathbb{R}$

## Differential Calculus

### Taylor expansion

Let $f : x \mapsto f(x)$, then

$$\begin{aligned} f(x+\varepsilon) &= f(x) + \varepsilon f'(x) + \frac{\varepsilon^2}{2} f''(x) + ... && (3.54) \\ &= \sum_{n=0}^{+\infty} \frac{\varepsilon^n}{n!} f^{(n)}(x) && (3.55) \end{aligned}$$

### Differential of a function of several variables

Let $f : (x, y, z) \mapsto f(x, y, z)$, then

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz \qquad (3.56)$$

## Vectorial operators

### $\nabla$ operator

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \qquad (3.57)$$

### Gradient

$$\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix} \tag{3.58}$$

### Divergence

Let $\mathbf{A} : (x, y, z) \mapsto \mathbf{A}(x, y, z) = \begin{pmatrix} A_x(x, y, z) \\ A_y(x, y, z) \\ A_z(x, y, z) \end{pmatrix}$ be a vectorial function, then

$$\nabla.\mathbf{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} \tag{3.59}$$

### Curl

$$\nabla \times \mathbf{A} = \begin{pmatrix} \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \\ \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \\ \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \end{pmatrix} \tag{3.60}$$

### Laplacian

For a vectorial function

$$\Delta \mathbf{A} = \nabla \left( \nabla.\mathbf{A} \right) - \nabla \times \left( \nabla \times \mathbf{A} \right) \tag{3.61}$$

For a scalar function

$$\Delta f = \nabla^2 f \tag{3.62}$$

## Fourier Transforms

### Definition

Let $f : t \mapsto f(t)$ be a function $\mathbb{R} \to \mathbb{R}$. Then the Fourier transform of $f$ is a function $\tilde{f}(\omega)$ of $\mathbb{R} \to \mathbb{C}$ defined by[14]

$$\tilde{f}(\omega) = \int_{-\infty}^{+\infty} f(x) e^{-i\omega t} dt \tag{3.63}$$

The inverse Fourier transform is defined by

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{f}(\omega) e^{i\omega t} d\omega \tag{3.64}$$

---

[14] We are defining the Fourier transform in terms of a scalar function, but all the definitions here extend very naturally to vector functions and we just need to replace every scalar function by a vector function to extend the definitions.

### Parseval-Plancherel theorem

$$\int_{-\infty}^{+\infty} |f(t)|^2 \, dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left| \tilde{f}(\omega) \right|^2 d\omega \tag{3.65}$$

### Convolution theorem

$$\tilde{f} * \tilde{g} = \widetilde{f \times g} \tag{3.66}$$

where the convolution product is defined by

$$(f * g)(t) = \int_{-\infty}^{+\infty} f(t - t')g(t')dt' \tag{3.67}$$

## Solide angle

An infintesimal solid angle $d\Omega$ is defined as the ratio of an infinitesimal unit surface $d\mathbf{S}$ by the square of the distance $r$ to that surface. The direction of $\mathbf{S}$ is normal to the surface and we have

$$d\Omega = \frac{dS}{r^2} \tag{3.68}$$

In spherical coordinates, we find

$$d\Omega = \sin\theta d\theta d\phi \tag{3.69}$$

Over an entire (spherical) space $\mathbb{R}^3$, the total solid angle is

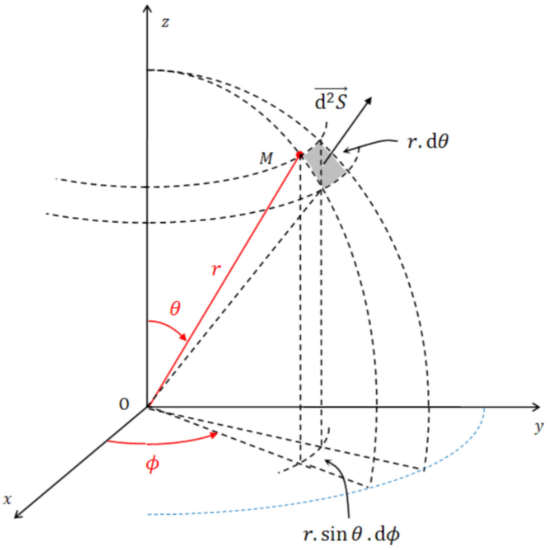

Figure 3.17: Illustration of the solid angle in spherical coordinates.

$$\Omega_{\mathbb{R}^3} = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \sin\theta d\theta d\phi = 4\pi \tag{3.70}$$

This solid angle is also equal to the surface of any sphere of radius r, divided by the square radius of the sphere

$$\Omega_{\mathbb{R}^3} = \frac{4\pi r^2}{r^2} = 4\pi \tag{3.71}$$

# Bibliography

[1] Charles Kittel. Introduction to solid state physics. 1976.

[2] Peter B Johnson and R-WJPrB Christy. Optical constants of the noble metals. *Physical review B*, 6(12):4370, 1972.

[3] Stefan Alexander Maier. *Plasmonics: fundamentals and applications*. Springer Science & Business Media, 2007.

[4] Craig F Bohren and Donald R Huffman. *Absorption and scattering of light by small particles*. John Wiley & Sons, 2008.

[5] Nikitas Papasimakis, VA Fedotov, Vassili Savinov, TA Raybould, and NI Zheludev. Electromagnetic toroidal excitations in matter and free space. *Nature materials*, 15(3):263, 2016.

[6] Milton Kerker. *The scattering of light and other electromagnetic radiation*. Elsevier, 2016.