
Optical Properties of Thermochromic Granular Films

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Abstract

Abstract.. abstract.

1 INTRODUCTION

Today, in the light of global warming, the importance of reducing the amount of released greenhouse gases into the atmosphere is more crucial than ever. But because the use of fossil fuel is so well implemented in our society and constitute such an important energy source it is difficult to find replacements. However, by identifying the most energy unefficient components of any system and being able to improve these, could help to reduce the overall energy consumption and the related emissions of carbon dioxide. A relatively large portion of the energy consumption worldwide is due to the building sector. Today the energy consumption of buildings in developed countries constitute about 30-40% of their total energy usage. In humid regions, this increases to roughly 30%-50% [3, 4, 5]. In 2010, 41% of the primary energy of the U.S., being the second largest energy consumer globally and accounting for 7% of the global energy use, were consumed by the building sector. This resulted in approximately 40% of the total energy-related carbon dioxide emission in the US. For comparison, the building sector in China accounted for 18% of the CO₂ emission of the country, whereas worldwide the building energy consumption is the cause of 8% of the total carbon dioxide emission. [2, 6]. Because this in total makes such a significant impact worldwide, it should motivate measures to be taken to reduce the building energy consumption, in order to reduce the related CO₂ emissions. In addition to lowering the energy consumption, it would also lower the energy related costs, such as costs due to electricity. So reducing the overall building energy usage would have both economical and environmental benefits.

When considering the energy consumption of buildings, devices which are responsible for heating, ventilation and airconditioning (HVAC) and in general help to maintain a comfortable indoor climate, are accounting for a significant amount of the overall energy usage.

HVAC devices are used to compensate for heat loss through the building's envelope, e.g. walls, roof, windows or any element separating the indoor from the outdoor, or excessive heating due to the thermal radiation from the sun. Together with lighting, HVAC were responsible for about 60% of the total building energy consumption in 2010 (???in the U.S. or in general???). [2]. The approaches to increase the energy efficiency of buildings can be divided into two categories: active strategies, including improving HVAC systems and lighting of the building; and passive strategies, such as improving the thermal properties of the building envelope. The latter includes measures like thermal insulation to walls, cool coatings on the roof tops or using windows with special coatings, altering the optical properties of the window [10, 11, 12, 13]. With the window being the most energy inefficient

component of the building [6] <- **burde sjekkes, men har ikke tilgang (har ikke prøvd VPN enda** , the measures focusing on improving the thermal properties of the window seems the most reasonable, as they try to solve the seemingly worst issue regarding the energy efficiency of the building envelope. [1]. <-**kanskje litt lang setning?**

The thermal properties of the window depend mainly on the outdoor conditions, such as shading, building orientation and type, in addition to the area of the window, its glass properties and glazing characteristics [8]. In window standards the latter is the most important, as the glazing characteristics determines the thermal transmittance coefficient, which again describes how much of the energy of the incident light that goes through the window. [9]. ([1], s.354 avsnitt 2)

One way of improving the thermal efficiency of the window is to add some additional mechanism, allowing the window to change its properties to the environment. An example of such improved windows are called "smart-" or "intelligent windows" and will be discussed in the next section.

(The information for this section was gathered by [1]) **FJERN DETTE eller INKLUDER DETTE PÅ EN BEDRE MÅTE (om det er verdt å nevne)**

[2]

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2 SMART/INTELLIGENT WINDOWS

A smart window or intelligent window is a type of window that manages to regulate the transmitted solar radiation by changing its optical properties. The change in the optical properties can be obtained by adding a controllable absorbing layer on the surface of the glass. The ability of the smart window to allow control of how the solar flux and daylight are transmitted, may help to reduce the electricity consumption regarding heating, cooling and lighting. They should optimally also be able to adapt to the differences created by the seasons. E.g. summertimes have a different demand than wintertimes with respect to the thermal properties of the window. In summertimes the ambient temperature is around or above the comfortable region and the window should therefore possess high reflectance in the infrared region to prevent further increase in temperature. In wintertimes on the other hand, the temperature is below the comfortable level and the reflectance should be low in order to allow the sun to heat up the indoor climate. This in addition to the transmission of light in the visible region, may reduce or remove the need for electrical heating, cooling or lighting such as HVAC devices or light bulbs. [4, 5, 8]

Windows with such a switchable layer can be categorized into two systems: active and passive. The active systems may be for example a switchable glazing with the opportunity to switch from one set of optical properties to another. An example of this is an electrochromic window, which uses a burst of electricity from an external energy source in order to change the opacity of the material. The passive devices on the other hand, do not require an external energy source, but switches automatically subject to environmental change. Examples of such devices are: photochromic windows, which reacts to light and thermochromic windows, which change in accordance to the temperature ([1]:[6]). The latter material will be discussed in more detail in the following section. As shown

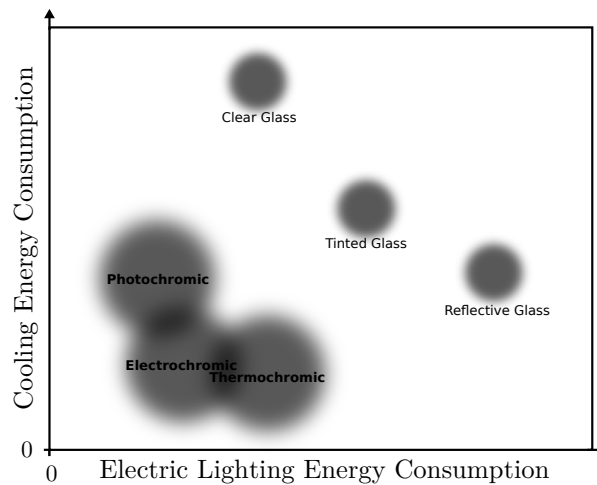


Figure 2.1: Comparison of the electric lighting energy and cooling energy consumption between different glazing types. Adapted from [3, p. 20]. For example, reflective glass reflects a large portion of the incident radiation, both visual light and radiant heat. This leaves it as a good option for hot climates where it can reduce the cooling load of the building. However, due to the low transmission of light additional lighting is required lowering the energy benefit to some extent.

in Figure 2.1 the resulting energy consumption varies for the different window and glazing technologies. It also demonstrates an important fact: even though using reflective glass would reduce cooling loads, a window should also be able to let visible light through. If the transmission of the visible spectrum is too low, it could cause the need for additional lighting, which again would increase the overall energy load ([1], [12]). Electrochromic and thermochromic windows usually result in lower cooling loads. In addition the electrochromic technology requires less energy for lighting due to the thermochromic coatings low optical transmission. However, as argued in the review of Kamalisarvestani et al. [1], this is not enough to exclude thermochromic layers as a good, low-priced alternative [14] <-fikk ikke tilgang, prøv VPN. For instance, a thermochromic window does not need any electrical wires as its electrochromic counterpart and the low visible transmission of the thermochromic windows can be increased by adding small quantities of a foreign material into the thermochromic coating. The process of adding small quantities of another element into a material is called doping and leads to changes in the electrical and optical properties [13, p. 39] (70).

3 THERMOCHROMIC MATERIALS

The technology behind intelligent windows and its diversity, is based on materials that change their optical properties when subjected to some external physical process. These materials are called chromic materials. The word chromic originates from the greek word "Chroma", which means color. If the induced change of optical properties results in changing the spectral reflectance in the visible spectrum, the material will change its color. *?CAN I SAY THIS WITHOUT A REFERENCE? ISN'T IT PRETTY OBVIOUS FROM ALL THE OTHER INFORMATION/ TAKEN FOR GRANTED? IT IS CORRECT RIGHT??* Chromic materials are again subdivided into categories dependent on what triggers their optical change. For example, photochromic and eletrochromic materials are two categories of chromic materials that changes their optical properties when subject to irradiation by light (photons) or an applied electric field, respectively. However, another subcategory is thermochromic materials and will be the category of interest in this assignment ([2],1).

"Thermos" is the greek word for warm or hot. As the name suggests, thermochromic materials change their optical properties, such as color, in response to heat or, in other words, the change in temperature. ([1]:(74)<-ikke tilgang(prøv VPN),[7]). [8] Typically, this change in color happens gradually over a range of temperatures. In this case it is called continuous thermochromism. Discontinuous thermochromism also occurs and involves a structural phase change at a certain characteristic "transition temperature" T_t . This phase change can be of first or second-order in nature, and may be reversible or irreversible ([2]:(1)).

Compounds like inorganic oxides, liquid cryctals ([2]:(2)), conjugated oligomers ([2]:(3)), leuco dyes ([2]:(4)) can exhibit thermochromic color changes reversibly, while thermochromic dyes, usually based on organic compounds, show color temperature dependent changes which are not reversible.

To explain the process behind the chromic behaviour, assume that the thermochromic material is initially in its cold state called the monoclinic state . Here it behaves as a semiconductor, being less reflective especially in the near-infrared(IR) region. Heating the material to a certain temperature, known as the transition temperature, will make it change from the monoclinic state to a rutile state. In the rutile or hot state the material acts like a semi-metal, reflecting a wide range of solar radiation. This change of state is called metal-to-semiconductor transition (MST) [10, p. 4565] and is fully reversible and co-occures with large variations in both electrical and optical properties in the near-IR range [11].

Because of these interesting properties, thermochromic materials have become increasingly important, espacially through the use as "smart coatings". Some potential thin film candidates for smart windows include substances such as Fe_3O_4 , FeSi_4 , NbO_2 , NiS , TiO_2 and VO_2 . [8].

4 THERMOCHROMIC WINDOWS

A thermochromic window, is a window with a thermochromic glazing, allowing the window as a whole to adopt the optical properties of the thermochromic material. Figure 4.1 is a pictorial representation of the influence of the thermochromic coating on the window. Below the transition temperature $T < T_t$, the window should trans-

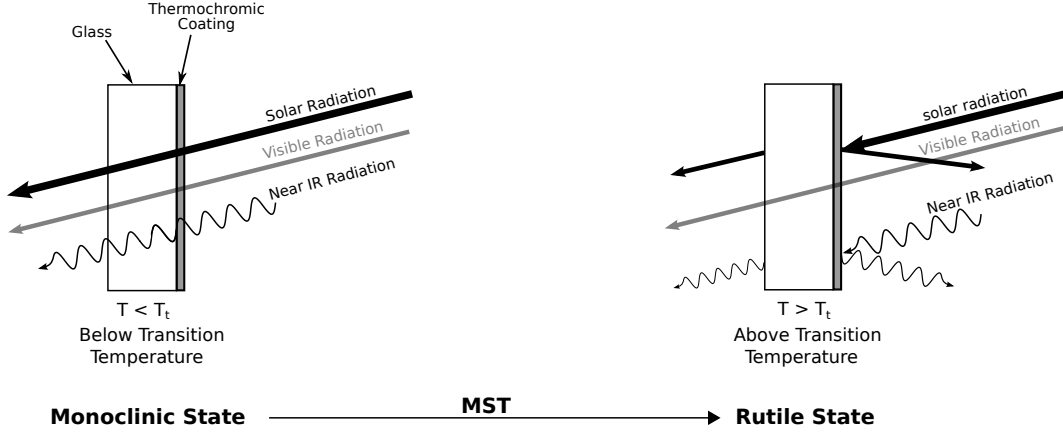


Figure 4.1: Schematic representation of thermochromic materials applied as an intelligent window coating [2].

mit the solar thermal radiation, heating up the interior of the building. If the temperature increases above the transition temperature T_t , the transmission of the thermal radiation should decrease significantly, lowering or removing the necessity of using cooling devices. For this to work, the transition temperature, which for most materials is significantly higher than room temperature, needs to be reduced down to a thermally comfortable level. Similarly to the transmission of the coating, this may be solved through doping with a foreign material or dopant. An example of such a dopant will be discussed in Section 4.2, which contains a closer look at a promising thermochromic coating candidate called vanadium dioxide.

The ideal spectral modulation of the thermochromic coating is given in Figure 4.2. This shows how the cold state should transmit the majority of the solar radiation, here modeled as a black body spectrum. In addition it shows how the hot state should reflect as much of the infrared and solar radiation as possible without compromising the transmission of the visible spectrum. If the transmission of daylight is poor, it would lead to an increase of the electrical load due to the accompanying additional lighting. [1]

As discussed by Blackman [10, p. 4569], the optical transmission of the film is depending on the thickness of the film. Control of the film thickness is crucial. Excessive coating thicknesses may lead to too much blocking of the visual light, leaving the coating unsuitable for architectural application. For the transmission of visible light to

Table 4.1: The ideal optical performance of thermochromic windows (taken from [1]) which adapted it from [12]

State	Monoclinic/cold ($T < T_t$)		Rutile/hot ($T > T_t$)	
Wavelength	Visible(%)	NIR (%)	Visible(%)	NIR (%)
Transmittance(T)	60-65	80	60-65	15
Reflectance(R)	17	12	17	77

be acceptable it should be higher than 60%. The ideal performance of a thermochromic window is shown in Table 4.1, showing that the modulation of the spectrum in the visible region should be the same for both the monoclinic and rutile state. Notice the transmission of 60%-65% of the visible light.

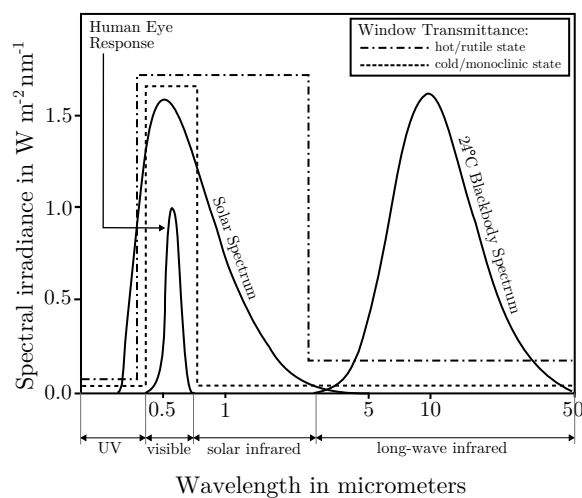


Figure 4.2: The spectral transmittance of a perfect thermochromic window, shown for both cold and hot environments (the monoclinic and rutile state, respectively). Adopted from [1, p. 15]

(The switchable reflective device (or dynamic tintable window))

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4.1 VANADIUM DIOXIDE VO₂; A PROMISING CANDIDATE

The most promising thermochromic material regarding thermochromic intelligent windows is vanadium (IV) oxide. Vanadium oxide can exist in four polymorphic forms; monoclinic, rutile and two metastable forms (2). The metal to semiconductor phase transition from the monoclinic to the rutile state occurs at 68°C and is fully reversible (3). In this transition, large changes in electrical conductivity and optical properties in the near-IR region occur (4), **while the change in optical region is relatively small [7, p. 395]**. Above T_t it behaves as a semi-metal, reflecting to a wide range of solar wavelengths, while below, it behaves as a semiconductor, reflecting significantly less in the near infrared region [10, p. 4565].

The transition temperature of 68°C is relatively low compared other thermochromic materials. 68°C is, however, far from the comfortable temperature region around ~20°C. This would leave the window in its monoclinic state for all natural ambient temperatures, never switching its state and leaving it unsuited as a smart coating [1, p. 358] [13, p. 39].

[1]:

TALK ABOUT DOPING (kamalisarvestani: The size and charge (84,86,87) of dopant ion, film's strain (88,89) as well as variations in electron carrier density are the determinant factors prevailing on the fall or rise of T_t (90)) Many studies regarding vanadium dioxide coatings have reported low transmittance in the visible range as discussed in the review of Kamalisarvestani et al. [1, p.358] and constitutes a the most critical weakness of VO₂ coatings. The switching efficiency η_T , defined as the change in transmittance over the transition temperature T_t , is a measure of the energy-saving efficiency and depends on doping (107,108), the materials microstructure (80,95,109-111) and the film thickness (80,88) (!!!!!Also Blackman [10, p. 4569] talk about the dependency on thickness of VO₂ films!!!! SO include this ref!!). The film thickness is the most important factor of the above parameters. However, because increasing it would reduce the transmittance of visual light, this parameter must be carefully tuned. **???Important? Film thickness:**

For VO₂ the ideal film thickness regarding visual transmission and switching efficiency is be between 40-90nm. Here the maximal thickness should be set correspondingly to the minimum acceptable optical transmission [1, p. 358] [10, p. 4569]. The ideal film would have the maximum acceptable thickness which corresponds to the minimum acceptable optical transmission. In our case this is in the range 70–90 nm thick. Also the film must be adherent and visually appealing.”

4.2 TUNGSTEN DOPING OF VO₂ COATINGS

The most efficient dopant of VO₂ coatings is the chemical element tungsten W. Tungsten is also known as wolfram and can be found in the periodic table under atomic number 74. When used as a dopant in VO₂ it reduces the transition temperature T_t of the MST and can optimally lower T_t down to about 25°C at 2 atom % loading [10, p. 4566]. There are also other problems regarding VO₂ coatings affecting their applicability other than T_t : vanadium dioxide have an unappealing yellow or brown color. However, this is also improved using tungsten as a dopant and give the coating a greener/bluer color. This is depending on the relative amount of tungsten and increases its aesthetical properties [10, p. 4565,4569].

5 BASIC THEORY

5.1 THE ELECTRIC POTENTIAL, LAPLACE'S EQUATION AND THE UNIQUENESS THEOREM

The usual task of electrostatics is to compute the electric field \mathbf{E} given a stationary electric charge distribution $\rho_E \mathbf{r}'$

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \rho(\mathbf{r}') d\mathbf{r}'. \quad (5.1)$$

The notation for Eq.(5.1) can be shown in Figure 5.1 and $\epsilon_0 = 8.85 \cdot 10^{-12} \text{C}^2/\text{Nm}^2$ is the permittivity of free space [2, . 58-62]. However, it is usually simpler to calculate the electric potential Ψ

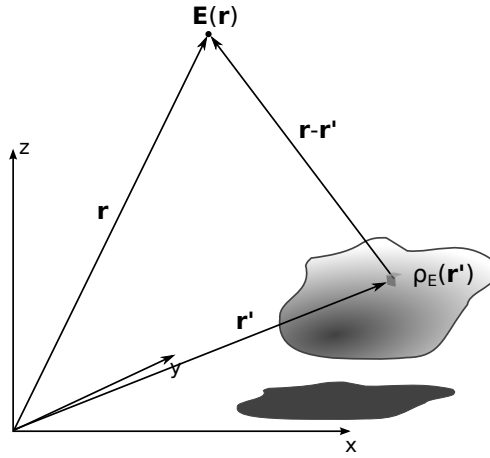


Figure 5.1: The electric field $\mathbf{E}(\mathbf{r})$ (at position \mathbf{r}) due to the charge distribution ρ_E located at \mathbf{r}' .

$$\Psi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') d\mathbf{r}' \quad (5.2)$$

first and then calculate the electric field from

$$\mathbf{E} = -\nabla\Psi. \quad (5.3)$$

This might in some situations, where do not necessarily know ρ but only the total amount of charge, also be to tough to handle analytically. In situations like these it is better to use Poisson's equation

$$\nabla^2\Psi = -\frac{1}{\epsilon_0} \rho, \quad (5.4)$$

which together with appropriate boundary conditions, is equivalent to Eq.(5.2). Very often, we are interested in finding the potential containing no charge (because the charge is located on the outside of our region of interest. In such cases Eq. (5.4) reduces to Laplace's equation ([2], p.110-111)

$$\nabla^2\Psi = 0. \quad (5.5)$$

According to the *Uniqueness Theorems*, the solution to Laplace's equation is uniquely determined in some volume if the potential is specified on the boundary of the volume. This easily extends to Poisson's equation by further requiring, in addition to the potential on the boundary, that the charge distribution throughout the region is known.

When considering conductors, charge are allowed to move freely and might start to rearrange themselves, leading to the *Second uniqueness theorem*, which states that the potential in a given volume, surrounded by conductors is uniquely determined if the total charge on each conductor is given.

The uniqueness theorem grants an enlarged mathematical freedom in the approach of finding the potential of a region of space. This is because the boundary uniquely determines the potential in the region enclosed region and any approach giving the correct boundary conditions would give you the correct potential function through Laplace's equation Eq. (5.5). This allows the use of tricks, like for example the classical *method of images* ([2], p.116-121).

5.2 POLARIZABILITY

When a neutral atom is placed in an electric field \mathbf{E} , the field tries to rip the atom apart by pushing the nucleus in the direction of the field and the electrons in the opposite direction. Because of the attraction between the positive and negative charge within the atom, an equilibrium displacement of the electrons compared to the nucleus is achieved, leaving the atom polarized and giving it a dipole moment. The dipole moment can be approximated by

$$\mathbf{p} = \alpha \mathbf{E}, \quad (5.6)$$

where α is the atomic polarizability and may depend on the detailed structure of the atom. For more complicated situations, like an asymmetrical molecule, the gained dipole moment of the molecule does not necessarily have to be in the same direction as the applied electric field. In such a case, the scalar polarizability in the expression above is replaced by a polarizability tensor

$$\boldsymbol{\alpha} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}. \quad (5.7)$$

In this way, an applied electric field induces many dipole moments in a material. In addition, any polar molecules will be subject to a torque, aligning it to the direction of the field. These two mechanisms leads to the polarization \mathbf{P} of the material

$$\mathbf{P} = \text{dipole moment per unit volume} = \epsilon_0 \chi_e \mathbf{E}. \quad (5.8)$$

In the above expression, there has been assumed a linear dielectric media, where χ_e is the electric susceptibility and depends on the microscopic structure of the material, in addition to the external temperature ([2], p.160-166, 179)

5.3 PLASMONS

5.4 THE DRUDE MODEL [1]

Defining the differences between the electrical properties of metals, semiconductors and insulators is not a trivial matter. To put it simple, metals are good conductors, while semiconductors and insulators are not. However, semiconductors such as silicon conduct electricity relatively well, so the picture is not quite that simple.

A simple model, with fundamental importance regarding electrical conductivity, was suggested by P. Drude in an attempt to explain the observed properties of metals. It is assumed that the electrons in a solid behave like a classical gas and do not interact with each other whatsoever. Coloumb interaction is also neglected. This is known as the *independent electron approximation*. The electron gas can be viewed as negatively charged particles bouncing about immobile positively charged ion cores. The only form of interaction in this model are instantaneous collision between the electrons and ions; see Figure 5.2. The simplification of removing the Coloumb ion-electron interaction is called the *free electron approximation*. The electrons reach thermal equilibrium with the lattice through the collisions, giving them the kinetic energy:

$$\frac{1}{2} m_e v_t^2 = \frac{3}{2} k_B T. \quad (5.9)$$

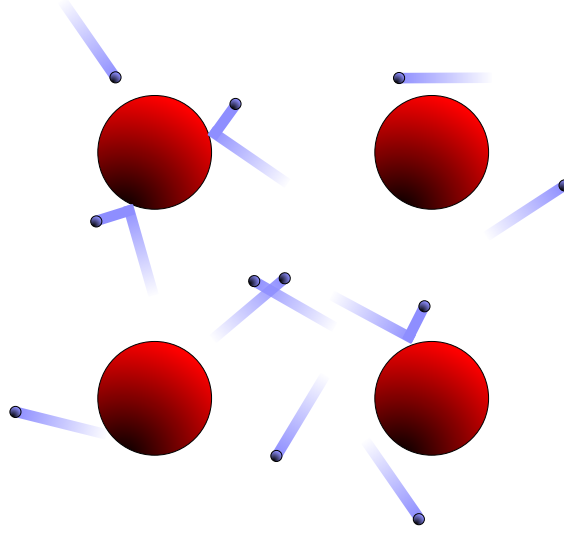


Figure 5.2: The Drude model. A non-interacting electron gas (blue) is swirling around and colliding with stationary positive ion cores (red). Since all Coloumb forces are neglected together with electron-electron collision, this ion-electron interaction is the only one being considered.

The average time between two collisions is called the relaxation time τ , with the corresponding mean free path defined as $\lambda = \tau v_t$. The probability for a electron to collide per unit time is assumed to be $1/\tau$.

It is necessary to determine the conduction electron density $\rho_{c,e}$ in order to describe properties such as electrical conductance. Assuming that every atom contributes every electron in its outermost shell N_e , e.g. that alkali metals contribute $N_e = 1$ and that earch alkaline earth metals contribute $N_e = 2$ etc. The number of atoms $N_a = \rho_m / m_a$, where ρ_m is the density of the metal in $[\text{kg}/\text{m}^{-3}]$ and m_a is the atomic mass in $[\text{kg}]$ (mass per atom).

5.5 CONDUCTIVITY; THE DRUDE MODEL

Subjecting the drude metal of an electric field \mathbf{E} will lead to a drift of the electrons

$$\frac{d\mathbf{v}}{dt} m_e = -e\mathbf{E}, \quad (5.10)$$

where e is the elementary charge. The solution is given by

$$\mathbf{v}(t) = \frac{-e\mathbf{E}t}{m_e}. \quad (5.11)$$

Assuming that the drift montion is destroyed in a collision, the average drift speed of the electrons become

$$\bar{\mathbf{v}}(t) = \frac{-e\mathbf{E}\tau}{m_e}, \quad (5.12)$$

which is very slow compared to the thermal movement of the electrons v_t .

Considering an area A perpendicular to the electric field, the amount of charge passing through the area is $-en_e|\bar{\mathbf{v}}|A$ and the resulting current density would be

$$\mathbf{j} = n\bar{\mathbf{v}}(-e) = \frac{n_e e^2 \tau}{m_e} \mathbf{E} \equiv \sigma \mathbf{E} = \mathbf{E} / \rho. \quad (5.13)$$

This is the familiar Ohm's law, with the conductivity

$$\sigma = \frac{n_e e^2 \tau}{m_e} \quad (5.14)$$

and the resistivity ρ . The e^2 dependence comes from the size of the pulling force due to the electric field, i.e. how fast the particles move, and the other is how the same charge, now moving, defines the current. This also means that we would get the same result for carriers with charge e instead of $-e$, which would be the case for semiconductors with positive holes.

5.6 OPTICAL REFLECTIVITY OF DRUDE METALS

The optical properties of materials are described by the complex refractive index $N(\omega)$ or the dielectric constant $\epsilon(\omega)$. To explain the reflectivity of metals we can consider an electron in an electromagnetic field induced by an optical incident wave with wavenumber $q = 2\pi N/\lambda_0$, where λ_0 is the wavelength of the wave in free space.

If ω is low, we basically retain the DC behavior. However, if ω is so high that $1/\omega \ll \tau$, the electrons does not manage to react fast enough and the collisions with the ions altogether can be ignored (this is fulfilled for optical frequencies when $\tau = 10^{-14}$ s). The electrons can now be treated as completely free, and a single electron follows

$$m_e \frac{d^2 x(t)}{dt^2} = -eE(t) = -eEe^{-i\omega t}. \quad (5.15)$$

A good ansatz for the solution is setting $x(t) = xe^{-i\omega t}$, which mean that the electron is oscillating along with the electric field. This gives an amplitude of

$$x = \frac{eR}{m_e \omega^2}. \quad (5.16)$$

The corresponding polarization due to the dipole moment of $-ex$ for a solid with conduction electron density n_e is

$$P = -n_e ex = -\frac{n_e e^2 E}{m_e \omega^2}. \quad (5.17)$$

From the constitutive relation

$$D = \epsilon \epsilon_0 E = \epsilon_0 E + P, \quad (5.18)$$

we get that

$$\epsilon = 1 + \frac{P}{\epsilon_0 E} = 1 - \frac{n_e e^2}{\epsilon m_e \omega^2} \equiv 1 - \text{frac} \omega_p^2 \omega^2, \quad (5.19)$$

with the plasma frequency ω_p defined as

$$\omega_p = \frac{n_e e^2}{m_e \epsilon_0}. \quad (5.20)$$

We can distinguish between two different cases and resulting outcome can be seen from the the electromagnetic plane wave

$$E(z, t) = E_0 e^{i(2\pi N z / \lambda_0 - \omega t)}. \quad (5.21)$$

In case 1) $\omega < \omega_p$ and ϵ is a real and negative, $\epsilon = \Re\{\epsilon\} < 0$. Therefore, $N = \sqrt{\epsilon}$ is purely imaginary, and the wave penetrating the solid is exponentially damped. Because Eq.(5.15) contain no inelastic properties, nothing is absorbed. The light that is not transmitted into the medium must therefore, due to energy conservation, be reflected back. For $\omega > \omega_p$, the dielectric constant is real and positive, $\epsilon = \Re\{\epsilon\} > 0$, and so is, followingly, the index of refraction. The result is a plane wave that propagates into the metal. This explains why metals are so reflective, or shiny. They are reflective for low-frequency light, but transparent for high-frequency light. The transition happens at the plasma frequency, which can be calculated solely from the conduction electron density of the metal. For most metals, the plasma frequency is in the far UV region, making them reflective in the visible range. Frequently, the plasma energy $\hbar\omega_p$ is used instead of the plasma frequency ω_p .

5.7 SHORTCOMINGS OF THE DRUDE MODEL

The questionable assumptions of the Drude model is the removal of the electron-electron interaction together with all the Coulomb forces. In addition, the assumption of treating the electrons as particles is not justified due to the fact that their de Broglie wavelength, in the case of thermal electrons, is in the order of nanometers. The assumption would however only satisfy electrons moving in structures much larger than the de Broglie wavelength.

The resulting conductivity of the model is not high enough at low temperatures, and is due to the assumption of a fixed mean free path, given by the atomic spacing. Apparently, at low temperature, the electrons manage to sneak past the other electrons and ions.

Also, the conductivity of alloys, in which impurities drastically reduce the conductivity, finds no justification in the Drude model.

5.8 DIELECTRICS

5.9 MICROSCOPIC POLARIZATION

There are several mechanisms causing microscopic electric dipole moments that lead to macroscopic polarization. E.g. displacement of electronic clouds and core, opposite displacement of the ions in a solid or orientation of permanent dipoles such as water molecules, called orientational polarization.

5.10 THE LOCAL FIELD

To calculate the microscopic polarizability α of the atoms making up the solid, start with the constitutive relation and assume that \mathbf{P} can be written as the total dipole moment per unit volume

$$\mathbf{P} = (\epsilon - 1)\epsilon_0 \mathbf{E} = \frac{N}{V} \mathbf{p} = \frac{N}{V} \alpha \mathbf{E}. \quad (5.22)$$

Because a microscopic dipole within the solid does not simply feel the average electric field \mathbf{E} but a microscopic local and stronger electric field \mathbf{E}_{loc} , the polarizability can not be correctly calculated from the above expression. Without derivation, the approximate local field can be given by

$$\mathbf{E}_{loc} = \frac{1}{3}(\epsilon + 2)\mathbf{E}. \quad (5.23)$$

So, with

$$\mathbf{P} = \frac{N}{V} \alpha \mathbf{E}_{loc} \quad (5.24)$$

and approximating the polarization \mathbf{P} with Eq.(5.22), we get the so-called Clausius-Mossotti relation

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} \frac{3\epsilon_0 V}{N}, \quad (5.25)$$

relating the atomic polarizability to the dielectric constant.

5.11 FREQUENCY DEPENDENCE OF THE DIELECTRIC CONSTANT

The frequency dependent permittivity $\epsilon(\omega)$ is usually called the dielectric function. For insulators, $\epsilon(\omega)$ is complex and energy can be resonantly transferred to the solid for certain frequencies. $\epsilon(\omega)$ implies a frequency dependence of the refractive index $N(\omega)$. Most of the frequency dependence can be explained by a simple idea combined with knowledge about the polarization mechanisms and how the different polarization mechanisms manages to keep up with the oscillating electric field. E.g. orientation polarization and ionic polarization does not manage to oscillate fast enough at higher frequencies, while the atomic polarization will, see Figure 5.3.

For a quantitative description of the frequencydependence of ϵ we can consider a simplified version of ionic vibration. Light can couple to optical phonons, e.g in ionic crystals where the phonons correspond to an out-of-phase vibration of the positive and negative ions in the unit cell. These vibrations can be approximated by independent

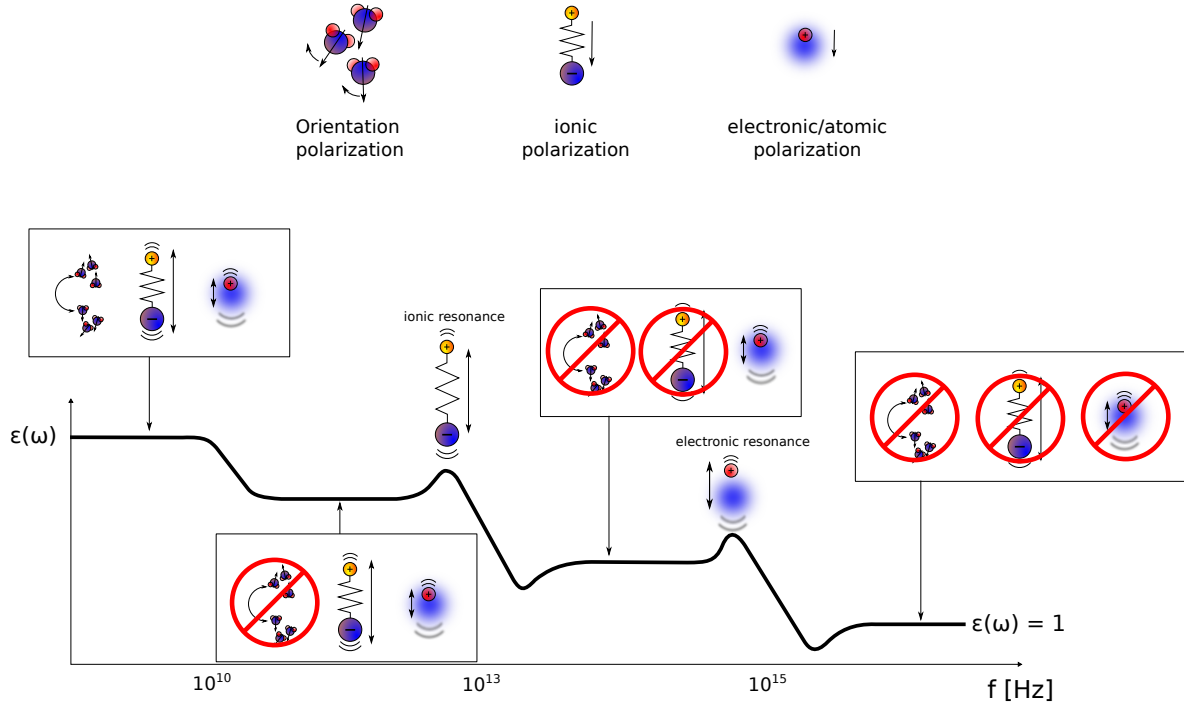


Figure 5.3: The contribution of orientation, ionic and electronic polarization. As the frequency of the applied electric field increases, the different polarization mechanisms fail to remain in step with the field when above a characteristic frequency. At sufficiently high frequencies the material no longer manages to polarize and the dielectric constant drops to 1, corresponding to the permittivity of free space. Figure is adapted from [2].

harmonic oscillators driven by an electric field $E e^{-i\omega t}$, with one such oscillator per unit cell of the crystal. Each oscillator have a resonant frequency of $\omega_o = (2\gamma/M)^{1/2}$, where γ is the force constant and M is the reduced mass of the two ions. The motion is damped by a term proportional to the velocity $\eta dx/dt$ and represents the excitation of other vibrations in the material, due to the large displacement. The resulting equation of motion is that of a driven harmonic oscillator with damping

$$\frac{d^2 x}{dt^2} + \eta \frac{dx}{dt} + \omega_o^2 x = \frac{eE}{M} e^{-i\omega t}. \quad (5.26)$$

A good ansatz for the solution is

$$x(t) = A e^{-i\omega t}, \quad (5.27)$$

resulting in the amplitude

$$A = \frac{eE}{M} \frac{1}{\omega_o^2 - \omega^2 - i\eta\omega} \quad (5.28)$$

$$= \frac{eE}{M} \left[\frac{\omega_o^2 - \omega^2}{(\omega_o^2 - \omega^2)^2 + \eta^2 \omega^2} + \frac{i\eta\omega}{(\omega_o^2 - \omega^2)^2 + \eta^2 \omega^2} \right] \quad (5.29)$$

Using this as the ionic vibration, we can calculate the total polarization for a crystal with N unit cells and volume V . Considering only one type of ions with a density N/V and effective atomic polarizability α , assuming both ionic and atomic polarization, $P_i(\omega)$, $P_a(\omega)$, the result reads

$$P(\omega) = P_i(\omega) + P_a(\omega) = \frac{N}{V} e A(\omega) e^{-i\omega t} + \frac{N}{V} \alpha E e^{-i\omega t}. \quad (5.30)$$

When dealing with two types of ions like in a NaCl crystal, the different polarizabilities can be taken care of by a suitable definition of α . The resulting dielectric function can be calculated from

$$\varepsilon(\omega)E(\omega) = P(\omega) + \varepsilon_0 E(\omega), \quad (5.31)$$

giving

$$\varepsilon(\omega) = \frac{P(\omega)}{\varepsilon_0 E e^{-i\omega t}} + 1 \quad (5.32)$$

$$= \frac{NeA(\omega)}{V\varepsilon_0} + \frac{N\alpha}{V\varepsilon_0} + 1 \quad (5.33)$$

$$= \frac{NeA(\omega)}{V\varepsilon_0} + \varepsilon_{opt}. \quad (5.34)$$

Here, ε_{opt} is the high frequency or optical limit, where the fields move so quickly for the ions to respond and $P_i(\omega) = 0$, i.e.

$$\varepsilon_{opt} = \lim_{\omega \rightarrow \infty} \varepsilon(\omega) = \frac{N\alpha}{V\varepsilon_0} + 1. \quad (5.35)$$

Plugging in the expression for $A(\omega)$ the real and complex values of the dielectric function $\varepsilon(\omega) = \varepsilon_{re}(\omega) + i\varepsilon_{im}(\omega)$ may be written as

$$\varepsilon_{re}(\omega) = \frac{Ne^2}{V\varepsilon_0 M} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \eta^2 \omega^2} + \varepsilon_{opt}, \quad \varepsilon_{im}(\omega) = \frac{Ne^2}{V\varepsilon_0 M} \frac{\eta\omega}{(\omega_0^2 - \omega^2)^2 + \eta^2 \omega^2} \quad (5.36)$$

The behaviour of the result is shown in Figure 5.4. The real part $\varepsilon_{re}(\omega)$ is almost constant away from the resonance

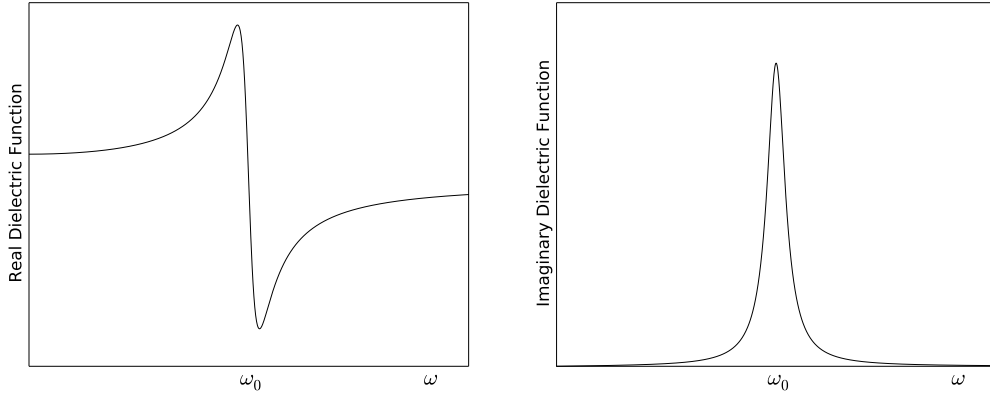


Figure 5.4: The dielectric function of an ionic crystal approximated by a driven harmonic oscillator with damping. The left and right figures show the behavior of the real and imaginary dielectric function close to the resonance frequency ω_0 .

frequency, but its value is higher at lower frequencies due to the loss of the contribution from the ionic polarization. The imaginary part $\varepsilon_{im}(\omega)$ is however zero everywhere except at the vicinity of the resonant frequency, where it shows a peak with a width given by the damping coefficient η .

To understand the meaning of $\varepsilon_{im}(\omega)$ and that the width of its resonance peak is connected to the damping coefficient η , one can consider the energy dissipation in the system. The instantaneous electrical power dissipated per unit volume is given by

$$P(t) = j(t)E(t) = j(t)E e^{-i\omega t} \quad (5.37)$$

where $j(t)$ is the current density. In an insulator, there are no free currents, only polarization currents

$$j(t) = -\frac{\partial D}{\partial t} = -\frac{\partial}{\partial t} \epsilon \epsilon_0 E e^{-i\omega t} = i\omega \epsilon \epsilon_0 E e^{-i\omega t} \quad (5.38)$$

The average dissipated power is found by averaging over one cycle $T = 2\pi/\omega$

$$P = \frac{1}{T} \int_0^T E(t) j(t) dt. \quad (5.39)$$

If ϵ is purely imaginary, $j(t)$ is out of phase with $E(t)$ and their product will always give a nonzero negative value, $-\epsilon_0 \epsilon_{3m}(\omega) E^2$. On the other hand, if ϵ is purely real, the phase shift will be $\pi/2$ and the integral will give $P = 0$. $\epsilon_{3m}(\omega)$ is therefore a measure of the energy dissipation of the electric field due to the solid, and is obviously highest at the resonance.

The discussion explains some of the optical behaviour of the material. This is however not the entire picture. E.g. the frequency dependence in the visible and UV region is not explained here. These effects are due to the valence electrons, which would need a quantum mechanical description of the electronic structure of the solid. From the band structure of solids, a qualitative understanding is obtainable. Figure 5.5 shows regions of high photon absorption due to the excitation of electrons, and how it is given by the imaginary dielectric function $\epsilon_{3m}(\omega) \propto \epsilon_i(\omega)$. Note that the photons do not have enough energy to change the electrons wave vector

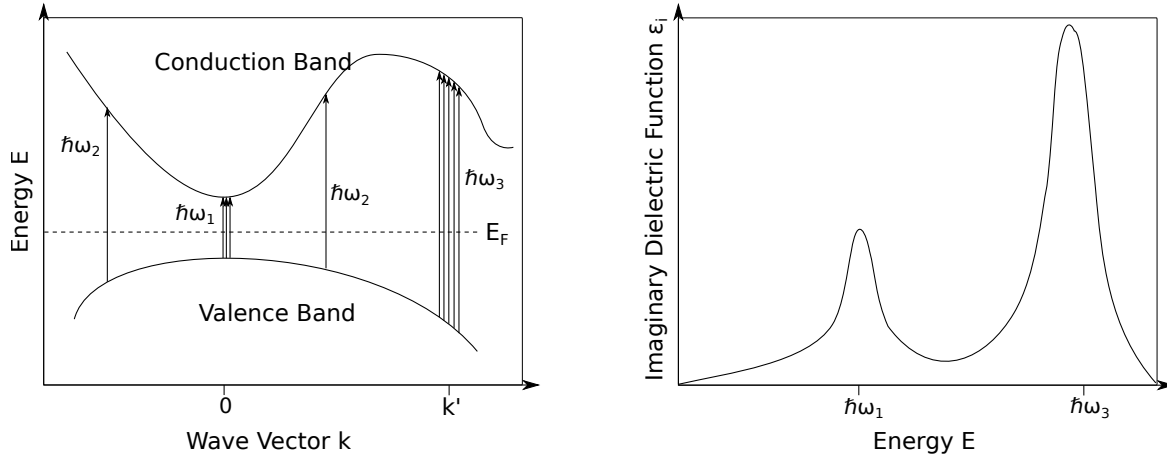


Figure 5.5: The left figure shows the photon-induced transitions between occupied and unoccupied states in the band structure of a solid. E_F is the fermi energy. In the regions where the valence band and conduction bands are parallel, a certain photon energy can excite several states. Here, the parallel regions are located at $\mathbf{k} = 0$ and $\mathbf{k} = \mathbf{k}'$ and result in higher transitions density. These transitions correspond to absorption of the electromagnetic wave given by the imaginary part of the dielectric function ϵ_i . The resulting resonances in ϵ_i due to the absorption of the $\hbar\omega_1$ and $\hbar\omega_2$ transitions are depicted in the right figure.

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5.12 COMPLEX PERMITTIVITY AND INDEX OF REFRACTION [1, p. 169-170]

The complex dielectric constant or relative permittivity $\hat{\epsilon}_r = \epsilon_r + i\tilde{\epsilon}_r$ of a material, is a measure of the material's response subject to an electromagnetic field. Here ϵ_r and $\tilde{\epsilon}_r$ denotes the real and imaginary components, respectively. The relative permittivity is related to the square of the refractive index,

$$N^2 = \hat{\epsilon}_r \quad (5.40)$$

which determines the optical properties of a given material. It is like the dielectric constant complex

$$N = n + ik. \quad (5.41)$$

The real and imaginary refractive indices are denoted by n and k , respectively. The choice of sign convention, i.e. using $n + ik$ rather than $n - ik$, is determined by the choice of the sign in the plane wave solution, $\exp i(\mathbf{q} \cdot \mathbf{r} - \omega t)$, of Maxwell's equations. From Eq.(5.40)

$$\hat{\epsilon}_r = N^2 \quad (5.42)$$

$$\epsilon_r + i\tilde{\epsilon}_r = (n + ik)^2 \quad (5.43)$$

$$\epsilon_r + i\tilde{\epsilon}_r = n^2 - k^2 + i2nk, \quad (5.44)$$

and with some simple comparison, the components of the permittivity can be expressed as

$$\epsilon_r = n^2 - k^2 \quad \tilde{\epsilon}_r = 2nk. \quad (5.45)$$

Taking the absolute value or modulus,

$$|\hat{\epsilon}_r| = \sqrt{\epsilon_r^2 + \tilde{\epsilon}_r^2} \quad (5.46)$$

$$|\hat{\epsilon}_r| = \sqrt{(n^2 - k^2)^2 + (2nk)^2} \quad (5.47)$$

$$|\hat{\epsilon}_r|^2 = n^4 + 2n^2k^2 + k^4 \quad (5.48)$$

$$|\hat{\epsilon}_r|^2 = (n^2 + k^2)^2 \quad (5.49)$$

$$|\hat{\epsilon}_r| = n^2 + k^2, \quad (5.50)$$

and putting it all together, gives the real and imaginary parts of N expressed through the relative permittivity

$$n = \left(\frac{|\hat{\epsilon}_r| + \epsilon_r}{2} \right)^{\frac{1}{2}} \quad k = \left(\frac{|\hat{\epsilon}_r| - \epsilon_r}{2} \right)^{\frac{1}{2}} \quad (5.51)$$

Considering a plane wave with a complex wave vector $\hat{q} = q + i\tilde{q}$ moving in the material [2, p. 402]

$$e^{i(\hat{q}z - \omega t)} = e^{-\tilde{q}z} e^{iqz - \omega t}, \quad (5.52)$$

one sees that the wave is attenuated. The quantity $\alpha \equiv 2\tilde{q}$ is called the absorption coefficient and is proportional to the optical conductivity σ , to $\tilde{\epsilon}$, and to k :

$$n\alpha = \frac{4\pi\sigma}{c} = \frac{\omega}{c} \tilde{\epsilon} \quad (5.53)$$

$$\Downarrow \quad (5.54)$$

$$\frac{\alpha}{2} = \frac{\omega}{c} k = \frac{1}{\delta} \quad (5.55)$$

k is usually called the extinction coefficient and is essentially the ratio of the free-space wave frequency ω to the skin depth δ .

n and k can be found experimentally by measuring the reflectivity R of a bulk, opaque sample, in addition to the transmittance T of a slab, which are given in terms of n and k as

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5.56)$$

$$T = \frac{(1-R)^2 e^{-2\omega kd/c}}{1 - R^2 e^{-4\omega kd/c}}, \quad (5.57)$$

where d is the sample thickness. The slab multiple-reflection effects are averaged, so that interface fringes are not resolved.

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6 THEORY BEHIND THE GRANFILM SOFTWARE

This section recapitulate the theoretical background behind GranFilm, a software used to calculate the optical properties of granular thin films.

6.1 THEORETICAL INTRODUCTION; FLAT SURFACE SCATTERING

Starting from basic electromagnetic theory, the simplest case of electromagnetic scattering is the transmission and reflection of light, hitting a flat, smooth interface between two different half-infinite media. The electric permittivity ϵ and magnetic permeability μ of the media are given with subscript + for the upper media, and – for the lower media, see Figure 6.1. Assuming that the incoming electromagnetic wave is a plane wave, the reflection

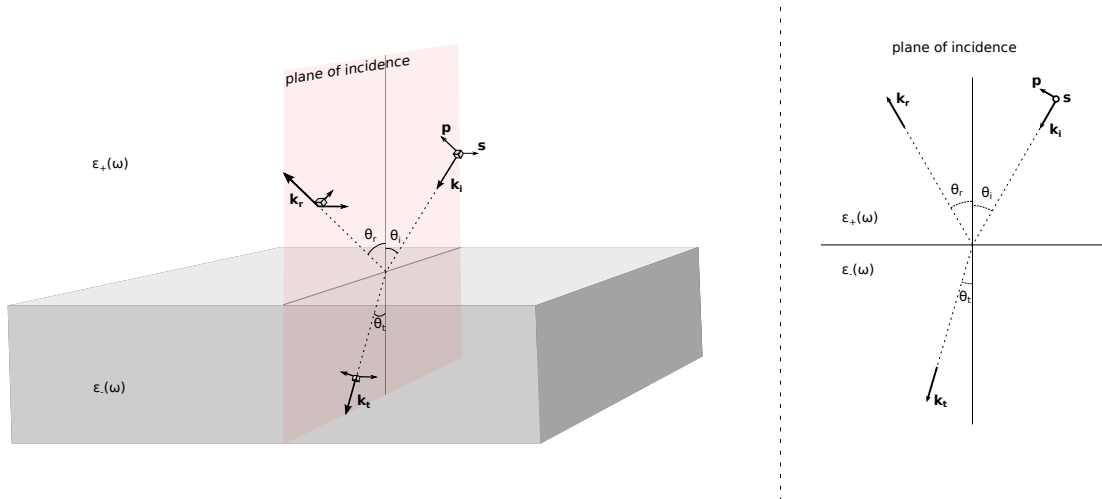


Figure 6.1: The reflection and transmission of an incident electromagnetic plane wave on a flat interface between two media. The dielectric functions for the upper and lower media are $\epsilon_+(\omega)$ and $\epsilon_-(\omega)$, respectively. The polarization direction \mathbf{p} is the polarization parallel to or inside the plane of incidence, while \mathbf{s} , which comes from the german word senkrecht meaning perpendicular, is the perpendicular polarization. The figure is adopted from ([1], p.125).

and transmission of the wave can be calculated from Maxwell's equations,

$$\nabla \cdot \mathbf{D} = \rho_f \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (6.1a)$$

$$\nabla \cdot \mathbf{B} = 0 \quad \nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t}, \quad (6.1b)$$

which describe the general behavior of electromagnetic waves. Here the electric field \mathbf{E} , the electric displacement \mathbf{D} , the magnetic field \mathbf{H} and the magnetic induction \mathbf{B} are pairwise related through

$$\mathbf{D} = \epsilon \mathbf{E}, \quad \mathbf{H} = \frac{1}{\mu} \mathbf{B} \quad (6.2)$$

(assuming linear media) ([2], p.330). Further assuming that there is no free charge or free current at the interface, Maxwell's equation provide the boundary conditions ([2], p.333)

$$D_{\perp}^{+} = D_{\perp}^{-} \quad \mathbf{E}_{\parallel}^{+} = \mathbf{E}_{\parallel}^{-} \quad (6.3a)$$

$$B_{\perp}^{+} = B_{\perp}^{-} \quad \mathbf{H}_{\parallel}^{+} = \mathbf{H}_{\parallel}^{-}. \quad (6.3b)$$

(\perp and \parallel denotes the perpendicular and parallel komponent with respect to the surface boundary. By enforcing these boundary conditions on the incident, reflected and transmitted waves, on the entire boundary, the reflection and transmission coefficients may be calculated. The coefficients are given by

$$R \equiv \frac{I_r}{I_i} \quad T \equiv \frac{I_t}{I_i}, \quad (6.4)$$

$$(6.5)$$

where $I_x, x \in [i, r, t]$ is the intensity or power per unit area stricking/leaving the interface for the incident, reflected and transmitted light, respectively ([2], p.386-391). The calculation can be found in any standard optics textbook *NEED OPTICS BOOK REFERENCE* and gives

$$R = r^2 \quad T = \frac{n_- \cos \theta_t}{n_+ \cos \theta_i}. \quad (6.6)$$

$$(6.7)$$

n_+ and n_- are the indices of refraction for the media above (+) and below (-) the interface, while θ_i and θ_t gives the incident and transmitted lights direction with respect to the surface normal. The coefficients r and t are called the Frensel coefficients and their values depend on the polarization of the incident light. For the flat interface the coefficients take the form *NEED ANOTHER OPTICS BOOK REFERENCE*

$$r_s = \frac{n_+ \cos \theta_i - n_- \cos \theta_t}{n_+ \cos \theta_i + n_- \cos \theta_t} \quad t_s = \frac{2n_+ \cos \theta_i}{n_+ \cos \theta_i + n_- \cos \theta_t}, \quad (6.8a)$$

$$r_p = \frac{n_- \cos \theta_i - n_+ \cos \theta_t}{n_+ \cos \theta_t + n_- \cos \theta_i} \quad t_p = \frac{2n_+ \cos \theta_i}{n_+ \cos \theta_t + n_- \cos \theta_i} \quad (6.8b)$$

so the reflection and transmission are different for the two polarization directions, which can be seen in Figure 6.1.

6.2 SCATTERING ON ROUGH SURFACES: EXCESS FIELDS AND SURFACE SUSCEPTIBILITIES

When moving away from a flat surface, looking at a more complicated geometry of the boundary between the two media, the behavior of the dielectric function gets correspondingly diffucult. Situations like these might be encountered for rough surfaces or granular thin films, where the latter means that a foreign material is distributed as small island on top of a substrate. In these situations the calculation of the Fresnel coefficients turns increasingly complex ([1], p.125).

However, in order to calculate such complicated surfaces, Bedeaux and Vlieger ([1], (7-12)) developed an approach in which the exact knowledge of the electromagnetic fields close to the surface is not required. Their formalism is based on the notion of excess quantities. The excess fields are defined as the differene between the real fields and the bulk fields extrapolated to the surface, where the bulk field simply means the field given sufficiently far away from the scattering surface. E.g. for the electric field $E(r)$ the excess quantity is defined as

$$\mathbf{E}_{ex}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) - \mathbf{E}^{-}(\mathbf{r})\theta(-z) - \mathbf{E}^{+}(\mathbf{r})\theta(z), \quad (6.9)$$

where $\theta(z)$ is the Heaviside function and the superscript \pm are used to indicate the region above (+) and below (-) the dividing interface at $z = 0$. In addition, the optical frequency ω is implicitly included in the notation. Furthermore, the excess field is only significant close to the surface, since $\mathbf{E}(\mathbf{r}, \omega) \rightarrow \mathbf{E}^{\pm}(\mathbf{r}, \omega)$ when $z \rightarrow \pm\infty$.

???is this correct??? By integrating these excess fields along the z-axis, which is set normal to the surface,

$$\mathbf{D}_{\parallel}^s(\mathbf{r}) = \int_{-\infty}^{+\infty} dz \mathbf{D}_{ex,\parallel}(\mathbf{r}), \quad E_z^s(\mathbf{r}) = \int_{-\infty}^{+\infty} dz E_{ex,z}(\mathbf{r}) \quad (6.10a)$$

$$\mathbf{B}_{\parallel}^s(\mathbf{r}) = \int_{-\infty}^{+\infty} dz \mathbf{B}_{ex,\parallel}(\mathbf{r}), \quad H_z^s(\mathbf{r}) = \int_{-\infty}^{+\infty} dz H_{ex,z}(\mathbf{r}), \quad (6.10b)$$

and gathering them in a singular Dirac term, $\delta(z)$, located at the surface ($z=0$) (see Figure 6.2, the fields may be

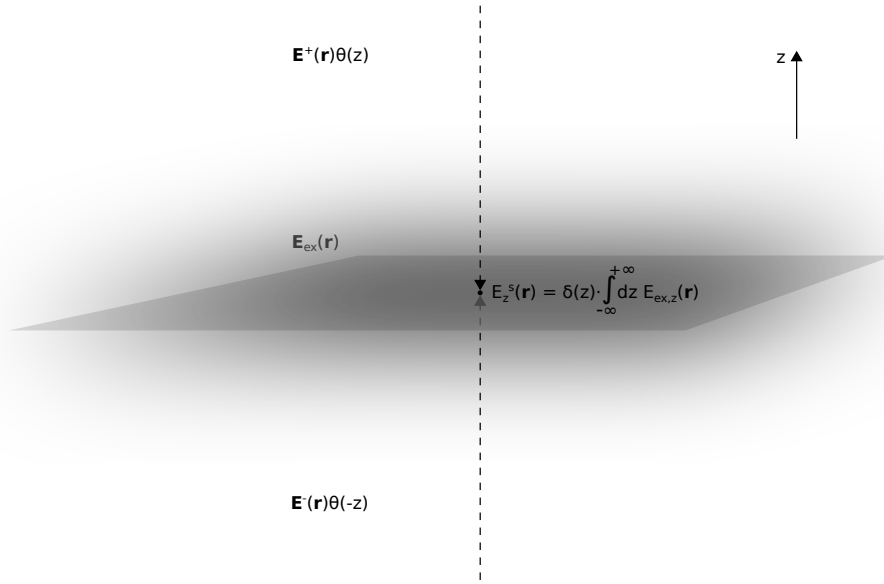


Figure 6.2: The excess fields are integrated over all values of z over the entire surface. Here this is visualized for the electric excess field, visualized by the fog surrounding the surface, as the excess field, is only significant close to the surface. Note however that the excess field is complicated and not correctly represented by the fog. ([1], p.126).

rewritten on the form (here shown for just the electric field)

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^-(\mathbf{r})\theta(-z) + \mathbf{E}^s(\mathbf{r})\delta(z) + \mathbf{E}^+(\mathbf{r})\theta(z). \quad (6.11)$$

Demanding that the fields given by Eq. (6.11) fulfill the Maxwell equations ([1], (7-9)) one ends up with the following boundary conditions

$$[\mathbf{E}_{\parallel}^+(\mathbf{r}) - \mathbf{E}_{\parallel}^-(\mathbf{r})] \Big|_{z=0} = i\omega \hat{z} \times \mathbf{M}_{\parallel}^s(\mathbf{r}_{\parallel}) - \nabla_{\parallel} P_z^s(\mathbf{r}_{\parallel}) \quad (6.12a)$$

$$[D_z^+(\mathbf{r}) - D_z^-(\mathbf{r})] \Big|_{z=0} = -\nabla_{\parallel} \mathbf{P}_{\parallel}^s(\mathbf{r}_{\parallel}) \quad (6.12b)$$

$$[\mathbf{H}_{\parallel}^+(\mathbf{r}) - \mathbf{H}_{\parallel}^-(\mathbf{r})] \Big|_{z=0} = i\omega \hat{z} \times \mathbf{P}_{\parallel}^s(\mathbf{r}_{\parallel}) - \nabla_{\parallel} M_z^s(\mathbf{r}_{\parallel}) \quad (6.12c)$$

$$[B_z^+(\mathbf{r}) - B_z^-(\mathbf{r})] \Big|_{z=0} = -\nabla_{\parallel} \mathbf{M}_{\parallel}^s(\mathbf{r}_{\parallel}), \quad (6.12d)$$

which is derived in Vlieger and Bedaux's *Optical Properties of Surfaces* (p.21). Here ∇_{\parallel} is the nabla operator parallel to the surface, while z denotes the vector component in the direction normal to the surface at $z = 0$. In addition,

the quantities with superscript s are the so-called excess polarization and magnetization densities

$$\mathbf{P}^s(\mathbf{r}_{\parallel}) = (\mathbf{D}_{\parallel}^s(\mathbf{r}_{\parallel}), -\varepsilon_0 E_z^s(\mathbf{r}_{\parallel})) \quad (6.13a)$$

$$\mathbf{M}^s(\mathbf{r}_{\parallel}) = (\mathbf{B}_{\parallel}^s(\mathbf{r}_{\parallel}), -\mu_0 H_z^s(\mathbf{r}_{\parallel})), \quad (6.13b)$$

Here, in Eq.(6.13), the quantities on the right hand side are the integrated excess fields. Even though Maxwell's equations have been included, demanding that the fields follow the boundary conditions of (6.12), they do not uniquely determine the physical situation. Maxwell's equations in matter (6.1), given in Section 6.1, includes \mathbf{E} and \mathbf{D} , together with \mathbf{B} and \mathbf{H} , but does not state how they depend on each other. In other words, Eq. (6.1) does not contain more information than Maxwell's equations given in free space. So, to fully explain how the fields interact with material and the interface, constitutive relations characteristic to the surface must be given (like the relations in Eq.(6.2) given for the flat interface example) ([2], p. 330). The constitutive relations link the interfacial polarisation and magnetization density ($\mathbf{P}^s(\mathbf{r}_{\parallel})$ and $\mathbf{M}^s(\mathbf{r}_{\parallel})$) and the bulk fields extrapolated to the surface. If the perturbed surface layer thickness d is negligible compared to the optical wavelength λ , the excess fields are only significant or non-negligible close to the surface, which followed from the notation for the excess fields assumed earlier in Eq. (6.9). Because of this, the constitutive relations are local and the extrapolated bulk fields may be written on the form $\mathbf{E}_{\parallel,\Sigma} = \{\mathbf{E}_{\parallel}^+(\mathbf{r}_{\parallel}) + \mathbf{E}_{\parallel}^-(\mathbf{r}_{\parallel})\}/2$. For simplicity we restrict our discussion to non-magnetic materials, i.e. that $\mathbf{M}^s(\mathbf{r}_{\parallel}) = 0$. The simplest constitutive relation can be written on the form

$$\mathbf{P}^s(\mathbf{r}_{\parallel}) = \xi_e^s [\mathbf{E}_{\parallel,\Sigma}(\mathbf{r}_{\parallel}), -D_{z,\Sigma}(\mathbf{r}_{\parallel})]. \quad (6.14)$$

By further assuming that the interface is homogeneous and isotropic, the interfacial tensor reduces to a diagonal matrix:

$$\xi_e^s = \begin{bmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \beta \end{bmatrix}, \quad (6.15)$$

With the first order surface susceptibilities γ and β . The reason why they are called first order susceptibilities is because the discussion above limits the dependence between the integrated excess quantities and the extrapolated bulk fields to a local relation (second order would require a spatial relation). In fact, even though they are not included in this discussion, GranFilm also takes account for the non-local dependence, described by the constitutive coefficients of second order δ and τ ([1], (7,15)). These quantities are of the order d/λ smaller than the first order coefficients. Linear combinations of δ and τ together with the first order susceptibilities γ and β can construct invariants, which are independent of the choice of the separation surface. Furthermore, the Fresnel quantities, which all are measurable, are also independent of where we choose to put the surface in our coordinate system and can be uniquely expressed as a function of these constructed invariants. This discussion will continue to only consider the first order susceptibilities γ and β , which are the dominating factors when considering granular layers consisting of metallic islands.

6.3 THE FRESNEL COEFFICIENTS

Using the same method as for the flat Fresnel surface, the Fresnel coefficients in terms of the surface susceptibilities can be derived. The derivation is tedious and will not be done here. It can however be found in Bedeaux and Vlieger's book ([3], p.45) ([6], p.10). In addition to the classical approach, the excess field boundary conditions (6.12), together with the constitutive relation between the interface and the extrapolated bulk fields (6.14). A property of this approach, is that the complicated surface, approximated by the perturbed layer, does not change the fact of *Snell's law*, which pops out of the boundary conditions when calculating the classical flat surface problem ([2], p388). In other words,

$$\theta_i = \theta_r \quad (6.16a)$$

$$n_+ \sin \theta_i = n_- \sin \theta_t. \quad (6.16b)$$

is still used to find the angle of incidence θ_i , reflection θ_r and transmission θ_t . They are, so to speak, unmodified by the perturbed layer. However, the Fresnel coefficients, which decide the reflection and transmission amplitudes, do depend on the perturbed layer through the surface susceptibilities. For s-polarization, the resulting Fresnel

coefficients are given by

$$r_s(\omega) = \frac{n_- \cos \theta_i - n_+ \cos \theta_t + i(\omega/c)\gamma}{n_- \cos \theta_i + n_+ \cos \theta_t - i(\omega/c)\gamma} \quad (6.17a)$$

$$t_s(\omega) = \frac{2n_- \cos \theta_i}{n_- \cos \theta_i + n_+ \cos \theta_t - i(\omega/c)\gamma}. \quad (6.17b)$$

For p-polarization the expressions are more complicated

$$r_p(\omega) = \frac{\kappa_- (\omega) - i(\omega/c)\gamma \cos \theta_i \cos \theta_t + i(\omega/c)n_- n_+ \epsilon_- \beta \sin^2 \theta_i}{\kappa_+ (\omega) - i(\omega/c)\gamma \cos \theta_i \cos \theta_t - i(\omega/c)n_- n_+ \epsilon_- \beta \sin^2 \theta_i}, \quad (6.18a)$$

$$t_p(\omega) = \frac{2n_- \cos \theta_i [1 + (\omega/2c)^2 \epsilon_- \gamma \beta \sin^2 \theta_i]}{\kappa_+ (\omega) - i(\omega/c)\gamma \cos \theta_i \cos \theta_t - i(\omega/c)n_- n_+ \epsilon_- \beta \sin^2 \theta_i}, \quad (6.18b)$$

where there has been introduced two quantities κ_{\pm} defined as

$$\kappa_{\pm} = [n_+ \cos \theta_i \pm n_- \cos \theta_t] \left[1 - \frac{\omega^2}{4c^2} \epsilon_- \gamma \beta \sin^2 \theta_i \right]. \quad (6.18c)$$

The simplicity of the expressions for s-polarization (6.17) compared to p-polarization (6.18), is due to the fact that s-polarized light only manages to excite modes parallel to the surface. This is reflected in the equations by the fact that $r_s(\omega)$ and $t_s(\omega)$ only depend on the parallel surface susceptibility γ . P-polarized light on the other hand, can excite modes both parallel and perpendicular to the interface, and gives rise to the increased complexity of $r_p(\omega)$ and $t_p(\omega)$, with the dependency of both γ and β .

If the surface susceptibilities in the expressions above are set to zero ($\gamma = \beta = 0$), this means that the perturbation from the flat interface, caused by the granular layer, disappears and the Fresnel coefficients, (6.17) and (6.18), reduce to the flat Fresnel coefficients, (6.8a) and (6.8b), respectively.

In addition to the source frequency ω , the refractive indices n_{\pm} and the incident angle θ_i are input parameters. The three latter provide, through Snell's law (6.16) as mentioned above, the calculation of the angle of transmittance θ_t . However, the surface susceptibilities γ and β are not known and, in order to calculate the Fresnel coefficients for the perturbed surface layer, these quantities must be found.

6.4 SURFACE SUSCEPTIBILITIES OF ISLAND LAYER

To this point, there has been no assumptions regarding the geometrical nature of the surface layer. The kind of layer to be considered is a discontinuous thin film of nm-sized island, constituting a granular layer. If the islands are much smaller than the optical wavelength, the scattering from the granular film will be negligible and the resulting angular distribution of light will be similar to that of a flat interface ([?].p.11, (2,p.99) <- **fjern Lie, sjekk og bruk kilde?**). In this case, the density of islands, or the number of island per unit surface area ρ , together with their ability to react to the applied field, decide the surface polarization density $\mathbf{P}^s(\mathbf{r}_{\parallel})$

$$\gamma = \rho \alpha_{\parallel} \quad \beta = \rho \alpha_{\perp} \quad (6.19)$$

The surface's ability to react to the applied field is called the polarizability α of the surface, where α_{\parallel} is the polarizability parallel to the surface, while α_{\perp} is perpendicular to the surface. ([?], (7,11,12,24))

In other words, the optical properties in this situation is essentially driven by the polarizability of the island. The *GranFilm* software, supports the calculation of both truncated spheres and truncated oblate or prolate spheroids. These two particle shapes can represent a great number of experimental situations, with the latter including shapes ranging from discs to needles. ([1], p.128)

To calculate the surface polarizabilities, the first step is to solve Laplace's equation for the electrostatic potential

$$\nabla^2 \Psi(\mathbf{r}) = 0 \quad (6.20)$$

in the quasi-static limit. An easy way to understand the quasistatic limit of Maxwell's equations is, as stated in ([4],p.238), to let $c \rightarrow \infty$, which would neglect all effects due to time retardation. This means that any charge or

current distribution at any instant in time, would decide the resulting fields at the same instant, in all of space. In other words: the effect of the sources will be instantaneous. The validity of the result depends on the distance to the source and how fast the fields are fluctuating, making the approximation valid if the distances are sufficiently short or if the fluctuations of the fields are sufficiently slow ([2], p.308-309). In the case of the granular film, the approximation is valid for sub-wavelength-sized island, in correspondence to the assumption of the layer thickness compared to the wavelength of the incident light.

Assuming spherical island geometry, the potential can be expanded in a multipolar basis of separable solutions to (6.20)

$$\Psi(\mathbf{r}) = \sum_{lm} A_{lm} r^{-l-1} Y_l^m(\theta, \phi) + \sum_{lm} B_{lm} r^l Y_l^m(\theta, \phi) \quad (6.21)$$

Here (r, θ, ϕ) are the spherical coordinates centered at the expansion point, A_{lm} and B_{lm} are the multipole expansion coefficients and $Y_l^m(\theta, \phi)$ are the spherical harmonics. The coordinate system for the expansion is

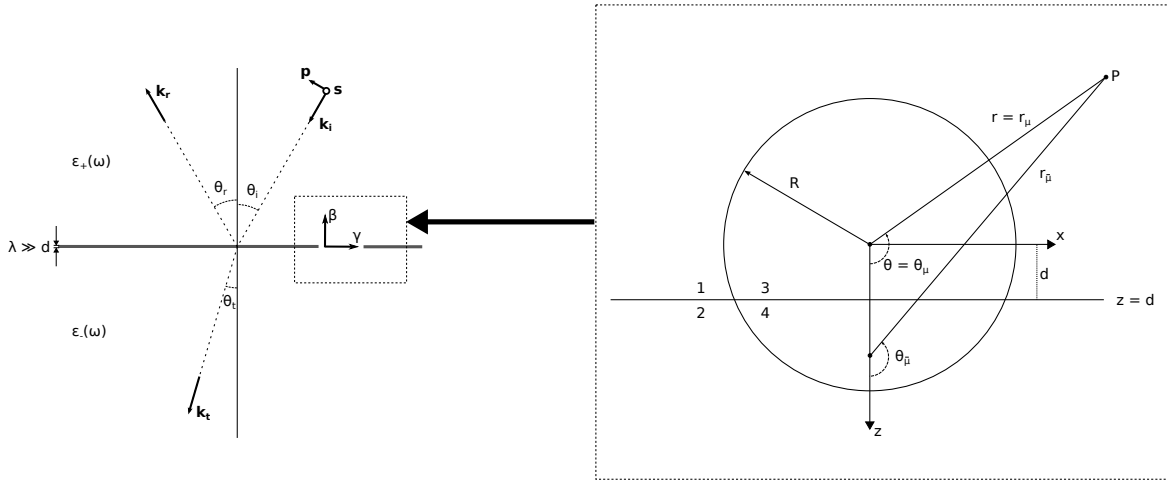


Figure 6.3: To the left: the transmission and reflection of a perturbed surface layer with thickness d , which is assumed to be much smaller than the optical wavelength λ of the incoming wave. The reflection and transmission amplitudes depend on the surface susceptibilities. The first order surface susceptibilities, γ and β , describe the ability of the surface to polarise in the parallel or perpendicular direction. These coefficients can be calculated from evaluating the geometry of the truncated spheres (shown to the right), making up the granular thin film ([1], p.126). Adopted from ([1], p.125)

given in Figure 6.3, with μ denoting the center of expansion, which may be centered at the truncated sphere or varied along the vertical symmetry axis. To deal with the boundary truncating the sphere, the classical image technique is used ([1], (13)). This is done by having a image expansion center located at the opposite side of the surface, compared to μ , inside the substrate. The image expansion point is denoted by $\bar{\mu}$. **Should I also mention t_r and the difference between $t_r > 0$ and $t_r < 0$?** As shown in Figure 6.3, mathematical approach assumes 4 different media, even though region 4 is part of the substrate. When specifying the material in the software region 2 and 4, which constitute the substrate, are usually set to be the same. Using Eq.(6.21) to expand the potential

around the expansion center and the image, the potential in the different regions take the form:

$$\Psi_1(\mathbf{r}) = \Psi_i(\mathbf{r}) + \sum_{lm}^{l \neq 0} A_{lm} r_\mu^{-l-1} Y_l^m(\theta_\mu, \phi_\mu) + \sum_{lm}^{l \neq 0} A_{lm}^r r_{\bar{\mu}}^{-l-1} Y_l^m(\theta_{\bar{\mu}}, \phi_{\bar{\mu}}) \quad (6.22a)$$

$$\Psi_2(\mathbf{r}) = \Psi_t(\mathbf{r}) + \sum_{lm}^{l \neq 0} A_{lm}^t r_\mu^{-l-1} Y_l^m(\theta_\mu, \phi_\mu) \quad (6.22b)$$

$$\Psi_3(\mathbf{r}) = \psi_0(\mathbf{r}) + \sum_{lm}^{l \neq 0} B_{lm} r_\mu^l Y_l^m(\theta_\mu, \phi_\mu) + \sum_{lm}^{l \neq 0} B_{lm}^r r_{\bar{\mu}}^l Y_l^m(\theta_{\bar{\mu}}, \phi_{\bar{\mu}}) \quad (6.22c)$$

$$\Psi_4(\mathbf{r}) = \psi_0(\mathbf{r}) + \sum_{lm}^{l \neq 0} B_{lm}^t r_\mu^l Y_l^m(\theta_\mu, \phi_\mu) \quad (6.22d)$$

Here, the $r^l|_{l=0}$ terms of the expansion are constant and have been extracted, giving the value $\psi_0(\mathbf{r})$ inside the sphere (region 3 and 4, see Fig.6.3). The negative terms $r^{-l-1}|_{l=0} = r^{-1}$ represents free charge, which has been assumed to be zero, and are removed. Outside the sphere (region 1 and 2) the potential is set to zero, simply because the potential reference point can be chosen freely. In addition to the $l = 0$ -terms, the incident field gives rise to the potential $\Psi_i(\mathbf{r})$. Some of the incident light is transmitted directly into the substrate and the resulting scalar field is given by $\Psi_t(\mathbf{r})$. **Burde kanskje ta med at $\Psi_i(\mathbf{r}), \Psi_t(\mathbf{r}) \sim -\mathbf{r} \cdot \mathbf{E}_0$. Men forstår det ikke... (se evt. M.thesis Leif Amind Lie)** Comparing Eqs. (6.22) to Eq. (6.21), note that all the r^l -terms in region 1 and 2, r^{-l-1} -terms in region 3 and 4 are removed due to the divergence of the potential as $r \rightarrow \infty$ and $r \rightarrow 0$, respectively.

The boundary conditions for the electric potential is given by ([2], p.89-90)

$$\varepsilon_i(\omega) \partial_n \Psi_i(\mathbf{r}) = \varepsilon_j(\omega) \partial_n \Psi_j(\mathbf{r}) \quad \Psi_i(\mathbf{r}) = \Psi_j(\mathbf{r}) \quad (6.23)$$

where $\partial_n = \hat{n} \cdot \nabla$ is the derivative with respect to the normal direction \hat{n} to the boundary surface, and the indices $i, j \in \{1, 2, 3, 4\}$, $i \neq j$ denotes the different media included at the different boundaries. From the boundary conditions the relation between the multipole coefficients are found

$$A_{lm}^r = (-1)^{l+m} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} A_{lm} \quad (6.24a)$$

$$A_{lm}^t = \frac{2\varepsilon_1}{\varepsilon_1 + \varepsilon_2} A_{lm} \quad (6.24b)$$

$$B_{lm}^r = (-1)^{l+m} \frac{\varepsilon_3 - \varepsilon_4}{\varepsilon_3 + \varepsilon_4} B_{lm} \quad (6.24c)$$

$$B_{lm}^t = \frac{2\varepsilon_3}{\varepsilon_3 + \varepsilon_4} B_{lm}. \quad (6.24d)$$

However, there are still 4 unknowns for each multipole order (every configuration of l and m). By using the orthogonality of the spherical harmonics $Y_l^m(\theta, \phi)$ to treat the boundary of the sphere, called the weak formulation of the boundary conditions, give two infinite linear systems for the multipolar coefficients A_{lm} and B_{lm} for $l = 1, m = 0, \pm 1$. To solve this system in practice, some cut-off value $l = M$ for the expansion is set. Based on investigations by Simonsen and Lazzari [5] a truncation at $M = 16$ appeared to be sufficient in most cases. This result is based on post-checking the boundary condition for the potential and the normal displacement at the surface; and convergence tests of the first term of the multipolar expansion. Keep in mind, that for cases like spherical caps (truncated at the upper hemisphere) or entire spheres on top of a substrate the convergence could be slower, requiring a truncation $M > 16$. Finally, knowing the first multipolar coefficients the polarizability of the islands can be found

$$\alpha_\perp \simeq A_{10} \quad \alpha_\parallel \simeq A_{11}. \quad (6.25)$$

The first $l = 0$ terms of region 1 A_{lm} are representing the dipole contribution, which dominates in the far-field limit ([?]: Bedeaux and Vlieger->(2), **Må sjekkes!**).

6.5 INTER-ISLAND COUPLING; COLLECTIVE CONTRIBUTION

So far, the discussion has only included the response of a single island and would perhaps give reasonable result in the low coverage limit. However, this would lead to an increase in error for larger coverages and create the need for a correction due to the increasing island-island interaction ([2], p. 20). By assuming that the islands are sufficiently close to one another such that their mutual separation is negligible compared to the optical wavelength, a correction to the low-coverage result can be obtained. In this limit, the islands would be excited by the same incident field and have similar responses to the field. Assuming a dipole response, the islands would be affected by the dipole fields excited in the neighboring particles. If the spheres are truncated by the substrate through their lower hemisphere, the modified polarizabilities compared to the isolated polarizabilities, α_{\perp} , α_{\parallel} , become

$$\alpha_{\perp}^{\text{mod}} = \frac{\alpha_{\perp}}{1 - 2\alpha_{\perp} I_{\perp}^{20}} \quad \alpha_{\parallel}^{\text{mod}} = \frac{\alpha_{\parallel}}{1 + 2\alpha_{\parallel} I_{\parallel}^{20}}. \quad (6.26)$$

The defined functions in the correction are called the interaction functions

$$I_{\perp}^{20} = \frac{1}{\sqrt{20\pi}L^3\epsilon_-} \left[S_{20} - \left(\frac{\epsilon_- - \epsilon_+}{\epsilon_- + \epsilon_+} \right) \tilde{S}_{20}^r \right] \quad (6.27a)$$

$$I_{\parallel}^{20} = \frac{1}{\sqrt{20\pi}L^3\epsilon_-} \left[S_{20} + \left(\frac{\epsilon_- - \epsilon_+}{\epsilon_- + \epsilon_+} \right) \tilde{S}_{20}^r \right], \quad (6.27b)$$

where

$$S_{20} = \sum_{i \neq 0} \left(\frac{L}{r} \right)^3 Y_2^0(\theta, \phi) \Big|_{r=R_i} \quad (6.28a)$$

$$S_{20}^r = \sum_{i \neq 0} \left(\frac{L}{r} \right)^3 Y_2^0(\theta, \phi) \Big|_{r=R_i^r} \quad (6.28b)$$

are the direct and image lattice sums, describing the interaction with the other direct and image dipoles, respectively. L stands for the lattice constant. The $i = 0$ term in the summation gives the contribution from the interaction with the corresponding image of an island. This is taken into account when calculating the isolated response and is therefore not needed in Eq.(6.28). The validity of the dipolar approximation was tested by Lazzari and Simonsen for hemispherical silver islands layed out in a hexagonal pattern on a MgO substrate ([1], p.129-130). The polarizabilities were computed for $M = 16$ and showed that the relative error of the dipole approximation compared quadrupole approximation is *sim*1% up to 40% coverage, which is higher than the interesting limits encountered in experiments.

the fields above $E^+(\mathbf{r})$ and below $E^-(\mathbf{r})$ the interface can be calculated for a incident plane wave (same goes for \mathbf{B} , \mathbf{D} and \mathbf{H}). So far, the boundary between the two half-infinite media has been considered to be a sharp, flat discontinuity in $\epsilon(z)$ and $\mu(z)$. As soon as the surface roughness, thickness and/or impurities are taken into account, the complexity of the problem increases.

Føler jeg burde ha referance til masteroppgaven jeg har sett på også... er dette en grei ting å gjøre?

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7 METHOD

By searching through various scientific articles, thermochromic data for a material in the form of either a complex dielectric constant $\hat{\epsilon}(\omega, T)$ or complex refractive index $N(\omega, T)$ was found. By the use of a program called ENGAUGE DIGITIZER graphically represented data, such as graphs or plots, could be extracted for use in numerical calculations. ENGAUGE DIGITIZER is an open source digitizing software and can be found on <http://digitizer.sourceforge.net/>. It can convert image files of type .bmp, .jpeg or other, containing a graph or a map, into numbers. The conversion from graphical to numerical data is obtained through defining three points in the image, e.g. the origin, largest x-value and largest y-value for a function $y = f(x)$, which define the x,y-axes together with their scale. The target data can be marked automatically or manually, depending on the quality of the image. The data can then be exported to a spreadsheet and used in numerical calculation.

The material data input to be read by GRANFILM must however be on a specific form. GRANFILM requires a complex refractive index N as a discrete function of energy or wavelength. The real and imaginary values of N must be given for each point of its domain. In addition, the values of the domain must consist of equidistant values. The resulting data through the use of ENGAUGE DIGITIZER is not equidistant and because the real and imaginary data is usually extracted from different image files, their values do not correspond to the same discrete domain.

Because of this mismatch between the extracted image data and the input file format of GRANFILM, some conversion had to be done. A generic conversion program was made, set to handle data of either N or $\hat{\epsilon}$ in some expected units, such as $\hat{\epsilon}(E, T)$, $N(E, T)$, with $[E]=\text{eV}$, and $\hat{\epsilon}(\lambda, T)$, $N(\lambda, T)$, with $[\lambda] \in \{\text{m}, \mu\text{m}, \text{nm}\}$. It was also encountered data as a function of frequency in Hz. This situation was not implemented, but should have been included if further work were to be made.

The converted data were then stored in a database with one file representing the spectral optical index, $N(E, T_i)$, $N(\lambda, T_i)$, for a specific temperature T_i . The data could then be fed into GRANFILM one file at the time and simulated.

Due to lacking overlap between the already included material data in GRANFILM and the new extracted data, only data from Kang et al. [1, p. 3], containing the dielectric constant of VO_2 have been used. Based on the produced code, it would not be a lot of work extracting more data to expand the thermochromic database, maybe including several thermochromic materials. However, the extraction of the data with ENGAUGE DIGITIZER depends on the quality and separation of the functions and could in the worst cases be very tedious.

7.1 CHOICE OF PARAMETERS

Due to the quasistatic approximation where it was assumed that the layer thickness or the size of the spheres should be negligible compared to the wavelength of the incident light $d, r \ll \lambda$.

- talk about the corresponding interval we're simulating (the energy range and the corresponding wavelength range).
- Then talk about how large sphere sizes we're then allowed to use.
- relate this up towards the mentioned thickness mentioned by the sources and comment on it.

(...)can not use the thin optimal film layer thickness between 40-90nm as mentioned by Kamalifarvestani et al. [1] and Blackman et al. [10].

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Er dette greit? Finner ikke sidetall osv.

8 RESULTS

The following simulations are done with an incident plane wave of direction $(\theta_i, \phi_i) = (45^\circ, 0^\circ)$, on VO_2 particles supported by a SiO_2 substrate with truncation ratio $t_r = 0$. The surrounding medium is air with $\epsilon(\omega, T) = 1$. The

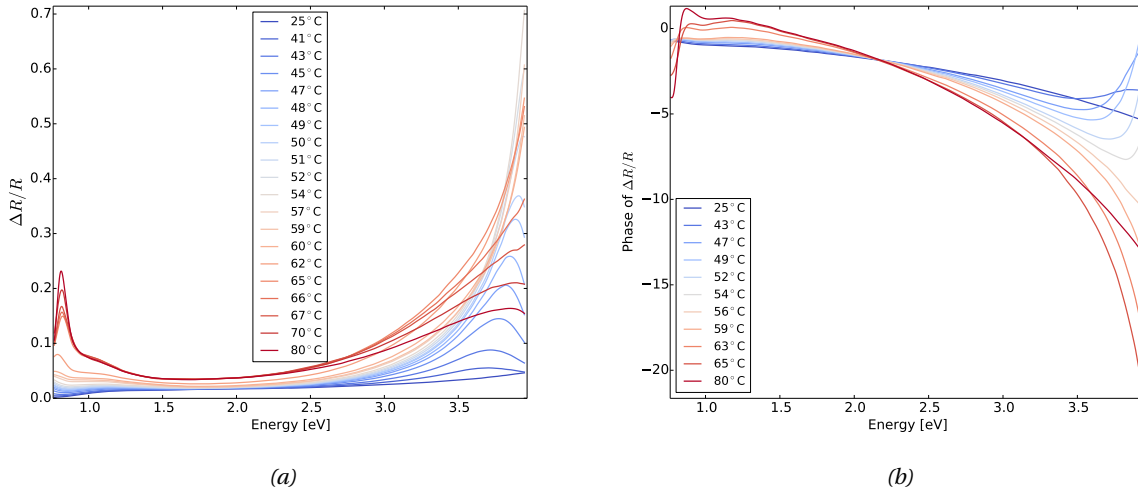


Figure 9.1: Relative reflectance $\Delta R/R$

particles are arranged in a square lattice with lattice constant $L = 45\text{nm}$ and the particle-particle interaction is given by a dipole contribution. The multipole truncation is set to $M = 16$.

9 SIMULATION 1; $R = 10\text{nm}$, P-POLARIZED INCIDENT LIGHT

10 SIMULATION 2; $R = 10\text{nm}$, S-POLARIZED INCIDENT LIGHT

11 SIMULATION 3; $R = 15\text{nm}$, P-POLARIZED INCIDENT LIGHT

12 SIMULATION 4; $R = 15\text{nm}$, S-POLARIZED INCIDENT LIGHT

13 DISCUSSION

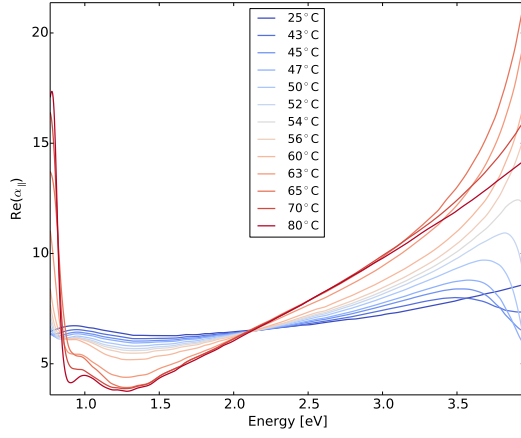
14 CONCLUSION

15 INTRODUCTION TO GRANFILM

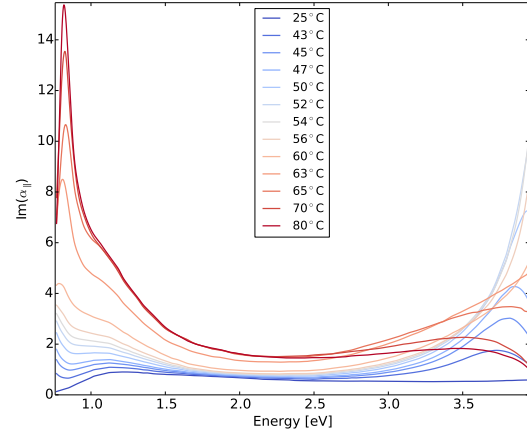
This section is included as a brief summary of the practical situations one encounter when using GranFilm. Even though the software provides the information required and would be self-explanatory for some, this would be for the less experienced reader to avoid any unnecessary confusion.

15.1 SOFTWARE OVERVIEW

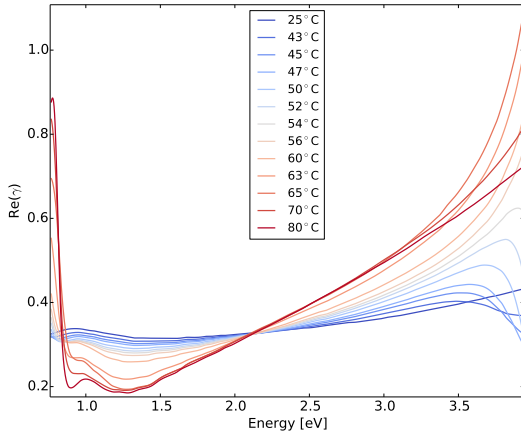
GRANFILM is a program written in FORTRAN 90 and serves as a tool for simulating and interpreting optical spectra from surfaces or thin films. The program takes in parameters specifying the incoming angle, polarization and energy range of the incoming plane wave, in addition to the radius and truncation ratio t_r of the sphere, the materials for region 1,2,3 and 4, the arrangement of the islands and finally the multipole order M .



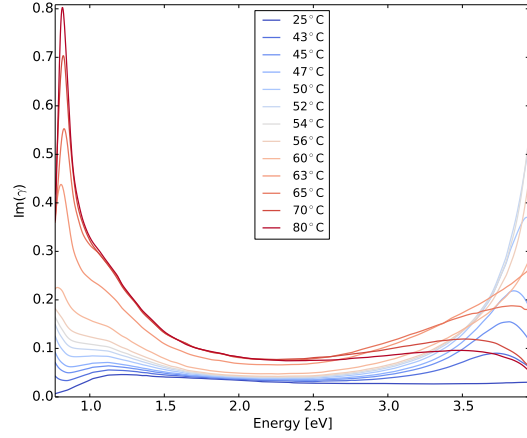
(a)



(b)

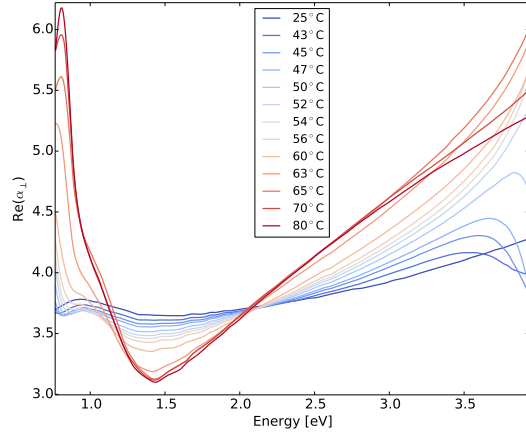


(c)

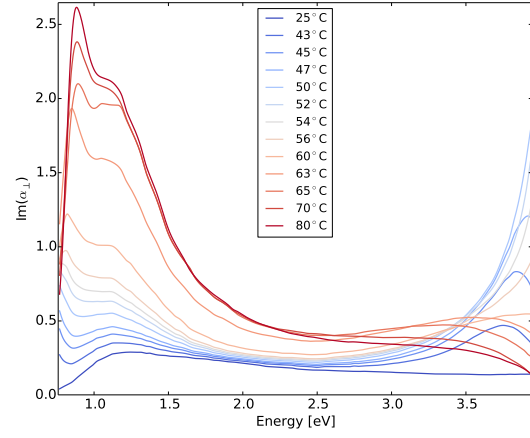


(d)

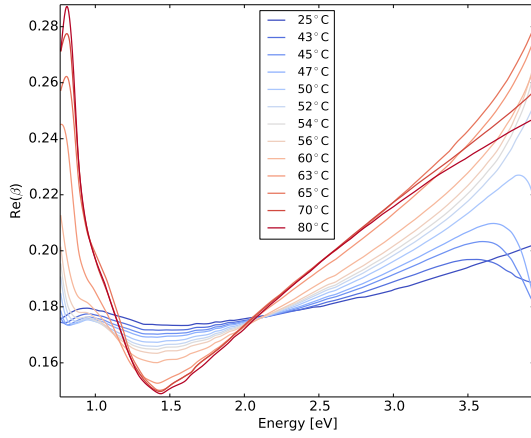
Figure 9.2: Relative reflectance $\Delta R/R$



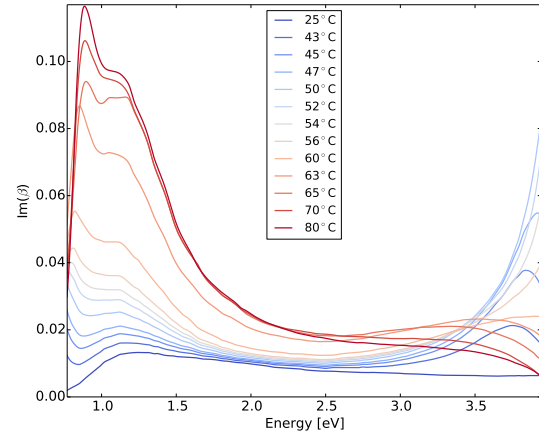
(a)



(b)

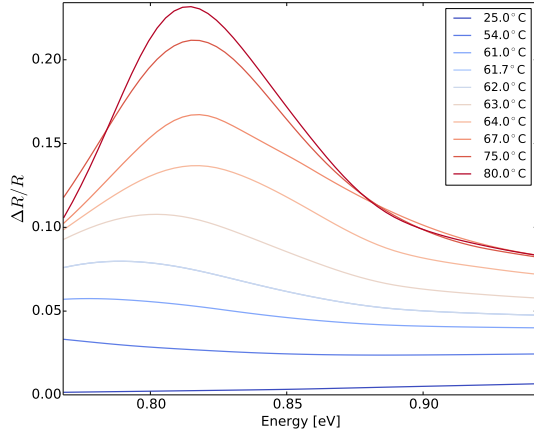


(c)

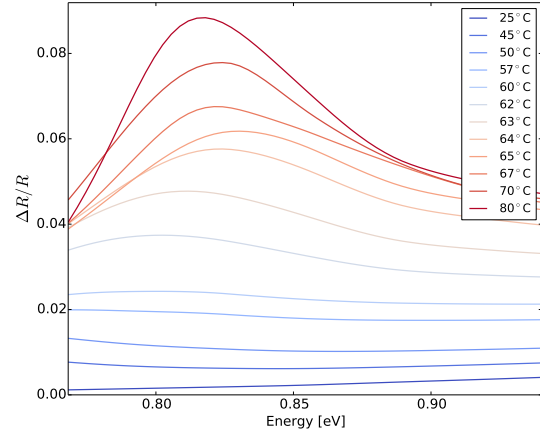


(d)

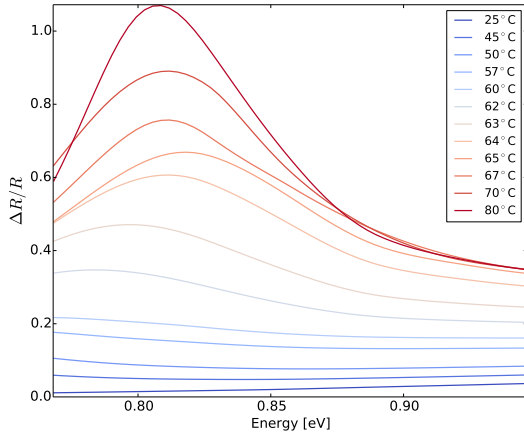
Figure 9.3: Relative reflectance $\Delta R/R$



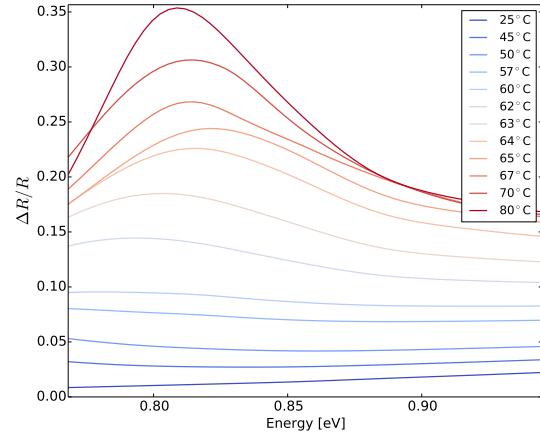
(a) $R = 10\text{nm}$, p -polarization



(b) $R = 10\text{nm}$, s -polarization



(c) $R = 15\text{nm}$, p -polarization



(d) $R = 15\text{nm}$, s -polarization

Figure 12.1: Relative reflectance $\Delta R/R$

16 METHOD

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Er dette greit? Finner ikke sidetall osv.

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