CHAPTER 10

The Optical Constants

10.1. Introduction

The most apparent properties of metals, their luster and their color, have been known to mankind since metals were known. Because of these properties, metals were already used in ancient times for mirrors and jewelry. The color was utilized 4000 years ago by the ancient Chinese as a guide to determine the composition of the melt of copper alloys: the hue of a preliminary cast indicated whether the melt, from which bells or mirrors were to be made, already had the right tin content.

The German poet Goethe was probably the first one who explicitly spelled out 200 years ago in his *Treatise on Color* that *color* is not an absolute property of matter (such as the resistivity), but requires a living being for its perception and description. Applying Goethe's findings, it was possible to explain qualitatively the color of, say, gold in simple terms. Goethe wrote: "If the color *blue* is removed from the spectrum, then blue, violet, and green are missing and red and yellow remain." Thin gold films are bluish–green when viewed in transmission. These colors are missing in reflection. Consequently, gold appears reddish–yellow.

This chapter treats the optical properties from a completely different point of view. Measurable quantities such as the index of refraction or the reflectivity and their spectral variations are used to characterize materials. In doing so, the term "color" will almost completely disappear from our vocabulary. Instead, it will be postulated that the interactions of light with the valence electrons of a material are responsible for the optical properties. As in previous chapters, where an understanding of the electrical properties

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was attempted, an atomistic model and later a quantum mechanical treatment will be employed. Thus, the electron theory of metals, as introduced in the first six chapters, will serve as a foundation.

Light comprises only an extremely small segment of the entire electromagnetic spectrum, which ranges from radio waves, via microwaves, infrared, visible, ultraviolet, and X-rays, to γ rays, as depicted in Fig. 10.1. Many of the considerations that will be advanced in this chapter are therefore also valid for other wavelength ranges, e.g., for radio waves or X-rays.

At the beginning of this century the study of the interactions of light with matter (black body radiation, etc.) laid the foundations for quantum theory. Today, optical methods are among the most important tools for elucidating the electron structure of matter. Most recently, a number of optical devices, such as lasers, photodetectors, waveguides, light-emitting diodes, flat-panel displays, etc., have gained considerable technological importance. They are used in communication, fiber optics, medical diagnostics, night viewing, solar applications, optical computing, or for other optoelectronic purposes. Traditional utilizations of optical materials for windows, antireflection coatings, lenses, mirrors, etc., should be likewise mentioned. All taken, it is well justified to spend a major part of this book on the optical properties of materials.

Before we start our discourse, we need to define the optical constants. We make use of some elements of physics.

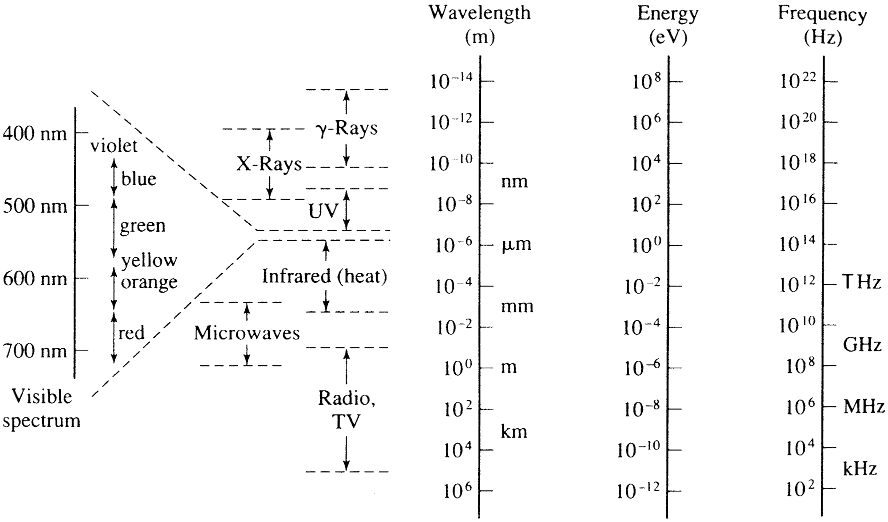

Figure 10.1. The spectrum of electromagnetic radiation. Note the small segment of this spectrum that is visible to human eyes.

10.2. Index of Refraction, *n*

When light passes from an optically "thin" into an optically dense medium, one observes that in the dense medium, the angle of refraction, β, (i.e., the angle between the refracted light beam and a line perpendicular to the surface) is generally smaller than the angle of incidence, α see Fig. 10.2. This well-known phenomenon is used for the definition of the refractive power of a material and is called **Snell's law**,

$$\frac{\sin\alpha}{\sin\beta} = \frac{n_{\text{med}}}{n_{\text{vac}}} = n. \tag{10.1}$$

Commonly, the **index of refraction** for vacuum, n_{vac}, is arbitrarily set to be unity. The refraction is caused by the different velocities, c, of the light in the two media,

$$\frac{\sin\alpha}{\sin\beta} = \frac{c_{\text{vac}}}{c_{\text{med}}}. \tag{10.2}$$

Thus, if light passes from vacuum into a medium, we find

$$n = \frac{c_{\text{vac}}}{c_{\text{med}}} = \frac{c}{v}. \tag{10.3}$$

The magnitude of the refractive index depends on the wavelength of the incident light. This property is called **dispersion**. In metals, the index of refraction varies, in addition, with the angle of incidence. This is particularly true when n is small.

As can be seen in Table 10.1, the index of refraction is not always larger than 1 as for example, for metals. Likewise, for X-rays, n can be smaller than 1.

In summary, when light passes from vacuum into a medium, its velocity as well as its wavelength, λ, generally decrease in order to keep the frequency, and thus, the energy, constant.

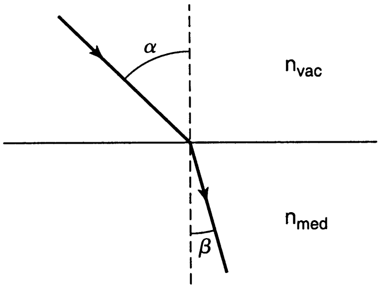

Figure 10.2. Refraction of a light beam when traversing the boundary from an optically thin medium into an optically denser medium.

Table 10.1. Optical Constants for Some Materials ($\lambda = 600$ nm).

	n	k	W (nm)	$R\%$[b]
Metals				
Copper	0.14	3.35	14.2	95.6
Silver	0.05	4.09	11.7	98.9
Gold	0.21	3.24	14.7	92.9
Aluminum	0.97	6.0	7.9	90.3
Ceramics				
Silica glass (Vycor)	1.46	[a]		3.50
Soda-lime glass	1.51	[a]		4.13
Dense flint glass	1.75	[a]		7.44
Quartz	1.55	[a]	3×10^8	4.65
Al_2O_3	1.76	[a]		7.58
Polymers				
Polyethylene	1.51	[a]		4.13
Polystyrene	1.60	[a]		5.32
Polytetrafluoroethylene	1.35	[a]		2.22
Semiconductors				
Silicon	3.94	0.025	1,910	35.42
GaAs	3.91	0.228	209	35.26

[a] The damping constant for dielectrics is about 10^{-7}.
[b] The reflection is considered to have occurred on one reflecting surface only.

10.3. Damping Constant, k

Metals damp the intensity of light in a relatively short distance. Thus, to characterize the optical properties of metals, an additional materials constant is needed.

We make use of the electromagnetic wave equation, which mathematically describes the propagation of light in a medium. The derivation of this wave equation from the well-known Maxwell equations does not further our understanding of the optical properties. (The interested reader can find the derivation in specialized texts.[1])

For simplification, we consider a plane-polarized wave that propagates along the positive z-axis and which vibrates in the x-direction (Fig. 10.3). We neglect possible magnetic effects. For this special case, the electromagnetic wave equation reads[2]

$$c^2 \frac{\partial^2 \mathscr{E}_x}{\partial z^2} = \varepsilon \frac{\partial^2 \mathscr{E}_x}{\partial t^2} + \frac{\sigma}{\varepsilon_0} \frac{\partial \mathscr{E}_x}{\partial t}, \tag{10.4}$$

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[1] For instance: R.E. Hummel, *Optische Eigenschaften von Metallen und Legierungen*, Springer-Verlag, Berlin (1971).

[2] See also Appendix 1.

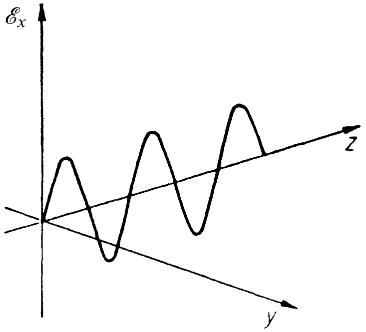

Figure 10.3. Plane-polarized wave which propagates in the positive z-direction and vibrates in the x-direction.

where $\mathscr{E}_x$ is the x-component of the electric field strength,[3] ε is the dielectric constant,[4] σ is the (a.c.) conductivity and ε_0 is a constant, called the permittivity of empty space (see Appendix 4). The solution to (10.4) is commonly achieved by using the following trial solution:

$$\mathscr{E}_x = \mathscr{E}_0 \exp\left[i\omega\left(t - \frac{zn}{c}\right)\right], \tag{10.5}$$

where $\mathscr{E}_0$ is the maximal value of the electric field strength and $\omega = 2\pi\nu$ is the angular frequency. Differentiating (10.5) once with respect to time, and twice with respect to time *and* z, and inserting these values into (10.4) yields

$$\hat{n}^2 = \varepsilon - \frac{\sigma}{\varepsilon_0\omega} i = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0\nu} i. \tag{10.6}$$

Equation (10.6) leads to an important result: The index of refraction is generally a complex number, as inspection of the right-hand side of (10.6) indicates. We denote for clarity the complex index of refraction by $\hat{n}$. As is true for all complex quantities, the complex index of refraction consists of a real and an imaginary part,

$$\hat{n} = n_1 - in_2. \tag{10.7}$$

In the literature, the imaginary part of the index of refraction, n_2, is often denoted by "k" and (10.7) is then written as

$$\hat{n} = n - ik. \tag{10.8}$$

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[3] We use for the electric field strength the symbol $\mathscr{E}$ to distinguish it from the energy.

[4] See Section 9.5.

We will call n_2 or k the **damping constant**. (In some books n_2 or k is named the *absorption constant*. We will not follow this practice because the latter term is extremely misleading. Other authors call k the *attenuation index* or the *extinction coefficient*, which we will not use either in this context.) Values for k for some materials are given in Table 10.1.

Squaring (10.8) yields, together with (10.6),

$$\hat{n}^2 = n^2 - k^2 - 2nki = \varepsilon - \frac{\sigma}{2\pi\varepsilon_0 v} i. \tag{10.9}$$

Equating individually the real and imaginary parts of (10.9) yields two important relations between electrical and optical constants,

$$\varepsilon = n^2 - k^2, \tag{10.10}$$

$$\sigma = 4\pi\varepsilon_0 nkv. \tag{10.11}$$

Let us return to (10.9). The right-hand side is the difference between two dielectric constants (a real one and an imaginary one). Thus, the left side must be a dielectric constant too, and (10.9) may be rewritten as

$$\hat{n}^2 = n^2 - k^2 - 2nik \equiv \hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2. \tag{10.12}$$

Equating individually the real and imaginary parts in (10.12) yields

$$\varepsilon_1 = n^2 - k^2 \tag{10.13}$$

and (with (10.11))

$$\varepsilon_2 = 2nk = \frac{\sigma}{2\pi\varepsilon_0 v}. \tag{10.14}$$

Similarly as above, ε_1 and ε_2 are called the real and the imaginary parts of the complex dielectric constant, $\hat{\varepsilon}$, respectively. (ε_1 in (10.13) is identical to ε in (10.10).) ε_2 is often called the *absorption product* or, briefly, the **absorption**.

We consider a special case: For insulators ($\sigma \approx 0$) it follows from (10.11) that $k \approx 0$ (see also Table 10.1). Then (10.10) reduces to $\varepsilon = n^2$ (**Maxwell relation**).

From (10.10), (10.11), (10.13), and (10.14) one obtains

$$n^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0 v}\right)^2} + \varepsilon\right) = \frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1\right), \tag{10.15}$$

$$k^2 = \frac{1}{2}\left(\sqrt{\varepsilon^2 + \left(\frac{\sigma}{2\pi\varepsilon_0 v}\right)^2} - \varepsilon\right) = \frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1\right). \tag{10.16}$$

It should be emphasized that (10.10)–(10.16) are only valid if ε, σ, n, and k are measured at the same wavelength, because these "constants" are wavelength dependent. For small frequencies, however, the d.c. values for ε and σ can be used with good approximation, as will be shown later. Finally, it should be noted that the above equations are only valid for optically isotropic media; otherwise ε becomes a tensor.

We return now to (10.5) in which we replace the index of refraction by the complex index of refraction (10.8). This yields

$$\mathscr{E}_x = \mathscr{E}_0 \exp\left[i\omega\left(t - \frac{z(n - ik)}{c}\right)\right], \tag{10.17}$$

which may be rewritten to read

$$\boxed{\mathscr{E}_x = \underbrace{\mathscr{E}_0 \exp\left[-\frac{\omega k}{c} z\right]}_{\text{Damped amplitude}} \cdot \underbrace{\exp\left[i\omega\left(t - \frac{zn}{c}\right)\right]}_{\text{Undamped wave}}.} \tag{10.18}$$

Equation (10.18) is now the complete solution of the wave equation (10.4). It represents a damped wave and expresses that in matter the amplitude decreases exponentially with increasing z (Fig. 10.4). The constant k determines how much the amplitude decreases, i.e., k expresses the degree of damping of the light wave. We understand now why k is termed the *damping constant.*

The result which we just obtained is well known to electrical engineers. They observe that at high frequencies the electromagnetic waves are conducted only on the outer surface of a wire. They call this phenomenon the (*normal*) *skin effect.*

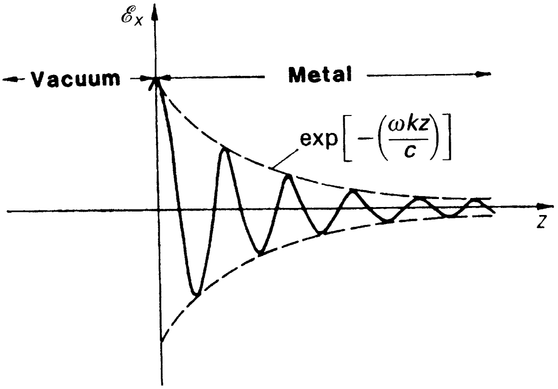

Figure 10.4. Modulated light wave. The amplitude decreases exponentially in an optically dense material. The decrease is particularly strong in metals, but less intense in dielectric materials, such as glass.

10.4. Characteristic Penetration Depth, *W*, and Absorbance, α

The field strength, $\mathscr{E}$, is hard to measure. Thus, the intensity, I, which can be measured effortlessly with light sensitive devices (such as a photodetector, see Section 8.7.6) is commonly used. The intensity equals the square of the field strength. Thus, the damping term in (10.18) may be written as

$$I = \mathscr{E}^2 = I_0 \exp\left(-\frac{2\omega k}{c} z\right). \tag{10.19}$$

We define a **characteristic penetration depth**, W, as that distance at which the intensity of the light wave, which travels through a material, has decreased to $1/e$ or 37% of its original value, i.e., when

$$\frac{I}{I_0} = \frac{1}{e} = e^{-1}. \tag{10.20}$$

This definition yields, in conjunction with (10.19),

$$z = W = \frac{c}{2\omega k} = \frac{c}{4\pi \nu k} = \frac{\lambda}{4\pi k}. \tag{10.21}$$

Table 10.1 presents values for k and W for some materials obtained by using light having $\lambda = 600$ nm.

The inverse of W is called the **absorbance** or sometimes the (exponential) *attenuation*, which is, by making use of (10.21), (10.14), and (10.11), given by,

$$\alpha = \frac{4\pi k}{\lambda} = \frac{2\pi \varepsilon_2}{\lambda n} = \frac{\sigma}{n c \varepsilon_0} = \frac{2\omega k}{c}. \tag{10.22}$$

Its unit is a reciprocal length, for example, cm^{-1}. It should be emphasized that, as already defined in equation (10.14)

$$\varepsilon_2 = 2nk$$

is called the **absorption** which is unitless. In other words, absorbance and absorption are *not* the same quantities. In Section 12.2 we will deepen our understanding concerning the absorption of light (that is, light quanta or photons) by explaining that if photons are interacting with matter they may be absorbed by electrons, then transfer their energy to them and, as a consequence, are excited into a higher, allowed energy state.

The **energy loss** per unit length (given for example in decibels, dB, per centimeter) is obtained by multiplying the absorbance, α, with 4.34, see Problem 13.6. (1 dB $= 10 \log I/I_0$.)

*In analytical (spectroscopic) chemistry which mostly deals with dilute liquids, α is called the **absorption coefficient**. Combining equation (10.19) with (10.22) yields

$$I/I_o = \exp\left(-2\omega kz/c\right) = \exp\left(-\alpha z\right), \tag{10.23}$$

where I and I_o are, as above, the transmitted and the incident light intensities, respectively. Equation (10.23) is known by the name **Beer–Lambert** (or Lambert– Beer–Bouguer) **law**. (It should be noted, however, that *not all* incident light is transferred into other energy forms e.g. heat, but instead, may be reflected, scattered, or as just mentioned, transmitted). Taking the natural logarithm of (10.23) yields

$$-\ln I/I_o = \alpha z = A_\lambda, \tag{10.24}$$

where A_λ is called the (wavelength-dependent) **optical density** or, unfortunately also *absorbance*. The variable z is, as above, the path length which the light travels through the material. To confuse the matter even further, analytical chemists often replace the natural logarithm, ln, by the common (base 10) logarithm which introduces a multiplication factor. Further, chemists relate α to the product of the **molar absorptivity** of the substance and to its concentration in the solvent. This means that A_λ is, within certain limits, linearly related to the concentration. However, the Beer–Lambert law breaks down for high concentrations, particularly when the substance is highly scattering.

10.5. Reflectivity, *R*, and Transmittance, *T*

Metals are characterized by a large reflectivity. This stems from the fact that light penetrates a metal only a short distance, as shown in Fig. 10.4 and Table 10.1. Thus, only a small part of the impinging energy is converted into heat. The major part of the energy is reflected (in some cases close to 99%, see Table 10.1). In contrast to this, visible light penetrates into glass much farther than into metals, i.e., approximately seven orders of magnitude more, see Table 10.1. As a consequence, very little light is reflected by glass. Nevertheless, a piece of glass about one or two meters thick eventually dissipates a substantial part of the impinging light into heat. (In practical applications, one does not observe this large reduction in light intensity because windows are as a rule only a few millimeters thick.) It should be noted that typical window panes reflect the light on the front as well as on the back surface.

The ratio between the reflected intensity, I_R, and the incoming intensity, I_0, of the light serves as a definition for the **reflectivity**:

$$R = \frac{I_R}{I_0}. \tag{10.25}$$

Quite similarly, one defines the ratio between the transmitted intensity, I_T, and the impinging light intensity as the **transmissivity**, or **transmittance**:

$$T = \frac{I_T}{I_0}. \tag{10.26}$$

Experiments have shown that for insulators, R depends solely on the index of refraction. For perpendicular incidence one finds

$$R = \frac{(n-1)^2}{(n+1)^2}. \tag{10.27}$$

This equation can also be derived from the Maxwell equations.

We know already that n is generally a complex quantity. By definition, however, R has to remain real. Thus, the modulus of R becomes

$$R = \left| \frac{\hat{n}-1}{\hat{n}+1} \right|^2, \tag{10.28}$$

which yields

$$R = \frac{(n-ik-1)}{(n-ik+1)} \cdot \frac{(n+ik-1)}{(n+ik+1)} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{10.29}$$

(**Beer equation**). The reflectivity is a unitless materials constant and is often given in percent of the incoming light (see Table 10.1). R is, like the index of refraction, a function of the wavelength of the light.

The reflectivity is also a function of ε_1 and ε_2. We shall derive this relationship by performing a few transformations. Equation (10.29) is rewritten as

$$R = \frac{n^2 + k^2 + 1 - 2n}{n^2 + k^2 + 1 + 2n}, \tag{10.30}$$

$$\begin{aligned}(1)\ \ n^2 + k^2 &= \sqrt{(n^2+k^2)^2} = \sqrt{n^4 + 2n^2k^2 + k^4} \\ &= \sqrt{n^4 - 2n^2k^2 + k^4 + 4n^2k^2} = \sqrt{(n^2-k^2)^2 + 4n^2k^2} \\ &= \sqrt{\varepsilon_1^2 + \varepsilon_2^2},\end{aligned} \tag{10.31}$$

$$(2)\ \ 2n = \sqrt{4n^2} = \sqrt{2(n^2+k^2+n^2-k^2)} = \sqrt{2\left(\sqrt{\varepsilon_1^2+\varepsilon_2^2} + \varepsilon_1\right)}. \tag{10.32}$$

Inserting (10.31) and (10.32) into (10.30) provides

$$R = \frac{\sqrt{\varepsilon_1^2+\varepsilon_2^2} + 1 - \sqrt{2\left(\sqrt{\varepsilon_1^2+\varepsilon_2^2} + \varepsilon_1\right)}}{\sqrt{\varepsilon_1^2+\varepsilon_2^2} + 1 + \sqrt{2\left(\sqrt{\varepsilon_1^2+\varepsilon_2^2} + \varepsilon_1\right)}}. \tag{10.33}$$

10.6. Hagen–Rubens Relation

Our next task is to find a relationship between reflectivity and conductivity. For small frequencies (i.e., $\nu < 10^{13}\ \mathrm{s}^{-1}$) the ratio $\sigma/2\pi\varepsilon_0\nu$ for metals is very large, that is, $\sigma/2\pi\varepsilon_0 \approx 10^{17}\ \mathrm{s}^{-1}$. With $\varepsilon \approx 10$ we obtain

$$\frac{\sigma}{2\pi\varepsilon_0\nu} \approx \frac{10^{17}}{10^{13}} \gg \varepsilon. \tag{10.34}$$

Then (10.15) and (10.16) reduce to

$$n^2 \approx \frac{\sigma}{2\pi\varepsilon_0\nu} \approx k^2. \tag{10.35}$$

The reflectivity may now be rewritten by combining the slightly modified equation (10.30) with (10.35) to read

$$R = \frac{n^2 + 2n + 1 + k^2 - 4n}{n^2 + 2n + 1 + k^2} = 1 - \frac{4n}{2n^2 + 2n + 1}. \tag{10.36}$$

If $2n + 1$ is neglected as small compared to $2n^2$ (which can be done only for small frequencies for which n is much larger than 1), then (10.36) reduces by using (10.35) to

$$R = 1 - \frac{2}{n} = 1 - 4\sqrt{\frac{\nu}{\sigma}\pi\varepsilon_0}. \tag{10.37}$$

Finally, we set $\sigma = \sigma_0$ (d.c. conductivity) which is again only permissible for small frequencies, i.e., in the infrared region of the spectrum. This yields the **Hagen–Rubens relation**,

$$\boxed{R = 1 - 4\sqrt{\frac{\nu}{\sigma_0}\pi\varepsilon_0},} \tag{10.38}$$

which states that in the infrared (IR) region metals with large electrical conductivity are good reflectors. This equation was found empirically by Hagen and Rubens from reflectivity measurements in the IR and was derived theoretically by Drude. As stated above, the Hagen–Rubens relation is only valid at frequencies below $10^{13}\ \mathrm{s}^{-1}$ or, equivalently, at wavelengths larger than about 30 μm.

Problems

1. Complete the intermediate steps between (10.5) and (10.6).
2. Calculate the conductivity from the index of refraction and the damping constant for copper (0.14 and 3.35, respectively; measurement at room temperature and $\lambda = 0.6\ \mu$m).

Compare your result with the conductivity of copper (see Appendix 4). You will notice a difference between these conductivities by several orders of magnitude. Why? (Compare only the same units!)

3. Express n and k in terms of ε and σ (or ε_1 and ε_2) by using $\varepsilon = n^2 - k^2$ and $\sigma = 4\pi\varepsilon_0 nk\nu$. (Compare with (10.15) and (10.16).)
4. The intensity of Na light passing through a gold film was measured to be about 15% of the incoming light. What is the thickness of the gold film? ($\lambda = 589$ nm; $k = 3.2$. *Note:* $I = \mathscr{E}^2$.)
5. Calculate the reflectivity of silver and compare it with the reflectivity of flint glass ($n = 1.59$). Use $\lambda = 0.6$ μm.
6. Calculate the characteristic penetration depth in aluminum for Na light ($\lambda = 589$ nm; $k = 6$).
7. Derive the Hagen–Rubens relation from (10.33). (*Hint*: In the IR region $\varepsilon_2^2 \gg \varepsilon_1^2$ can be used. Justify this approximation.)
8. The transmissivity of a piece of glass of thickness $d = 1$ cm was measured at $\lambda = 589$ nm to be 89%. What would the transmissivity of this glass be if the thickness were reduced to 0.5 cm? (Note: Neglect the reflectance of the glass.)