

## CHAPTER 11

# Atomistic Theory of the Optical Properties

### 11.1. Survey

In the preceding chapter, the optical constants and their relationship to electrical constants were introduced by employing the “continuum theory.” The continuum theory considers only macroscopic quantities and interrelates experimental data. No assumptions are made about the structure of matter when formulating equations. Thus, the conclusions which have been drawn from the empirical laws in Chapter 10 should have general validity as long as nothing is neglected in a given calculation. The derivation of the Hagen–Rubens equation has served as an illustrative example for this.

The validity of equations derived from the continuum theory is, however, often limited to frequencies for which the atomistic structure of solids does not play a major role. Experience shows that the atomistic structure does not need to be considered in the far infrared (IR) region. Thus, the Hagen–Rubens equation reproduces the experimental results of metals in the far IR quite well. It has been found, however, that proceeding to higher frequencies (i.e., in the near IR and visible spectrum), the experimentally observed reflectivity of metals decreases faster than predicted by the Hagen–Rubens equation (Fig. 11.1(a)). For the visible and near IR region an atomistic model needs to be considered to explain the optical behavior of metals. Drude did this important step at the turn of the 20<sup>th</sup> century. He postulated that some electrons in a metal can be considered to be free, i.e., they can be separated from their respective nuclei. He further assumed that the free electrons can be accelerated by an external electric field. This preliminary Drude model was refined by considering that the moving electrons collide with certain metal atoms in a nonideal lattice.

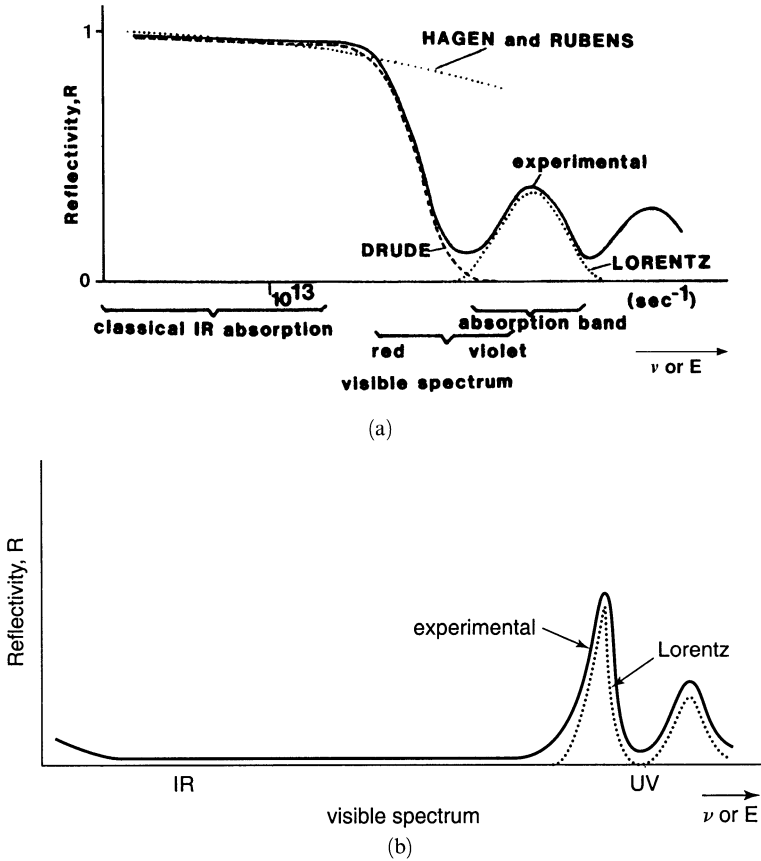


Figure 11.1. Schematic frequency dependence of the reflectivity of (a) metals, (b) dielectrics, experimentally (solid line) and according to three models.

The free electrons are thought to perform periodic motions in the alternating electric field of the light. These vibrations are restrained by the abovementioned interactions of the electrons with the atoms of a nonideal lattice. Thus, a **friction force** is introduced, which takes this interaction into consideration. The calculation of the frequency dependence of the optical constants is accomplished by using the well-known equations for vibrations, whereby the interactions of electrons with atoms are taken into account by a damping term which is assumed to be proportional to the velocity of the electrons. The free electron theory describes, to a certain degree, the dispersion of the optical constants of metals quite well. This is schematically shown in Fig. 11.1(a), in which the spectral dependence of the reflectivity is plotted for a specific case. The Hagen–Rubens relation reproduces the

experimental findings only up to  $10^{13} \text{ s}^{-1}$ . In contrast to this, the Drude theory correctly reproduces the spectral dependence of  $R$  even in the visible spectrum. Proceeding to yet higher frequencies, however, the experimentally found reflectivity eventually rises and then decreases again. Such an **absorption band** cannot be explained by the Drude theory. For its interpretation, a new concept needs to be applied.

Lorentz postulated that the electrons should be considered to be bound to their nuclei and that an external electric field displaces the positive charge of an atomic nucleus against the negative charge of its electron cloud. In other words, he represented each atom as an electric dipole. Retracting forces were thought to occur which try to eliminate the displacement of charges. Lorentz postulated further that the centers of gravity of the electric charges are identical if no external forces are present. However, if one shines light onto a solid, i.e., if one applies an alternating electric field to the atoms, then the dipoles are thought to perform forced vibrations. Thus, a dipole is considered to behave similarly as a mass which is suspended on a spring, i.e., the equations for a harmonic oscillator may be applied. An oscillator is known to absorb a maximal amount of energy when excited near its resonance frequency (Fig. 11.2). The absorbed energy is thought to be dissipated mainly by diffuse radiation. Figure 11.2 resembles an absorption band as shown in Fig. 11.1.

Forty or fifty years ago, many scientists considered the electrons in metals to behave at low frequencies as if they were free and at higher frequencies as if they were bound. In other words, electrons in a metal under the influence of light were described to behave as a series of classical free electrons and a series of classical harmonic oscillators. Insulators and semiconductors, on the other hand, were described by harmonic oscillators only, see Fig. 11.1(b).

We shall now treat the optical constants of materials by applying the above-mentioned theories.

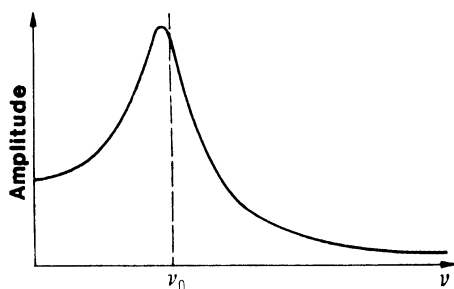


Figure 11.2. Frequency dependence of the amplitude of a harmonic oscillator that is excited to perform forced vibrations, assuming weak damping.  $\nu_0$  is the resonance frequency.

## 11.2. Free Electrons Without Damping

We consider the simplest case at first and assume that the free electrons are excited to perform forced but undamped vibrations under the influence of an external alternating field, i.e., under the influence of light. As explained in Section 11.1, the damping of the electrons is thought to be caused by collisions between electrons and atoms of a nonideal lattice. Thus, we neglect in this section the influence of lattice defects. For simplicity, we treat the one-dimensional case because the result obtained this way does not differ from the general case. Thus, we consider the interaction of plane-polarized light with the electrons. The momentary value of the field strength of a plane-polarized light wave is given by

$$\mathcal{E} = \mathcal{E}_0 \exp(i\omega t), \quad (11.1)$$

where  $\omega = 2\pi\nu$  is the angular frequency,  $t$  is the time, and  $\mathcal{E}_0$  is the maximal value of the field strength. The equation describing the motion of an electron that is excited to perform forced, harmonic vibrations under the influence of light is (see Appendix 1 and (7.6))

$$m \frac{d^2 x}{dt^2} = e\mathcal{E} = e\mathcal{E}_0 \exp(i\omega t), \quad (11.2)$$

where  $e$  is the electron charge,  $m$  is the electron mass, and  $e \cdot \mathcal{E}$  is the modulus of the excitation force. The stationary solution of this vibrational equation is obtained by forming the second derivative of the trial solution  $x = x_0 \exp(i\omega t)$  and inserting it into (11.2). This yields

$$x = -\frac{e\mathcal{E}}{m4\pi^2\nu^2}. \quad (11.3)$$

The vibrating electrons carry an electric dipole moment, which is the product of the electron charge,  $e$ , and displacement,  $x$ , see (9.12). The polarization,  $P$ , is defined to be the sum of the dipole moments of all  $N_f$  free electrons per cubic centimeter:

$$P = exN_f. \quad (11.4)$$

The dielectric constant can be calculated from polarization and electric field strength by combining (9.14) and (9.15):

$$\varepsilon = 1 + \frac{P}{\varepsilon_0 \mathcal{E}}. \quad (11.5)$$

Inserting (11.3) and (11.4) into (11.5) yields

$$\hat{\varepsilon} = 1 - \frac{e^2 N_f}{4\pi^2 \varepsilon_0 m \nu^2}. \quad (11.6)$$

(It is appropriate to use in the present case the *complex* dielectric constant, see below.) The dielectric constant equals the square of the index of refraction,  $n$ , (see (10.12)). Equation (11.6) thus becomes

$$\hat{n}^2 = 1 - \frac{e^2 N_f}{4\pi^2 \epsilon_0 m v^2}. \tag{11.7}$$

We consider two special cases:

- (a) For small frequencies, the term  $e^2 N_f / 4\pi^2 \epsilon_0 m v^2$  is larger than one. Then  $\hat{n}^2$  is negative and  $\hat{n}$  imaginary. An imaginary  $\hat{n}$  means that the real part of  $\hat{n}$  disappears. Equation (10.25) becomes, for  $n = 0$ ,

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

i.e., the reflectivity is 100% (see Fig. 11.3).

- (b) For large frequencies (UV light), the term  $e^2 N_f / 4\pi^2 \epsilon_0 m v^2$  becomes smaller than one. Thus,  $\hat{n}^2$  is positive and  $\hat{n} \equiv n$  real (but smaller than one). The reflectivity for real values of  $\hat{n}$ , i.e., for  $k = 0$ , becomes

$$R = \frac{(n - 1)^2}{(n + 1)^2},$$

i.e., the material is essentially transparent for these wavelengths (and perpendicular incidence) and therefore behaves optically like an insulator, see Fig. 11.3.

We define a characteristic frequency,  $\nu_1$ , often called the **plasma frequency**, which separates the reflective region from the transparent region (Fig. 11.3). The plasma frequency can also be deduced from (11.6) or (11.7). We observe in these equations that  $e^2 N_f / 4\pi^2 \epsilon_0 m$  must have the unit of the square of a frequency, which we define to be  $\nu_1$ . This yields

$$\nu_1^2 = \frac{e^2 N_f}{4\pi^2 \epsilon_0 m}. \tag{11.8}$$

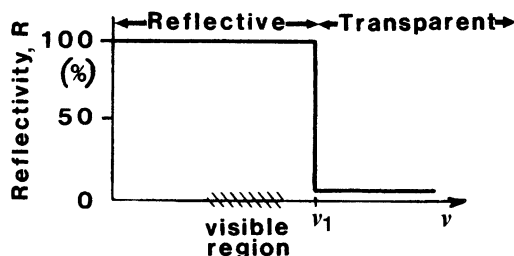


Figure 11.3. Schematic frequency dependence of an alkali metal according to the free electron theory without damping.  $\nu_1$  is the plasma frequency.

Because of (11.8) we conclude from (11.6) that the dielectric constant becomes zero at the plasma frequency.  $\hat{\epsilon} = 0$  is the condition for a **plasma oscillation**, i.e., a fluid-like oscillation of the entire electron gas. We will discuss this phenomenon in detail in Section 13.2.2.

The alkali metals behave essentially as shown in Fig. 11.3. They are transparent in the near UV and reflect the light in the visible region. This result indicates that the  $s$ -electrons<sup>5</sup> of the outer shell of the alkali metals can be considered to be free.

Table 11.1 contains some measured, as well as some calculated, plasma frequencies. For the calculations, applying (11.8), *one* free electron per atom was assumed. This means that  $N_f$  was set equal to the number of atoms per volume,  $N_a$ . (The latter quantity is obtained by using

$$N_a = \frac{N_0 \cdot \delta}{M}, \quad (11.9)$$

where  $N_0$  is the Avogadro constant,  $\delta$  = density, and  $M$  = atomic mass.)

We note in Table 11.1 that the calculated and the observed values for  $\nu_1$  are only identical for sodium. This may be interpreted to mean that only in sodium does exactly *one* free electron per atom contribute to the electron gas. For other metals an “effective number of free electrons” is commonly introduced, which is defined to be the ratio between the observed and calculated  $\nu_1^2$  values:

$$\frac{\nu_1^2 \text{ (observed)}}{\nu_1^2 \text{ (calculated)}} = N_{\text{eff}}. \quad (11.10)$$

The **effective number of free electrons** is a parameter of great interest, because it is contained in a number of nonoptical equations (such as the Hall constant, electromigration, superconductivity, etc.). Since for most metals the plasma frequency,  $\nu_1$ , cannot be measured as readily as for the alkalis, another avenue for determining  $N_{\text{eff}}$  has to be found. For reasons which will become clear later,  $N_{\text{eff}}$  can be obtained by measuring  $n$  and  $k$  in the red or

Table 11.1. Plasma Frequencies and Effective Numbers of Free Electrons for Some Alkali Metals.

Metal	Li	Na	K	Rb	Cs
$\nu_1$ ( $10^{14} \text{ s}^{-1}$ ), observed	14.6	14.3	9.52	8.33	6.81
$\nu_1$ ( $10^{14} \text{ s}^{-1}$ ), calculated	19.4	14.3	10.34	9.37	8.33
$\lambda_1$ nm (= $c/\nu_1$ ), observed	150	210	290	320	360
$N_{\text{eff}}$ [free electrons/atom]	0.57	1.0	0.8	0.79	0.67

<sup>5</sup>See Appendix 3.

IR spectrum (i.e., in a frequency range without absorption bands, Fig. 11.1) and by applying

$$N_{\text{eff}} = \frac{(1 - n^2 + k^2) v^2 4\pi^2 \epsilon_0 m}{e^2}. \quad (11.10a)$$

Equation (11.10a) follows by combining (11.6) with (10.10) and replacing  $N_f$  by  $N_{\text{eff}}$ .

### 11.3. Free Electrons With Damping (Classical Free Electron Theory of Metals)

The simple reflectivity spectrum as depicted in Fig. 11.3 is seldom found for metals. We need to refine our model. We postulate that the motion of electrons in metals is damped. More specifically, we postulate that the velocity is reduced by collisions of the electrons with atoms of a nonideal lattice. Lattice defects may be introduced into a solid by interstitial atoms, vacancies, impurity atoms, dislocations, grain boundaries, or thermal motion of the atoms.

To take account of the damping, we add to the vibration equation (11.2) a damping term,  $\gamma(dx/dt)$ , which is proportional to the velocity (See Appendix 1 and (7.7)):

$$m \frac{d^2x}{dt^2} + \gamma \frac{dx}{dt} = e\mathcal{E} = e\mathcal{E}_0 \exp(i\omega t). \quad (11.11)$$

We determine first the damping factor,  $\gamma$ . For this we write a particular solution of (11.11) which is obtained by assuming that the electrons drift under the influence of a steady or slowly varying electric field (see Section 7.3) with a velocity  $v' = \text{const.}$  through the crystal. (The drift velocity of the electrons, which is caused by an external field, is superimposed on the random motion of the electrons.) The damping is depicted to be a friction force which counteracts the electron motion.  $v' = \text{const.}$  yields

$$\frac{d^2x}{dt^2} = 0. \quad (11.12)$$

By using (11.12), Equation (11.11) becomes

$$\frac{e\mathcal{E}}{\gamma} = \frac{dx}{dt} = v'. \quad (11.13)$$

The drift velocity is

$$v' = \frac{j}{eN_f} \quad (11.14)$$

(see (7.4)), where  $j$  is the current density (i.e., that current which passes through an area of one square centimeter).  $N_f$  is the number of free electrons per cubic centimeter. The current density is connected with the d.c. conductivity,  $\sigma_0$ , and the field strength,  $\mathcal{E}$ , by Ohm's law (7.2),

$$j = \sigma_0 \mathcal{E}. \quad (11.15)$$

Inserting (11.14) and (11.15) into (11.13) yields

$$\gamma = \frac{N_f e^2}{\sigma_0}. \quad (11.16)$$

Thus, (11.11) becomes

$$m \frac{d^2 x}{dt^2} + \frac{N_f e^2}{\sigma_0} \frac{dx}{dt} = e \mathcal{E} = e \mathcal{E}_0 \exp(i\omega t). \quad (11.17)$$

We note that the damping term in (11.17) is inversely proportional to the conductivity, i.e., proportional to the resistivity. This result makes sense.

The stationary solution of (11.17) is obtained, similarly as in Section 11.2, by differentiating the trial solution  $x = x_0 \exp(i\omega t)$  by the time, and inserting first and second derivatives into (11.17), which yields

$$-m\omega^2 x + \frac{N_f e^2}{\sigma_0} x \omega i = \mathcal{E} e. \quad (11.18)$$

Rearranging (11.18) provides

$$x = \frac{\mathcal{E}}{\frac{N_f e \omega}{\sigma_0} i - \frac{m\omega^2}{e}}. \quad (11.19)$$

Inserting (11.19) into (11.4) yields the polarization,

$$P = \frac{e N_f \mathcal{E}}{\frac{N_f e \omega}{\sigma_0} i - \frac{m\omega^2}{e}}. \quad (11.20)$$

With (11.20) and (11.5) the complex dielectric constant becomes

$$\hat{\epsilon} = 1 + \frac{P}{\epsilon_0 \mathcal{E}} = 1 + \frac{1}{\frac{2\pi\epsilon_0 v}{\sigma_0} i - \frac{m4\pi^2\epsilon_0}{N_f e^2} v^2}. \quad (11.21)$$

The term  $N_f e^2/m4\pi^2\epsilon_0$  is set, as in (11.8), equal to  $v_1^2$ , which reduces (11.21) to

$$\hat{\epsilon} = 1 + \frac{1}{\frac{2\pi\epsilon_0 v}{\sigma_0} i - \frac{v^2}{v_1^2}} = 1 + \frac{v_1^2}{iv \frac{2\pi\epsilon_0 v_1^2}{\sigma_0} - v^2}. \quad (11.22)$$



The term  $2\pi\varepsilon_0v_1^2/\sigma_0$  in (11.22) has the unit of a frequency. Thus, for abbreviation, we define a **damping frequency**

$$v_2 = \frac{2\pi\varepsilon_0v_1^2}{\sigma_0} = 2\pi\varepsilon_0v_1^2\rho_0. \quad (11.23)$$

(Table 11.2 lists values for  $v_2$  which were calculated using experimental  $\rho_0$  and  $v_1$  values.) Now (11.22) becomes

$$\hat{\varepsilon} = 1 + \frac{v_1^2}{ivv_2 - v^2}, \quad (11.24)$$

where  $\hat{\varepsilon}$  is, as usual, identical to  $\hat{n}^2$ ,

$$(\hat{n})^2 = n^2 - 2nki - k^2 = 1 - \frac{v_1^2}{v^2 - vv_2i}. \quad (11.25)$$

Multiplying the numerator and denominator of the fraction in (11.25) by the complex conjugate of the denominator ( $v^2 + vv_2i$ ) allows us to equate individually real and imaginary parts. This provides the Drude equations for the optical constants,

$$n^2 - k^2 = \varepsilon_1 = 1 - \frac{v_1^2}{v^2 + v_2^2} \quad (11.26)$$

and

$$2nk = \varepsilon_2 = \frac{v_2}{v} \frac{v_1^2}{v^2 + v_2^2}, \quad (11.27)$$

with the characteristic frequencies

$$v_1 = \sqrt{\frac{e^2N_f}{4\pi^2\varepsilon_0m}} \quad (11.8)$$

and

$$v_2 = \frac{2\pi\varepsilon_0v_1^2}{\sigma_0}. \quad (11.23)$$

Table 11.2. Resistivities and Damping Frequencies for Some Metals.

Metal	Li	Na	K	Rb	Cs	Cu	Ag	Au
$\rho_0$ ( $\mu\Omega$ cm) <sup>a</sup>	8.55	4.2	6.15	12.5	20	1.67	1.59	2.35
$v_2$ ( $10^{12}$ s <sup>-1</sup> )	10.1	4.8	3.1	4.82	5.15	4.7	4.35	5.9

<sup>a</sup> *Handbook of Chemistry and Physics*, 1977; room-temperature values.

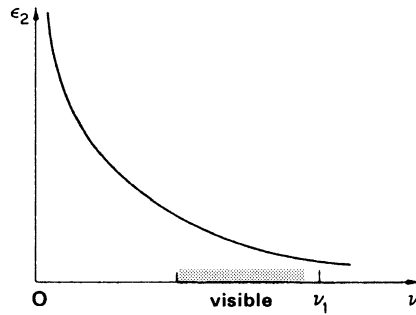


Figure 11.4. The absorption,  $\epsilon_2 = 2nk$ , versus frequency,  $\nu$ , according to the free electron theory (schematic).

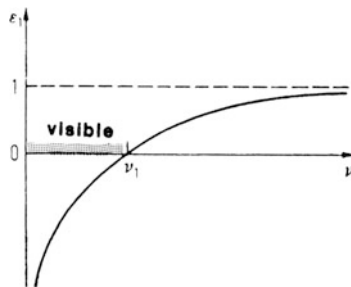


Figure 11.5. The dielectric polarization,  $\epsilon_1 = n^2 - k^2$ , as a function of frequency according to the Drude theory for metals (schematic).

The functions  $\epsilon_2$  (absorption) and  $\epsilon_1$  (which is proportional to the dielectric polarization, see Fig. 9.19), are plotted in Figs. 11.4 and 11.5 as a function of frequency, making use of (11.27) and (11.26).

## 11.4. Special Cases

For the *UV*, *visible*, and *near IR* regions, the frequency varies between  $10^{14}$  and  $10^{15} \text{ s}^{-1}$ . The average damping frequency,  $\nu_2$ , is  $5 \times 10^{12} \text{ s}^{-1}$  (Table 11.2). Thus,  $\nu^2 \gg \nu_2^2$ . Equation (11.27) then reduces to

$$\epsilon_2 = \frac{\nu_2}{\nu} \frac{\nu_1^2}{\nu^2}. \quad (11.28)$$

With  $\nu \approx \nu_1$  (Table 11.1) we obtain

$$\epsilon_2 \approx \frac{\nu_2}{\nu}. \quad (11.29)$$

Equation (11.29) confirms that  $\epsilon_2$  plotted versus the frequency yields a hyperbola with  $\nu_2$  as parameter (Fig. 11.4).

For *very small frequencies* ( $\nu^2 \ll \nu_2^2$ ), we may neglect  $\nu^2$  in the denominator of (11.27). This yields, with (11.23),

$$nk\nu = \frac{\sigma}{4\pi\epsilon_0} = \frac{1}{2} \frac{\nu_1^2}{\nu_2} = \frac{\sigma_0}{4\pi\epsilon_0}. \tag{11.30}$$

Thus, in the far IR the a.c. conductivity,  $\sigma$ , and the d.c. conductivity,  $\sigma_0$ , may be considered to be identical. We have already made use of this condition in Section 10.6. In general, however,  $\sigma$  is *not* identical to the d.c. conductivity,  $\sigma_0$ . (The same is true for the dielectric constant,  $\epsilon$ .)

### 11.5. Reflectivity

The reflectivity of metals is calculated using (10.29) in conjunction with (11.26) and (11.27), see Fig. 11.6. We notice that the experimental behavior for not-too-high frequencies (Fig. 11.1) is essentially reproduced. See also in this context the experimentally obtained reflectivities in Figs. 13.7, 13.10, and 13.12. For higher frequencies, however, we need to resort to a model different from the one discussed so far. This will be done in the next chapter.

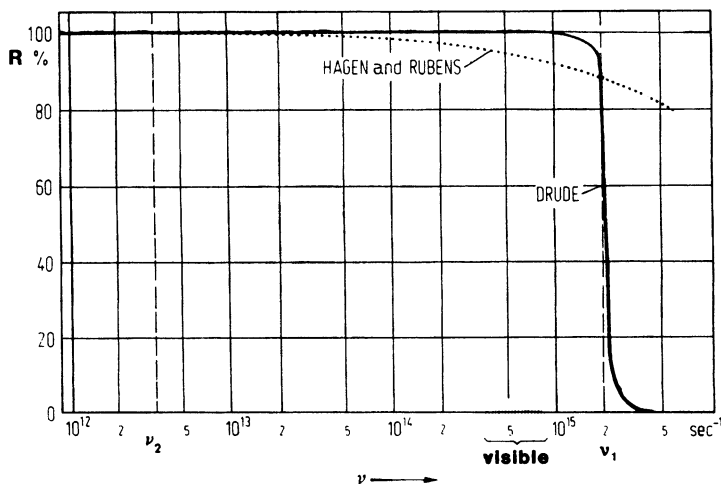


Figure 11.6. Calculated spectral reflectivity for a metal using the exact Drude equation (solid line), and the Hagen–Rubens equation (10.34) using  $\nu_1 = 2 \times 10^{15} \text{ s}^{-1}$  and  $\nu_2 = 3.5 \times 10^{12} \text{ s}^{-1}$ .

## 11.6. Bound Electrons (Classical Electron Theory of Dielectric Materials)

The preceding sections have shown that the optical properties of metals can be described and calculated quite well in the low-frequency range by applying the free electron theory. We mentioned already that this theory has its limits at higher frequencies, at which we observe that light is absorbed and reflected by metals as well as by nonmetals in a narrow frequency band. To interpret these absorption bands, Lorentz postulated that the electrons are bound to their respective nuclei. He assumed that under the influence of an external electric field, the positively charged nucleus and the negatively charged electron cloud are displaced with respect to each other (Fig. 11.7). An electrostatic force tries to counteract this displacement. For simplicity, we describe the negative charge of the electrons to be united in one point. Thus, we describe the atom in an electric field as consisting of a positively charged core which is bound quasielastically to *one* electron (electric dipole, Fig. 11.8). A bound electron, thus, may be compared to a mass which is suspended from a

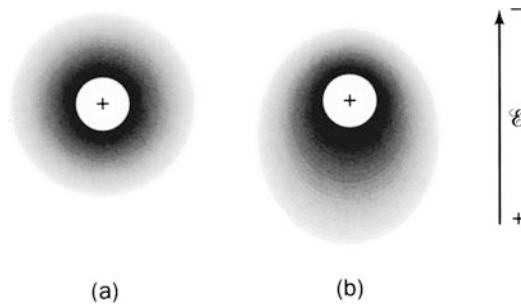


Figure 11.7. An atom is represented as a positively charged core and a surrounding, negatively charged electron cloud (a) in equilibrium and (b) in an external electric field.

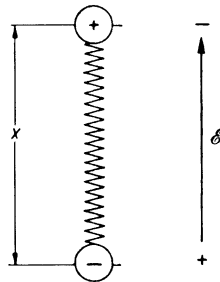


Figure 11.8. Quasi-elastic bound electron in an external electric field (harmonic oscillator).

spring. Under the influence of an alternating electric field (i.e., by light), the electron is thought to perform forced vibrations. For the description of these vibrations, the well-known equations of mechanics dealing with a harmonic oscillator may be applied. This will be done now.

We first consider an isolated atom, i.e., we neglect the influence of the surrounding atoms upon the electron. An external electric field with force

$$e\mathcal{E} = e\mathcal{E}_0 \exp(i\omega t) \quad (11.31)$$

periodically displaces an electron from its rest position by a distance  $x$ . This displacement is counteracted by a restoring force,  $\kappa \cdot x$ , which is proportional to the displacement,  $x$ . Then, the vibration equation becomes (see Appendix 1)

$$m \frac{d^2x}{dt^2} + \gamma' \frac{dx}{dt} + \kappa x = e\mathcal{E}_0 \exp(i\omega t). \quad (11.32)$$

The factor  $\kappa$  is the *spring constant*, which determines the binding strength between the atom and electron. Each vibrating dipole (e.g., an antenna) loses energy by radiation. Thus,  $\gamma'(dx/dt)$  represents the damping of the oscillator by radiation ( $\gamma'$  = damping parameter). The stationary solution of (11.32) for weak damping is (see Appendix 1)

$$x = \frac{e\mathcal{E}_0}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2\omega^2}} \exp[i(\omega t - \phi)], \quad (11.33)$$

where

$$\omega_0 = 2\pi\nu_0 = \sqrt{\frac{\kappa}{m}} \quad (11.34)$$

is called the **resonance frequency** of the oscillator, i.e., that frequency at which the electron vibrates freely without an external force.  $\phi$  is the phase difference between forced vibration and the excitation force of the light wave. It is defined to be (see Appendix 1)

$$\tan \phi = \frac{\gamma'\omega}{m(\omega_0^2 - \omega^2)} = \frac{\gamma'v}{2\pi m(v_0^2 - v^2)}. \quad (11.35)$$

As in the previous sections, we calculate the optical constants starting with the polarization,  $P$ , which is the product of the dipole moment,  $e \cdot x$ , of *one* dipole times the number of all dipoles (oscillators),  $N_a$ . As before, we assumed *one* oscillator per atom. Thus,  $N_a$  is identical to the number of atoms per unit volume. We obtain

$$P = exN_a. \quad (11.36)$$

Inserting (11.33) yields

$$P = \frac{e^2 N_a \mathcal{E}_0 \exp[i(\omega t - \phi)]}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}}. \quad (11.37)$$

With

$$\exp[i(\omega t - \phi)] = \exp(i\omega t) \cdot \exp(-i\phi) \quad (11.38)$$

we obtain

$$P = \frac{e^2 N_a \mathcal{E}}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}} \exp(-i\phi), \quad (11.39)$$

which yields with (11.5) and (10.12)

$$\hat{\epsilon} = n^2 - k^2 - 2nki = 1 + \frac{e^2 N_a}{\epsilon_0 \sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}} \exp(-i\phi). \quad (11.40)$$

Equation (11.40) becomes with<sup>6</sup>

$$\exp(-i\phi) = \cos \phi - i \sin \phi, \quad (11.41)$$

$$\begin{aligned} n^2 - k^2 - 2nki = 1 + \frac{e^2 N_a}{\epsilon_0 \sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}} \cos \phi \\ - i \frac{e^2 N_a}{\epsilon_0 \sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}} \sin \phi. \end{aligned} \quad (11.42)$$

The trigonometric terms in (11.42) are replaced, using (11.35), as follows:

$$\cos \phi = \frac{1}{\sqrt{1 + \tan^2 \phi}} = \frac{m(\omega_0^2 - \omega^2)}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}}, \quad (11.43)$$

$$\sin \phi = \frac{\tan \phi}{\sqrt{1 + \tan^2 \phi}} = \frac{\gamma' \omega}{\sqrt{m^2(\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2}}. \quad (11.44)$$

<sup>6</sup>See Appendix 2.

Separating the real and imaginary parts in (11.42) finally provides the optical constants

$$\varepsilon_1 = n^2 - k^2 = 1 + \frac{e^2 m N_a (\omega_0^2 - \omega^2)}{\varepsilon_0 [m^2 (\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2]},$$

that is,

$$\varepsilon_1 = 1 + \frac{e^2 m N_a (v_0^2 - v^2)}{\varepsilon_0 [4\pi^2 m^2 (v_0^2 - v^2)^2 + \gamma'^2 v^2]}, \quad (11.45)$$

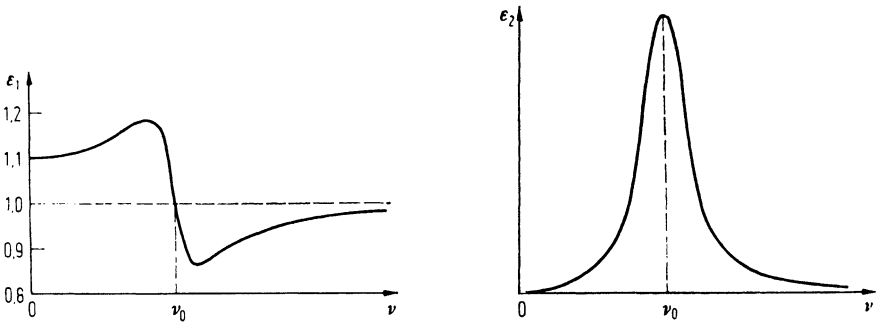
and

$$\varepsilon_2 = 2nk = \frac{e^2 N_a \gamma' \omega}{\varepsilon_0 [m^2 (\omega_0^2 - \omega^2)^2 + \gamma'^2 \omega^2]},$$

or

$$\varepsilon_2 = \frac{e^2 N_a \gamma' v}{2\pi \varepsilon_0 [4\pi^2 m^2 (v_0^2 - v^2)^2 + \gamma'^2 v^2]}. \quad (11.46)$$

The frequency dependencies of  $\varepsilon_1$  and  $\varepsilon_2$  are plotted in Figs. 11.9 and 11.10. Figure 11.9 resembles the dispersion curve for the index of refraction as it is experimentally obtained for dielectrics. Figure 11.10 depicts the absorption product,  $\varepsilon_2$ , in the vicinity of the resonance frequency,  $\nu_0$ , (absorption band) as experimentally observed for dielectrics. Equations (11.45) and (11.46) reduce to the Drude equations for  $\nu_0 \rightarrow 0$  (no oscillators).



Figures 11.9 and 11.10. Frequency dependence of the dielectric polarization,  $\varepsilon_1 = n^2 - k^2$ , and absorption,  $\varepsilon_2 = 2nk$ , as calculated with (11.45) and (11.46), respectively, using characteristic values for  $N_a$  and  $\gamma'$ .

## \*11.7. Discussion of the Lorentz Equations for Special Cases

### 11.7.1. High Frequencies

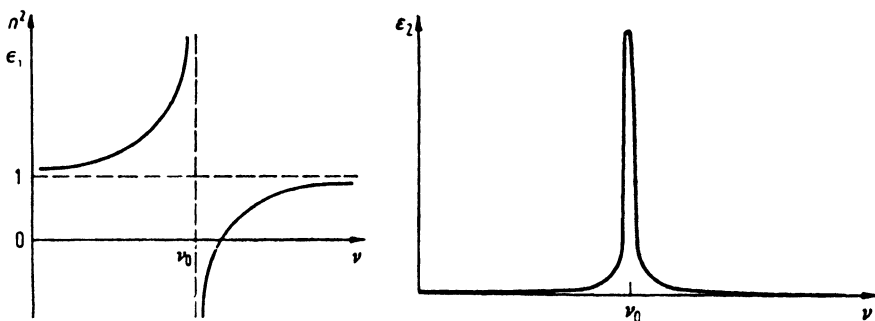
We observe in Fig. 11.10 that  $\epsilon_2$  approaches zero at high frequencies and far away from any resonances (absorption bands). In the same frequency region,  $\epsilon_1 = n^2 - k^2$  and, thus, essentially  $n$ , assumes the constant value 1 (Fig. 11.9). This is consistent with experimental observations that X-rays are not refracted and are not absorbed by many materials. (Note, however, that highly energetic X-rays interact with the *inner* electrons, i.e., they may be absorbed by the K, L, . . . , etc. electrons. Metals are, therefore, opaque for high-energetic X-rays).

### 11.7.2. Small Damping

We consider the case for which the radiation-induced energy loss of the oscillator is very small. Then,  $\gamma'$  is small. With  $\gamma'v^2 \ll 4\pi^2m^2(v_0^2 - v^2)^2$  (which is only valid for  $v \neq v_0$ ), equation (11.45) reduces to

$$\epsilon_1 = n^2 - k^2 = 1 + \frac{e^2N_a}{4\pi^2\epsilon_0m(v_0^2 - v^2)}. \quad (11.47)$$

Figure 11.11 depicts a sketch of (11.47). We observe that for small damping,  $\epsilon_1$  (and thus essentially  $n^2$ ) approaches infinity near the resonance frequency. A dispersion curve such as Fig. 11.11 is indeed observed for many dielectrics (glass, etc.).



Figures 11.11 and 11.12. The functions  $\epsilon_1$  ( $n^2$ ) and  $\epsilon_2$ , respectively, versus frequency according to the bound electron theory for the special case of small damping.



### 11.7.3. Absorption Near $\nu_0$

Electrons absorb most energy from light at the resonance frequency, i.e.,  $\epsilon_2$  has a maximum near  $\nu_0$ . For small damping, the absorption band becomes an absorption line (see Fig. 11.12). Inserting  $\nu = \nu_0$  into (11.46) yields

$$\epsilon_2 = \frac{e^2 N_a}{2\pi\epsilon_0 \gamma' \nu_0}, \quad (11.48)$$

which shows that the absorption becomes large for small damping ( $\gamma'$ ).

### 11.7.4. More Than One Oscillator

At the beginning of Section 11.6 we assumed that *one* electron is quasielastically bound to a given nucleus; in other words, we assumed *one* oscillator per atom. This assumption is certainly a gross simplification, as one can deduce from the occurrence of multiple absorption bands in experimental optical spectra. Thus, each atom has to be associated with a number of  $i$  oscillators, each having an oscillator strength,  $f_i$ . The  $i$ th oscillator vibrates with its resonance frequency,  $\nu_{0i}$ . The related damping constant is  $\gamma'_i$ . (This description has its equivalent in the mechanics of a system of mass points having one basic frequency and higher harmonics.) If all oscillators are taken into account, (11.45) and (11.46) become

$$\epsilon_1 = n^2 - k^2 = 1 + \frac{e^2 m N_a}{\epsilon_0} \sum_i \frac{f_i (\nu_{0i}^2 - \nu^2)}{4\pi^2 m^2 (\nu_{0i}^2 - \nu^2)^2 + \gamma_i'^2 \nu^2}, \quad (11.49)$$

$$\epsilon_2 = 2nk = \frac{e^2 N_a}{2\pi\epsilon_0} \sum_i \frac{f_i \nu \gamma'_i}{4\pi^2 m^2 (\nu_{0i}^2 - \nu^2)^2 + \gamma_i'^2 \nu^2}. \quad (11.50)$$

Equations (11.49) and (11.50) reduce for weak damping (see above) to

$$\epsilon_1 = n^2 - k^2 \approx n^2 = 1 + \frac{e^2 N_a}{4\pi^2 \epsilon_0 m} \sum_i \frac{f_i}{\nu_{0i}^2 - \nu^2}, \quad (11.51)$$

$$\epsilon_2 = 2nk = \frac{e^2 N_a}{8\pi^3 \epsilon_0 m^2} \sum_i \frac{f_i \nu \gamma'_i}{(\nu_{0i}^2 - \nu^2)^2}. \quad (11.52)$$

### 11.8. Contributions of Free Electrons and Harmonic Oscillators to the Optical Constants

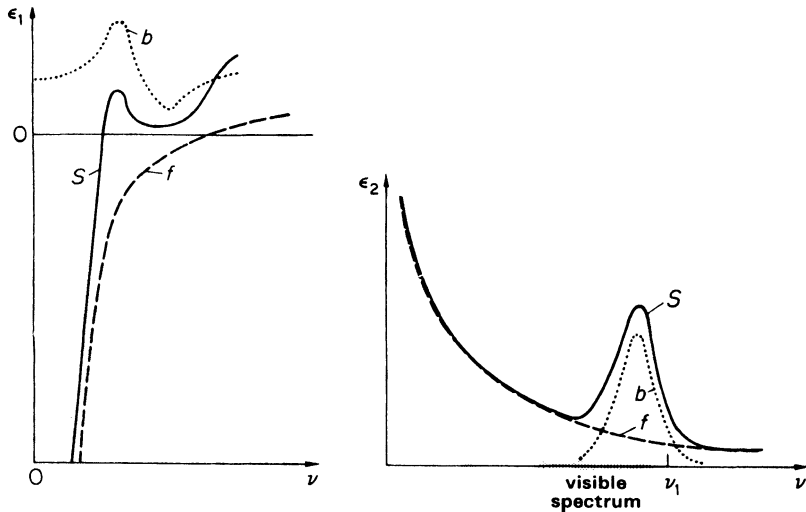
In the previous section, we ascribed two different properties to the electrons of a solid. In Section 11.4 we postulated that  $N_f$  electrons move freely in metals under the influence of an electric field and that this motion is damped by collisions of the electrons with vibrating lattice atoms and lattice defects. In Section 11.6 we postulated that a certain number of electrons are quasielastically bound to  $N_a$  atoms which are excited by light to perform forced vibrations. The energy loss was thought to be by radiation.

The optical properties of metals may be described by postulating a certain number of free electrons and a certain number of harmonic oscillators. Both the free electrons and the oscillators contribute to the polarization. Thus, the equations for the optical constants may be rewritten, by combining (11.26), (11.27), (11.49), and (11.50),

$$\epsilon_1 = 1 - \frac{v_1^2}{v^2 + v_2^2} + \frac{e^2 m N_a}{\epsilon_0} \sum_i \frac{f_i (v_{0i}^2 - v^2)}{4\pi^2 m^2 (v_{0i}^2 - v^2)^2 + \gamma_i'^2 v^2}, \tag{11.53}$$

$$\epsilon_2 = 2nk = \frac{v_2}{v} \frac{v_1^2}{v^2 + v_2^2} + \frac{e^2 N_a}{2\pi\epsilon_0} \sum_i \frac{f_i v \gamma_i'}{4\pi^2 m^2 (v_{0i}^2 - v^2)^2 + \gamma_i'^2 v^2}. \tag{11.54}$$

Figures 11.13 and 11.14 depict schematically the frequency dependence of  $\epsilon_1$  and  $\epsilon_2$  as obtained by using (11.53) and (11.54). These figures also



Figures 11.13 and 11.14. Frequency dependence of  $\epsilon_1$  and  $\epsilon_2$  according to (11.53) and (11.54). ( $i = 1$ ).  $f$  = free electron theory;  $b$  = bound electron theory;  $S$  = summary curve (schematic).

show the contributions of free and bound electrons on the optical constants. The experimentally found frequency dependence of  $\epsilon_1$  and  $\epsilon_2$  resembles these calculated spectra quite well. We will elaborate on this in Chapter 13, in which experimental results are presented.

## Problems

1. Calculate the reflectivity of sodium in the frequency ranges  $\nu > \nu_1$  and  $\nu < \nu_1$  using the theory for free electrons without damping. Sketch  $R$  versus frequency.
2. The plasma frequency,  $\nu_1$ , can be calculated for the alkali metals by assuming *one* free electron per atom, i.e., by substituting for  $N_f$  the number of atoms per unit volume (atomic density,  $N_a$ ). Calculate  $\nu_1$  for potassium and lithium.
3. Calculate  $N_{\text{eff}}$  for sodium and potassium. For which of these two metals is the assumption of *one* free electron per atom justified?
4. What is the meaning of the frequencies  $\nu_1$  and  $\nu_2$ ? In which frequency ranges are they situated compared to visible light?
5. Calculate the reflectivity of gold at  $\nu = 9 \times 10^{12} \text{ s}^{-1}$  from its conductivity. Is the reflectivity increasing or decreasing at this frequency when the temperature is increased? Explain.
6. Calculate  $\nu_1$  and  $\nu_2$  for silver ( $0.5 \times 10^{23}$  free electrons per cubic centimeter).
7. The experimentally found dispersion of NaCl is as follows:

$\lambda$ [ $\mu\text{m}$ ]	0.3	0.4	0.5	0.7	1	2	5
$N$	1.607	1.568	1.552	1.539	1.532	1.527	1.519

Plot these results along with calculated values obtained by using the equations of the “bound electron theory” assuming small damping. Let

$$\frac{e^2 N_a}{4\pi^2 \epsilon_0 m} = 1.81 \times 10^{30} \text{ s}^{-2} \quad \text{and} \quad \nu_0 = 1.47 \times 10^{15} \text{ s}^{-1}.$$

8. The optical properties of an absorbing medium can be characterized by various sets of parameters. One such set is the index of refraction and the damping constant. Explain the physical significance of those parameters, and indicate how they are related to the complex dielectric constant of the medium. What other sets of parameters are commonly used to characterize the optical properties? Why are there always “sets” of parameters?
9. Describe the damping mechanisms for free electrons and bound electrons.
10. Why does it make sense that we assume *one* free electron per atom for the alkali metals?
11. Derive the Drude equations from (11.45) and (11.46) by setting  $\nu_0 \rightarrow 0$ .
12. Calculate the effective number of free electrons per cubic centimeter and per atom for silver from its optical constants ( $n = 0.05$  and  $k = 4.09$  at 600 nm). (*Hint:* Use the free

electron mass.) How many free electrons per atom would you expect? Does the result make sense? Why may we use the free electron theory for this wavelength?

13. *Computer problem.* Plot (11.26), (11.27), and (10.29) for various values of  $\nu_1$  and  $\nu_2$ . Start with  $\nu_1 = 2 \times 10^{15} \text{ s}^{-1}$  and  $\nu_2 = 3.5 \times 10^{12} \text{ s}^{-1}$ .
14. *Computer problem.* Plot (11.45), (11.46), and (10.29) for various values of  $N_a$ ,  $\gamma'$ , and  $\nu_0$ . Start with  $\nu_0 = 1.5 \times 10^{15} \text{ s}^{-1}$  and  $N_a = 2.2 \times 10^{22} \text{ cm}^{-3}$  and vary  $\gamma'$  between 100 and 0.1.
15. *Computer problem.* Plot (11.51), (11.52), and (10.29) by varying the parameters as in the previous problems. Use one, two or three oscillators. Try to “fit” an experimental curve such as the ones in Figs. 13.10 or 13.11.