

### INTERACTION OF ELECTROMAGNETIC WAVES WITH SUBSTANCE

#### 5.1. Dispersion of light

We know that visible light consists of electromagnetic waves with the lengths band of 400–760 nm (corresponding frequency range  $\nu = (0.39 - 0.75) \cdot 10^{15}$  Hz). In vacuum, all light waves propagate with the same phase velocity  $c = 3 \cdot 10^8$  m/s. Light entering from vacuum to another optically transparent medium changes the phase velocity which in turn leads to the refraction of light in the case of slope falling to the border of separation of two optically different media.

*The dependence of the phase velocity on the wavelength (frequency) is called dispersion of light.* Thus, for waves of different lengths the speed of light in a medium is different. This means that the absolute refractive index depends on the wave length (frequency). All environments are characterized by dispersion of light except vacuum.

Newton experimentally found in 1672 that violet rays are refracted more than red ones in the glass prism. This means that the refractive index of the glass prism depends on the wavelength of the incident light  $n = f(\lambda_0)$ , where  $\lambda_0$  is the light wavelength in vacuum.

Unfortunately, Maxwell's electromagnetic theory, which unites electromagnetic and optical phenomena, could not explain the phenomenon of dispersion. According to Maxwell's theory, refractive index is determined by the dielectric constant  $\epsilon = n^2$ , which is constant for a given environment. Therefore, the refractive index would also be a constant.

Remember some of the conclusions of the Maxwell theory. If a ray of light falls from vacuum (in practice from air) on an isotropic transparent dielectric, the light phase velocity in the dielectric  $v < c$ , then according to Snell's law of refraction we have:

$$\frac{\sin \vartheta}{\sin \vartheta''} = \frac{c}{v} = n, \quad (\vartheta > \vartheta''), \quad (5.1)$$

where  $\vartheta$  and  $\vartheta''$  are the angles between the directions of the incident and refracted rays and the normal to the surface vacuum-dielectric border;  $n$  is the absolute refractive index of the dielectric material.

Summarizing the law of refraction when light passes from one substance to another, we find an equation for the *relative refractive index* of the second medium with respect to the first:

$$\frac{\sin \vartheta}{\sin \vartheta''} = \frac{v_1}{v_2} = \frac{v_1 c}{v_2 c} = \frac{c/v_2}{c/v_1} = \frac{n_2}{n_1} = n_{12}, \quad (5.2)$$

where  $v_1$  and  $v_2$  are the phase velocities of light waves in the first and second media.

When an electromagnetic wave propagates in a homogeneous medium with dielectric permittivity  $\epsilon$  and permeability  $\mu$ , the theory of Maxwell states that

$$v = \frac{1}{\sqrt{\epsilon\epsilon_0\mu\mu_0}}. \quad (5.3)$$

In vacuum  $\epsilon = \mu = 1$ ,  $c = \frac{1}{\sqrt{\epsilon_0\mu_0}}$ ; hence, the absolute refractive index of the medium can be written as:

$$n = \frac{c}{v} = \sqrt{\epsilon\mu}. \quad (5.4)$$

The permeability  $\mu \approx 1$  for majority of optically transparent dielectric media; so, the formula (5.4) is simplified:

$$n = \frac{c}{v} = \sqrt{\epsilon} \Rightarrow \epsilon = n^2. \quad (5.5)$$

The frequency of electromagnetic wave is unchanged when light passes from one medium to another. The phase velocity of wave propagation in the medium can be determined through the frequency  $v = \lambda/T = \lambda\nu$  ( $c = \lambda_0\nu$  in vacuum). Then, taking into account the constant frequency, the equation for the relative refractive index takes the form:

$$n_{12} = \frac{v_1}{v_2} = \frac{\lambda_1}{\lambda_2}. \quad (5.6)$$

If a ray of light goes into the environment from the vacuum, we obtain:

$$n = \frac{\lambda_0}{\lambda} \Rightarrow \lambda = \frac{\lambda_0}{n}, \quad (5.6a)$$

where  $\lambda_0$  is the light wavelength in the vacuum;  $\lambda$  is the light wavelength in the medium;  $n$  is the medium absolute refractive index.

Dispersion of light can be explained by considering the interaction of light with matter. Electrons motion in an atom is described by the laws of quantum mechanics; in particular, the notion of a trajectory of an electron in an atom does not exist. However, as it is shown by Lorenz, the classical concepts are enough for the qualitative description of the dispersion of light; the concepts lead to the same results as the quantum theory.

According to the classical electron theory, dispersion of light is caused by light waves interaction with the electrons in atoms of a dielectric material. Atoms can be represented as electric dipoles, which perform forced oscillations under the influence of the electromagnetic field of the light with the frequency of oscillation of the incident wave. Electromagnetic radiation caused by the dipoles oscillations excites the secondary waves, which propagate with the same speed as the primary light wave.

Adding these secondary waves to the primary one gives a resultant wave which phase depends on the phase of the primary wave and the amplitudes and the phases of the secondary waves. The amplitude and the phase of each elementary secondary wave depends on the amplitude and the phase of the forced oscillations of the corresponding dipole. Since these dipoles have their natural (resonant) frequency  $\omega_0$ , their amplitudes and phases strongly depend on the ratio of the primary wave frequency and the natural frequency.

Thus, the phase of the resulting wave that propagates through matter is different from the initial phase of the propagating wave in the vacuum and depends on its frequency. Hence, waves with different wavelengths (frequencies) propagate in matter with the different phase speeds and have different refractive indexes.

For simplicity, we assume that the atoms of the dielectric isotropic medium have only one optical electron (hydrogen atoms). An optical electron in an atom is considered as a harmonic oscillator; the oscillator

differential equation of motion is well known from the theory of oscillations; it is the equation of the forced oscillations:

$$m\ddot{x} = -r\dot{x} - kx + eE,$$

where  $m$  is an electron mass;  $e$  is an electron charge;  $r\dot{x}$  is the resistance force;  $kx$  is the force that keeps the electron in equilibrium and has the character of elastic force, so, it is called quasielastic;  $E$  is the intensity of the alternating electric field of the incident wave along the  $x$  direction.

Divided by the mass the classical equation will look like:

$$\ddot{x} + 2\beta\dot{x} + \omega_0^2 x = eE/m, \quad (5.7)$$

where  $\omega_0^2 = k/m$  is the natural frequency;  $\beta = r/2m$  is the damping factor.

It is known from the theory of oscillations that equation (5.7) is a differential equation of the forced oscillations. For these oscillations, the amplitude of the oscillator reaches maximum value (resonance) at the frequency  $\omega \approx \omega_0$  of the external electromagnetic field; so, natural frequency  $\omega_0$  is also called *resonance* frequency.

It has been assumed that the intensity  $E$  is directed along  $x$  and, since electromagnetic waves are transverse, we can assume that the incident plane wave propagates along the direction  $z$ . The wave equation in the complex form is as following:

$$E(z, t) = E_0 e^{i\omega(t-z/c)} = E_0 e^{i(\omega t - \omega z/c)} = E_0 e^{i(\omega t - kz)}, \quad (5.8)$$

where  $\omega/c = k$  is the wave number .

The solution of the equation (5.7) is well known from the theory of oscillations:

$$x(t) = A e^{i\omega t}, \quad (5.9)$$

where  $A$  is the complex amplitude;  $\omega$  is the frequency of the incident electro-magnetic wave.

Differentiation of the equation (5.9) gives  $\dot{x} = i\omega x$ ,  $\ddot{x} = -\omega^2 x$ . Substituting these equations in the equation (5.7), we obtain:

$$(-\omega^2 + i\omega 2\beta + \omega_0^2)x = eE/m; \quad (5.10)$$

the solution of (5.10) is:

$$x = \frac{e/m}{\omega_0^2 - \omega^2 + i\omega 2\beta} E. \quad (5.11)$$

The dipole moment of an atom, which electron has been shifted from the equilibrium point  $x = 0$  in the point  $x$  is:

$$p = ex = \frac{e^2 / m}{\omega_0^2 - \omega^2 + i\omega 2\beta} E. \quad (5.12)$$

If there are  $N_0$  atoms that undergo polarization in the volume of unit of the medium, the electric moment of the volume unit, (polarization of the medium  $P$ ) is:

$$P = N_0 p = \frac{N_0 e^2 / m}{\omega_0^2 - \omega^2 + i\omega 2\beta} E. \quad (5.13)$$

Taking into account the equation for the electric field induction

$$D = \epsilon_0 E + P = \epsilon_0 \epsilon E, \quad (5.14)$$

we can find an equation for the dielectric constant:

$$\epsilon = 1 + \frac{N_0 e^2 / (\epsilon_0 m)}{\omega_0^2 - \omega^2 + i\omega 2\beta}. \quad (5.15)$$

The equation (5.15) shows that the dielectric constant of the medium depends on the frequency  $\epsilon = \epsilon(\omega)$  and in general it is a complex quantity. *The dependence of the dielectric constant of the medium on a light frequency means that the phase velocity of light (5.3) in the medium also depends on the frequency, i.e., there is light dispersion.*

### 5.1.1. Normal and abnormal dispersion

Using the equation (5.15), the refractive index can be represented as

$$\tilde{n}^2 = \epsilon = 1 + \frac{N_0 e^2 / (\epsilon_0 m)}{\omega_0^2 - \omega^2 + i\omega 2\beta}, \quad (5.16)$$

or

$$\tilde{n} = \sqrt{\epsilon} = \left( 1 + \frac{N_0 e^2 / (\epsilon_0 m)}{\omega_0^2 - \omega^2 + i\omega 2\beta} \right)^{1/2}, \quad (5.16a)$$

where  $\tilde{n}$  is a complex value. Submit it in the form

$$\tilde{n} = n - i\kappa, \quad (5.17)$$

where  $n$  and  $\kappa$  are the real and imaginary parts of  $\tilde{n}$ . Dimensionless quantity  $\kappa$  is called the *index of absorption or extinction*; it characterizes the diminishing amplitude of a plane wave propagating along a certain direction.

Let us consider a simplified case where the modulus of the refractive index  $|\tilde{n}|$  differs a little from one. This case is typical for many gases in visible light as well as for X-rays. In this case, the equation (5.16a) can be expanded in a Taylor series, being limited by the second term:

$$\tilde{n} = n - i\kappa = \sqrt{\epsilon} \approx 1 + \frac{N_0 e^2 / (2\epsilon_0 m)}{\omega_0^2 - \omega^2 + i\omega 2\beta} \quad (5.18)$$

(we have used the decomposition of functions  $(1+x)^n \approx 1+nx$ , where  $n=1/2$ ).

Multiplying and dividing the equation (5.18) by  $\omega_0^2 - \omega^2 - i\omega 2\beta$  and dividing into real and imaginary parts, we obtain:

$$n = 1 + \frac{N_0 e^2}{2\epsilon_0 m} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + 4\beta^2 \omega^2}; \quad (5.19)$$

$$\kappa = \frac{N_0 e^2}{2\epsilon_0 m} \cdot \frac{2\beta \omega}{(\omega_0^2 - \omega^2)^2 + 4\beta^2 \omega^2}. \quad (5.20)$$

The dependence of  $n$  and  $\kappa$  on the frequency  $\omega$  is shown in Fig. 5.1 *a*. The dependence  $n = f(\omega)$  shows that the refractive index increases with the frequency increasing at both sides at some distance from the resonance frequency  $\omega_0$ .

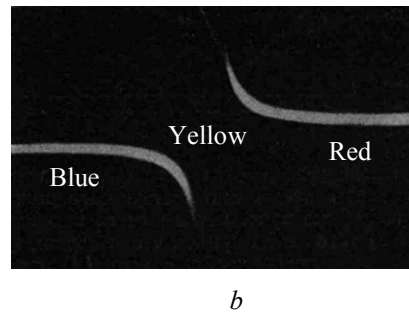
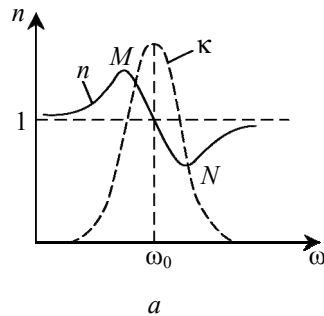


Fig. 5.1

Frequency range  $dn/d\omega > 0$  corresponds to *normal dispersion*. The refractive index decreases with the frequency increasing  $dn/d\omega < 0$  on the zone  $MN$  of the curve. This frequency range corresponds to *abnormal dispersion*. The frequency range of abnormal dispersion coincides with the absorption band (dashed curve), which has a maximum value near the resonance frequency of the optical electron oscillations in an atom.

The place of rupture of the curve corresponds to the total absorption of resonance wavelength of the yellow sodium D-line 589 nm.

Fig. 5.1 shows that the index of absorption  $\kappa$  tends to zero outside the absorption band. This means that the damping factor in the equation (5.20) tends to zero  $\beta \rightarrow 0$ ; therefore, the imaginary part of the equation (5.15) can be neglected:

$$\epsilon = n^2 = 1 + \frac{N_0 e^2 / (\epsilon_0 m)}{(\omega_0^2 - \omega^2)}. \quad (5.21)$$

Graphical dependence (5.21)  $n^2 = f(\omega)$  is shown in Fig. 5.2; it shows that the normal dispersion is observed for the frequencies  $0 < \omega < \omega_0$  and  $\omega > \omega_0$ . Assumption that  $n^2 \rightarrow \pm \infty$  is the result of neglecting of damping; hence, the dependence (5.21) near the resonance frequency has no real physical meaning.

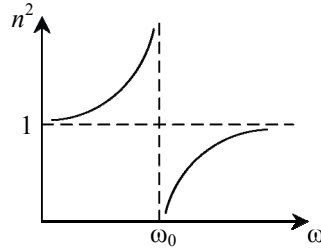


Fig. 5.2

### 5.1.2. Oscillator strength, static dielectric permittivity

In general, atoms contain many electrons; so, it can be several natural oscillation frequencies may. Consider this fact.

Suppose, there is the substance with the concentration of the atoms  $N_0$ ; each atom has  $f_1$  oscillators with the natural frequency  $\omega_{01}$  and the

damping factor  $\beta_1$ ,  $f_2$  oscillators with the natural frequency  $\omega_{02}$  and the damping factor  $\beta_2$  and so on. Then the concentration of oscillators with frequency  $\omega_{0i}$  and damping factor  $\beta_i$  can be written as:  $N_i = N_0 f_i$ .

To consider the effectiveness of all oscillators in the equations (5.16), (5.19)–(5.21), we replace  $N_0$ ,  $\omega_0$ ,  $\beta$  with  $N_0 f_i$ ,  $\omega_{0i}$ ,  $\beta_i$  and perform summing over all possible values of  $i$  (i.e., for all sorts of oscillators). Then,

$$\tilde{n}^2 = 1 + \frac{N_0 e^2}{\epsilon_0 m} \sum_i \frac{f_i}{\omega_{0i}^2 - \omega^2 + i\omega 2\beta_i}. \quad (5.22)$$

Outside the absorption bands in the equation (5.22), the imaginary part can be neglected:

$$n^2 = 1 + \frac{N_0 e^2}{\epsilon_0 m} \sum_i \frac{f_i}{\omega_{0i}^2 - \omega^2}. \quad (5.23)$$

If a refractive index is close to one, we obtain from the equations (5.19) and (5.20):

$$n = 1 + \frac{N_0 e^2}{2\epsilon_0 m} \sum_i \frac{f_i (\omega_{0i}^2 - \omega^2)}{(\omega_{0i}^2 - \omega^2)^2 + 4\beta_i^2 \omega^2}; \quad (5.24)$$

$$\kappa = \frac{N_0 e^2}{2\epsilon_0 m} \sum_i \frac{f_i 2\beta_i \omega}{(\omega_{0i}^2 - \omega^2)^2 + 4\beta_i^2 \omega^2}. \quad (5.25)$$

Where  $f_i$  are constant coefficients that are called *oscillator strengths*.

If there are several natural frequencies, the dispersion curves splits into several branches (Fig. 5.3). Each natural frequency has its own absorption band; the refractive index varies abnormally near the band.

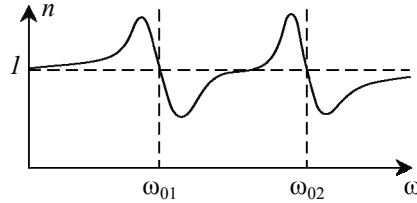


Fig. 5.3



In general, the dispersion in substance is created not only by the oscillation of electrons, but the ions oscillations. Because of the high mass, the ions natural oscillations frequency is much smaller than the frequency of the electrons natural oscillations. The ions natural frequencies are in the far infrared band and do not affect the dispersion curve in the visible spectrum.

However, they play a major role in explaining the difference between the values of the static dielectric constant and the value of dielectric permeability in the visible spectrum. Indeed, if the frequencies are low ( $\omega \rightarrow 0$ ), the static refractive index can be represented from equation (5.23) as:

$$n_{st}^2 = 1 + \frac{N_0}{\epsilon_0} \sum_i \frac{e_i^2 f_i}{m_i \omega_{0i}^2}. \quad (5.26)$$

The equation (5.26) shows that  $n_{st}$  is independent from the frequency  $\omega$  of the incident wave. Physically, this means that at the low frequencies the instantaneous polarization of the medium is almost the same as in the case of the static fields; so, the values  $\epsilon$  and  $n$  do not depend on  $\omega$ .

### 5.1.3. Lorentz–Lorenz Formula

In the calculations above, the external electric field with intensity  $E$  is considered instead of the internal field  $E'$ . Thus, the difference between these fields was ignored  $E' \approx E$ , it can do for rarefied gases. But, let us find out what the consequence of taking into account the interaction of molecules polarized by the electric field of the incident light would be.

For the most optically transparent materials (gases, liquids), natural frequencies of electrons oscillations correspond to the ultraviolet light. These frequencies are much higher than the visible light frequencies so the visible frequency range is far from the absorption band. Therefore, we can neglect absorption and think that  $\beta = 0$ . So, the equation (5.13) is simplified and it takes the form for each natural frequency:

$$P = N_0 p = \frac{N_0 f e^2 / m}{\omega_0^2 - \omega^2} E. \quad (5.27)$$

Lorentz has shown that for an isotropic medium:

$$\vec{E}' = \vec{E} + \frac{\vec{P}}{3\epsilon_0}. \quad (5.28)$$

Substituting  $\vec{E}$  by  $\vec{E}'$  in equation (5.27) gives an equation for the electric moment per unit volume:

$$\vec{P} = \frac{N_0 f e^2 / m}{(\omega_0^2 - \omega^2) - N_0 f e^2 / (3m\epsilon_0)} \vec{E}. \quad (5.29)$$

Taking into account the relation (5.14), we obtain the equation for the dielectric constant:

$$\epsilon = 1 + \frac{N_0 f e^2 / (m\epsilon_0)}{(\omega_0^2 - \omega^2) - N_0 f e^2 / (3m\epsilon_0)}. \quad (5.30)$$

Performing mathematical transformation of (5.30), we obtain:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n^2 - 1}{n^2 + 2} = \frac{N_0 f e^2}{3m\epsilon_0(\omega_0^2 - \omega^2)} = \frac{1}{3} N_0 \alpha, \quad (5.31)$$

where  $\alpha = \frac{f e^2}{m\epsilon_0(\omega_0^2 - \omega^2)}$  is the polarizability of the atom (molecule), which dimension is  $[m^3]$ .

For rarefied gases,  $n$  is close to one, i.e.  $n^2 + 2 \approx 3$ . Then, the formula (5.31) turns to formula (5.21):

$$n^2 - 1 = \frac{N_0 e^2}{m\epsilon_0(\omega_0^2 - \omega^2)}.$$

The equation (5.21) was simultaneously received by Dutch physicist Lorentz and Danish physicist L. Lorentz; so, it is called Lorentz-Lorentz formula.

Lorentz-Lorentz formula shows that for a given substance ( $e$ ,  $m$ ,  $\omega_0$ ) at the constant frequency ( $\omega = \text{const}$ ), the relation is true:

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho} = \frac{\alpha}{3m_0} = \text{const}, \quad (5.32)$$

where  $\rho = N_0 m_0$  is density;  $m_0$  is the mass of one atom (molecule) of a substance.

The value of  $r$  is called the *specific refraction*, and, according to the relation (5.32), it should not change when you change the density of the transparent material  $\rho$ .

The product of specific refraction and the molar mass  $M$  is called *molar refraction*  $R$ :

$$R = Mr = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{1}{3} N_0 \frac{M}{\rho} \alpha = \frac{1}{3} N_0 \frac{m_0 N_A}{m_0 N_0} \alpha = \frac{1}{3} N_A \alpha, \quad (5.33)$$

where  $N_A$  is Avogadro constant.

Since the polarizability of the molecule has the dimension  $[\text{m}^3]$ , then we write it in the form  $\alpha = 4\pi r^3$ , where  $r$  is the radius of an atom (molecule). Then, the equation (5.33) takes the form:

$$R = \frac{4\pi r^3}{3} N_A = N_A v_0, \quad (5.34)$$

where  $v_0$  is the volume of a single molecule.

Thus, the molar refraction  $R$  is equal to the volume of all the molecules in one mole of a substance.

If the substance does not consist of one type of molecules, the molar refraction of the mixture is the sum of the ingredients refractions.

Let the volume unit of the mixture contains  $N_1$  molecules with polarizability  $\alpha_1$ ,  $N_2$  molecules with polarizability  $\alpha_2$ , etc. Experiments show that the mixture refraction is the sum of the refractions of the components:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} (N_1 \alpha_1 + N_2 \alpha_2 + \dots). \quad (5.35)$$

Multiplying equation (5.35) by  $N_A / N_0$  ( $N_0$  is the total amount of molecules in  $\text{m}^3$ , i.e. concentration), we obtain:

$$\begin{aligned} \frac{n^2 - 1}{n^2 + 2} \frac{N_A}{N_0} &= \frac{1}{3} N_A \left( \frac{N_1}{N_0} \alpha_1 + \frac{N_2}{N_0} \alpha_2 + \dots \right) = \\ &= \frac{1}{3} N_A (g_1 \alpha_1 + g_2 \alpha_2 + \dots) = g_1 R_1 + g_2 R_2 + \dots, \end{aligned} \quad (5.35a)$$

where  $g_i = N_i / N_0$  characterizes the molar concentration of  $i$ -th component of the mixture;  $R_1, R_2, \dots, R_n$ , are the molar refractions of the mixture components.

Since the density of the mixture is:

$$\rho = \frac{M_1 N_1 + M_2 N_2 + \dots}{N_A} = \frac{N_0}{N_A} \frac{M_1 N_1 + M_2 N_2 + \dots}{N_0} = \frac{N_0}{N_A} \bar{M},$$

where  $M_1, M_2, \dots, M_n$  are the components molar masses;  $\bar{M}$  is the average molar mass. Finally,

$$\bar{R} = \frac{n^2 - 1}{n^2 + 2} \frac{\bar{M}}{\rho} = g_1 R_1 + g_2 R_2 + \dots, \quad (5.35b)$$

where  $\bar{R}$  is the average molar refraction or molar refraction of the mixture.

Determination of refraction (refractive index) is an important analytical method of study of the chemical nature of the molecules; refractometric methods are widely used in modern physics-chemical studies.

#### 5.1.4. Dispersion of plasma

Plasma is an ionized gas; it has nearly equal concentrations of negative electrons and positive ions. Electrons in plasma are free; so, dielectric constant of plasma is mainly determined by the electrons. Their natural frequency can be regarded as zero. Putting in (5.15)  $\omega_0 = 0$  and neglecting damping, we obtain:

$$n^2 = \epsilon = 1 - \frac{N_e e^2}{\epsilon_0 m \omega^2}, \quad (5.36)$$

or

$$n^2 = \epsilon = 1 - \frac{\omega_p^2}{\omega^2}. \quad (5.37)$$

$N_e$  is the free electrons concentration in plasma;  $\omega_p^2 = N_e e^2 / \epsilon_0 m$  is the natural frequency of plasma.

If  $\omega_p > \omega$ , it follows from the formula (5.37) that the value  $\epsilon$  (and the refractive index  $n = \sqrt{\epsilon}$ ) is positive but less than one. If the electromagnetic wave frequency is less than the plasma frequency  $\omega < \omega_p$ , the permittivity is negative  $\epsilon < 0$ ; hence, the refractive index for these frequencies becomes imaginary  $n = -i\kappa$ . Let us find out what it means.

The electromagnetic wave equation in the complex form according to equation (5.8) is:

$$E(z, t) = E_0 \exp(-\kappa k_0 z) e^{i\omega t}, \quad (5.38)$$

where  $k = 2\pi/\lambda$ ,  $\lambda = \lambda_0/n$  is the wavelength in the medium,  $\lambda_0$  is the wavelength in vacuum,  $k_0 = 2\pi/\lambda_0$ , and  $n = -i\kappa$ .

The standing wave amplitude decreases by the exponential law. Physically, this means that an electromagnetic wave cannot penetrate through plasma. In fact, the wave penetrates only in a thin surface layer of plasma and undergoes complete reflection on it.

Dispersion of plasma explains ability of the long-range radio communications in the earth's atmosphere. There is a spherical ionized layer called the ionosphere, which begins approximately 60 km altitude and extends to about 20,000 km. The main source of ionization of the ionosphere is the Sun ultraviolet radiation and soft X-ray emission of the solar corona.

The only way to reach the receiver is a reflection of radio waves from the ionosphere. It allows to transmit radio signals over long distances, up to thousands kilometers. The most stable long-range radio communication is realized using long radio waves.

With the frequency increase  $\omega \geq 10^8$  Hz, the refractive index increases too and when  $n \approx 1$ , waves pass freely through the ionosphere without refraction and reflection. This limits their use for radio broadcasting but provides an opportunity to make radio contact with the cosmos, to execute radar of the Moon and planets.

## 5.2. Group velocity

The value of the refractive index less than one ( $n < 1$ ) means that the phase velocity of the wave in the substance is greater than the speed of light in vacuum. An excess of phase velocity relatively to the speed of light does not contradict the theory of relativity.

According to the math Fourier theorem, any real wave can be represented as a superposition of monochromatic waves with the different amplitudes and frequencies inside of a frequency interval  $\Delta\omega$ . Superposition of waves with a small difference of frequencies ( $\Delta\omega \ll \omega$ ) is called *wave packet*. Inside of the limits, the

monochromatic components mutually reinforce each other; outside the package, they almost extinguish each other (Fig. 5.4).

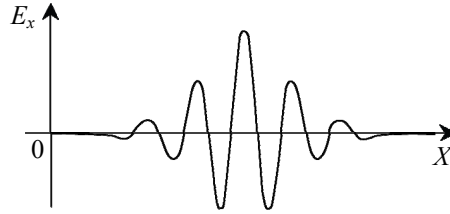
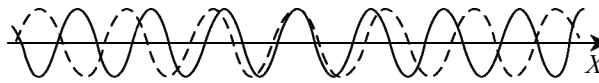


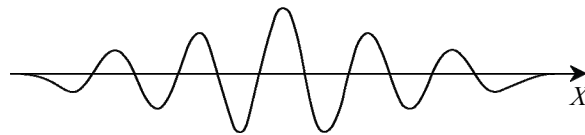
Fig. 5.4

In a vacuum, all monochromatic waves create a wave packet with the same phase velocity  $v = c$ .

If a medium dispersion is small (air), the wave packet deforms very slowly and it can be described by a velocity of its maximum  $u$ . Let us suppose two waves with the equal amplitudes but slightly different frequencies (Fig. 5.5, *a*). The result of their superposition is shown on Fig. 5.5, *b*.



*a*



*b*

Fig. 5.5

If the number of components in the wave packet is increased, the width of the wave packet decreases. In the case of superposition of an infinite number of similar frequencies, a wave packet is converted into a pulse. Mathematically, this means that the impulse can be represented as a Fourier integral. Calculations show that the more components in the wave packet (the larger the frequencies  $\Delta\omega$  and wavenumbers  $\Delta k$

intervals), the smaller the width of the wave packet  $\Delta x$ , and the more it is similar in shape to a narrow pulse:

$$\Delta k \Delta x \approx 2\pi.$$

Let us consider the simplest case of a superposition of two waves (initial phases are equal to zero):

$$E_1 = A \cos(\omega t - kx);$$

$$E_2 = A \cos[(\omega + d\omega)t - (k + dk)x].$$

Their addition gives:

$$E_1 + E_2 = 2A \cos \frac{td\omega - xdk}{2} \cos(\omega t - kx) \quad (5.39)$$

( $d\omega$  neglected compared to  $\omega$ ,  $dk$  neglected compared to  $k$ ).

The speed of the maximum amplitude of the resultant wave is the speed of the wave packet, i.e. the *group velocity*. The equation (5.39) can be regarded as the equation of a plane monochromatic wave with the amplitude:

$$A_0 = \left| 2A \cos \frac{td\omega - xdk}{2} \right|.$$

We have several amplitude maxima, defined by

$$\cos \frac{td\omega - xdk}{2} = \pm 1 \Rightarrow \frac{td\omega - xdk}{2} = \pm m\pi \quad (m = 0, 1, 2, \dots).$$

Each of these maxima can be considered as a maximum (or center) of the group of waves. Since the maxima are exactly the same, any of them can be selected as the initial. Then,  $td\omega - xdk = 0$ , and the equation for the group velocity is:

$$u = \frac{x}{t} = \frac{d\omega}{dk}. \quad (5.40)$$

Thus, the phase velocity is defined by  $v = \omega/k$  and the group velocity by  $u = d\omega/dk$ .

Let us find the connection between the group and phase velocities (remember that  $\omega = vk$ ):

$$u = \frac{d}{dk}(vk) = v + k \frac{dv}{dk}. \quad (5.41)$$

As  $k = 2\pi/\lambda$ ,  $dk = -(2\pi/\lambda^2)d\lambda$ , where  $\lambda$  is wavelength in the medium; the equation (5.41) turns into

$$u = v - \lambda \frac{dv}{d\lambda}. \quad (5.42)$$

This is *Rayleigh formula*, which indicates that the group velocity  $u$  can be either smaller or larger than the phase velocity  $v$ . If the dispersion is normal ( $dn/d\lambda_0 < 0$ ), the group velocity is less than the phase velocity; if dispersion is abnormal ( $dn/d\lambda_0 > 0$ ), the group velocity is more than the phase velocity.

### 5.3. Absorption of light

The passage of light through a substance causes the appearance of the oscillations of the electrons under the influence of the electromagnetic field of the incident wave and is accompanied by a loss of energy of the wave, which is spent to excitation of the electrons oscillations.

This phenomenon is called *absorption of light*. The absorbed energy can be converted into the energy of the secondary radiation that has a different spectral composition and other directions of radiation (photoluminescence). Absorption of light can cause heating the substance, excitation and ionization of atoms or molecules, photochemical reactions and so on.

The propagating wave equation along  $z$  in a complex form is:

$$E(z, t) = E_0 e^{i(\omega t - k'z)}.$$

If we use the equation (5.5), the wave number  $k' = \omega/v$  ( $v$  is the phase velocity of light in the substance) can be given as:

$$k' = \omega/v = \omega\sqrt{\epsilon}/c. \quad (5.43)$$

Replacing the equation  $\sqrt{\epsilon}$  by  $\sqrt{\epsilon} = n - i\kappa$  gives:

$$k' = \omega n/c - i\omega\kappa/c, \quad (5.44)$$

after substitution of (5.44) in (5.8), we obtain:

$$E(z, t) = E_0 e^{i(\omega t - k'z)} = E_0 e^{-\omega\kappa z/c} e^{i(\omega t - \omega n z/c)}. \quad (5.45)$$



The formula (5.45) contains the wave amplitude  $E_0 e^{-\omega\kappa z/c}$  with exponential factor with the rate of absorption  $\kappa$ . This means that the wave propagation in a dielectric medium is accompanied by a decrease of its amplitude. Thus, the phenomenon of absorption is explained by the electrons damping oscillations in an atom, i.e. the imaginary part of the refractive index describes the damping of a plane wave during its propagation in the dielectric.

According to the equation (5.19), where the frequency of the incident wave approaches the resonance frequency  $\omega \rightarrow \omega_0$ , then  $n \rightarrow 1$  and the rate of absorption  $\kappa$  (5.20) takes the maximum value (see Fig. 5.1). Thus, absorption is the main cause of the damping of the electromagnetic waves in the region of the resonant frequency.

For example, the light emitted by the Sun passes through the solar atmosphere (as well as through the Earth's atmosphere), and the frequencies that coincide with the resonance frequency of the atoms in the solar atmosphere are strongly absorbed. Due to this, dark lines (absorption lines) are observed in the solar spectrum.

The observation of the similar spectral lines allows to discover the resonance frequencies of the atoms and, hence, the chemical composition of the solar atmosphere. Similarly, the absorption spectra of stars give information about the composition of stellar matter. We now know that the chemical elements in the Sun and the stars are the same as on the Earth.

### 5.3.1. Bouguer law

According to the equation (5.45), the amplitude of the damped waves is:

$$|E| = E_0 e^{-\omega\kappa z/c} = E_0 e^{-\frac{2\pi\nu}{c}\kappa z} = E_0 e^{-\frac{2\pi}{\lambda_0}\kappa z} \quad (5.46)$$

( $\lambda_0 = c/\nu$  is the wavelength in vacuum).

The second power of (5.46) gives the intensity of the wave after passing a distance  $z$ :

$$I = I_0 e^{-\frac{4\pi}{\lambda_0}\kappa z}. \quad (5.47)$$

The equation (5.47) is equivalent to Bouguer's law, which was originally established empirically and theoretically grounded by Bouguer (1729).

Let us take an infinitely thin flat layer of thickness  $dx$  in a substance. Obviously, the relative change in intensity is proportional to  $dx$ :

$$\frac{dI}{I} = -\mu dx, \quad (5.48)$$

where  $\mu$  is a coefficient of proportionality.

The sign «minus» shows that the intensity of light passed through the substance decreases with the increase of thickness of the layer of the absorbing substance.

Integrating equation (5.48) from  $I_0$  to  $I$  and from  $x=0$  to  $x=l$ , we obtain:  $\ln(I/I_0) = -\mu l$ , then

$$I = I_0 e^{-\mu l}. \quad (5.49)$$

The coefficient of proportionality is called the *linear absorption coefficient* (or extinction) and has the dimension of the inverse length [ $\text{m}^{-1}$ ].

Comparing the equations (5.47) and (5.49), we find the relationship between the absorption coefficient  $\mu$  and the index of absorption  $\kappa$ :

$$\mu = \frac{4\pi}{\lambda_0} \kappa, \quad (z = l). \quad (5.50)$$

The index of absorption and the absorption coefficient depend on the wavelength (frequency). This means that absorption is selective in nature for all substances, which is due to the presence of the resonant frequencies. This explains the coloration of absorbing media.

An interesting effect is observed during selective absorption and reflection of light by gold. Gold is yellow.

However, if you make a very thin film of gold and observe light through the film, it will be blue. In the first case, the color of gold is due to selective reflection; in the second one, the color is due to selective absorption.

If atoms (molecules) do not interact with each other (gases and metals vapor at low pressures, where the atoms or molecules can be considered free), absorption coefficients for the most of the wavelengths are close to zero; only for very narrow spectral bands (width of several hundredths of angstrom), there are observed clear maxima.

As an example, Fig. 5.6 schematically shows some doublets of sodium vapor absorption. These peaks correspond to the resonance frequencies of oscillations of electrons in atoms.

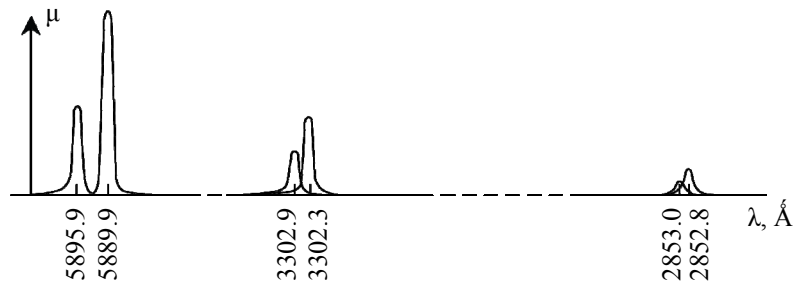


Fig. 5.6

High pressure gases, liquids, and solids are characterized by the broad absorption bands (Fig. 5.7). A high pressure gas absorption spectrum is close to the absorption spectra of liquids. This suggests that the expansion of narrow absorption bands is the result of the interaction of atoms with each other.

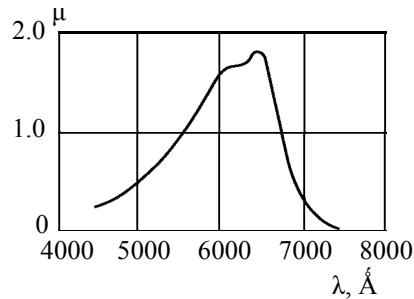


Fig. 5.7

Metals are almost opaque to visible light. The absorption coefficient  $\mu$  for them is  $10^6 \text{ m}^{-1}$  (a glass absorption coefficient  $\mu \approx 1 \text{ m}^{-1}$ ). This is due to the fact that metals have free electrons.

The electric field of the light wave causes the free electrons motion. As a result, microcurrents appear in the metal; it is accompanied by the release of Joule heat. So, the energy of the light is quickly transformed in the metal internal heat.

### 5.3.2. Bouguer-Beer law

Bouguer concluded that light can undergo similar changes when faced with the same number of particles that can delay or scatter the rays. So, absorption depends on the masses of substances contained in these thicknesses.

This fact is of great practical importance. Experiments show that the absorption coefficient is proportional to the number of absorbing molecules per the length unit of the light wave path or per the volume unit that is proportional to the concentration  $c$ . In this case, the absorption coefficient is:

$$\mu = a_0 c, \quad (5.51)$$

where  $a_0$  is a new factor, which is independent from concentration and is characteristic for the absorption material molecules.

Then, the generalized Bouguer law takes the form:

$$I = I_0 e^{-a_0 c l}. \quad (5.52)$$

The statement that  $a_0$  is an independent value from the concentration constant is often called the law of Beer; he reached this conclusion after measurements of light absorption by colored fluids (1852). Therefore, the law (5.52) is called the Bouguer-Beer law.

The analysis of the molecular composition of complex mixtures based on measuring the absorption of ultraviolet and infrared parts of the spectrum is especially important. Spectra of many organic molecules are very characteristic. These allow determining both the molecular composition and the quantitative content of individual components in the mixture.

### 5.4. Scattering of light

The emission of the secondary waves by the electrons causes scattering of light. Because of light scattering in the sideways directions, intensity of a primary wave is reduced. It should be noted that the coherent secondary waves completely extinguish one another in all sideways directions except the direction of propagation of the primary wave *in a completely homogeneous medium*. So, scattering of light does not occur in a completely homogeneous medium.

If a substance is characterized by certain heterogeneity, the primary light waves are diffracted by the small in comparison to the wavelength inhomogeneities ( $r_0 \sim 0,1\lambda$ ) and create relatively uniform distribution of the light intensity in all directions. This is called *diffuse scattering of light*.

Substances with a strong optical inhomogeneity are called *turbid media*. They are smokes (suspensions of tiny solid particles in gases), mists (suspensions of small droplets of liquid in gases), and emulsions (suspensions of small droplets of one liquid in another). For example, an emulsion is normal milk where fat droplets float in water.

Light scattering in turbid media with the particles size  $r_0 \sim (0.1-0.2)\lambda$  is called the Tyndall phenomenon. A typical example of dispersion is shown on Fig. 5.8.

Natural light creates a parallel beam of rays that pass through the cell with water. If the water is thoroughly cleaned of any contaminants, the beam is barely visible when observing the side. This means that the primary beam is not scattered in the sideways areas. If we drop milk into the cell, the beam of light becomes clearly visible from all sides. If the thickness of the cell is sufficient, almost all of the light is scattered in all directions and the primary beam is not observed clearly.

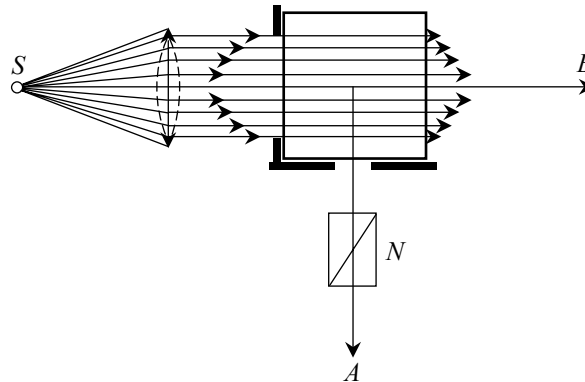


Fig. 5.8

Observation of the scattered at the right angle to the primary beam light through the polaroid  $N$  shows that the scattered light is completely polarized (line  $A$ , Fig. 5.8), while the primary light (direction  $B$ ) is natural.

If we estimate the intensity of light scattered in different directions, it is symmetrical with respect to the primary beam and relative to the line that is perpendicular to it. The curve that graphically shows the intensity distribution of scattered light in different directions is called the *scattering indicatrix*. If the incident light is natural, the scattering indicatrix in the plane has the form shown in Fig. 5.9, and is given by:

$$I_{\vartheta} = I_{\pi/2}(1 + \cos^2 \vartheta), \quad (5.53)$$

where  $I_{\pi/2}$  is the intensity of light scattered at the right angle to the incident (primary) beam ( $\vartheta = \pi/2$ ). Spatial indicatrix can be obtained by the rotation of Fig. 5.9 around the axis  $BB$ .

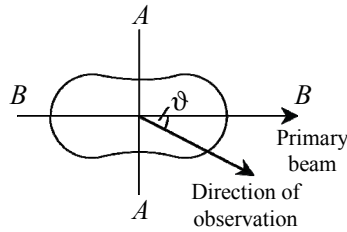


Fig. 5.9

As a result of the light scattering in the sideways directions, the light intensity in the primary direction decreases faster than in the case of only absorption. Therefore, besides the absorption factor  $\kappa$  the additional scattering factor  $\kappa'$  should be in the equation (5.50) for the linear absorption coefficient for a turbid medium:

$$\mu = \frac{4\pi}{\lambda_0}(\kappa + \kappa') = \tau + \sigma, \quad (5.54)$$

where  $\tau$  is the linear coefficient of absorption;  $\sigma$  is the linear coefficient of dispersion. Taking into account (5.54), Bouguer law can be written as:

$$I = I_0 e^{-\mu l} = I_0 e^{-(\tau + \sigma)l}. \quad (5.55)$$

#### 5.4.1. Rayleigh law

If a light wave falls onto a particle of  $r_0 \sim 0.1\lambda$  size, it simultaneously excites oscillations of all the electrons in the particle, i.e. they oscillate together as a unit with the same phase. Since the

oscillations of all electrons are in phase, then the particle can be considered as a «great» dipole.

This dipole oscillates with the frequency of the incident light wave and emits light in all directions with the average power

$$\langle P \rangle = \frac{\mu_0}{12\pi c} \omega^4 p_0^2, \text{ where } p_0 \text{ is the dipole moment.}$$

Dividing this equation by the area of a spherical surface  $4\pi R^2$ , we obtain an equation for the intensity at a distance  $R$ :

$$I = \frac{\mu_0}{48\pi^2 R^2 c} \omega^4 p_0^2.$$

Thus, the intensity of the dipole radiation is proportional to the fourth power of the frequency and inversely proportional to the fourth power of the wavelength:

$$I \sim \omega^4 \sim \frac{1}{\lambda^4}. \quad (5.56)$$

This dependence is called the *Rayleigh law*, which indicates that the short-wave part of the spectrum is dissipated more rapidly than the long-wave part.

The ratio of the wavelength of the red light ( $\lambda = 6500 \text{ \AA}$ ) to the wavelength of the blue light ( $\lambda = 4500 \text{ \AA}$ ) is equal to 1.44. The fourth power of the ratio is 4.3.

Thus, the blue light is scattered four times more intense than the red one.

Smoluchowski (1908) theoretically proved that the cause of optical inhomogeneities in a completely clean substance is the *density fluctuations*.

That is statistical deviations within the small volumes of the substance density due to the chaotic thermal motion of molecules. This means that the density fluctuations cause the occurrence of the fluctuations of the refractive index, which makes environment muddy.

Light scattering caused by fluctuations of density is called *molecular scattering*. This explains the blue color of the sky and the reddish light of the Sun.



## Test Questions

1. Give a definition of light dispersion.
2. What is the cause of the phenomenon of dispersion?
3. What is the difference between normal and abnormal dispersion of light?
4. What is the essence of the Lorentz-Lorenz formula?
5. What are the X-rays dispersion specifics?
6. What is a wave packet?
7. Give a definition of the group velocity.
8. Write the formula for the Rayleigh connection of the group and phase speeds of light.
9. How can we explain the absorption of light?
10. Explain the law of Bouguer.
11. Explain the law of Bouguer-Beer.
12. What is the nature of the light scattering?
13. What is called the scattering indicatrix?
14. What is the Rayleigh scattering of light?