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Physics. — "*On the scattering of light by molecules*". By Prof. H. A. LORENTZ.

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§ 1. It was pointed out many years ago by Lord RAYLEIGH¹⁾ that a beam of light can be scattered to all sides not only by particles of dust, but also by the molecules of the medium in which the propagation takes place. According to his theory the coefficient of extinction due to this cause in the case of a body of small density, a gas for instance, is determined by the formula

$$h = \frac{32\pi^3(\mu-1)^2}{3N\lambda^4}, \quad \dots \quad (1)$$

in which μ is the index of refraction, λ the wave-length and N the number of molecules per unit of volume, the meaning of the coefficient h itself being that the intensity is diminished in the ratio of 1 to e^{-hl} when a distance l is travelled over.

RAYLEIGH has deduced his equation by calculating the energy radiating from the molecules whose particles are put in motion by the incident rays, and by taking into account that the quantities of energy traversing two successive sections of the beam must differ from each other by an amount equal to the energy that is emitted by the molecules lying between those sections.

The problem may, however, also be treated in a different manner. In many theories the ordinary absorption of light is explained by a resistance opposing the motion of the vibrating particles and giving rise to a development of heat. Similarly, the extinction which we are now considering may be ascribed to a certain resistance which, however, is not accompanied with a heating effect, but is intimately connected with the radiation from the molecules. According to the theory of electrons²⁾ a force of this kind acts on an electron whenever its velocity v ³⁾ is variable; it is represented by the expression

$$\frac{e^2}{6\pi c^3} \frac{d^2 v}{dt^2}, \quad \dots \quad (2)$$

in which e is the charge of the electron, and c the velocity of light in the ether.

¹⁾ RAYLEIGH, On the transmission of light through an atmosphere containing small particles in suspension, and on the origin of the blue of the sky, *Phil. Mag.* (5) 47 (1899), p. 375 (*Scientific Papers* 4, p. 397).

²⁾ See, for instance, LORENTZ, *Math. Encyklopädie*, V, 14, § 20.

³⁾ German letters represent vector quantities.

In the case of a simple harmonic motion the sign of the second differential coefficient of v is opposite to that of v itself, so that, like the resistance assumed in the theory of absorption, the force (2) is opposite to the velocity. As to the connexion between this force and the radiation from the vibrating electron, it becomes apparent if we remark that during a full period the work of the force which is required for maintaining a constant amplitude, and which must be equal and opposite to (2), is exactly equal to the amount of the radiated energy.

In a recent paper NATANSON¹⁾ has shown that RAYLEIGH's formula can be obtained by introducing the force (2) into the equation of motion of each vibrating electron.

§ 2. This result is very satisfactory, but still there are some points which require further consideration.

In RAYLEIGH's theory it is necessary to take into account the interference between the vibrations which are produced, at some definite point of space, by all the molecules in the beam, and, on the other hand, a consideration of the resistances will be incomplete if one does not keep in view the mutual action between the molecules. Whether we prefer one course or the other, it may be shown that a scattering can only take place when the molecules are irregularly distributed, as they are in gases and liquids; in a body whose molecules have a regular geometrical arrangement, a beam of light is propagated without any diminution of its intensity.

Let us begin with the second method, and let us observe in the first place that, according to (2), the resistance per unit of charge is given by

$$\frac{e}{6\pi c^3} \frac{d^2 v}{dt^2}.$$

If r is the displacement of an electron from the position of equilibrium which it has in a molecule, this expression may be replaced by

$$\frac{e}{6\pi c^3} \frac{d^2 r}{dt^2},$$

for which we may also write

$$\frac{1}{6\pi c^3} \frac{d^2 p}{dt^2}, \quad \dots \dots \dots (3)$$

if we put

¹⁾ L. NATANSON, On the theory of extinction in gaseous bodies, Bulletin de l'Acad. des Sciences de Clacovie, déc. 1909, p. 915.

$$e r = p .$$

This latter quantity is the electric moment of the molecule, if e is the only movable electron contained in it.

The above expression contains the *third* differential coefficient of r or p with respect to the time, and it is easily seen that terms of this kind, or, in general, terms of odd order, are the only ones in the equations determining the propagation of light which can give rise to an extinction of the beam. This circumstance will enable us to distinguish the terms with which we shall be principally concerned, from others which determine, not the extinction but the velocity of propagation, and which it will not be necessary to consider in detail.

§ 3. It is important to remark that the field belonging to a molecule with an alternating moment p acts with a force like (3), not only on the electron e in the molecule itself, but also on electrons lying outside the particle, at distances that are very small in comparison with the wave-length.

At a point (x, y, z) , at a distance r from the molecule, the scalar potential φ and the vector potential a are determined by the equations

$$\varphi = -\frac{1}{4\pi} \operatorname{div} \frac{[p]}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$a = \frac{1}{4\pi c r} \left[\frac{dp}{dt} \right], \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which the square brackets serve to indicate that, if we want to know the potentials for the time t , we must use the values of the enclosed quantities corresponding to the time $t - \frac{r}{c}$. Hence, $[p]$ is a function of x, y, z, t , and we may write for the vector potential

$$a = \frac{1}{4\pi c r} \frac{\partial [p]}{\partial t}.$$

Now, if r is very small with respect to the wave-length, we have

$$[p] = p - \frac{r}{c} \frac{dp}{dt} + \frac{r^2}{2c^2} \frac{d^2p}{dt^2} - \frac{r^3}{6c^3} \frac{d^3p}{dt^3} + \dots$$

For our purpose it will suffice to consider the part of φ corresponding to the fourth term of this series, and the part of a corresponding to the second term. In equation (4) the quantity $\frac{[p]}{r}$ may therefore be replaced by

$$-\frac{r^2}{6c^3} \frac{d^3 \mathbf{p}}{dt^3},$$

a vector whose components are

$$-\frac{r^2}{6c^3} \frac{d^3 p_x}{dt^3}, -\frac{r^2}{6c^3} \frac{d^3 p_y}{dt^3}, -\frac{r^2}{6c^3} \frac{d^3 p_z}{dt^3},$$

and whose divergence is

$$-\frac{1}{3c^3} \left(x \frac{d^3 p_x}{dt^3} + y \frac{d^3 p_y}{dt^3} + z \frac{d^3 p_z}{dt^3} \right),$$

if the point from which r is reckoned, is taken as origin of coordinates.

We have therefore

$$\varphi (=) \frac{1}{12\pi c^3} \left(x \frac{d^3 p_x}{dt^3} + y \frac{d^3 p_y}{dt^3} + z \frac{d^3 p_z}{dt^3} \right),$$

denoting by the symbol $(=)$ that terms irrelevant to our purpose have been omitted.

The differential coefficients of the quantity within the brackets with respect to x, y, z are

$$\frac{d^3 p_x}{dt^3}, \frac{d^3 p_y}{dt^3}, \frac{d^3 p_z}{dt^3},$$

so that we find

$$\text{grad } \varphi (=) \frac{1}{12\pi c^3} \frac{d^3 \mathbf{p}}{dt^3}.$$

Combining this with

$$\mathbf{a} (=) -\frac{1}{4\pi c^2} \frac{d^2 \mathbf{p}}{dt^2},$$

we are led to the expression

$$\frac{1}{6\pi c^3} \frac{d^3 \mathbf{p}}{dt^3},$$

which has already been mentioned, for the force acting on unit charge

(which is given in general by $-\frac{1}{c} \dot{\mathbf{a}} - \text{grad } \varphi$).

Simple examples may serve to show that this result agrees with the law of energy. Suppose, for instance, that two molecules placed very near each other contain equal electrons vibrating with equal amplitudes and phases along parallel straight lines. Then the flow of energy across a closed surface surrounding the molecules will be equal to four times the flow that would belong to one of the particles taken by itself. Hence, for each molecule, the work necessary for maintaining its vibrations must be doubled by the influence of the other particle. This is really the case because the resistance is doubled, each molecule contributing an equal part to it.

Again, if the two vibrations have opposite phases, the amplitudes still being equal, the two forces acting on one of the electrons according to our formulae — one produced by the field of the electron itself and the other by the field of the other molecule — will annul each other. But in this case the system of the two molecules does not lose any energy by radiation.

§ 4. The preceding considerations show that a correct explanation of the extinction of light, by means of the forces acting on the vibrating electrons, can only be obtained by examining the mutual actions between the molecules. In order to take these into account I shall follow the same method which I have used on previous occasions.

We shall start from the fundamental equations by means of which the electromagnetic field between the electrons and even inside these small particles can be described in all its details. Let \mathfrak{d} and \mathfrak{h} be the electric and the magnetic force, ϱ the density of the electric charge, and v its velocity. Then

$$\begin{aligned} \operatorname{div} \mathfrak{d} &= \varrho, \\ \operatorname{div} \mathfrak{h} &= 0, \\ \operatorname{rot} \mathfrak{h} &= \frac{1}{c} (\dot{\mathfrak{d}} + \varrho v), \\ \operatorname{rot} \mathfrak{d} &= -\frac{1}{c} \dot{\mathfrak{h}}. \end{aligned}$$

Any electromagnetic state which satisfies these conditions may be represented by means of a scalar potential φ and a vector potential \mathfrak{a} . These are determined by the equations

$$\varphi = \frac{1}{4\pi} \int \frac{[\varrho]}{r} dS, \dots \dots \dots (6)$$

$$\mathfrak{a} = \frac{1}{4\pi c} \int \frac{[\varrho v]}{r} dS, \dots \dots \dots (7)$$

in which the integrations are to be extended over all space, and we have

$$\mathfrak{d} = -\frac{1}{c} \frac{\partial \mathfrak{a}}{\partial t} - \operatorname{grad} \varphi.$$

We may now pass on to the equations that may be used for a description of the phenomena in which the details depending on the molecular structure and inaccessible to our means of observation are omitted. We obtain these by simply replacing each term in the above formulae by its mean value over a space S surrounding the point considered, whose dimensions are so small that, in so far as

it can be observed, the state of the medium may be regarded as the same at all points of S , and at the same time so great that S contains a large number of molecules. A space of this kind may be called "infinitely small in a physical sense" and the mean value of any scalar or vector quantity A is defined by the equation

$$\bar{A} = \frac{1}{S} \int A dS,$$

in which the integration extends over the small space S .

We shall suppose the medium to contain neither conduction- nor magnetization-electrons, but only polarization-electrons, i. e. charged particles whose displacement from their positions of equilibrium produces the electric moments of the molecules. Let \mathfrak{P} be the electric polarization (the electric moment per unit of volume). Then ¹⁾

$$\begin{aligned}\bar{\rho} &= -\operatorname{div} \mathfrak{P}, \\ \bar{\rho v} &= \dot{\mathfrak{P}},\end{aligned}$$

and, if we put $\bar{\mathfrak{E}} = \mathfrak{E}$ (electric force), $\mathfrak{E} + \mathfrak{P} = \mathfrak{D}$ (dielectric displacement), $\bar{\mathfrak{H}} = \mathfrak{H}$, $\bar{\varphi} = \phi$, $\bar{\mathfrak{A}} = \mathfrak{A}$,

$$\left. \begin{aligned}\operatorname{div} \mathfrak{D} &= 0, \\ \operatorname{div} \mathfrak{H} &= 0, \\ \operatorname{rot} \mathfrak{H} &= \frac{1}{c} \dot{\mathfrak{D}}, \\ \operatorname{rot} \mathfrak{E} &= -\frac{1}{c} \dot{\mathfrak{H}},\end{aligned} \right\} \dots \dots \dots (8)$$

$$\mathfrak{E} = -\frac{1}{c} \frac{\partial \mathfrak{A}}{\partial t} - \operatorname{grad} \phi \dots \dots \dots (9)$$

In those cases in which the field is produced by polarization-electrons only, we have by (6) and (7)

$$\begin{aligned}\phi &= -\frac{1}{4\pi} \int \frac{[\operatorname{div} \mathfrak{P}]}{r} dS, \\ \mathfrak{A} &= \frac{1}{4\pi c} \int \frac{1}{r} \left[\frac{\partial \mathfrak{P}}{\partial t} \right] dS. \dots \dots \dots (10)\end{aligned}$$

In the first of these two equations it has been tacitly assumed that there is nowhere a discontinuity in the polarization \mathfrak{P} . Whenever such a discontinuity exists at some surface σ , the equation must be replaced by

$$\phi = -\frac{1}{4\pi} \int \frac{[\operatorname{div} \mathfrak{P}]}{r} dS - \frac{1}{4\pi} \int \frac{1}{r} \{[\mathfrak{P}_{n_2}] - [\mathfrak{P}_{n_1}]\} d\sigma, \dots (11)$$

¹⁾ Math. Encyklopädie V 14, § 30.

where n means the normal to the surface σ , drawn from the side 1 towards the side 2.

§ 5. The fundamental equations show that the field may be considered as produced by the electrons contained in the source of light and in the media traversed by the rays. Let σ be a closed surface in the medium with which we are concerned and let the value of \mathfrak{E} at some point on the inside of σ be decomposed into two parts, the first of which (\mathfrak{E}_1) is due to all the electrons lying outside the surface, whereas the second part (\mathfrak{E}_2) has its origin in the state of the medium within σ . This latter part can be determined by the equations (9), (10) and (11), if, for a moment, we confine ourselves to the matter enclosed by σ , with the values of \mathfrak{p} existing in it. Then, drawing the normal to σ towards the outside, we have $\mathfrak{p}_{n_2} = 0$ and we may write

$$\phi = \frac{1}{4\pi} \int \frac{[\mathfrak{p}_n]}{r} d\sigma, \quad (12)$$

if we omit the index 1 in \mathfrak{p}_n and if we take for granted that the vibrations are transverse, so that $\text{div } \mathfrak{p} = 0$.

Confining the integration in (10) to the space within σ , we find for the second part of \mathfrak{E}

$$\mathfrak{E}_2 = -\frac{1}{c} \frac{\partial \mathfrak{A}}{\partial t} - \text{grad } \phi. \quad (13)$$

As to the first part

$$\mathfrak{E}_1 = \mathfrak{E} - \mathfrak{E}_2,$$

it represents the value which \mathfrak{E} would have at a point within the surface, if we removed all the particles contained in it, without changing anything in the state of the matter on the outside.

In what follows we shall conceive the cavity made in this way to be infinitely small in a physical sense. But, nevertheless, we shall suppose its dimensions to be very great in comparison with those of the space S that has been mentioned in the definition of the mean values. Under these circumstances and if we except those points of the cavity which are very near the walls, there will be no difference between the mean value of \mathfrak{d} and this vector itself. Hence, \mathfrak{E}_1 may be considered as the real value of \mathfrak{d} within the cavity.

§ 6. In order to find the laws of the propagation of light, we have to combine the equations (8) with the relation between \mathfrak{D} (or \mathfrak{p}) and \mathfrak{E} , which can be deduced from the equation of motion of the electrons vibrating in the molecules.

We shall simplify by assuming that each molecule contains no more than one vibrating electron. Let us fix our attention on a single molecule M and let us denote by r the displacement of its movable electron from the position of equilibrium, by $p = e r$ the moment of the molecule, and by m the mass of the electron. The forces acting on the electron are: 1. the quasi-elastic force, for which we shall write $-f$; 2. the resistance (3), and 3. the force $e \mathfrak{d}$, if \mathfrak{d} is the electric force produced at the place of M by all the surrounding electrons. Now, after having described around M an infinitely small surface σ , such as has been considered in § 5, we may conceive \mathfrak{d} to be made up of two parts, the vector \mathfrak{E}_1 that has already been mentioned, and the part that is due to the molecules Q surrounding M and lying within the surface σ . Let \mathfrak{d}_q be the part contributed by one of these molecules, and let the symbol Σ refer to all the molecules Q . Then, the equation of motion becomes

$$m \frac{d^2 r}{dt^2} = -f + \frac{e}{6\pi c^3} \frac{d^3 p}{dt^3} + e(\mathfrak{E} - \mathfrak{E}_1) + e \Sigma \mathfrak{d}_q \quad (14)$$

and here, on account of what has been said in § 3, we may put

$$\Sigma \mathfrak{d}_q (=) \frac{1}{6\pi c^3} \Sigma \frac{d^3 p_q}{dt^3}, \quad (15)$$

if we confine ourselves to the resistances.

The determination of the sum occurring on the right-hand side would be a very simple matter, if the molecules were arranged in some regular way, if, for example, they occupied the points of a parallelepipedic net. In such a case, the moment p_q of any one of the molecules Q may be considered as equal to that of the particle M itself, for which we want to write down the equation of motion (because the dimensions of σ are very small with respect to the wavelength). On the contrary, in a system of particles having an irregular distribution, unequalities may arise from the mutual electromagnetic actions; this is easily seen if one considers that the distance to the nearest particle is not the same for the different molecules. On account of this circumstance, it would be very difficult accurately to calculate the sum for a liquid body.

In the case of a gas the problem becomes more simple. Indeed, it can be safely assumed that in such a body the influence of the molecules on the propagation of light is rather feeble. It is only in a small measure that the state in a definite molecule depends on that of the surrounding ones; it is chiefly determined by the state of the ether, and this may be taken to be nearly the same that could exist if the beam were propagated in a vacuum. Consequently, in

the equation of motion of the electron belonging to a definite molecule, the terms expressing the action of the other molecules are small in comparison with the remaining terms, and we shall neglect only quantities that may be said to be of the second order, if, in calculating the terms in question, we reason as if the moments of the molecules Q and that of M itself were wholly independent of the mutual action between these particles. But in this case all these moments would be equal to each other. Therefore, in calculating the sum in (15), we shall take each p_i to be equal to the mean value of p for all the molecules M contained in an infinitely small space. Distinguishing mean values of this kind by a double bar above the letter, and writing ν for the number of the molecules Q , i. e. for the number of particles, with the exception of M , lying within the closed surface σ , we may replace (15) by

$$\Sigma d_i (=) \frac{\nu}{6\pi c^3} \frac{d^3 \bar{p}}{dt^3}.$$

§ 7. It remains to consider the electric force \mathfrak{E}_2 determined by (10), (12) and (13). Let us put for this purpose

$$[\mathfrak{P}] = \mathfrak{P} + \Omega,$$

and let each of the three quantities ϕ , \mathfrak{A} and \mathfrak{E}_2 be decomposed into two parts in a way corresponding to this formula. The first part of \mathfrak{E}_2 depends only on the values of \mathfrak{P} which are found, at the definite moment t , on the surface σ and inside it, and even if account had to be taken of the changes of \mathfrak{P} from one point to another — which can be represented by means of the differential coefficients of \mathfrak{P} with respect to the coordinates, it could be shown that the part in question contains differential coefficients of even order only, at least if the form of σ is symmetrical with respect to three planes passing through M and parallel to the planes of coordinates. It will therefore suffice for our purpose to consider the second part of \mathfrak{E}_2 , and to substitute in (13) the values

$$\phi = \frac{1}{4\pi} \int \frac{\Omega_n}{r} d\sigma \dots \dots \dots (16)$$

and

$$\mathfrak{A} = \frac{1}{4\pi c} \int \frac{1}{r} \frac{\partial \Omega}{\partial t} dS \dots \dots \dots (17)$$

In the following transformations, whose object is the determination of \mathfrak{E}_2 , the coordinates of the point M for which we want to know ϕ , \mathfrak{A} and \mathfrak{E}_2 are denoted by x', y', z' , and those of a point on the surface σ or within it, by x, y, z .

It may be remarked in the first place that (16) may be written in the form

$$\phi = \frac{1}{4\pi} \int \left(\frac{\partial}{\partial x} \frac{\Omega_x}{r} + \frac{\partial}{\partial y} \frac{\Omega_y}{r} + \frac{\partial}{\partial z} \frac{\Omega_z}{r} \right) dS \quad . \quad . \quad . \quad (18)$$

and that here the differential coefficients with respect to x, y, z , may be replaced by those with respect to x', y', z' with the signs inverted. In order to show this, put

$$\Psi_x = f_1(x, y, z, t), \Psi_y = f_2(x, y, z, t), \Psi_z = f_3(x, y, z, t)$$

and write $f'_{1x}(x, y, z, t)$ etc. for the partial derivatives, taken for a constant t , of these expressions with respect to x, y, z . The vibrations being transverse, we have

$$f'_{1x}(x, y, z, t) + f'_{2y}(x, y, z, t) + f'_{3z}(x, y, z, t) = 0, \quad . \quad . \quad (19)$$

and also

$$\begin{aligned} f'_{1x}\left(x, y, z, t - \frac{r}{c}\right) + f'_{2y}\left(x, y, z, t - \frac{r}{c}\right) + \\ + f'_{3z}\left(x, y, z, t - \frac{r}{c}\right) = 0, \quad . \quad . \quad . \quad (20) \end{aligned}$$

because (19) is true for any value of t .

Now,

$$\begin{aligned} \frac{\Omega_x}{r} &= \frac{1}{r} \left\{ f_1\left(x, y, z, t - \frac{r}{c}\right) - f_1(x, y, z, t) \right\}, \\ \frac{\Omega_y}{r} &= \frac{1}{r} \left\{ f_2\left(x, y, z, t - \frac{r}{c}\right) - f_2(x, y, z, t) \right\}, \\ \frac{\Omega_z}{r} &= \frac{1}{r} \left\{ f_3\left(x, y, z, t - \frac{r}{c}\right) - f_3(x, y, z, t) \right\}, \end{aligned}$$

and, if this is substituted in (18), we get two groups of terms, some depending on the explicit occurrence in $\frac{\Omega_x}{r}$ etc. of x, y, z and the remaining ones arising from the variability of r . Equations (19) and (20) show that the terms of the first group annul each other, and we may replace (18) by

$$\phi = \frac{1}{4\pi} \int \left(\frac{\partial}{\partial x'} \frac{\Omega_x}{r} + \frac{\partial}{\partial y'} \frac{\Omega_y}{r} + \frac{\partial}{\partial z'} \frac{\Omega_z}{r} \right) dS \quad . \quad . \quad . \quad (21)$$

because

$$\frac{\partial r}{\partial x'} = -\frac{\partial r}{\partial x}, \text{ etc.}$$

Let us next substitute in (21) (cf. § 3)

$$\Omega = [\mathfrak{p}] - \mathfrak{p} = -\frac{r}{c} \frac{\partial \mathfrak{p}}{\partial t} + \frac{r^2}{2c^2} \frac{\partial^2 \mathfrak{p}}{\partial t^2} - \frac{r^3}{6c^3} \frac{\partial^3 \mathfrak{p}}{\partial t^3} + \dots, \quad . \quad (22)$$

where the differential coefficients $\frac{\partial \Omega}{\partial t}$ etc. are independent of x', y', z' .

After this expansion none of the terms in $\frac{\Omega}{r}$ contains a negative power of r , and in differentiating (21) with respect to x', y', z' , as is necessary for the determination of $\text{grad } \phi$, we may effect the operation under the sign of integration. Thus

$$-\frac{\partial \phi}{\partial x'} = \frac{1}{4\pi} \int \left(\frac{\partial^2}{\partial x'^2} \frac{\Omega_x}{r} + \frac{\partial^2}{\partial x' \partial y'} \frac{\Omega_y}{r} + \frac{\partial^2}{\partial x' \partial z'} \frac{\Omega_z}{r} \right) dS, \text{ etc.}$$

or, confining ourselves to the part of this expression corresponding to the last term in (22),

$$-\frac{\partial \phi}{\partial x'} (=) -\frac{1}{12\pi c^3} \int \frac{\partial^3 \mathfrak{p}_x}{\partial t^3} dS, \text{ etc.,}$$

i. e.

$$-\text{grad } \phi (=) -\frac{1}{12\pi c^3} \int \frac{\partial^3 \mathfrak{p}}{\partial t^3} dS.$$

As to the term $-\frac{1}{c} \frac{\partial \mathfrak{I}}{\partial t}$, it will suffice to substitute in (17) the first term of (22), so that

$$-\frac{1}{c} \frac{\partial \mathfrak{I}}{\partial t} (=) \frac{1}{4\pi c^3} \int \frac{\partial^3 \mathfrak{p}}{\partial t^3} dS.$$

The result of our calculation is

$$\mathfrak{E}_x (=) \frac{1}{6\pi c^3} \int \frac{\partial^3 \mathfrak{p}}{\partial t^3} dS,$$

or, since $\frac{\partial^3 \mathfrak{p}}{\partial t^3}$ may be considered as constant throughout the small space enclosed by σ , if the magnitude of that space is denoted by U ,

$$\mathfrak{E}_x (=) \frac{1}{6\pi c^3} U \frac{\partial^3 \mathfrak{p}}{\partial t^3}.$$

Finally, the equation of motion (14) takes the form

$$m \frac{d^2 r}{dt^2} = -f r + e \mathfrak{E} + \frac{e}{6\pi c^3} \left(\frac{d^3 \mathfrak{p}}{dt^3} + v \frac{d^3 \bar{\mathfrak{p}}}{dt^3} - U \frac{\partial^3 \beta}{\partial t^3} \right) + \mathfrak{F}, \quad (23)$$

where several actions of which we have not spoken and which are not to be reckoned among the resistances, are taken together in the term \mathfrak{F} .

§ 8. We have now to distinguish two cases.

a. Let the molecules have a regular arrangement in such a manner that each occupies the centre of one of a system of equal paralle-

lepipeds which are formed by three groups of planes. In this case there is no difference between \mathfrak{p} and $\overline{\mathfrak{p}}$. Further, if $\frac{1}{N}$ is the volume of one of the elementary parallelepipeds, and if we take for the space U a parallelepiped consisting of k elementary ones,

$$\mathfrak{P} = N\mathfrak{p},$$

$$U = \frac{k}{N}.$$

By this the expression enclosed in brackets in (23) becomes

$$(1 + \nu - k) \frac{\partial^3 \mathfrak{p}}{\partial t^3}.$$

But, $\nu + 1$ being the total number of particles in the space U , we have

$$\nu + 1 = k,$$

so that, after all, there is no resistance, and there can be no extinction of the rays of light.

b. The case of an irregular distribution of the molecules is best treated by applying equation (23) to each of the molecules within an infinitely small space and taking the mean value of each term. Since

$$\mathfrak{P} = N\overline{\mathfrak{p}},$$

N being the number of molecules per unit of volume, we get

$$m \frac{d^2 \overline{\mathfrak{r}}}{dt^2} = -\overline{f\mathfrak{r}} + e\overline{\mathfrak{z}} + \frac{e}{6\pi c^3} (1 + \overline{\nu} - NU) \frac{\partial^3 \overline{\mathfrak{p}}}{\partial t^3} + \overline{\mathfrak{y}}. \quad (24)$$

Now, the number of particles in the space U considered in § 7 was $1 + \nu$, and therefore it would almost seem at first sight as if the mean value $1 + \overline{\nu}$ were equal to NU . In fact, however, we have, in the case of an irregular distribution

$$\overline{\nu} = NU. \quad (25)$$

In order to see this, we must remember that $1 + \nu$ represented the total number of particles lying in a space U *that had been chosen around a molecule M on which we had previously fixed our attention.* Let us imagine in the gas a volume V very great in comparison with the infinitely small space U , and let us conceive the NV molecules which this volume is to contain, to be placed in it at random, no difference being made between one part of space and another. After having assigned its position to the first molecule, we choose around it the small space U and we ask how many of the remaining $NV - 1$ particles will, in the mean, come to lie in that space, if the experiment of placing the $NV - 1$ molecules in the

volume V is repeated many times. Obviously, this mean number, which we may take for \bar{v} , is

$$\frac{U}{V}(NV - 1) = NU - \frac{U}{V}$$

and this may be replaced by (25), because $\frac{U}{V}$ is a very small fraction.

Our conclusion must therefore be that the coefficient $1 + \frac{U}{V} - NU$ in (24) has the value 1, and we may express this by saying that among the terms in (23) which represent resistances, one only remains, namely the term that is due to the field belonging to the molecule itself which we are considering.

Finally, in order to give a more convenient form to the equation of motion (24) we shall multiply it by $\frac{eN}{m}$, replacing at the same time the vector $Ne\vec{r} = N\vec{p}$ by \mathfrak{p} . We shall also put

$$\frac{eN}{m}\vec{\mathfrak{p}} = \gamma \mathfrak{p},$$

where, with sufficient approximation, γ may be considered as a constant coefficient, and

$$\frac{f}{m} - \gamma = n_0^2.$$

In this way we are led to the formula

$$\frac{\partial^2 \mathfrak{p}}{\partial t^2} = -n_0^2 \mathfrak{p} + \frac{e^2 N}{m} \mathfrak{E} + \frac{e^2}{6\pi c^2 m} \frac{\partial^3 \mathfrak{p}}{\partial t^3},$$

from which, if it is combined with (8), RAYLEIGH's extinction coefficient can be deduced.

§ 9. We shall conclude by briefly showing that, like the method which we have now followed, that of RAYLEIGH, namely the direct calculation of the energy emitted by the molecules, leads to a scattering of the light, only for a system whose molecules are irregularly distributed.

Let us consider a bundle of parallel homogeneous rays, and let L be a line or a very narrow cylinder having the direction of the rays, AB a part of L very long in comparison with the wave-length, AP a line making a certain angle with AB , and P a point of that line whose distance from A is many times greater than AB . We shall take the axis of x along AB and we shall simplify by assuming that, for each molecule situated on the line L or in the narrow

cylinder, the electric moment may be represented by an expression of the form

$$a \cos (n t + p),$$

in which p is a linear function of x . The amplitude a may be regarded as constant, if we neglect the unequalities that may arise from the mutual action between the molecules of a gas or a liquid (comp. § 6), and if we suppose the extinction along the length of AB to be very feeble.

For one of the components of the light vector at P , so far as it depends on one molecule, we may now put

$$b \cos (n t + q),$$

where b is a constant, and q a linear function of x , and we have to calculate the sum

$$s = \Sigma b \cos (n t + q), \quad . \quad . \quad . \quad . \quad . \quad (26)$$

extended to all the molecules.

Suppose in the first place that k molecules occupy equidistant positions on the line AB . Then the values of q form an arithmetical series $q_1, q_1 + \Delta, q_1 + 2 \Delta$, etc. and we have

$$\begin{aligned} s &= \frac{b}{2 \sin \frac{1}{2} \Delta} [\sin \{n t + q_1 + (k - \frac{1}{2}) \Delta\} - \sin \{n t + q_1 - \frac{1}{2} \Delta\}] = \\ &= b \frac{\sin \frac{1}{2} k \Delta}{\sin \frac{1}{2} \Delta} \cos \{n t + q_1 + \frac{1}{2} (k-1) \Delta\}. \end{aligned}$$

It appears from the first form that the resulting disturbance of equilibrium can be conceived as consisting of two vibrations emitted by points near the extremities of the row of molecules, and the second form shows that, when the length of the row is increased constantly, the amplitude of s remains comprised between $+\frac{b}{\sin \frac{1}{2} \Delta}$ and $-\frac{b}{\sin \frac{1}{2} \Delta}$. Though there is a certain residual vibration, its intensity cannot be said to increase with the length of AB .

§ 10. This conclusion also holds when the molecules of a gas are distributed in such a manner over the cylinder L that equal parts of it, separated from each other by normal sections, contain exactly equal numbers of particles. Then, for an element dx , the number will be $f dx$, with a constant f , and we have instead of (26)

$$s = b f \int \cos (n t + q) dx = b f \frac{l}{q'' - q'} \{ \sin (n t + q'') - \sin (n t + q') \},$$

l being the length of AB , and q', q'' the extreme values of q . While

l increases, the ratio $\frac{l}{q''-q'}$ remains constant, and, like in the former case, the resulting vibration may be considered as made up of two components emitted by the extremities of AB .

In order not to encumber our formulae with this small residual vibration, I shall suppose the difference $q'' - q'$ to be a multiple of 2π .

When the distribution of the molecules is an irregular one, equal parts of the cylinder L will *not* contain exactly the same number of particles, and we shall now show that these differences must cause a real scattering of the rays. For this purpose we begin by dividing the cylinder AB into a number of parts AA' , $A'A''$ etc., such that along each of them q changes by 2π . Next, always using normal sections, we divide each of these parts into a great number, say k , of smaller ones, all of equal length dx . Having done this, we take together the first part of AA' , the first of $A'A''$, etc., considering their sum as *one* part of the cylinder AB ; in the same manner we combine into a *second* part of it the second part of AA' , the second of $A'A''$, and so on, so that after all the whole cylinder is divided into k parts of equal volume. For all the molecules lying in one of these parts the phases of the vibrations which they produce at the point P , may be taken to be equal. Let the k phases be determined by the quantities q_1, q_2, \dots, q_k , which form an arithmetical series.

Now, if g_1, g_2, \dots, g_k are the numbers of molecules contained in the k parts of the cylinder, we have

$$s = b [g_1 \cos (nt + q_1) + g_2 \cos (nt + q_2) + \dots + g_k \cos (nt + q_k)] . \quad (27)$$

According to what has been said, this would be zero if all the numbers g_1, g_2, \dots, g_k were equal. Consequently we may also write

$$s = b [h_1 \cos (nt + q_1) + h_2 \cos (nt + q_2) + \dots + h_k \cos (nt + q_k)],$$

if we understand by h_1, h_2, \dots, h_k the deviations of the numbers g_1, g_2, \dots, g_k from their mean value. We shall denote this mean value itself by g .

The radiation across an element of surface lying at the point P is determined by the square of s , and our problem may therefore be put as follows: What will be the mean value of s^2 in a large number of experiments in which, all other things remaining the same, the distribution of the particles is different, a number kg of molecules being each time distributed at random over the k parts of the cylinder?

In considering this we must keep in mind that, among the numbers h_1, h_2, \dots, h_k there must always be negative as well as positive ones ;

since $h_1 + h_2 + \dots + h_k = 0$, neither the positive nor the negative values will predominate.

Now it is clear that the mean value of any product of two different h 's, relating to any two definite among the k parts, must of necessity be zero, in as much as there is no reason for a different probability of equal or unequal signs of those two deviations.

Hence, the mean value in question becomes

$b^2 [\overline{h_1^2} \cos^2 (n t + q_1) + \overline{h_2^2} \cos^2 (n t + q_2) + \dots + \overline{h_k^2} \cos^2 (n t + q_k)]$,
and on an average, for a full period,

$$\frac{1}{2} b^2 (\overline{h_1^2} + \overline{h_2^2} + \dots + \overline{h_k^2}).$$

But, by a well known theorem in the theory of probabilities,

$$\overline{h_1^2} = \overline{h_2^2} = \dots = \overline{h_k^2} = g,$$

so that our result becomes

$$\frac{1}{2} k g b^2,$$

showing that, in order to find the intensity of the radiation issuing from the cylinder L , we must multiply the intensity $\frac{1}{2} b^2$ that is produced by one molecule, by the number kg of particles in the cylinder. This conclusion can easily be extended to a part of the beam of any size. Indeed, the k vibrations occurring in (27) mutually destroy each other for the greater part by interference, and the vibration of which we have calculated the intensity is no more than a small residual disturbance of equilibrium. It may have any phase whatever according as the molecules happen to be disseminated in one way or another. Now, if a part of the beam of any magnitude is divided into a number of cylinders L such as we have considered in the last paragraphs, there will be no connexion between the distribution of the molecules in these several cylinders. The phases of the residual vibrations due to each of them will be wholly independent of each other, and it will be allowable, simply to take the sum of their intensities.

Physics. — “*Quasi-association or molecule-complexes.*” By Prof. J. D. VAN DER WAALS.

(Communicated in the Meeting of May 28, 1910).

In the Meeting of this Academy of January 1906 I delivered an address on what I then called “Quasi-association”. I demonstrated that the phenomena, particularly in the liquid state, led to the

conclusion that the equation of state $p = \frac{RT}{v-b} - \frac{a}{v^2}$ was not in har-