

VIII. *On the Molecular Scattering of Light in Dense Vapours and Gases.* By C. V. RAMAN, M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University; and K. R. RAMANATHAN, M.A., Demonstrator in Physics, Maharajah's College, Trivandrum, and University of Madras Research Scholar*.

1. Introduction.

AS is well-known, the theory advanced by the late Lord Rayleigh † explaining the blue light of the sky as due to the molecular scattering of sunlight has of recent years been amply confirmed by accurate measurements of sky-radiation and of the attenuation of the sun's rays in traversing the earth's atmosphere, and also by the laboratory experiments of Cabannes ‡ and of the present Lord Rayleigh § which have demonstrated the scattering of light by dust-free gases and shown that its magnitude is in agreement with the theory. Apart from its special application to the explanation of the blue light of the sky, the subject of the molecular scattering of light possesses very great interest, standing as it does in intimate relationship with the fundamental problems of optics, such as the propagation of light and the reflexion, refraction, dispersion, and extinction of light in transparent media. Its study has already yielded information which is of first-rate importance in testing theories of atomic and molecular structure, and promises to prove even more fruitful in future in the same direction. It is also not improbable that the study of the problems of molecular scattering of light may serve to elucidate the nature of radiation itself, that is, to determine whether it consists of some form of continuous disturbance moving through space, as contemplated by Maxwell's electromagnetic theory, or whether it consists of discrete entities or "quanta," as conceived of by Einstein. It is proposed in this paper to consider the very important problem of the scattering of light in *dense* media, such as vapours and gases under high pressure, in which circumstances, as was pointed out by the late Lord Rayleigh himself, the simple treatment proposed by him is not applicable. Fresh experimental evidence bearing on the subject will also be referred to.

* Communicated by the Authors.

† Phil. Mag. xlvii. pp. 375-384 (1899). Scientific Papers, vol. iv. p. 397.

‡ *Annales de Physique*, xv. pp. 1-150.

§ Proc. Roy. Soc. xciv. p. 453 (1918) *et seq.*

Phil. Mag. S. 6. Vol. 45. No. 265. Jan. 1923..

2. *Rayleigh's Theory of Light-Scattering.*

As a preliminary to the discussion of the problem of light-scattering in highly compressed gases and vapours, it is useful to recall very briefly the principles on which the case of gases under ordinary conditions was dealt with by Lord Rayleigh. Reduced to its essentials, the treatment is on the following lines:—

The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbours. There is, of course, a definite phase-relation between the primary wave when it reaches a given molecule and the secondary wave emitted from it. *In the direction of propagation of the primary waves* the secondary radiations emitted by all the molecules in a given layer are in identical phase, for the differences in the phase of the primary wave when it reaches different molecules are exactly compensated by the acceleration or retardation due to the scattered waves having to traverse a shorter or greater path, as the case may be. *In other directions*, however, owing to the molecules being distributed at random within the volume of the gas, the phases of the scattered waves do not stand in any invariable relation to each other, and hence, in order to find the average expectation of intensity of the scattered light emerging from within the gas, the *intensities*, not the amplitudes of the waves scattered by the individual molecules, should be added up. In all ordinary cases there is very little difference of phase between the primary wave reaching an individual molecule and the secondary wave sent out by it so far as the direction of original propagation of the wave is concerned. When, however, the effect of all the molecules contained in a stratum parallel to the plane of the primary wave is integrated by the usual method of subdivision of the stratum into Fresnel zones, and the resultant is combined with the primary wave, a change of phase appears which may be identified as the retardation associated with the passage of waves through a refractive medium. A relation is thus obtained between the scattering power of the molecules, their number per unit volume, and the refractivity of the medium. Thus, taking the light-vector in the primary waves to be represented by $R_0 \cos(\omega t - lx)$, where x is measured from the position of the scattering molecule, the vector in the scattered wave arising from it may be written as

$$A_1 \cos(\omega t - lr) R_0 \sin \theta/r, \quad (1)$$

when r is the distance from the molecule and θ is the angle between the vibration at the origin and the scattered ray. On carrying out the calculations indicated, the relation obtained is

$$n_1 A_1^2 = \frac{4\pi^2(\mu - 1)^2}{n_1 \lambda^4}, \dots \dots \dots (2)$$

where n_1 is the number of molecules in unit volume, λ is the wave-length of the light, and μ is the refractive index of the gas.

The energy scattered by the molecules in the interior of the gas must be derived from the primary beam, and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The coefficient of attenuation may be readily evaluated by a simple calculation of the total energy scattered by an individual molecule, and then multiplying this by the number n_1 of molecules per unit volume. We thus obtain the intensity of the transmitted light to be $I = I_0 e^{-kx}$, where k the coefficient of attenuation is given by the relation

$$k = \frac{32\pi^3(\mu - 1)^2}{3n_1 \lambda^4} \dots \dots \dots (3)$$

This expression for the attenuation coefficient may also be derived directly by a more accurate investigation, which does not neglect the small difference of phase between the primary wave and the secondary waves originating at a molecule. It is then found that on compounding the effects of the primary wave with those of the secondary wave arising from a stratum of molecules, there appears, in addition to the alteration of phase of the primary wave, also a small diminution in its intensity which is exactly that expected in view of the lateral scattering of part of the energy.

3. *Justification of the Principle of Random Phase.*

It will be seen from the foregoing that the Rayleigh law of scattering depends for its validity on the principle that the phases of the waves laterally scattered by the individual molecules are absolutely at random. This point is clearly brought out in the detailed analyses of the problem which have been given H. A. Lorentz* and by the late Lord Rayleigh himself †, and it appears that the necessary random character of the phases of the scattered waves can only arise

* Proc. Roy. Soc. of Sciences, Amsterdam, xiii. p. 92 (1910).

† Phil. Mag. xxxvi. pp. 429-449 (1918).

from a random arrangement in space of the molecules under consideration. If we deny the random character of this distribution of phase of the scattered waves, we must also deny the applicability of Rayleigh's law expressing the intensity of the scattered light in terms of the refractivity of the medium. The fact that even in a gas at atmospheric pressure there are about 10^6 molecules in a cube of the size of a wave-length of light, so that the scattered waves arising from adjacent molecules differ in phase by only 10^{-2} of the period, has been felt as a difficulty by some writers in this connexion. In fact, Larmor* has raised the question whether in view of this closeness of packing we are really justified in considering the phases of the individual scattered waves to be distributed entirely at random. It may be easily shown, however, that no appreciable deviation from a random distribution of phase, and therefore, also, from the Rayleigh law of scattering, can arise so long as the pressure-volume relation of the gas does not sensibly deviate from Boyle's law. For, all that is necessary is that the chance that a given molecule finds itself in a specified finite element of volume should be a random one, that is, is sensibly uninfluenced by the other molecules in the gas. This is true provided the total volume occupied by all the molecules, or rather by all their spheres of mutual action, forms a small fraction of the total space in the containing vessel, which is obviously also the condition that the compressibility of the gas should not appreciably deviate from that given by Boyle's law.

Larmor has made the suggestion † that Rayleigh's principle of random phase is not correct in the form in which it is stated, but that the random character of the phases of the scattered waves when they reach the observer is secured by the Doppler effect, due to the motion of the scattering molecules. The view he proposes is, in fact, that the phases of the scattered radiations emerging from the column of gas may be correlated at first, but after traversing 10^6 wave-lengths, or 50 cms., they would have become fortuitous and the energy-effects thus additive. Larmor's suggestion is, however, not acceptable. For, if it were correct, we should find that the aggregate intensity of the scattered light should be small immediately after emergence from the column of gas, that is, when it is observed within a distance of a centimetre or two from the track of the primary beam, and should increase at a greater distance from it. Such a result is

* *Phil. Mag.* xxxvii. p. 161 (1919).

† *Loc. cit.*

obviously quite inadmissible, besides being contrary to experience. The fallacy lies in Larmor's assumption that the change of wave-length (Doppler effect) has an effect on the relative phases of the scattered waves, whereas in reality it has none. To make this clear, we may consider two neighbouring molecules A and B. The scattered waves originating from them travel outwards with an identical velocity which is quite unaffected by any movements of these molecules. The phase-difference at any epoch therefore remains unaffected as the waves move out, being exactly the same as when the portions of the wave-train under consideration left the molecules. In other words, the phase-difference at each stage is exactly the same as if the molecules had remained fixed from the instant of emission of the scattered light. The scattering from any appreciable volume of gas would thus remain unaffected if all the molecules were assumed suddenly to be fixed in their instantaneous positions, and the Doppler effect due to their movement exerts no influence whatever on the observed results. Larmor's suggestion, therefore, clearly fails, and we have to fall back upon the view already expressed that the *principle of random phase of the scattered waves rests upon the random character of the distribution of the molecules in space in a gas obeying Boyle's law.*

4. Application of Boltzmann's Distribution Law.

It is clear from the preceding discussion that if the distribution of the molecules of a gas or vapour in space is *not* a random arrangement, the intensity of the light scattered would not be given by the Rayleigh law, that is, would cease to be simply proportional to the number of molecules per unit volume. In the usual treatments of the kinetic theory of gases, the molecules are conceived to exert forces on each other, and if the time during which the forces acting on any individual molecule are sensible forms an appreciable fraction of the whole time, the arrangement of the molecules would not be a random one. The influence of the molecules on each other would not then be negligible, and the energy-effects of the individual molecules could not be added up to find the total light scattered in the manner contemplated by the simple theory. It is, however, possible to make a calculation of the altered scattering power of the gas. Let $\phi(r)$ be the law of repulsive force between any two molecules whose centres are at a distance r from each other. By a suitable assumption regarding the nature of $\phi(r)$, it is possible to

include in this function the cohesive or van der Waals's forces which act when the molecules are not in collision with each other, and also the large repulsive forces occurring during actual impact. According to a well-known theorem due to Boltzmann*, the chance that two molecules find themselves at a finite distance r apart is less than the chance that they are at a very great distance apart in the ratio

$$e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \dots \dots \dots (4)$$

where $\int_r^\infty \phi(r) dr$ obviously expresses the potential energy of the configuration. The probability of groups of three, four, or more molecules being found at specified distances apart may be similarly expressed in terms of the potential energies of the respective configurations. If we assume that the deviation from Boyle's law is not very large, expression (4) will suffice to enable us to take into account the mutual influence of the molecules in determining their ordering in space. Consider a sphere of radius l drawn round the instantaneous position of a given molecule as centre. If n be the whole (actual) number of molecules in the volume of the gas or vapour, the number to be expected within this sphere of volume $\frac{4}{3}\pi l^3$ is

$$\int_0^l A \cdot 4\pi r^2 dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \dots \dots \dots (5)$$

where A is a constant to be presently determined. Integrating by parts, (5) reduces to

$$A \left[\frac{4}{3} \pi r^3 e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} - \frac{1}{RT} \int_0^l \frac{4}{3} \pi r^3 \phi(r) dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \right]_0^l \dots (6)$$

To enable this expression to be reduced, we will assume that the force $\phi(r)$ between two molecules vanishes sensibly when $r \geq \sigma$, where σ is the range of molecular action. The expression (6) then reduces to

$$A \cdot \frac{4}{3} \pi l^3 - \frac{A}{3RT} \int_0^\sigma 4\pi r^2 r \phi(r) dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \dots (7)$$

provided $l \geq \sigma$. When l is very great, the first term in (7) will be very large in comparison with the second, and since (7) must then give the total number of molecules, we find at once $A = \frac{n}{v}$. We may denote the integral in (7) by C ;

* *Vorlesungen über Gastheorie's* II. See also Jeans' 'Dynamical Theory of Gases,' 3rd ed. p. 132.

and putting $l = \sigma$, we find that, on the average, the number of molecules which we may expect to find within the sphere of action of the specified molecule is

$$\frac{n}{v} \cdot \frac{4}{3} \pi \sigma^3 - \frac{nC}{v \cdot 3RT}, \dots \dots \dots (8)$$

and is thus smaller than the number corresponding to a random distribution of the molecules by $\frac{nC}{v \cdot 3RT}$. (If C be negative, the number will be greater.)

In order to evaluate the intensity of the scattered light, we may now apply the general method developed by the late Lord Rayleigh*. The disturbance due to the scattered waves may be represented by the summation

$$\sum \cos (pt + \epsilon_1), \dots \dots \dots (9)$$

where ϵ_1 represents the phase of the scattered wave arising from a molecule and is easily expressed in terms of the position of the molecule and the directions of the incident and scattered rays. The intensity of the scattered light is obviously represented by

$$\begin{aligned} & [\cos \epsilon_1 + \cos \epsilon_2 + \cos \epsilon_3 + \dots]^2 \\ & + [\sin \epsilon_1 + \sin \epsilon_2 + \sin \epsilon_3 + \dots]^2 \\ & = n + 2 \sum \cos (\epsilon_1 - \epsilon_2), \dots \dots \dots (10) \end{aligned}$$

where n is the number of molecules and the summation $\sum \cos (\epsilon_1 - \epsilon_2)$ has to be made for all the $\frac{1}{2}n(n-1)$ pairs of molecules contained in the volume. For a random distribution, $\sum \cos (\epsilon_1 - \epsilon_2)$ vanishes, as has been shown by Lorentz and by Rayleigh. In the present case, the distribution differs from a random one in that the average number of molecules present within the sphere of action of a molecule is smaller by $\frac{n}{v} \frac{C}{3RT}$. The summation indicated in (10) will

not therefore reduce to n simply. Since the radius of action σ of the molecules is much less than the wave-length of the light, the value of $(\epsilon_1 - \epsilon_2)$ for the missing molecules may without appreciable error be taken to be zero, and hence, when the summation is carried out for all the molecules in the volume v , (10) will reduce to

$$n \left(1 - \frac{n}{v} \cdot \frac{C}{3RT} \right), \dots \dots \dots (11)$$

* Phil. Mag. xxxvi. pp. 429-449 (1918).

From this it is seen that if C be positive, the intensity of the scattered light is less than that given by the Rayleigh law, while if C be negative, it is *greater*.

In order to interpret the result contained in (11), we notice that, the integral in the second term of (7) which we have denoted by C when multiplied by $\frac{1}{2} \frac{n^2}{v^2}$ represents the *virial function* for the gas or vapour. The virial equation is in fact simply *

$$pv = nRT + \frac{1}{6} \frac{n^2}{v} C. \quad \dots \quad (12)$$

By differentiating (12), the compressibility β of the gas or vapour may be written as

$$\beta = -\frac{1}{v} \frac{dv}{dp} = \frac{1}{n \frac{RT}{v} \left(1 + \frac{n}{v} \frac{C}{3RT}\right)} \quad \dots \quad (13)$$

$$= \frac{v}{nRT} \left(1 - \frac{n}{v} \frac{C}{3RT}\right), \quad \dots \quad (14)$$

to the same degree of approximation as used previously. On comparing (14) with (11), it is seen that the intensity of the light scattered per unit of volume, instead of being proportional to $\frac{n}{v}$ as required by the Rayleigh law, is proportional to

$$\frac{n^2}{v^2} RT\beta, \quad \dots \quad (15)$$

and thus varies directly as the absolute temperature, the square of the density of the substance and its compressibility.

In the case of a gas obeying Boyle's law, $\beta = \frac{1}{p}$ and $pv = nRT$, and (15) becomes simply $\frac{n}{v}$ in agreement with the Rayleigh law.

5. *The Theory of Density Fluctuations.*

The result deduced by us in the preceding section from the principles of the kinetic theory for the case of moderately compressed gases agrees with the general formula obtained

* This agrees with Keesom's approximate equation of state, containing only the first two terms in the expansion of the virial function. Proc. Roy. Acad. Sciences, Amsterdam, vol. xv. p. 264.

in an entirely different manner by Einstein * in developing an explanation given by Smoluchowski † of the phenomenon of opalescence exhibited by fluids in the vicinity of the critical state. Einstein's reasoning is of a very general character and makes no use whatever of the molecular hypothesis. It is based on the following train of ideas. If, in the condition of equilibrium, the medium is conceived of as a completely uniform homogeneous system, there can be no scattering of the light-waves passing through it. Actually, however, as Smoluchowski showed from thermodynamical considerations, the density of the substance must vary from point to point, and also fluctuate from instant to instant, the density as measured by our ordinary appliances being merely a statistical average. Hence, in framing the electromagnetic equations, the dielectric constant (which is assumed to vary with the density in the manner contemplated by the Lorentz-Mossotti formula) must be regarded as varying from point to point, and the solution of the equations for wave-propagation contains, besides the regularly transmitted waves, also an opalescence radiation which is a volume-effect and represents the scattered light resulting from the local inequalities of density. Einstein's treatment naturally therefore falls into two parts: firstly, the determination of the magnitude of the fluctuations of the dielectric constant for the elements of volume, secondly, the calculation of the opalescent radiation.

The magnitude of the density-fluctuations is calculated by Einstein in the following manner:—Boltzmann's well-known thermodynamical principle connects the entropy S of a system with the probability W to which the entropy S relates by the equation

$$S = R \log W + \text{constant}, \dots \dots \dots (16)$$

where R is the gas-constant. Einstein points out that the entropy S of the whole system does not completely define the physical conditions of the small individual parts of the system at any instant, and hence (16) should be understood as referring to an *ensemble* of different possible conditions of the system in each of which its entropy is S . If we consider particular parts of the system and particular instants of time, fluctuations from the ideal thermodynamic equilibrium must appear, the magnitude of which is determined by the corresponding changes of entropy of the parts of the system. For an isothermal compression or rarefaction, the change of

* *Annalen der Physik*, xxxiii. p. 1294 (1910).

† *Loc. cit.* xxv. p. 205 (1908).

entropy is simply the work done divided by the absolute temperature. Boltzmann's theorem may be written in the form

$$W = e^{\frac{S - S_0}{R}}, \dots \dots \dots (17)$$

where S_0 is the entropy in the state of thermodynamic equilibrium. Taking ν to be the deviation of some observable physical variable, *e. g.* in this case the density, from the value corresponding to thermodynamic equilibrium, Einstein writes (17) in the form

$$W(\nu)d\nu = Ae^{-\frac{1}{2RT}a\nu^2} d\nu, \dots \dots \dots (18)$$

where $W(\nu)d\nu$ is the probability that ν lies between ν and $\nu + d\nu$, A is a constant, and $\frac{1}{2}a\nu^2$ is the work done in altering ν from 0 to ν . (18) evidently has the same form as Gauss's error-law, and it follows that

$$\overline{\frac{1}{2}a\nu^2} = \frac{1}{2}RT, \dots \dots \dots (19)$$

where the bar indicates the *mean* value of the quantity under consideration. If we identify ν with $(\Delta\rho)$ the fluctuation of density, its mean square may be evaluated from (19) and written in the form

$$(\overline{\Delta\rho})^2 = \frac{RT\beta\rho_0^2}{\phi}, \dots \dots \dots (20)$$

where β is the isothermal compressibility, ϕ is the small element of volume under consideration, and ρ_0 is the mean density.

For the deduction of the light-scattering from (21) with the aid of Maxwell's electromagnetic equations, reference should be made to Einstein's original paper. We may follow here an abbreviated treatment which gives an identical result.

At right angles to the incident light the intensity of scattered light is given by the expression *

$$\frac{\pi^2\phi^2(\Delta\epsilon)^2}{2\lambda^4} \frac{1}{r^2}, \dots \dots \dots (21)$$

$(\Delta\epsilon)$ being the variation of the dielectric constant.

Now, as the individual local variations of the dielectric constant are irregularly distributed, the phases of the various scattered beams are also quite arbitrary, and hence for calculating the total intensity of scattered light we have

* Rayleigh, *Phil. Mag.* p. 81 (1881); *Sc. Papers*, vol. i. p. 526.

merely to sum up the above expression over the total volume v . The expression contains a factor

$$\Sigma(\Delta\epsilon)^2\phi^2,$$

which may be evaluated by use of the Mosotti-Lorentz law

$$\frac{\epsilon-1}{\epsilon+2} = \text{const. } \rho.$$

Differentiating, we obtain

$$(\Delta\epsilon)^2 = \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \left(\frac{\Delta\rho}{\rho_0}\right)^2. \quad (22)$$

Substituting in this the value given above for fluctuation of density, we obtain

$$\frac{(\epsilon-1)^2(\epsilon+2)^2}{9} RT\beta \Sigma \phi = RT\beta \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \cdot v. \quad (23)$$

Thus the intensity of light scattered by a cubic centimetre of fluid at right angles to the incident rays is

$$\frac{\pi^2}{18} RT\beta \frac{(\epsilon-1)^2(\epsilon+2)^2}{\lambda^4} = \frac{\pi^2}{18} RT\beta \frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4}. \quad (24)$$

In the cases of gases and vapours, whether obeying Boyle's law or not, the formula (24) may be appreciably simplified by assuming $(\mu^2+2)=3$, and $(\mu^2-1)^2=4(\mu-1)^2$ approximately, and it may then be written in the form

$$\frac{2\pi^2(\mu-1)^2 RT\beta}{\lambda^4}. \quad (25)$$

If the gas or vapour obeys Boyle's law, $\beta = \frac{1}{p}$ and $pv = nRT$, and (25) becomes identical with the Rayleigh law. In other cases, (25) is seen to agree with formula (15) when the omitted multiplying factors are restored.

It may be pointed out that the expression giving the magnitude of the density-fluctuation might have been derived immediately from the principle of equipartition of energy, as is indeed evident from the form of the relation (19). In the case of a gas obeying Boyle's law in which the molecules are distributed at random throughout the space, the mean square of the density-fluctuation may also be derived by direct application of the theory of probabilities, and the intensity of the scattering calculated therefrom. This has been done by Lorentz *, and the result naturally agrees with that obtained by Rayleigh.

* Proc. Roy. Soc. Amsterdam, xiii. p. 92 (1911).

6. *Experimental Tests of the Einstein-Smoluchowski Formula.*

The expression given by Einstein for the light-scattering in a direction transverse to the primary beam, viz. :

$$\frac{\pi^2}{18} \frac{R_1 T \beta}{N_1} \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{\lambda^4},$$

where R_1 and N_1 represent the gas-constant and the Avogadro-number respectively for a *gram-molecule*, was originally developed by him to explain the opalescence exhibited by fluids in the vicinity of the critical state. It should, however, possess a far wider and *general* application, and indeed be regarded as superseding the Rayleigh law of scattering, which should only be valid in the special case of gases accurately obeying Boyle's law. It is thus of great importance to test the validity of the Einstein-Smoluchowski formula over a very wide range of cases. So far as the authors are aware, the only experimental tests that have so far been made of it for the case of a single substance in the gaseous state are those of Kammerlingh Onnes and Keesom* on the opalescence of ethylene vapour, but the work of these investigators was confined to a range of only 2.5 degrees of temperature *above* the critical temperature of this substance. A far more comprehensive and general test of the formula for several substances over the widest possible range of temperatures and pressures is obviously desirable, and researches with this object have been undertaken in the authors' laboratory. The first substance chosen was ether. This substance has a high refractivity and therefore a large scattering power in the state of vapour, and its critical temperature and pressure are moderate, and it also possesses a high degree of chemical stability under the action of heat and light. It is therefore very well suited for quantitative work. The detailed account of the determinations carried out with it by one of us (K. R. Ramanathan) will be published in a separate paper, and it will suffice here to indicate the general scope of the work and the results obtained. The light-scattering power of ether has been determined separately for the substance in the saturated vapour and in the liquid phases for temperatures from 30° C. to the critical temperature 194° (.), and for the gaseous phase from 194° C. to 217° C. The vapour and gaseous phases deviate very largely from Boyle's law, the compressibility being larger than the reciprocal of the pressure, especially at the higher temperatures, and the

* *Loc. cit.* (1908).

measurements throughout the whole range show that the *Rayleigh law of scattering completely breaks down* and strikingly confirm the correctness of the Einstein-Smoluchowski formula. The scattering power of the vapour when it is dense is in fact several times larger than that given by the Rayleigh law, and this feature is more and more pronounced as the critical temperature is approached from either side. The Einstein-Smoluchowski formula also shows itself to be equally applicable to the case of liquids over the whole range of temperature tried.

7. Polarization of the Scattered Light.

It should be noted that, according to Einstein's investigation, the light scattered in a direction transverse to the primary beam should be completely polarized. Actually, however, this is not the case. The imperfectness of the polarization of the light scattered by gases was first discovered by Strutt (the present Lord Rayleigh), and measurements of the magnitude of the effect have been made by a photographic method by him* and by Cabannes† and also by Gans‡. The imperfect polarization can be detected visually even in the case of dust-free air at atmospheric pressure §, and with the gases at high pressure, the increased intensity enables *visual measurements* to be carried out. In the case of ether vapour, the effect is very feeble, the polarization in the transversely scattered light being nearly complete (about 98·5 per cent.), but the great intensity of the scattered light enables *visual measurements* to be carried out, and it is found that with increasing density of the vapour, the percentage of polarization does not appreciably change. In the case of the liquid, specially interesting effects are observed which will be dealt with in a separate paper.

Cabannes|| has shown that owing to the imperfect polarization, the intensity of the transversely scattered light is increased and is greater than that given by the Rayleigh law in the ratio $\frac{6(1+\rho)}{6-7\rho}$, where ρ is the ratio of the weaker to the stronger component of polarization. It is found that the Einstein-Smoluchowski formula should be modified by a similar correcting factor in order to give results in agreement with experiment. The correction becomes very important when ρ is large.

* Proc. Roy. Soc. xciv. p. 453 (1918).

† *Ann. de Physique*, xv. pp. 1-150.

‡ *Ann. der Physik*, lxxv. p. 97 (1921).

§ 'Nature,' Jan. 19, 1922.

|| *Loc. cit.*

8. *Relation of Molecular Scattering to Critical Opalescence.*

As we have already seen, the Einstein-Smoluchowski formula shows that there is a perfect continuity between the comparatively feeble light-scattering shown by gases and vapours under ordinary conditions and the extremely large scattering or opalescence which develops as the critical state is approached. At the critical point itself, the compressibility of the substance is infinite, and it follows that the Einstein-Smoluchowski formula gives an infinite value for the scattering power. This is obviously inadmissible, and Einstein* himself has pointed out that for a *very minute* region at and round the critical point, the neglect of second-order terms in the expression for the work done in altering the density is not permissible and the formula requires modification. This point has, however, not much importance for our present purpose, as the range of temperature over which the neglect of the second-order terms is not permissible is exceedingly small. It may be mentioned that the matter has been further discussed by Ornstein and Zernike†, who have proposed an amended formula applicable in the immediate neighbourhood of the critical point which leads to a finite value for the scattering at this point. The bearing of Ornstein and Zernike's results on the phenomena observed with ether will be dealt with separately.

9. *The Case of Carbon Dioxide and the permanent gases.*

The experimental confirmation of the Einstein-Smoluchowski formula for the case of ether vapour, and also in the case of various ordinary liquids, shows that its theoretical basis is thoroughly firm and that the formula may be justly expected to apply equally well in the case of other gases and vapours. It is therefore very important that the case of carbon dioxide and the permanent gases, *e. g.* oxygen, nitrogen, argon, &c., should be thoroughly investigated. The scattering power of saturated carbon dioxide vapour at 21° C. (that is, ten degrees below the critical temperature) has been determined by the present Lord Rayleigh, and found to be 102 times that of the gas at atmospheric pressure. The compressibility of carbon dioxide at this temperature is very great, and the Einstein-Smoluchowski formula shows that the scattering power of saturated carbon dioxide at 21° C. should have been about 855 times that of the gas at atmospheric pressure. The observed result thus apparently supports the Rayleigh law of scattering (the density of carbon dioxide at this temperature being about

* *Ann. der Physik*, xxxiii. p. 1275 (1910).† *Proc. Amsterdam*, xvii. p. 793 (1914).

110 times the density of atmospheric pressures), and not the Einstein-Smoluchowski formula. The experimental result is however open to question, as Rayleigh mentions that his observation tube had a leak, and the density of the gas was therefore probably much less than that corresponding to the saturation pressure. Some observations made in a Cailletet tube containing CO_2 liquid and vapour by the authors show that both carbon dioxide liquid and vapour scatter light very strongly at and for a few degrees below the critical temperature, but the scattering power falls off very quickly with decreasing temperature. It is hoped to carry out a series of measurements at different temperatures with improved apparatus, and to obtain data in order decisively to settle the question whether the Einstein-Smoluchowski formula does really break down for carbon dioxide. Probably standing in very close relation to this is the fact that has been observed by Kammerlingh Onnes and his co-workers at the Leiden Laboratory, that pure oxygen, nitrogen*, and argon do not show the phenomenon of critical opalescence. It is obviously of the greatest importance to investigate whether in these cases the Einstein-Smoluchowski formula is applicable or not.

Till further data are available, it is probably not safe to venture an opinion, but it seems clear that the applicability of the thermodynamic reasoning of Einstein and Smoluchowski stands on an unchallengeable basis at least at ordinary temperatures and so far as gases and liquids are concerned. It will be noticed that the formula was derived on the basis of the classical theory of light in which it is assumed to consist of some form of continuous wave-propagation. In view of recent work in various modern fields of physics, and the known failure of the classical theory in explaining the facts regarding the emission and absorption of light, the question arises whether we are justified in assuming that the classical wave theory is necessarily capable of giving a strict quantitative explanation of the facts regarding the molecular scattering of light? Is it not possible that in the case of substances whose molecules have a relatively small light-scattering power, the infinite sub-divisibility of the energy of the incident waves which the classical theory assumes might break down? Then again is it not possible that the statistical-mechanical considerations on which the validity of Boltzmann's principle rests might require modification in the sense of the quantum theory, particularly in dealing with fluids at low temperatures? The answer to these questions can only be given when a more thorough experimental investigation of the facts of molecular

* Proc. Amsterdam Academy, xviii. p. 950 (1915).

scattering in dense vapours has been carried out. Such investigation has been undertaken by the authors, and it is hoped that before long the necessary data will be available.

10. *Summary.*

The paper considers the problem of the molecular scattering of light in dense vapours and gases *not* obeying Boyle's law. The following are the principal results:—

(1) It is shown by a discussion that the Rayleigh law of scattering, which is based on the assumption of a random distribution of the molecules in space, should not be applicable in these cases.

(2) Assuming the non-random distribution of the molecules in space to be given by Boltzmann's theorem, a calculation is made of the scattering power of the medium. The result obtained is interpreted with the aid of the virial equation, and it is shown that the scattering power per unit volume is proportional to the absolute temperature, to the square of the density of the substance, and to its compressibility. If the gas obeys Boyle's law, the expression reduces to the Rayleigh law.

(3) The result thus deduced directly from the principles of the kinetic theory agrees with the general formula derived from the thermodynamical theory of density fluctuations, developed by Einstein and Smoluchowski, of which a brief account is given.

(4) Experiments carried out with ether vapour and liquid over a large range of temperature both below and above the critical point completely confirm the Einstein-Smoluchowski formula for this substance.

(5) The corrections of the formula necessary in view of the imperfectness of the polarization of the transversely scattered light, and also in the immediate neighbourhood of the critical point when the compressibility becomes excessively great, are indicated.

(6) The cases of carbon dioxide and of the permanent gases are referred to and the possible significance of the results obtained in their cases is discussed.

Calcutta, India.

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Note added in proof (6th August): Since the paper was sent in, experiments on the light-scattering in the vapours of benzene and pentane at different temperatures and also in *carbon dioxide* at high pressure contained in sealed bulbs have been carried out, and these definitely confirm the Einstein-Smoluchowski formula and show that the Rayleigh law of scattering is not valid except in gases obeying Boyle's law.