MOLECULAR DIFFRACTION OF LIGHT

CHAPTER I

Fundamental principles

1. The whole edifice of modern physics is built up on the fundamental hypothesis of the atomic or molecular constitution of matter. In common with other branches of the science, physical optics has to concern itself intimately with the attributes of these molecules or atoms under different conditions and in different states of aggregation and the manner in which they determine the observed properties of substances. The propagation of light through refractive media is in a special degree related to and determined by the molecular structure of these media. The question is, does any departure from perfect regularity of the light-propagation arise from the discontinuous structure of the medium? The answer to this question forms the subject of the present essay. Under the description of the molecular diffraction of light, we may include such deviations from simple wave propagation as can be attributed to the ultimate structure of matter.

Rayleigh's theory

2. The principles on which the problem of molecular diffraction may be handled, at least in the case of gaseous media, were first indicated by the late Lord Rayleigh in one of his well-known papers on the origin of the blue of the sky.* Reduced to its essentials, as has been done by Schuster,† 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

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[*] Philos. Mag. **47**, 1899, pp. 375–384, *Scientific Papers*, Vol. IV, p. 397.

[†] *Theory of Optics*, 2nd edition, p. 325.

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 sub-division 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

$$A_1 \cos(\omega t - lr) \cdot R_0 \sin\theta / r \tag{1}$$

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

$$NA_1^2 = \frac{4\pi^2(\mu - 1)^2}{N\lambda^4} \tag{2}$$

where N is the number of molecules in unit volume, λ is the wavelength of the light and μ is the refractive index of the gas.

3. 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 of molecules per unit volume. We thus obtain the intensity of the transmitted light to be $I = I_0 \exp - (\kappa v)$ where κ the coefficient of attenuation is given by the relation

$$\kappa = \frac{32\pi^3(\mu - 1)^2}{3N\lambda^4}. \tag{3}$$

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 waves 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.

Criticism of the theory

4. In connection with the treatment outlined above, two distinct points come up for remark. According to Lord Rayleigh's treatment, $(\mu - 1)$ is proportional to the number of particles per unit volume of the gas, in other words varies directly as the density when the pressure is increased. In other words, the theory leads to Gladstone and Dale's law for the relation between refractive index and the density. It is well-known however that this law is only an approximation, a more accurate relation between the refractive index μ and the density ρ being the Lorentz-Mossoti formula

$$\frac{\mu^2 - 1}{\mu^2 + 2} = \text{constant}\,\rho. \tag{4}$$

The derivation of this formula has been discussed by Rayleigh* and it is clear that to be quite strict, the treatment of the problem of molecular diffraction should be modified so that it leads to (4) as the relation connecting the density with the refractive index. It may be mentioned however that in the case of gases at ordinary pressures the error involved in overlooking this point would not be appreciable.

5. A more important question is the justification for the view that the phases of the waves laterally scattered by the individual molecules are absolutely at random, so that their energy effects are additive. In the earlier treatment given by Lord Rayleigh, this was by no means made entirely clear, and on a superficial view of the matter it might be questioned (as indeed it has been by Sir Joseph Larmor)† whether the phase relation of the scattered waves arising from the molecules in any small volume is indeed in reality subject to such large and arbitrary variations that the energies due to the individual molecules may be summed up without any sensible error from their mutual interference. Larmor points out that in the case of a gas at atmospheric pressure, there are 10^6 molecules in a cubic wavelength so that the scattered waves arising from adjacent

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*[*] *Philos. Mag.*, **34**, pp. 481–502, 1892, *Scientific Papers*, Vol. IV, p. 19.

[†] *Philos. Mag.*, Jan. 1919, p. 161. These comments of Larmor were made with reference to a paper by Rayleigh in the *Philos. Mag.* for Dec. 1918, dealing with the general problem of the light emitted from a random distribution of luminous sources.

molecules differ in phase by only 10^{-2} of the period and asks, in view of this closeness of packing of the molecules whether, if they could be regarded as fixed while the radiation was passing, they ought not in conjunction to scatter far less than they would do separately? The difficulty will perhaps appear even more acutely if we consider a gas at fairly high pressure, say 64 atmospheres. The average difference of phase for adjacent molecules is in this case only $2{\cdot}5 \times 10^{-3}$ of a period, and the mean free path of a molecule would be only about $0{\cdot}02 \times 10^{-5}$ cm, that is, less than 1/250 of the wavelength of sodium light. Could we in the circumstances consider the phases of the scattered waves arising from individual molecules to be distributed entirely at random?

6. The difficulty referred to in the preceding paragraph appears to have impressed Larmor so greatly that in order to find a way of escape from it, he has suggested a somewhat different logical basis for the empirically observed correctness of the result deduced from Rayleigh's theory. It seems best to quote Larmor's own words: "The molecules of the atmosphere are in thermal motion, with velocities in correlated directions which are at ordinary temperatures of the order of 10^{-6} of that of the radiation. The wavelength of the radiation scattered from them will thus vary within a range of 10^{-6} of itself. If the phases of the scattered radiations are correlated at first, after traversing 10^6 wavelengths or 50 cm they will have become fortuitous, and the energy effects thus additive. This consideration, if justified would find the source of Lord Rayleigh's principle in the uncoordinated thermal motion of the molecules."

Justification of the principle of random phase

7. With regard to the remarks by Larmor quoted above, it may be pointed out that the difficulty raised cannot be evaded in the manner proposed by him. The suggestion made is that the phases of the scattered radiations emerging from the column of gas may be correlated at first but after traversing 10^6 wavelengths or 50 cm, they would have become fortuitous and the energy effects thus additive. If this 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 obviously quite inadmissible, besides being contrary to experience. The fallacy lies in the assumption that the change of wavelength (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.

8. What then is the justification of Rayleigh's principle? The answer to this question becomes plain when we consider the implications contained in the propositions under discussion. In order that the phases of the scattered waves arising from the individual molecules should be entirely fortuitous, it is clearly necessary and sufficient that the distribution of the molecules in the space enclosed within the walls of the containing vessel should be itself entirely fortuitous. This again in its turn would be true, if the probability that a given molecule is found within a small specified volume is independent of the presence of any other molecules, in other words if the probability that two or more given molecules are found together within a specified space is the product of the probabilities of each of them separately being found within the space. This will be true provided the total volume of the molecules or rather of the spheres of influence within which their mutual action on each other is sensible forms a sufficiently small fraction of the total space occupied by the molecules. This is precisely the condition necessary that the relation between the pressure and volume of a gas should be that given by Boyle's law. In other words, we have a truly random distribution of the molecules provided the compressibility of the gas at the pressure under consideration does not appreciably deviate from that derived from Boyle's law. So long as this is the case, Rayleigh's principle must be substantially valid, and neither the closeness of the packing nor the smallness of the free path of the molecules in relation to the wavelength of light can influence the result appreciably.

9. A precisely similar result is also arrived at if we investigate the condition necessary that the light scattered by an appreciable proportion of the molecules in the given volume may be extinguished by their mutual interference. It is obvious immediately that if the molecules be distributed *uniformly* throughout the containing vessel, we may divide up the entire volume into a large number of very small equal elements each containing a few molecules, and take them off in pairs situated at such distances from each other that in any specified direction, the scattered waves from the components of each pair differ in phase by π and therefore cut each other out by interference. In such a case, it is clear that there would be no scattered light emerging from within the gas. (A few elements of volume might be left over surplus and uncompensated near the boundaries of the vessel. These would give a surface-effect with which we are not here concerned.) If however we attempt to apply similar reasoning in the case of an actual gas the argument breaks down. The distribution of the molecules is no doubt such that

the density of the medium does not vary by any appreciable fraction of itself when we consider any appreciable volume, say one cubic wavelength. But when the sub-division of the space is carried further, deviations from the equality of the number of molecules present in equal elements of volume become relatively more important, until finally when we consider volume elements of molecular dimensions the probability that a molecule will be found inside such an element becomes small and in the case of a gas obeying Boyle's law with accuracy, vanishingly small. Thus if we take two volume elements of molecular size at a distance *exactly* $\lambda/2$ apart, the expectation that they would both simultaneously hold molecules whose effects would mutually extinguish one another is vanishingly small. Thus again we see that no appreciable proportion of the energy scattered by the individual molecules is taken off as the result of interference.

10. The foregoing discussion makes two points clear. The validity of the principle of random phase depends on the conditions being such that the compressibility of the medium is given with sufficient accuracy by Boyle's law. Secondly, the ultimate justification of the principle rests on the complete non-uniformity in the spatial distribution of the molecules in so far as very small volume elements are concerned. As we shall see later on, it is precisely these factors, namely, the compressibility of the medium and the non-uniformity of the spatial distribution of molecules, which enter into the general theory of light-scattering developed according to the principles laid down by Einstein and Smoluchowski, and which, as has been pointed out by these writers, in the case of *gases* obeying Boyle's law leads to results substantially identical with those obtained from Rayleigh's formula. It is important therefore to notice that in respect of gases at any rate, the special theory developed by Rayleigh and the more general theory of Einstein and Smoluchowski rest on exactly the same logical bases and differ only in the detailed mode of calculation of the intensity of the light scattered.