THE RECIPROCITY THEOREM IN COLLOID OPTICS.

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1. *Introduction.*

In a paper[1] on the depolarisation of the Tyndall scattering in colloidal solutions contributed to these Proceedings, the author derived the simple algebraic relation

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

connecting the three quantities ρ_u, ρ_v, ρ_h which denote the measure of the depolarisation of the light transversely scattered in a horizontal direction by a colloidal solution when the incident light is respectively (1) unpolarised, (2) polarised with electric vector vertical, and (3) polarised with electric vector horizontal. The relation was derived on the basis of reasoning involving somewhat conjectural assumptions, the truth of which however appeared *prima facie* to be highly probable. It has, however, since been found that it is not necessary to make such special assumptions in order to obtain the relation (1). The object of the present paper is to show that the aforesaid relation can be derived as a consequence of the very general *Principle of Reciprocity* due originally to Helmholtz and expounded in detail by the late Lord Rayleigh. Further, it has been found that the validity of the application of the reciprocity principle to the problem of light-scattering admits of a very simple and direct experimental test, which has been carried out and found to be completely satisfied for all kinds of disperse media, irrespective of the size, shape, structure or distribution of the particles contained in them and of any non-uniformity of the particles.

2. *Application of the Reciprocity Principle.*

Consider a horizontal beam of light polarised with its electric vibrations vertical and traversing a diffusing medium. The light scattered transversely can be supposed to be made up of two components, the vertical

[1] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1935, 1, 717.

component V_v and the horizontal component H_v. Then the depolarisation ρ_v of the transversely scattered light is given by

$$\rho_v = H_v/V_v \qquad (2)$$

When the incident light is polarised with its electric vector horizontal, let the vertical and horizontal components of the intensity of the light scattered transversely in the horizontal direction be V_h and H_h respectively. The depolarisation ρ_h is then given by

$$\rho_h = H_h/V_h \qquad (3)$$

When the incident light is unpolarised, the two components of intensity of the scattered light would be (V_v+V_h) and (H_v+H_h), and ρ_u would be given by

$$\rho_u = (H_v + H_h)/(V_v + V_h) \qquad (4)$$

From (2), (3) and (4) we obtain

$$\rho_u = (1 + 1/\rho_h)H_v/(1 + 1/\rho_v)V_h \qquad (5)$$

The quantities H_v and V_h appearing in equation (5) are related to each other in a reciprocal fashion, the direction of the electric vibration in the incident and scattered radiations being interchanged in the two cases. The theories of light-scattering due to Rayleigh and Mie show that when polarised light is incident on spherical isotropic particles of any size, the light scattered transversely in the horizontal direction is always completely polarised in the same way as the incident light, *i.e.*, H_v and V_h are both equal to zero. In the more general case of non-spherical or anisotropic particles, the two components H_v and V_h have finite values and they arise from the same cause, *i.e.*, the anisotropy or the non-spherical shape of the scattering particles. We may therefore write

$$H_v = V_h \qquad (6)$$

a relation which may be regarded as a special case of the very general "Theorem of Reciprocity," stated by the late Lord Rayleigh[2] in the following words:—"*A force of any type acting alone produces a displacement of a second type equal to the displacement of the first type due to the action of an equal force of the second type.*" It may be mentioned in this connection that the relation $H_v = V_h$ has been proved in a different manner by Rayleigh[3] for the special case of scattering by a cloud of small ellipsoidal particles. But its validity is far more general, and in fact, the relation should hold good for all particles irrespective of their size, shape, orientation, uniformity or distribution in space. Writing $H_v = V_h$ in equation (5), we obtain equation

[2] Lord Rayleigh, I., *Theory of Sound,* Vol. **I**, page 93.

[3] Lord Rayleigh, I., *Phil. Mag.,* 1918, **35**, 373.

(1) immediately. This latter relation should be true for any scattering medium consisting of particles, large or small, spherical or non-spherical, isotropic or anisotropic and either uniformly or non-uniformly distributed. It should be equally true for a medium consisting of a mixture of various kinds of particles.

3. *Special Case of Small Ellipsoidal Particles.*

In the case of small anisotropic particles, the relation (1) can be simplified further. The law of distribution of light scattered transversely by a cloud of small ellipsoidal particles was worked out by the late Lord Rayleigh[4] and afterwards generalised for the case of molecules in dense media by Raman and Ramanathan,[5] yielding a very simple result, namely that the three quantities H_v, V_h and H_h are equal in intensity. Consequently ρ_h becomes equal to unity. Introducing this in (1) we get

$$\rho_u = 2\rho_v/(1+\rho_v) \quad \ldots \quad (7)$$

This is a well-known relation applicable to most cases of the molecular scattering of light.

4. *Method of Experimental Test.*

Equations (1) and (6) represent essentially the same physical fact and are alternative forms of stating the reciprocity theorem in colloid optics. In the author's paper on the "Depolarisation of Tyndall scattering in colloids," equation (1) was tested against experimental data for ρ_u, ρ_v and ρ_h obtained by Mr. D. S. Subbaramaiya for some colloidal systems. It should be remarked in this connection that in the measurements made by Mr. D. S. Subbaramaiya ρ_u, ρ_v and ρ_h were determined separately and independently. The form of equation (1) is such that any experimental errors in the measurement of ρ_v which is usually a small quantity would introduce appreciable differences between the observed and the calculated values of ρ_u. Further it is known that in many cases, *e.g.*, that of sulphur suspensions considered in the paper referred to, there is a progressive change in the size, shape and structure of the particles due to their growth or aggregation. In consequence, the values of ρ_u, ρ_v and ρ_h measured at successive intervals of time would correspond to different groups of particles and we cannot expect them to satisfy relation (1) accurately. Considering the circumstances mentioned above, the agreement found between the data and equation (1) must be thought rather satisfactory except in the case of casein solutions, where the discrepancies noticed may be due to the disturbing effect on the measurements of the optical activity of the medium.

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[4] Lord Rayleigh, I., *Loc. cit.*

[5] C. V. Raman and K. R. Ramanathan, *Phil. Mag.*, 1923, **45**, 113.

The various sources of error possible in the determination of the depolarisation and consequently also in testing equation (1) are avoided in a direct experimental test of relation (6) by the following method. The principle of this method consists in splitting the incident unpolarised light into two beams of equal intensity, one with vibrations vertical and the other with vibrations horizontal by passing the incident beam through a double-image prism. The colloidal solution is placed in the track of both the two beams which enter it side by side and the light scattered transversely is viewed through another double-image prism. Four images of the track would then be seen corresponding respectively to the components V_v, H_v, V_h and H_h. By properly placing the two double-image prisms, the two components V_h and H_v can be brought into juxtaposition and their intensities compared. If they are identical in intensity and colour, equation (6) and therefore also equation (1) stands verified. This method is very delicate and is capable of detecting small differences in intensities of the components.

5. *Details of the Experiment.*

The light from a 20-ampere projection lantern was condensed on a small square aperture (2 mm. square). The light emerging from the aperture passed through a long focus lens. A big double-image prism (2″ square) sufficiently large to cover the full aperture of the long focus lens was placed normally in the track of the beam after the lens, as shown in Fig. 1, and its

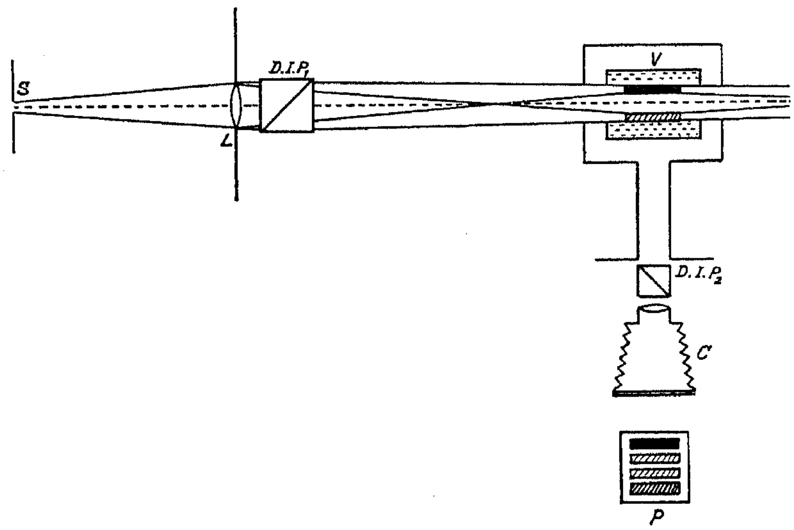


FIG. 1.

S = Illuminated square aperture (2 mm. square).
L = Long focus lens.
$D.I.P_1$ = Double-image prism.
V = Rectangular glass cell containing the colloidal solution.
$D.I.P_2$ = Second double-image prism.
C = Camera.
P = Pattern as seen on the ground glass plate of the camera.

position was adjusted so that the two mutually perpendicularly polarised beams were separated from each other at the focus by more than twice the width of either. The double-image prism was placed in such a manner that the upper beam was polarised with vibrations vertical. At the focus, the two beams of light passed through a rectangular cell of cemented glass which contained the scattering medium. The cell was enclosed in a wooden box provided with three small windows, one for the entrance of light, one for its exit and the third for observation. Just at the focus, the tracks in the scattering medium were found to be parallel. A small length of the track at this portion was chosen for observation. The scattered light was observed through another double-image prism placed with its axis perpendicular to the axis of the tracks inside the scattering medium, and it was so turned that the upper image as seen through the prism corresponded to the vertical vibrations. The tracks of the scattered light were viewed transversely through an adjustable tube suitably darkened on its inner surfaces, which was attached to the wooden box. Four images of the tracks were seen, each of the incident beam giving rise to two images, one corresponding to the vertical vibrations and the other corresponding to the horizontal vibrations. Various types of scattering media such as tap water, dilute milk, castor oil, soap solution, starch solution, gelatine solution, sulphur suspensions, arsenic sulphide sols, kaolin suspensions, ferric oxide sols, and silver colloid were successively examined. The tracks were first examined visually, and subsequently photographed. Typical photographs are reproduced in the attached plate.

6. *Results.*

Each set of photographs exhibits four images of the scattered light consisting respectively of the beams V_v, H_v, V_h and H_h in the order stated. The ratio of the intensity of the second to that of the first gives ρ_v; the ratio of the third to the fourth gives ρ_h, while the ratio of the sum of the intensities of the second and the fourth to the sum of the intensities of the first and the third gives a measure of ρ_u. In the various cases studied, it is found that the two middle components are always exactly identical in intensity and colour, establishing thereby the validity of the reciprocity theorem as applied to the phenomenon of light-scattering, irrespective of the nature of the dispersing medium. The colour and intensity of the two outermost components usually differ greatly from each other and from those of the middle components, and these differences furnished indications regarding the size and shape of the scattering particles. If the last three components are all of equal intensity and colour, it may be inferred that the scattering particles are exceedingly small (of molecular dimensions) but anisotropic in shape or structure. On the other hand, if the particles are large and nearly isotropic in shape and structure, the two outer components would be very strong and the two middle ones very weak. The changes in the colour and relative intensity of the four beams with increasing size of the particles may be conveniently followed in the case of sulphur suspensions. In the earlier stages, when the particles are small, all the four components are blue in colour; but as the particles grow, the colour of the two outer components tend to become white and their intensities tend to equality, while the two middle components remain weaker than the outer ones. In the case of castor oil, the fourth component is definitely brighter than each of the middle ones. But it is not yet fully established whether the increased brightness of the fourth component is really due to the presence of molecular aggregates or to the presence of dust. The picture taken with gelatine solution shows an apparent difference in intensity between the second and third components. Visually it was observed that these two components were exactly identical in intensity. But since they were very weak in intensity compared with that of the first component, the plate had to be over-exposed. Consequently, photographic halation has slightly vitiated the result in gelatine solution, which could have been avoided by using backed plates. The last picture is taken with silver colloid. In this case the anisotropic components are comparatively bright, demonstrating the high anisotropy of the metallic colloidal particles.

In conclusion, the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for rendering valuable help and guidance during the progress of this investigation.

7. *Summary.*

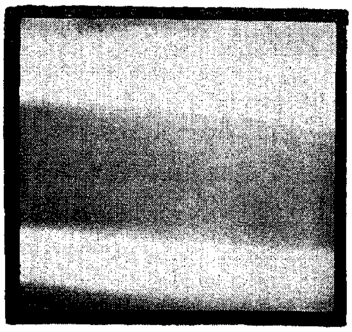
A simple method of deriving the following algebraic relation between ρ_u, ρ_v and ρ_h is given,

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v)$$

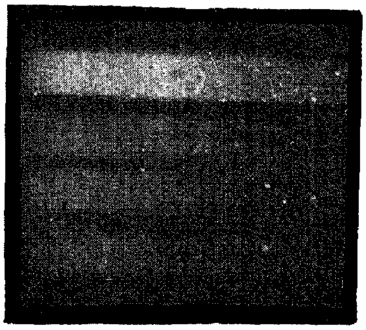
applying the general dynamical *Principle of Reciprocity* formulated by Helmholtz and Rayleigh, where ρ_u, ρ_v and ρ_h are the measures of the depolarisation of the Tyndall scattering when the incident light is respectively (1) unpolarised, (2) polarised with its electric vector vertical, and (3) polarised with its electric vector horizontal. The conclusions derived from the reciprocity principle admit of a very simple and direct experimental test which has been carried out and found to be satisfied by all kinds of colloidal solutions, emulsions, suspensions, protein solutions, etc., irrespective of size, shape or structure of the particles contained in them or of their non-uniformity. The principle of the experimental method employed to test the relation consists of splitting the incident unpolarised light by means of a

double-image prism into two beams of equal intensity but polarised perpendicularly. The scattered light is also viewed through another double-image prism. The four images of the tracks corresponding to the components V_v, H_v, V_h and H_h can be viewed at the same time and their intensities compared. In all the cases studied, H_v is found to be equal to V_h which is equivalent to the relations stated above. The relative intensity of the four track-images furnishes useful indications of the size and shape of the particles in the dispersing medium.

1. Tap water

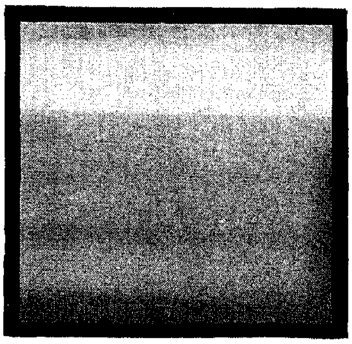


2. Dilute milk

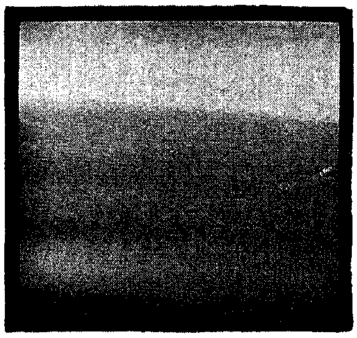


3. Castor oil

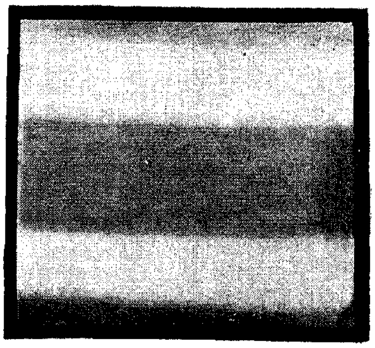
4. Soap Soln



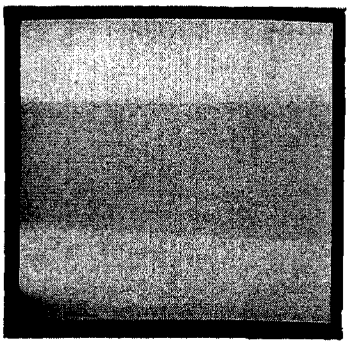
5. Starch Soln



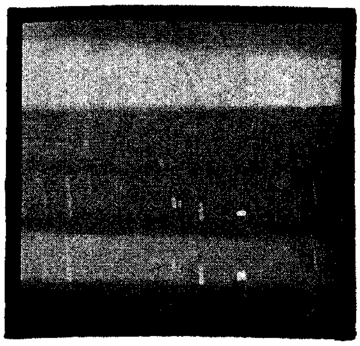
6. Gelatine Soln



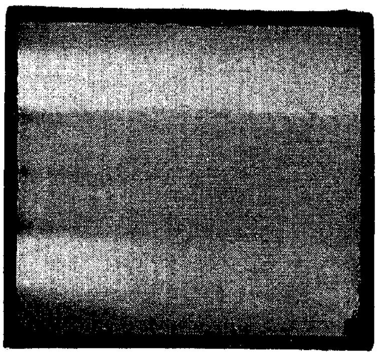
7. Sulphur Suspension (1)



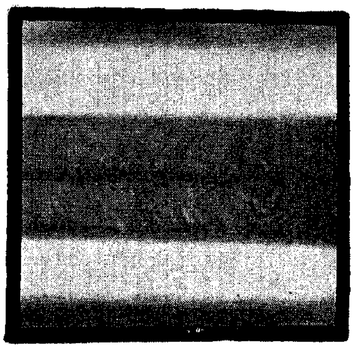
8. Sulphur Suspension (2)



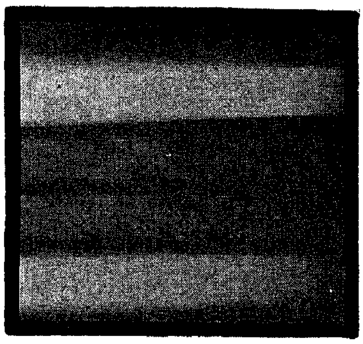
9. Arsenic Sulphide Sol.



10. Kaolin soln



11. Ferric oxide Sol.



12. Silver Colloid