

ON THE DEPOLARISATION OF TYNDALL SCATTERING IN COLLOIDS.

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1. Introduction.

THE study of the size, shape and structure of the particles in colloidal suspensions is obviously a matter of great interest. Amongst the methods available, one of the most useful and important is that based on the study of the Tyndall effect or light scattering in the solutions. This includes the measurement of the intensity of the Tyndall effect as well as the determination of the state of polarisation of the transversely scattered light. To obtain the maximum of information regarding the condition of the particles, it is not sufficient to measure the depolarisation employing incident unpolarised light as is usually done. For, the depolarisation actually observed may arise from two causes, (1) the size of the particles being comparable with the wave-length of light and (2) the varying orientations of the particles which may be non-spherical in shape or anisotropic in structure. In the case of particles which are spherical in shape and isotropic in structure, the size of the particles can be calculated from the observed depolarisation using incident unpolarised light and the formulæ for the intensity of scattering derived by Mie.¹ In the general case, however, to separate the effects of finite size from those due to the non-spherical shape or anisotropy of the particles, the depolarisation of the Tyndall scattering should be measured with the incident light, (1) unpolarised, (2) vertically polarised and (3) horizontally polarised, giving us the three quantities, ρ_u , ρ_h and ρ_v .^{*} The importance of measuring all these three quantities was pointed by the author in a previous paper entitled "Optical evidence for molecular clustering in fluids".² In a paper having the same title as this paper and appearing in these *Proceedings*, Mr. Subbaramaiya³ has published some measurements of the three quantities ρ_u , ρ_v and ρ_h in colloidal solutions and emulsions. The object of the present investigation is to obtain a relation connecting the three quantities ρ_u , ρ_v and ρ_h and to test the same with the aid of the data obtained by him.

^{*} The depolarisation is defined as the ratio of the weak to the strong component. ρ_h as thus defined is the reciprocal of the ρ_h used in the author's earlier paper quoted below.

2. Theoretical Considerations.

In obtaining an expression for the depolarisation of Tyndall scattering in colloids, one has to take into consideration the optical properties of the colloidal particles, their distribution and orientations in space, the field acting on them and the nature of the surrounding medium. The scattering by the surrounding medium which is in most cases water can be neglected compared with that of the colloidal particles. It is assumed that the particles are polarisable differently along the three mutually perpendicular directions fixed in them. All the particles can be supposed to be identical in size, shape and structure, their freedom of orientation is assumed to be unrestricted and their distribution in space is taken as random.

Depolarisation due to "Orientation Scattering".—In the case of small anisotropic particles with unrestricted freedom of orientation, the difference between the intensity of scattering actually observed and that which would be observed if the particles were replaced by spherically symmetrical particles of the same average polarisability, gives us a measure of the scattering due to the varying orientations of the anisotropic particles. The law of distribution in direction of the orientation scattering by small ellipsoidal particles has already been indicated by Gans.⁴ In the case of larger colloidal particles also, the diminution in the intensity of scattering caused by the replacement of the actual particles by spherical and isotropic particles having the same volume and the same average polarisability, may be defined as the scattering arising from the varying orientations of the colloidal particles. We may also assume that the law of distribution in direction of the orientation scattering by larger particles is the same as that for very small ones. *Prima facie*, this assumption does not seem unjustifiable, since in the case of very small particles, the law of distribution in direction of the orientation scattering is derived from kinematical considerations based on their unrestricted freedom of orientation, and the same considerations would apply equally also in the case of larger particles so long as the freedom of orientation is unrestricted.

Let a beam of plane polarised light be incident along the x -axis of a system of co-ordinates x, y, z with the electric vector along the z -axis. Let the x - y plane be the horizontal plane, the transverse observation being made along the y -axis. The two components, *i.e.*, x and z components of the scattered light will be along the horizontal and vertical planes respectively. The horizontal and vertical components of the intensity of the orientation scattering when the incident electric vector is vertical are A and $\frac{4}{3}A$, where A is a constant depending on the incident electric intensity and also on the nature of the scattering particle. When the incident electric vector is horizontal,

the two components of the intensity of scattered light are A and A respectively. For incident unpolarised light the two components are $2A$ and $7/3A$.

Depolarisation due to finite size.—According to the theory of Lord Rayleigh⁵ and G. Mie⁶ a spherical isotropic particle of finite size does not actually depolarise the light scattered by it. The depolarisation observed when the incident beam is unpolarised is only apparent, since when the incident beam is polarised with its vibrations vertical or horizontal, the light scattered transversely in the horizontal direction is also completely polarised. If the horizontal component of the intensity of the scattered light with the incident electric vector horizontal be denoted by X , the vertical components of the same is zero. If the vertical component of the intensity of the scattered light with incident electric vector vertical be denoted by Z , the horizontal component of the same is zero. The values of X and Z in terms of the size and refractive index of the particles have been given by Mie.⁷ The ratio X/Z i.e., the apparent depolarisation due to finite size is a function of the size of the scattering particles.

The depolarisation due jointly to finite size and varying orientations.—From the manner in which the orientation scattering is defined, the individual effects arising from the finite size and varying orientation of the anisotropic particles can be added to get the resultant effect.

TABLE I.

Direction of incident electric vector	Horizontal component of scattered light	Vertical component of scattered light	Depolarisation
1. Vertical	A	$Z + 4/3 A$	$\rho_v = A/(Z + 4/3 A)$
2. Horizontal	$X + A$	A	$\rho_h = A/(X + A)$
3. Unpolarised	$X + 2A$	$Z + 7/3 A$	$\rho_u = \frac{(X + 2A)}{(Z + 7/3 A)}$

The three quantities ρ_u , ρ_v and ρ_h are seen to be related to one another thus :—

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

From a knowledge of any two of the three quantities, the third can be calculated. From ρ_v and ρ_h alone, the components X and Z can be evaluated in terms of the orientation scattering component A . The depolarisation X/Z due to finite size can also be calculated. Moreover, this method affords an estimate of the relative importance of the orientation scattering and the scattering due to finite size.

3. Numerical Calculations.

The experimental data reported in the preceding paper by Mr. Subbaramaya⁸ with colloids, emulsions and protein solutions are employed in this paper for a test of the relation between ρ_u , ρ_v and ρ_h .

(a) Arsenic Sulphide Suspensions.

TABLE II.

Depolarisation	Fresh sample	After 5.5 hrs.	After 18.5 hrs.
ρ_v	2.1%	4.9%	6.9%
ρ_h	90 %	70 %	55 %
ρ_u (Calculated)	4.4%	11.5%	18 %
ρ_u (Observed)	4.7%	11.5%	16 %

The respective values of X in terms of A are 0.1A, 0.4A and 0.8A. The values of Z are 46A, 19A and 13A respectively. The relative values of X, A and Z for the fresh sample show that the particles are at first small, but nevertheless are definitely anisotropic. The relative values of X, Z and A in the later stages indicate that the particles grow in size with time and simultaneously become more and more irregular in shape or anisotropic in structure. The excellent agreement between the observed and the calculated values of ρ_u illustrates the validity of the assumptions made regarding the law of distribution in direction of the orientation scattering for large particles.

(b) Castor-Oil Emulsion.

TABLE III.

Depolarisation	Fresh sample
ρ_v	7%
ρ_h	13%
ρ_u (Calculated)	57%
ρ_u (Observed)	55%
X = 7A. Z = 13A.	

In this case, the size effect preponderates over the orientation scattering. Nevertheless, the emulsified particles show a definite optical anisotropy. *Prima*

facie, it might have been supposed that the emulsified drops of one liquid suspended in another would have been spherical in shape and isotropic in structure. Since, however, the observations indicate an optical anisotropy, we have to infer that the droplets stick together forming irregularly shaped groups or else that the Brownian oscillations in shape of the particles may give rise to an observable depolarisation.

(c) *Sulphur Suspensions.*

TABLE IV.

Depolarisation	Fresh sample	After 6 hrs.
ρ_v	3 %	6 %
ρ_h	5.5 %	7 %
ρ_u (Calculated)	56 %	86 %
ρ_u (Observed)	48 %	70 %

X = 17A and 13A respectively, while Z = 32A and 15A respectively. From the above table it is seen that as time progresses the particles grow bigger and bigger in size, and the shape becomes more and more non-spherical. The agreement with theory is not so good as in the previous cases and it would be interesting to have some further data.

(d) *Casein Solutions.*

TABLE V.

P _x	Depolarisation	Fresh sample	After 36 hrs.	After 60 hrs.
2.2	ρ_v	19.4 %	24.3 %	26.5 %
	ρ_h	34 %	58.9 %	30.7 %
	ρ_u (Calculated)	64 %	53 %	89 %
	ρ_u (Observed)	44 %	48 %	58 %
5	ρ_v	78.3 %	100 %	98.2 %
	ρ_h	87 %	93.2 %	95.4 %
	ρ_u (Calculated)	94 %	96 %	98 %
	ρ_u (Observed)	87 %	(reversed) 98.5 %	(reversed) 100 %
6	ρ_v	19 %	19.7 %	27.1 %
	ρ_h	22 %	40.5 %	28.3 %
	ρ_u (Calculated)	89 %	57 %	96 %
	ρ_u (Observed)	33.3 %	56.8 %	66.8 %

In this case, the theoretical relation between ρ_v , ρ_h and ρ_u is not found to be in accordance with fact, and several anomalies are observed. It appears likely that in the case of protein solutions, the assumptions on which relations between the three quantities were derived, namely the independence of the particles as regards spacing and orientation, are not always valid. The matter however requires further theoretical and experimental examination.

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

4. Summary.

In this paper, an attempt has been made to obtain theoretically the relationship between the depolarisations ρ_u , ρ_v and ρ_h of the Tyndall scattering in colloids where ρ_u , ρ_v and ρ_h are the depolarisations of the transversely scattered light when the incident light is (1) unpolarised, (2) horizontally polarised, and (3) vertically polarised respectively, the plane of observation being the horizontal plane. The total scattering observed in the case of colloids and emulsions is divisible into two parts, (1) the scattering arising from the finite size of the particles assumed to be spherical and isotropic and (2) the scattering arising from the varying orientations of the actual non-spherical anisotropic particles. It is assumed that the law of distribution in direction of the orientation scattering by larger particles is the same as that for very small ellipsoidal particles. The following numerical relationship is then derived between ρ_u , ρ_v and ρ_h , namely,

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

Using the experimental values for the depolarisation obtained with arsenic sulphide sols, castor oil emulsions and sulphur suspensions, it is found that the formula obtained is in satisfactory agreement with observations. In the case of protein solutions, however, certain anomalies are observed. The method of separating the observed scattering into the two parts as stated, and of calculating the size of the particles from the observations is also indicated.

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