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The theory of the Christiansen experiment

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1. Introduction

In the well-known experiment due to Christiansen (1884), an optically isotropic solid, e.g., glass, is powdered and put inside a flat-sided cell which is then filled with liquid and the refractive index of the latter is adjusted suitably by varying its composition or altering its temperature. Beautiful chromatic effects are observed when the refractive index of the liquid is thus brought into coincidence with that of the powder for some chosen wavelength in the spectrum. The cell becomes transparent for a restricted region of the spectrum in the vicinity of that wavelength, while the rest of the incident light passing through the cell is diffused out in various directions and appears as a halo surrounding the light source. The range of wavelengths regularly transmitted by the cell diminishes as its thickness is increased and is also influenced by the other conditions of the experiment. Coarser powders give a sharper transmission band, while, *per contra*, the range of wavelengths transmitted may be made as large as we please by making the particles sufficiently fine. The difference in the dispersive powers of the solid and the liquid is also of importance. When it is large, the transmission band is sharp, while *per contra*, if it be small enough, nearly the whole spectrum can get through.

From the facts stated, it is clear that the effects observed in the Christiansen experiment are not capable of being understood on a purely geometric basis but require to be considered on the basis of wave-optics. This was appreciated by Rayleigh (1899), and he suggested that by considering the fluctuations in the number of particles encountered by a ray of light traversing the cell and the resulting variations in optical path, it might be possible to make a theoretical estimate of the width of the transmission band in the spectrum. The subject was, however, not further pursued by him. At the suggestion of the present writer, N K Sethi (1920) undertook a study with a view to obtain some experimental data and develop a theory capable of explaining the facts. A considerable measure of success was achieved by him in both of these directions. His work was followed up by C M Sogani (1926), who made a detailed examination of the optical phenomena exhibited by the so-called chromatic emulsions. Later, B Mukhopadhyaya (1932) undertook to investigate the case of very finely powdered non-isotropic crystals. More recently, also, G N Ramachandran (1943) has sought to elucidate the subject further by considering the case in which the particles are of spherical shape and applying to it the principles of diffraction theory.

The present paper considers the subject afresh from a point of view which is different from that originally suggested by Rayleigh and is also simpler. The theory as now developed gives us a clear account of the phenomena and yields results in satisfactory accord with the facts of observation. Its publication has appeared desirable in view of the fact that of recent years, the importance of the Christiansen effect has been more widely appreciated. Many papers have been published and many references to it have appeared in text-books, concerning themselves chiefly with its practical application in optical filters capable of isolating narrow regions in the spectrum with the minimum loss of light. Strangely enough, however, one does not find in the literature of the subject any recognition of the fact that the performance of such a filter is determined by the principles of wave-optics.

2. Some general considerations

The powder-liquid mixture contained in a Christiansen cell is an optically heterogeneous medium, and its functioning depends on the fact that while this heterogeneity vanishes for the particular wavelength for which the two refractive indices (μ_1 of powder and μ_2 of liquid) are identical, it persists for adjoining wavelengths and disturbs the regular wave-propagation in their cases. In actual practice, the thickness of a Christiansen filter is of the order of a centimetre or even several centimetres, and hence, we shall not be justified in assuming a simple rectilinear propagation of the light rays for such wavelengths through the entire distance. To find the effect of the cell on the passage of the incident light-beam, we have to conceive of its total thickness as divided up into a sufficiently large number of individual layers, each of which in its turn produces its own independent effect, namely that of diverting part of the energy of the incident wave-train away from its original path in the form of diffracted waves. The wave-train finally emerging from the cell is that which has had its intensity cut down in this manner by the cumulative effect of the successive layers through which it has passed. To complete the picture, one has also to consider the diffracted radiations having their origin at these layers and emerging from the cell, since they are responsible for the halo observed in the experiment. The characters of the halo would evidently be determined by the intensities of these radiations as well as by their distribution in angle for various wavelengths.

In considering the problem from the point of view indicated above, it is evident that various quantities need to be known, viz., the size, shape and orientation of the particles of the powder, as well as the manner in which they are disposed within the cell with respect to their neighbours. In the circumstances of the actual experiment, however, none of these quantities can be considered as invariable. It is precisely this situation which justifies us in adopting the approach indicated above and dividing up the thickness of the cell into a large number of layers which could be considered as acting more or less independently of each other. Layers of the same thickness would not necessarily be similar in their behaviour, but such differences would be averaged out when the total effect of the whole cell is under consideration. Hence, it is permissible to base our discussion on the behaviour of a single layer which is representative of the material contained in the cell. The question arises as to what should be the choice for the thickness Δ of an elementary layer, if the theory developed on these assumptions should correctly describe the facts. It is obvious that the fluctuations in optical path arising within a given layer would be *relatively* the largest when its thickness is smallest. On the other hand, it would be clearly not permissible to carry the subdivision beyond the point at which the dimensions of an individual particle would exceed Δ. The choice which we shall accordingly make for Δ is that it is equal to the maximum distance which a light ray could travel within a single particle of average dimensions contained in the cell.

3. Formulation of the theory

By way of introducing the most general case, we shall first consider a particular example in which the elementary layers are assumed to be so constituted as to produce the maximum disturbance of the wave-propagation. This would obviously be the case when the entire thickness Δ of an elementary layer is occupied at various points on its area either by the solid alone or by the liquid alone, one-half of the aggregate area being thus occupied by the solid material and the other half by the liquid. The retardation of the wave-front in its passage through the layer would be $\mu_1\Delta$ in one case and $\mu_2\Delta$ in the other. Hence, if the wave-train before entry normally into the layer is represented by

$$\sin\frac{2\pi}{\lambda}(ct - Z), \tag{1}$$

the wave-train emerging from it is given by the summation

$$\tfrac{1}{2}\sin\frac{2\pi}{\lambda}(ct - Z - \mu_1\Delta) + \tfrac{1}{2}\sin\frac{2\pi}{\lambda}(ct - Z - \mu_2\Delta),$$

and may therefore be written as

$$\cos\frac{\pi(\mu_1 - \mu_2)\Delta}{\lambda}\sin\frac{2\pi}{\lambda}(ct - Z - \tfrac{1}{2}\Delta\cdot\overline{\mu_1 + \mu_2}). \tag{2}$$

The loss of intensity of the wave-train in its passage through the layer is obtained by squaring the amplitudes in (1) and (2) and taking the difference. It is evidently

$$\sin^2 \frac{\pi(\mu_1 - \mu_2)\Delta}{\lambda}, \tag{3}$$

while the retardation in phase produced by the layer is

$$\frac{\pi(\mu_1 + \mu_2)\Delta}{\lambda}. \tag{4}$$

The retardation in phase produced by passage through the entire cell would be merely the sum of the retardations produced by the individual layers. On the other hand, the reduction in intensity would be cumulative. It may be found by writing (3) in the form of a differential equation for the reduction of intensity, viz.,

$$\mathrm{d}I = -I \cdot \sin^2 \pi(\mu_1 - \mu_2)\Delta/\lambda \cdot \mathrm{d}z/\Delta. \tag{5}$$

On integrating (5) we obtain

$$I = I_0 \cdot \exp\left[-\sin^2 \pi(\mu_1 - \mu_2)\Delta/\lambda \cdot z/\Delta\right], \tag{6}$$

where z is the total thickness of the cell and Δ may be identified with the effective thickness of the particles of the powder. As an approximation, we may write (6) in the form

$$I = I_0 \cdot \exp\left[-\pi^2(\mu_1 - \mu_2)^2 \Delta z/\lambda^2\right]. \tag{7}$$

We may now readily generalize the foregoing treatment. For this purpose, we divide the cell-thickness as before into elementary layers of thickness Δ. Considering an individual layer of this thickness, we imagine its area divided into a large number N of equal parts. The disturbance incident normally on the layer being

$$\sin \frac{2\pi}{\lambda}(ct - Z),$$

the regularly emergent wave-train is given by the summation of the disturbances emerging from all the N elements of area, viz.,

$$\sum_N \sin \frac{2\pi}{\lambda}(ct - Z - \mu\Delta), \tag{8}$$

where μ is a quantity defined for each of the N elementary areas of the wave-front by the relations

$$\mu\Delta = \mu_1\Delta_1 + \mu_2\Delta_2 \quad \text{and} \quad \Delta_1 + \Delta_2 = \Delta. \tag{9}$$

Δ_1 and Δ_2 are the paths traversed in solid and liquid respectively in the particular area. On effecting the summation indicated in (8) and evaluating the resulting intensity, we find the diminution produced by passage through the layer to be

$$\frac{4}{N^2}\cdot\sum_{rs}\sin^2\frac{\pi(\mu_r-\mu_s)\Delta}{\lambda}, \tag{10}$$

where μ_r and μ_s are the values of μ respectively at two different elements of area and the summation indicated in (10) is made over all such pairs of elements, $N^2/2$ in number. We may, at this stage, make an approximation and write (10) in the form

$$\frac{4}{N^2}\sum_{rs}\cdot\frac{\pi^2(\mu_r-\mu_s)^2\cdot\Delta^2}{\lambda^2}. \tag{11}$$

If k_{rs} is a number defined by the relation

$$k_{rs}(\mu_1-\mu_2)=(\mu_r-\mu_s), \tag{12}$$

and using the abbreviation

$$k^2=\frac{4}{N^2}\sum_{rs}k_{rs}^2, \tag{13}$$

we may write (11) in the form

$$k^2\pi^2(\mu_1-\mu_2)^2\cdot\Delta^2/\lambda^2. \tag{14}$$

Finally, by integration over the whole thickness of the cell, we obtain as the expression for the transmission coefficient

$$\exp\left[-k^2\pi^2(\mu_1-\mu_2)^2\cdot\Delta z/\lambda^2\right]. \tag{15}$$

Our final formula (15) thus differs from (7) obtained earlier for an idealized case merely by the appearance of an additional numerical factor k^2 in the exponential. That this factor has a maximum value of unity and would in general be rather less may be shown by considering particular examples. If, for instance, $\mu\Delta$ is $\mu_1\Delta$ over σN elements of area of the wave-front and $\mu_2\Delta$ for the remaining $(1-\sigma)N$ elements, we obtain at once from (12) and (13) that

$$k^2=4\sigma(1-\sigma). \tag{16}$$

k^2 has thus the maximum value unity when $\sigma=\frac{1}{2}$, as in the case considered earlier. That k^2 would be less than unity when the thickness of the individual particles is less than Δ over a part of their area, is also fairly obvious on a consideration of the effect on the summations indicated in (12) and (13).

4. The case of spherical particles

It is of interest to consider the special case in which the particles of the powder are tiny spheres, since it forms an excellent illustration of the general theory, and also since it is an experimentally realisable case. We consider a layer of thickness Δ equal to the diameter of the spherules in which a fraction σ of the area of the wave-front is covered by the spherules, while in the remaining fraction $(1-\sigma)$ the light passes entirely through the surrounding liquid. The disturbance emerging from the layer may be written in the form

$$(1-\sigma)\sin\eta + \sigma\int_0^{\pi/2} 2\sin(\eta - \xi\cos\theta)\sin\theta\cos\theta d\theta, \tag{17}$$

where

$$\eta = \frac{2\pi}{\lambda}(ct - Z) \quad \text{and} \quad \xi = \frac{2\pi(\mu_1 - \mu_2)\Delta}{\lambda}. \tag{18}$$

The integration may be effected, enabling (17) to be written as

$$(1-\sigma)\sin\eta + 2\sigma\sin\eta\left[\frac{\sin\xi}{\xi} + \frac{\cos\xi}{\xi^2} - \frac{1}{\xi^2}\right]$$
$$+ 2\sigma\cos\eta\left[\frac{\cos\xi}{\xi} - \frac{\sin\xi}{\xi^2}\right]. \tag{19}$$

It is readily verified that in the limit when ξ is zero, (19) reduces to $\sin\eta$, as it should. We are interested in the cases when ξ is rather small, and (19) may then be written in the approximate form

$$(1 - \sigma\cdot\xi^2/4)\sin\eta - \sigma\cdot 2\xi/3\cdot\cos\eta. \tag{20}$$

Finally, we obtain for the coefficient of transmission, an expression of the same form as the general formula (14) in which the constant k^2 is given by

$$k^2 = (2\sigma - 16\sigma^2/9). \tag{21}$$

This has a maximum value 9/16 when $\sigma = 9/16$; in other words when the spherules cover a little over half the area in each layer. It is thus apparent that the spherical shape of the particles would result in a very considerable increase in the spectral width of the transmission band as compared with the case in which the particles are flat platelets.

5. The diffraction halo

That the halo seen surrounding the source of light in the Christiansen experiment is a diffraction effect, and not a simple matter of geometrical optics should be evident from the fact that it has its origin in the same set of circumstances which determine the spectral range of the regularly transmitted light, viz., the optical heterogeneity of the medium and its variations with wavelength. As remarked earlier in the paper, the halo is, in essence, a superposition of the diffracted radiations having their origin in the successive layers within the cell traversed by the incident beam of light.

In considering the problem of the distribution of light in the halo and the spectral character of the radiations composing it, it should be emphasised that the diffracted radiations have their origin at the *layers* parallel to the wave-front traversed by it, and hence that they represent the joint effect of all the particles in a layer. In other words, we have to consider the configuration of the whole wave-front after it has traversed the layer; the positions of the individual particles in the layer would determine the locations of the elevations or depressions (as the case may be) on the wave-front, while the size and shape of the particles and the value of $(\mu_1 - \mu_2)$ for the particular wavelength would determine their magnitude. In effect, each layer would form a two-dimensional laminar diffraction grating, though necessarily an irregular one. The theory of the haloes observed in the Christiansen experiment would thus be based on a description of the optical behaviour of such an irregular grating.

The theory of diffraction gratings has been well studied in the cases in which the rulings are regular and run in one direction only. We are here concerned with phase-change gratings, and the optical behaviour of such gratings may be readily described in terms of a quantity ζ which corresponds to $\pi(\mu_1 - \mu_2)\Delta/\lambda$ in our problem and represents the amplitude of the (harmonic) corrugations on the wave-front expressed as a phase-angle. When ζ is zero, the wave-front is plane and all the spectra vanish. When ζ is finite but small, only the first-order spectra on either side appear. Their intensity increases steadily as ζ increases and is quite considerable when ζ reaches the value 1, while the intensity of the higher order spectra is still quite small. The intensity of the first order spectra continues to increase till ζ is nearly equal to 2. At this stage, the second order has gained considerable strength, though still weaker than the first order, and the two orders between them contain nearly the whole of the incident energy. As ζ increases further, the spectra of still higher orders successively gain in strength, the orders having the maximum intensity being higher, the larger ζ is. The energy is distributed between several high orders for large values of ζ, so that individually they are rather weak.

The nature of the results to be expected in our present problem would necessarily be somewhat modified by various considerations. Nevertheless, one can indicate in general terms what they would be, on the basis of the results indicated above for a regular phase-change diffraction grating. Firstly, the diffracted radiations would be absent for the wavelength of maximum transmission for which $(\mu_1 - \mu_2)$ vanishes. They would rapidly increase in intensity as $(\mu_1 - \mu_2)$ becomes numerically larger and attain large values, but provided $(\mu_1 - \mu_2)$ is not too large, they would be concentrated principally in directions adjacent to that of regular transmission, the angular separation from it being determined by the average distance apart of the individual particles. (In a close-packed arrangement, this would also be the size of the individual particles.) As

$(\mu_1 - \mu_2)$ increases numerically beyond a certain limit, the diffracted radiations would spread out over a wider range of angles, and the direction of their maximum intensity would also move away further from that of regular transmission. Their intensity in any particular direction would simultaneously be much weakened.

Superficially, the results inferred above on the basis of diffraction theory resemble those which one might anticipate on the basis of geometrical optics as the result of irregular refractions by the particles of powder immersed in the surrounding liquid. Actually, however, they are different, since according to geometrical optics, the deviations of the rays would be determined by the *shape of the particles*, while in diffraction theory, it is *the size of the particles and their distances apart* in relation to the wavelength of light that principally determine the results.

6. Comparison with the facts

That the transmission band of a Christiansen cell does not exhibit a sharp cut-off in the spectrum in either direction was observed by Sethi (*loc. cit.*) in his investigations on the subject. He noticed that the visually observed spectral width could be increased by merely increasing the intensity of the light incident on the cell, and inferred from this that the transmission curve resembled a graph of the Gaussian error function. This was verified quantitatively by decreasing the intensity of the incident light by known large fractions and observing the corresponding decrease in width of the transmission band. Using powdered glass in which the particles had been sorted out into grades of different size, and also using varying thicknesses of the cell, he was enabled to establish that the variable which determined the spread of the exponential curve was proportional to the product of the thickness of the cell and the size of the particles. Finally, combining these observations with theoretical considerations of the kind indicated by Rayleigh (*loc. cit.*), Sethi derived a formula identical with our formula (7) above, except that an empirical constant appeared in the exponential instead of π^2. Sethi remarks that his data indicated the constant to be about 7. Sogani (*loc. cit.*) carried the matter further and sought to evaluate the constant appearing in the formula theoretically. Considering the case in which the particles had a spherical shape and occupied the largest possible fraction of the total volume, he calculated the constant to be $16\pi^2/9$ or 18, while his experimental observations showed the constant to be about 9. According to Ramachandran (*loc. cit.*), the theoretical value of the constant is 22 for the same case, obviously much in excess of that indicated by the actual facts. It is noteworthy that the formula of Mukhopadhyaya (*loc. cit.*) when evaluated gives the constant as about 5. The lower value is to be traced to his theoretical approach being more like that adopted in the present paper.

The general form of the transmission curve indicated by our theoretical formula (15) is thus supported by the experimental facts. Various authors have remarked upon the unsymmetrical form of the transmission curve which is steeper on the side of shorter wavelengths than on the long wavelength side. This effect, according to our formula, would be due to the joint effect of two factors, viz., due to $(\mu_1 - \mu_2)^2$ appearing in the numerator of the exponential increasing more rapidly towards shorter wavelengths and also due to the factor λ^2 appearing in the denominator. The increased sharpness of the transmission band when it is pushed towards shorter wavelengths by altering the temperature or varying the composition of the liquid, which has also been noticed in experiment, may similarly be explained as the joint effect of the same two factors in our theoretical formula. The appearance of λ^2 in the denominator is characteristic of wave-optics, and it is much to be desired that the influence of this factor is demonstrated by fresh quantitative data obtained with suitable material with which the transmission band could be shifted over a wide range of wavelengths, and by disentangling therefrom the effect of the variations of the factor $(\mu_1 - \mu_2)^2$ which appear simultaneously. In respect of the other factors, viz., the thickness of the cell and the size of the particles, the data already on record amply establish their influence. It would be desirable however to carry out further studies enabling the constant appearing in the formula to be evaluated in a number of cases, with a view to demonstrate the influence of the particle shape and of the closeness of packing on its numerical value.

In the practical use of a Christiansen filter, it is necessary, among other things, by suitable methods to separate the light regularly transmitted by the filter from that diffused or scattered by it. The discussion in the preceding section of the characters of the diffraction halo has an important bearing on this question. If the particles are very large, the diffracted light would appear in directions very close to that of the regularly transmitted light, and its separation from the latter would obviously become difficult. If, on the other hand, the particles are very small, the spectral width of the transmission would itself be greatly increased. There is thus an optimum size for the particles if the filter is to function most usefully. The work of Denmark and Cady (1935) is of interest in this connection. It may be remarked that the characters of the halo in directions adjacent to that of the transmitted light, as also in directions remote therefrom were very fully described and illustrated by a series of spectrograms in Sethi's paper of 1920. The features described by him find a satisfactory explanation on our present theory.

Summary

The effects exhibited by a Christiansen filter can only be explained or understood in terms of wave-optics. A theoretical formula is derived in the paper for the distribution of intensity in the spectrum of the transmitted light, the variables

involved being the wavelength of the light, the average size of the particles of the powder, the thickness of the cell and the difference in the refractive indices of the powder and the liquid for the wavelength under consideration. The characters of the halo observed around the light source are also discussed in terms of diffraction theory. The theory explains the facts of observation in a very simple manner and gives results in satisfactory accord with the available experimental data.

Bibliography
(In chronological order)

Christiansen C, *Ann. Phys.*, 1884, **23**, 298.
Christiansen C, *Ann. Phys.*, 1885, **24**, 439.
Rayleigh Lord, *Philos. Mag.*, 1885, **20**, 358.
Rayleigh Lord, *Nature* (*London*), 1899, **60**, 64.
Rayleigh Lord, *Scientific Papers*, **2**, 433 and **4**, 392.
R W Wood, *Physical Optics*, All editions.
Bodroux F, *Comptes Rendus*, 1913, **156**, 772.
Sethi N K, *Proc. Indian Assoc. Cultiv. Sci.*, 1920, **6**, 121.
Sethi N K, *Philos. Mag.*, 1921, **42**, 669.
Holmes and Cameron, *Am. Chem. Soc. J.*, 1922, **44**, 71.
Sogani C M, *Philos. Mag.*, 1926, **1**, 321.
Bhalla, Bhatnagar S S, and Yajnik, *Kolloid Z.*, 1927, **43**, 366.
Weigert, F and Staude H, *Z. Phys. Chem.*, 1927, **130**, 607.
Elvegard, E., Staude, H., and Weigert F, *Z. Phys. Chem.*, 1929, **B2**, 149.
Weigert F and Shidei J, *Z. Phys. Chem.*, 1930, **B9**, 329.
Kohn H and Fragstein K Von, *Phys. Z.*, 1932, **33**, 929.
Mukhopadhyaya B, *Indian J. Phys.*, 1932, **8**, 307.
Fragstein K Von, *Ann. Phys.*, 1933, **17**, 22.
Knudsen E, *Kolloid Z.*, 1934, **66**, 257.
Abbot C G, *J. Opt. Soc. Am.*, 1935, **25**, 42.
Denmark H S and Cady W M, *J. Opt. Soc. Am.*, 1935, **25**, 330.
McAlister E D, *Smithson. Misc. Collect.*, 1935, **93**, No. 7.
Barnes R B and Bonner L G, *Phys. Rev.*, 1936, **49**, 732.
Ramachandran G N, *Proc. Indian Acad. Sci.*, 1943, **A18**, 67.
Sinsheimer R L and Loofbourow J R, *Nature* (*London*), 1947, **160**, 674.