THE DETERMINATION BY PHYSICAL MEANS OF INFESTATION IN FISH

by

Gilbert E. McMurtrie

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PREFACE

The following report is a summary of an investigation undertaken on behalf of the Canadian fishing industry, more especially the inland fisheries of the Prairie provinces, by the Fisheries Research Board of Canada. The investigation was allotted to the Pacific Fisheries Experimental Station at Vancouver, the actual work being performed in the Physics Department of the University of British Columbia.

The application of physical methods of biological and other problems is becoming more prevalent. The case in hand is an example of the application of physics, more particularly the laws of light scattering, to determining the infestation of fish by Triaenophorus crassus. The arguments wherever possible have been stated in everyday language and notwithstanding the possibility of boring the informed reader, all experiments are described in detail. This, it is hoped, will accomplish two purposes. Firstly the biologist will have a better understanding of the investigation and secondly the application of physics to similar problems can be assessed.

Included at the end of the section on candling is an attempt to explain the formation of shadows by objects imbedded in turbid media. The argument is first given in simple language followed by a mathematical discussion. The complexity of the theory of scattered light in terms of ultimate processes need not be stressed. A treatment based
on the theory of M. Born is found in Appendix I.

The author wishes to express his gratitude to Dr. G.M. Shrum, Head of the Department of Physics who made available the facilities of the Department, without which the investigation would have been impossible. Sincere thanks are due to the General X-Ray Corporation for the loan of much equipment and aid. The author is deeply grateful to Dr. A.M. Crooker, friend and teacher who throughout the investigation contributed so freely of his time and knowledge.

Physics Department,  
University of British Columbia.  
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G.E. McMurtrie.
The determination of *Triaenophorus crassus* infestation in whitefish and tullibee by candling is dependent upon an understanding of the behaviour of light in the medium in which the parasites are imbedded. The "candling" technique is described and it is found to be limited in application. The absorption curve for fish flesh is obtained over a range from 2500 Å to 7000 Å. No transmission bands are found. Scattering experiments are performed and the results plotted as graphs showing variations in intensity over the surface for changing thickness and depth of object. X-rays are found capable of detecting some cysts but only using photographic methods. All attempts to utilize fluorescent screens have failed.

**INTRODUCTION**

The development of a method of detecting *Triaenophorus crassus* and the associated encysted plerocercoids in commercial fish, especially whitefish (*Coregonus clupeaformis*) and tullibee (*Leucichthys tullibee*) is of economic importance. The first intimation of this importance came in
1930 when a shipment of Canadian whitefish consigned to the United States of America was turned back at the border by American inspectors acting for the U.S. Food and Drug Administration as being unfit for human consumption. This was the first of a long series of similar rejections that has adversely affected the inland fishing industries causing a loss of markets and revenues. From the point of view of health the infestation has no bad effect for the T. crassus are non toxic and are incapable of using the human body as a host. The only objection is on the ground of esthetics -- the consumers' demand for "clean" fish.

In an attempt to retain foreign markets and to ensure the livelihood of the fishermen, the Government has undertaken investigations into every aspect of the problem including, control, eradication, selection, and detection and removal. Control and eradication were entertained as possibilities up until March 1945 when the full life cycle of the T. crassus finally became known and it was realized that it was economically if not physically impossible due to the large volume of water that has to be considered. Selection is the main method at present.

1 Fisheries Res. Bd. Memo. Director of Western Fisheries 1945
3 R.B. Miller The Life History of Trisenophorus crassus Fish. Branch, Dept. of Lands & Mines, Alberta, March 1945
employed. To ensure that shipments fulfil the entry requirements of the U.S. Food and Drug Administration all lakes have been surveyed and those in which the fish are within tolerance are labelled "clean" and only fish from these lakes are allowed to be exported in the round, i.e. without filleting and inspection. This is a severe restriction on the industry and further, brings about a consequent danger of depleting the clean fish reserves of the provinces.

While the fish of the remaining lakes exceed the tolerance as a group, it has been found that individually a high percentage could meet the requirements. Thus if a method could be developed to cull the heavily infested from the relatively clean it would bring hundreds of lakes into production that are now useless from a commercial aspect.

Any method employed to detect the presence and degree of infestation other than biological means, must depend upon the physical and/or chemical differences between the cyst and the medium in which it is imbedded. Due to the limited application it appeared to have, the difficulties and tedious work involved and the doubtful results, it was decided to forego the micro-analysis required for a determination of the chemical differences. The choice of physical differences capable of being utilised was governed by several considerations.

(1) What difference lent itself most readily to detection.
(2) What available methods were capable of displaying the selected difference. (There were considerations of expense, complexity and operating difficulties. For example a method that in a well equipped laboratory would be a matter of routine might be impossible of employment elsewhere.)

(3) Could the difference chosen be utilized within the limitations imposed by the commercial aspects of the problem, since:

(a) the cyst had to be detected "in situ". The greatest alteration that could be entertained was filleting.

(b) the fish had to remain unaffected from the standpoint of consumption.

These severe restrictions appeared to leave only one difference that could be considered, viz. the relative transparency of the fish flesh and cyst to ranges of the electro magnetic spectrum or to such portions of the spectrum as were feasible.

**EXPERIMENTAL**

The visible range 4000Å - 7000Å was selected first since an answer in this region of the spectrum, if found, would be the most advantageous requiring the least interpretation to adapt it to the human senses and furthermore it had the appearance of being the least expensive as
regards equipment.

(a) CANDLING

The employment of the above range is generally known as candling, the technique being similar to that of candling eggs (from which it derives its name). As far as is known this was first tried in the state of Minnesota and then abandoned to be taken up again in 1940 by two exporters operating on Lesser Slave Lake, which is infected beyond tolerance. The success claimed for the method when applied to fish from this lake was not verified by subsequent observations and it must be said that results were doubtful. The apparent success it enjoyed was due to the fact that in Lesser Slave Lake whitefish, the cysts lie close to the skin and in a badly infected fish one or more are likely to be detectable by candling.

In order to reach a decision as to whether candling as employed was reliable or not, a device similar to those used by the fish packing firms was constructed. Simple in construction, it consisted of a light tight box approximately 18" x 18" x 24" with an aperture in the centre of the upper surface over which was placed a glass plate for supporting the fish. Inside the box was placed the light source. To render the equipment more flexible the aperture was made variable as to size and configuration, facilities were provided for the insertion of filters beneath the glass supporting plate while the source, a tungsten arc was fitted with reflectors and lenses. The
arrangement is shown in figure 1.

![Diagram of arrangement](image)

The fish were placed on the plate and various combinations of illumination and filters were used in an attempt to detect the cysts. The positions of suspected shadows were marked and when the candling was completed the fish was carefully dissected. The percentage of cysts corresponding to suspected shadows was very small except where the cyst was large and lay directly beneath the skin. The natural variations in light from the skin pattern coupled with an overlying layer of scales served to hide all but the most obvious shadows.

It was at this point that the first basic alteration to the natural problem was introduced. The fish were skinned and the flesh lying above the lateral line and extending from the head to the dorsal fin was cut out in
Plate I
Hilger Medium Quartz Spectrograph
and
Spekker Spectrophotometer.
two blocks, one to each side of the bone structure. (It is in this area that 80% of all cysts are found.) These blocks were then candled as above. This simplification was introduced since if cysts could not be detected in pure flesh there would be no chance of detection when covered with skin and scales. Further to the above, brass rods of various diameters were sharpened at one end similar to meat skewers. With a sample of flesh in place the skewers were inserted horizontally into the flesh and perpendicular to the incident beam commencing at the bottom and repositioning toward the upper surface. It was found that within the range of sizes assumed by the cyst there was no difference in detection and the earliest that detection commenced was when the object was approximately one half inch below the viewing surface. The skewer being completely opaque represented an ideal cyst and no better could be expected when viewing the real object. The skewers were tried on fish in the round, i.e. with skin and scales and as before detection was certain only when the skewer lay next to the skin. Repositioning to a quarter of an inch into the flesh was sufficient to obliterate the shadow.

The foregoing was repeated for fish that had been frozen. The rate of freezing appeared to have no effect on the results which were poorer than with fresh fish. Fish flesh that had been frozen by packing in solid CO, and flesh frozen slowly in a refrigerator were both tried. It was thought that a large crystal size obtained by a slow freeze
would offer advantages over the quick freeze, but in neither case could the "cyst" be detected until complete thawing had taken place.

The only possibility of improving the candling method lay in finding a wavelength or band of wavelengths to which fish flesh was selectively transparent and then determining the behaviour of light in the flesh so that full advantage could be taken of the selected band. Detection depends upon "seeing a shadow" of the cyst on the viewing surface and thus despite the previous visual results incident conditions were almost certain to affect detection. That there was a preferred band could be inferred from general theory and the region was indicated by the fact that by transmitted light the flesh was reddish while by reflected light it was grey or white.

(b) ABSORPTION

Micro sections of flesh were prepared (the small thickness being necessary on account of the density of the medium) by freezing the flesh and sectioning with a microtome. The usual technique of imbedding in wax prior to cutting was found unsatisfactory, the wax lending insufficient support for the area desired. Furthermore, it was found necessary to keep the microtome as well as the sample well below freezing during the entire time of handling since with such thin sections the relatively warm blade melted the section as it cut, and any attempt at handling an unfrozen section resulted in the flesh falling to pieces. The cooling was
accomplished by passing a stream of air through copper coils immersed in a bath of solid carbon dioxide and alcohol and blowing the same directly onto the block of flesh and the blade of the microtome, the whole having been previously cooled by being packed in "dry ice". Even with rapid freezing the crystal structure was still large enough to cause tearing in sections less than 40 μ in thickness and in the thicker samples made accurate thicknesses impossible.

The micro sections (which were cut parallel to the plane containing the maximum length and depth of the fish) were placed between two circular quartz windows approximately 2 cm. in diameter and 1.5 m.m. thick, held together by brass sleeves (fig. 2) which permitted the passage of light through the sandwich.

![Diagram of fish flesh and quartz windows](image)

The cell was placed in the upper beam of a Spekker spectrophotometer mounted on a Hilger Medium Quartz Spectrograph (Plate 1) the lower beam passing through two quartz windows identical with the first. The useful range was from 2000Å to 12000Å depending upon the sensitivity of the
SPEKKER SPECTROPHOTOMETER

(fig 3.)
photographic plate and the type of source.

The principle of the instrument is that the two beams which are horizontal and parallel originate from a single source and in the beginning are equal in intensity this being ensured by an appropriate optical system (fig. 3). After each beam has traversed what has been interposed (which alters the intensities) they are again put through a set of prisms that places the bottom beam directly underneath the top one but not quite touching. The two beams that are now travelling in close company illuminate the slit of the spectrograph. The spectrograph splits the beams into their component wavelengths whose intensities can be ascertained from the blackening of the photographic plate. A typical plate is shown in Plate II where the two spectra may be discerned one directly above the other. At the origin of the lower beam is a device for altering the amount of light in this beam in known steps. Now if the light incident upon the micro section (the top beam) was transmitted with the relative intensities of different wavelengths unaffected by the micro section, on comparing it with the light from the lower beam the most that would be observed would be overall difference in intensity, as shown by the photographic plate. However, if the fish flesh transmitted or absorbed any particular band of wavelength it would appear on the plate as a change of intensity with respect to wavelength when compared with the spectrum of the clear beam. By varying the intensity of the lower beam and
Plate II

Absorption Spectrograms

of

Fish Flesh

To fac p10
11.

plotting points of equal densities for the two spectra against wavelength it is possible to obtain the absorption and transmission curves of the substance. Spectrograms were obtained in the above manner for thirty fish (examples are shown in Plate II.) The curves obtained from the plate all showed the same form, viz. an absorption that slowly increased from 7000Å to approximately 3400Å then a sharp rise to 2950Å (Plate III). Although only thirty determinations were made it would appear that this is a characteristic of the specie independent of age, sex or past history. The region in which the high absorption took place was close to the absorption band of vitamin A. To check that this was not the cause, micro sections were left exposed to air and ultra violet light for as long as twelve hours and used for redetermination. Within the limits of experimental error no change was observed.

It is well to point out that the curves as shown do not represent true absorption but absorption plus scattering for only a negligible amount of the light scattered by the specimen would reach the slit of the spectrograph and this loss would contribute to the shape of the curve. From the point of view of transmission it is readily seen that there is no preferred band in the

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1For a detailed account of this technique see Experimental Spectroscopy by Sawyer.
visible range but only a small improvement towards the longer wavelengths, which advantage would be more than offset by the sensitivity of the human eye.

If a transmission band had been found the use of a Bildwandler\(^1\) was proposed for interpretation. Plotted on the same wavelength scale Plate IV is the spectral sensitivity of the average human eye which is seen to have a maximum at 5500Å dropping rapidly on either side, and it is at this point that variations in surface intensity would be most readily detectable. In addition to the failure of the human eye in the long wavelengths, heavy absorption takes place due to the aqueous composition of the flesh and it is not until the far infra red is reached that transmission bands are encountered. The problem of a source let alone means of interpretation would render commercial use of this latter region out of the question.

It can be stated that candling using the visible portion of the spectrum has an extremely limited application. Using fish "in the round" only cysts directly beneath the skin are observable while for skinned fillets it is impossible to detect with certainty cysts lying deeper than one-half inch below the viewing surface. In frozen flesh the results are worse. Within the natural range of sizes assumed by the infestation there was no difference in maximum depth at which detection commenced. In other words,

\(^1\) A device for "changing" infra red wavelengths to the visible range used during the war for night vision.
SENSITIVITY OF THE HUMAN EYE

INTENSITY

ANGSTROMS

2000 3000 4000 5000 6000 7000 8000
if all cysta lay at a depth greater than one-half inch below the viewing surface, the probability of designating the fish as infested by means of candling is practically zero. However, if skinned fillets less than one inch thick were candled by a skilled operator most cysts should be observable. The substitution of an opaque object in lieu of a cyst proved that it was not a difference in optical density that was responsible for the difficulty and therefore the failure of the method must be attributed to the behaviour of light in the medium, thus precluding the necessity of experimenting with the cysts alone.

USE OF ULTRA VIOLET LIGHT

There remains one more point to consider. Although it was seen that absorption and scattering were large toward the ultra violet end of the spectrum there was a possibility that the cyst materials might fluoresce under the action of short wavelengths and appear as light spots in the flesh. To check this possibility entire cysts as well as cyst material from both frozen and unfrozen fish were placed on plates and irradiated with an ultra violet lamp as well as with a tungsten arc with appropriate filters. No fluorescence was seen. If there was any action it was far too weak to be of any use in detection

X-RAYS

That X-rays were capable of penetrating the fish was
X-RAY CIRCUIT

(fig. 4)
GRAPH OF X-RAY TRANSMISSION FOR BERYLLIUM AND PYREX WINDOWS OF THICKNESS 1 MM.
an assurity and from such a medium as flesh scattering would be negligible. The determining factor was however the difference in absorption between the cyst and the surrounding media. If this was small there would be little chance of utilizing X-rays.

A circuit was built to provide rectified and variable plate voltage to the X-ray tube for better control of the hardness or softness of the rays. A schematic diagram of the circuit is shown in fig. 4 while the apparatus is shown in Plate V. The reversal from the usual procedure of having the filament at ground potential and the target at a positive potential was employed to simplify the cooling problem. For long exposures it was necessary to have a water cooled target and if this was at ground potential it could be connected directly to the water system with no electric leakage or insulation difficulties arising. The final X-ray tube employed was a General X-ray CA6 diffraction tube with a chromium water cooled target but with the target and Beryllium windows modified to give a useful solid angle of radiation of approximately 40° instead of the usual 6°. The need of Beryllium windows if soft radiation is required is graphically illustrated in fig. 5 which shows the difference in the spectral energy curves for Beryllium and glass at three different voltages. Photographic film of fine grain was used since if it was impossible to obtain results in this manner it would be impossible otherwise. The film holder had to have a low coefficient of absorption
Plate V

View of X-Ray Apparatus.
for long wavelengths or else a large percentage of the soft rays would be lost consequently it was made of black light tight paper.

The fish were placed directly on top of the film holder and as close to the tube window as feasible. The exposure times being dependent upon the thickness of the fish, were determined by trial and error. The film was developed for maximum contrast in Eastman X-ray Developer, and dried in the usual manner.

The first indication of results was when small white spots foreign to the anatomy of the fish were seen in the area between the lateral line and dorsal fin. These spots can be seen by a careful inspection of Plate \( VI \). That they were due to cysts was verified by noting their position and dissetting the fish. It was found that all spots corresponded to cysts but not all cysts corresponded to spots. A large number of cysts were then removed from other fish and X-rayed separately. The results showed that not all cysts caused spots. Plate \( VII \) shows (a) an isolated cyst showing two groups of opaque spots, (b) a cyst imbedded in flesh with similar effects, and (c) an isolated \textit{T. crassus}. No worm by itself showed any evidence of spots, which fact indicated that whatever the cause it belonged to the cyst. It has been determined that the spots are small particles of calcium carbonate resulting from the onset of calcification of the cyst by the fish. This gave the reason why all cysts did not show spots. Calcification is a slow process.
Plate VI

X-ray of fish showing calcified cysts along upper portion of back
Plate VII

X-ray photograph showing (a) isolated cyst with calcified spots, (b) similar cyst imbedded in flesh, (c) isolated worm and (d) pure flesh.
and the cyst would have to be of a certain age before exhibiting the phenomenon. Thus the absence of spots could not be taken as proof that the fish was clean but only that no cysts were over a certain age.

It was thus necessary to obtain radiograms showing if possible, the entire cyst. By keeping the X-rays very soft and determining the exposure times as before, the outlines of cysts were found on the film (Plate(VIII ). Once again not all cysts gave results, but only those above a certain density. Referring back to Plate(VII ) (d) is pure fish flesh. It is seen that if there is a difference in density between cyst material (ignoring the spots) and pure flesh it is very small and in many cases would be insufficient to provide the needed contrast. However, cysts could be detected before calcification commenced. How much before could not be determined. Any commercial application of X-rays even though limited in scope could not use photographic film. The time involved, let alone the cost, would be prohibitive. It was necessary, if the method was to be used, to utilize a fluorescent screen. All experiments with such screens failed to give the required results. The reasons are first, the film is accumulative with respect to time, the screen is not, and secondly for good intensity the size of crystals in the screen is large which reduces the definition.

Once again it must be said that it is impossible to say definitely whether or not a fish is infected or to what
Plate VIII

Film showing outline of entire cysts imbedded in upper portion of back
extent if infection is found.

FORMATION OF SHADOWS

The following makes no attempt at explaining the microscopic behaviour of light in the medium but is rather a macroscopic discussion. The conditions under which a shadow is discernable while depending upon absolute intensity depends to a greater extent upon the intensity distribution across the surface. If the rate of change of intensity with respect to distance as measured from the "centre" outward across the surface is below a critical value detection becomes impossible. Consider a medium of given thickness \( d \) bounded by two parallel planes with the top surface illuminated by a parallel beam of light, large in extent, incident at right angles; fig. (XY). We assume that the intensity at any plane in the medium \( Z = k \) is for light in the \( Z \) direction given by

\[
I_k = I_o e^{-\mu(d-k)}
\]

(1)

where \( \mu \) is the sum of the coefficients of absorption and scattering, \( I_o \) is the incident intensity and \( (d-k) \) is of course the thickness of intervening medium.
Our problem is to find the effect that a small opaque object imbedded at say $Z = d$ will have on the intensity distribution across the bottom or viewing surface $S$. The object will be considered as very thin and circular in shape and to be parallel to the bounding faces. We will first find what the contribution of a similar area without the object would be at any point in $S$ and then consider it as a deletion when the object is inserted.
In fig (v) consider the flux through the element of area \( r \,dr\,d\theta \). In the \(-Z\) direction it is

\[ \Phi_z = I_z \, r \, dr \, d\theta \]  \hfill (2)

If we assume initially that the variation of intensity with direction obeys Lambert's law,

\[ I_\psi = I_z \cos \psi \]  \hfill (3)

for angles that are not too large, we have for the flux through the element in the \( R \) direction

\[ \Phi_\varphi = I_z \cos \psi \, r \, dr \, d\theta \]

This quantity will suffer an attenuation due to scattering and absorption such that on reaching point \( P \) we have

\[ \Phi_\psi = I_z \cos \psi \, e^{-\mu R} \, r \, dr \, d\theta \]  \hfill (4)

The point \( P \) is chosen on the \( X \)-axis for simplicity.

It is seen from symmetry that there is no loss in generality.

Finally the flux leaving the surface \( S \) at \( P \) is

\[ \Phi_P = I_z \cos^2 \psi \, e^{-\mu R} \, r \, dr \, d\theta \]  \hfill (5)

And the total contribution from the area \( A \) will be

\[ \Psi_P = \int_0^R \int_0^{2\pi} I_z \cos^2 \psi \, e^{-\mu R} \, r \, dr \, d\theta \]  \hfill (6)

\[ = I_z \int_0^R \int_0^{2\pi} \frac{Z^2 e^{-\mu \sqrt{Z^2 + (x^2 + r^2 - 2xr \cos \theta)}}}{[Z^2 + (x^2 + r^2 - 2xr \cos \theta)]} \, r \, dr \, d\theta \]  \hfill (7)
where
\[ R = \sqrt{Z^2 + (X^2 + r^2 - 2Xr \cos \theta)} \] (8)
and the integration is over the area \( A \).

We can find the amount that would be received at \( P \) in virtue of the entire plane in which \( A \) lies by putting \( X = 0 \) in (7) and extending the integration for \( r \) to infinity. We get
\[
\Psi_P = I_z \int_{0}^{2\pi} \int_{0}^{\infty} \frac{Z^2 e^{-\frac{\sqrt{r^2 + r'^2}}{Z^2 + r'^2}}} {r \, dr \, d\theta} \tag{9}
\]
Setting \( S = Z^2 + r^2 \) we obtain
\[
\Psi_P = 2\pi Z^2 I_z \int_{S}^{\infty} \frac{e^{-\frac{\sqrt{r^2}}{S}}} {S} \, ds \]

Let \( Z = 1 \) (that is unit distance). Then the expression becomes
\[
\Psi_P = 2\pi I_z \int_{1}^{\infty} \frac{e^{-\frac{r}{S}}} {S} \, ds \tag{10}
\]
Now \( \int_{1}^{\infty} \frac{e^{-\frac{r}{S}}} {S} \, ds = E_i(\mu) \) is a function which has been tabulated\(^1\) for \( \mu \) up to and including 10. Thus
\[
\Psi_P = 2\pi I_z E_i(\mu) \tag{11}
\]
We can find the change in intensity directly under our object \( A \) (at the surface \( S \)) by subtracting what it would contribute from (11) thus
\[
\Psi_P = 2\pi I_z E_i(\mu) - 2\pi I_z \int_{0}^{r} \frac{e^{-\frac{\sqrt{r^2 + r'^2}}{Z^2 + r'^2}}} {r \, dr}
\]

\(^1\) N.R.C. Div. of Atomic Energy M.T.I.
\[ \psi = 2\pi \int_0^1 \left[ \frac{e^{-r^2}}{s^2} \right] ds \]

\[ = 2\pi \int_0^1 \left[ \frac{e^{-r^2}}{s^2} \right] ds \]

\[ = 2\pi \int_0^1 \left[ \frac{e^{-r^2}}{s^2} \right] ds \]

The value of the integral for \((S^2 - 1)^{\infty}\) is given by the following

\[ \sum_{n=1}^{\infty} \frac{(-1)^n S^n}{n!} \]

which is rapidly convergent. Substituting this in (13) we have

\[ \psi = 2\pi \int_0^1 \left[ \psi - \left( \frac{\mu S}{n!} + \frac{\mu^2 S^2}{2 \cdot 2!} + \cdots - \frac{(-1)^n \mu^n S^n}{n \cdot n!} \right) \right] \]

changing back to our variable \(r\), (15) becomes

\[ \psi = 2\pi \int_0^1 \left[ \psi - \left( \frac{\mu S}{n!} + \frac{\mu^2 S^2}{2 \cdot 2!} + \cdots - \frac{(-1)^n \mu^n S^n}{n \cdot n!} \right) \right] \]

The intensity at any point \(P\) in the plane \(S\) is given by

\[ \psi = 2\pi \int_0^1 \left[ \psi - \left( \frac{\mu^2 S^2}{2 \cdot 2!} + \cdots - \frac{(-1)^n \mu^n S^n}{n \cdot n!} \right) \right] \]

which is the result when we subtract the contribution of \(A\) as given in (6) from the total intensity in the absence of
A as given in (10). We require the change of $\Psi_a$ with respect to $X$. Hence
\[ \frac{d\Psi_a}{dX} = -2\pi I_z \int_0^{2\pi} \int_0^\infty \frac{d\phi}{dx} (\cos^2 \phi e^{-\mu r^2}) r dr d\theta \] (18)

Since $X$ is independent of $\mu$ and $\theta$.

Thus from (16) we can find the change directly beneath $A$ for various $\mu$ if we know $\mu$, and (18) gives the change of intensity with $X$.

The evaluation of the integral
\[ \int_0^{2\pi} \int_0^\infty \frac{e^{-\mu \sqrt{z^2 + (x^2 + r^2 - z\cos \phi)}}}{z^2 + (x^2 + r^2 - z\cos \phi)} r dr d\theta \]
is attempted here since it is not found in the literature. One proceeds as follows. Consider
\[ \int_0^{2\pi} \frac{e^{-\mu \sqrt{z^2 + (x^2 + r^2)}}}{z^2 + (x^2 + r^2)} d\theta \]
and put $a = z + x + r^2$; $b = rX$

Now $X^2 - 2Xa + a^2 = 0$ being a perfect square we can say:
$X^2 + r^2 \geq 2XR$ and hence $a > 2b$

Expanding the integrand of
\[ \int_0^{2\pi} \frac{e^{-\mu \sqrt{a - 2b \cos \theta}}}{a - 2b \cos \theta} d\theta \]
we obtain
\[ \int_0^{2\pi} \left( \frac{1}{a - 2b \cos \theta} - \frac{\mu}{\sqrt{a - 2b \cos \theta}} + \frac{\mu^2}{2!} - \frac{\mu^3}{3!} \sqrt{a - 2b \cos \theta} + \frac{\mu^4}{4!} (a - 2b \cos \theta) + \cdots \right) d\theta \] (19)

Now since $0 > 2b$ we are justified in integrating term by term. We change to complex integration and for the first integral integrate around the unit circle. Thus
\[ i \oint \frac{dz}{bz^2 - az + b} \] (20)

which has a pole at $Z = \frac{a - \sqrt{a^2 - 4b^2}}{2b}$

Therefore the value of the integral is
\[ \frac{2\pi}{\sqrt{a^2 - 4b^2}} \] (21)
The second integral assumes the form
\[
- \frac{1}{\sqrt{d}} \oint \frac{dz}{z(a - dz - \frac{b}{z})^{\frac{1}{2}}} = - \frac{1}{\sqrt{d}} \oint \frac{dz}{\sqrt{-a} (1 - \frac{a}{d} z + z^*)^{\frac{1}{2}}}
\]
(22)

We recognise the bracket in the denominator as the generating function of Legendre Polynomials and we can write the integral as

\[
- \frac{1}{\sqrt{d}} \sum_{n=0}^{\infty} P_n\left(\frac{a}{d}\right) z^{-n-\frac{1}{2}} dz = - \frac{1}{\sqrt{d}} \sum_{n=0}^{\infty} P_n\left(\frac{a}{d}\right) \oint z^{-n-\frac{1}{2}} dz
\]
(23)

The integrand has an essential singularity at the origin thus we integrate around the contour as shown giving for the value after integration

\[
\frac{A}{\sqrt{d}} \sum_{n=0}^{\infty} \frac{P_n\left(\frac{a}{d}\right)}{2n+1}
\]
(24)

The third term is integrated by inspection giving

\[
2\pi \frac{u^3}{2!}
\]
(25)

The fourth term integrates as follows

\[
\int_{0}^{2\pi} \sqrt{a - 2b \cos \theta} d\theta = \sqrt{a} \int_{0}^{2\pi} (1 - \frac{2b}{a} \cos \theta)^{\frac{1}{2}} d\theta
\]
(26)

Now \( \int_{0}^{2\pi} \cos^s \theta d\theta = 0 \) if \( r \) is odd, therefore let \( r = 2n \) then

\[
\int_{0}^{2\pi} \cos^{2n} \theta d\theta = \frac{1}{2^{2n}} \left(\frac{2n}{n}\right) 2\pi
\]

And the value of the integral is

\[
- \sqrt{a} \sum_{n=0}^{\infty} \frac{\sqrt{n}! \cdot 2\pi}{2^{2n} (2n)! (n!)^2 (4n-1)} \left(\frac{1}{d}\right)^{2n}
\]
(27)

The integration of the remaining terms is straightforward and will not be done here.
Collecting what we have and arranging terms we have as an expression of our original integral

\[
\int [\frac{A}{\pi b} \sum_{n=0}^{\infty} P_n(\frac{a}{b}) \frac{A^{n+1} 2^n (\frac{b}{a})^{2n}}{2^{2n} (2n+1)! (N)^{2n+1}} - \int_{0}^{r} \frac{A^{n+1} 2^n (\frac{b}{a})^{2n}}{2^{2n} (2n+1)! (N)^{2n+1}} r dr + \int \text{Remaining Terms} ] dr + \int \text{Remaining Terms} \]

\[
\left. \right|_{r}^{\infty} + \frac{2^n \mu^2 r^2}{2} + \frac{2^n}{\sqrt{a^2 - b^2}} \frac{r^2}{2} = \Lambda
\]

The intensity at any point is then given by

\[
\Psi_r = E_r(\mu) - \Lambda 2 n I_z
\]

and if we wish to find the change of intensity along \( x \)

\[
\frac{d \Psi_r}{dX} = - \frac{d \Lambda}{dX} 2 n I_z
\]
Plate IX

View of scattering apparatus showing control circuit for mercury arc, quadrant with sample in place, microammeter etc.
In the beginning we made two assumptions that require justification. The first assumption was that for light leaving the medium at right angles to the surface the intensity is given by

$$I_\kappa = I_0 e^{-\mu(d-\kappa)}$$

where $I_0$ is the normal intensity entering the layer of thickness $X$. To check this the apparatus shown in Plate (IX) was constructed. Referring to fig (VIII)A, is a General Electric HS6 mercury arc situated at the focus of a good lens of large aperture. Due to the intensity of the light (60,000 lumens) the arc is water cooled. (It was found necessary to cool the lens and its surroundings as well by a continuous stream of cold air). On the centre axis of the parallel beam emerging from B a brass quadrant C, calibrated in degrees, carried a photo multiplier tube (981A) in front of which was placed a lens and diaphragm D in such a position that the tube received only parallel rays from the direction in which it pointed. The current through the final stage of the tube due to the light received was read directly from a microameter E. (The meter was shunted by factors of ten in order to extent its range).
LINE DIAGRAM OF PLATE IX

FIG 6
The intensity prior to taking readings was checked by placing (on the quadrant table at (a,a)) a block of paraffin kept for that purpose and the arc then adjusted until the desired reading was obtained. This permitted a comparison of results without the necessity of determining the absolute intensity for each experiment. The procedure was to place the medium on the quadrant table at right angles to the beam. The intensity of the transmitted light for different thicknesses and zero angle was then read directly from the microameter. The mean results for several determinations with paraffin blocks are plotted as a graph of intensity against thickness Plate (\( \chi \)). The intensity I is plotted as ordinate and is in arbitrary units since absolute intensities are not required. The graph was analysed and was found to be in good agreement with the function \( I = I_o e^{-bX} \) where \( I_o \) was chosen in such a manner as to have the two curves coincident at a point. We can therefore within the limits of experimental error accept the first assumption and take \( b = 3 \).

The second assumption made was \( I_\phi = I_z e^{\Delta \phi} \)

where \( I_\phi \) is the intensity observed at an angle \( \phi \) to the normal direction \( Z \) and \( I_z \) is the intensity in the latter direction. The arrangement was as before except that the photo tube was swung through an angle \( \phi \) and the intensity read from the meter. The results are shown graphically in Plate (\( \chi \)). From the geometry of the
GRAPH OF

INTENSITY / THICKNESS OF PARAFFIN

THICKNESS IN INCHES
apparatus it is seen that the curve has to be corrected to compensate for the increase in area visible to the phototube as the angle is increased. If A is the area effecting a reading in the normal direction then \( \frac{A}{\cos \phi} \) is the effective area at an angle \( \phi \) and it follows that the readings of intensity have all to be multiplied by \( \cos \phi \).

In addition to this correction for area a further correction must be applied to compensate for the increased thickness traversed by the light as the angle is increased. Using the value of \( \mu \) from above for computing the correction, the resulting curve is found to be a cosine curve within experimental error, and our second assumption is justified.
Graph of Intensity vs. Angle of Scattering

Curves corrected for area
Curves corrected for area and intensity

Intensity

Angle of Scattering
One is accustomed to call the phenomenon of light scattering the Tyndal Effect after the man Tyndal who was first to observe the luminous path of a light ray in turbid media and colloidal suspensions. Later in observing the light scattered from gases he observed that it was polarised. Now it can be shown that only in an ideal crystal grating at the lowest temperature does light behave strictly according to Maxwell's equations. In all other cases scattering is present due to the actual arrangement of the molecules being different from ideal or in consequence of thermal agitation. Thus in a dilute gas it permits the evaluation of the number of molecules per c.c. since the scattered light is a measure of the thermal fluctuations. In Rayleigh's formula for turbidity

1 Phil. Mag. 37, 384 (1896)
P.R.S. 17, 92, 222, 317, 1868

2 Phil. Mag. (4), 41, 107, 274, 447 (1871)
(47), 375, (1899).
\begin{align*}
\gamma &= \frac{8 \pi}{3} \left( \frac{2 \pi}{\lambda} \right)^4 \eta \alpha^2 \\
\eta_j \text{ may be solved for once and the polarizability is known and the latter can be found from } &\mu - 1 = \frac{2 \pi \eta \alpha}{\lambda} \\
\text{where } \mu \text{ is the index of refraction. Further observations of the polarisation of scattered light affords information on the anisotropy of molecules.} \\
\text{Let plane electromagnetic waves be incident on the medium then the scattered light is a function of the fluctuations of the electric moment per unit volume } P \\
\text{about its mean value } \overline{P}. \text{ The excess}
\end{align*}

\[ P - \overline{P} = \Delta P \]  

(1)

produces incoherent waves which do not completely cancel but spread out evenly in all directions as scattered light. We have therefore to investigate the origin of the electric field of a vibrating dipole and the radiated energy distribution. Writing

\begin{align*}
E &= \nabla \nabla \cdot \vec{\gamma} - \frac{1}{c} \ddot{\vec{\gamma}} \\
H &= \frac{1}{c} \nabla \times \vec{\gamma} \\
\end{align*}

(2)

where \( \vec{\gamma} = \frac{[P]}{r} = \frac{P(t - \frac{r}{c})}{r} \)  

(3)

is the moment of the vibrating dipole and signifies retardation

and since at large distances from the dipole only terms of lowest order in \( \frac{1}{r} \) are considered we have by calculation.
Let the dipole vibrate with $\mathbf{S}\mathbf{H}\mathbf{M.}$ so that

$$\mathbf{p} = p_0 \, e^{i\omega t}$$

then

$$E = -\frac{\omega^2}{c^2 r^3} \, \mathbf{r} \times (\mathbf{r} \times \mathbf{p}) , \quad H = \frac{\omega^2}{c^2 r^2} (\mathbf{r} \times \mathbf{p})$$

In the Tyndall Effect in turbid media the partial waves of the first order which are diffracted by small semi-conducting dielectric spheres can be represented as the fields of vibrating dipoles. For assume that the electric moment $\mathbf{p}$ vibrates in the $X$ direction, introduce polar coordinates and it follows from (6) that

$$E_x = \frac{\omega^2}{c^2} \, p_0 \left( \sin^2 \theta \, \sin^2 \phi + \cos^2 \phi \right) e^{-i\omega t} \frac{e^{-i\omega t}}{r}$$

$$E_y = -\frac{\omega^2}{c^2} \, p_0 \left( \sin^2 \theta \, \sin \phi \cos \phi \right) e^{-i\omega t} \frac{e^{-i\omega t}}{r}$$

$$E_z = -\frac{\omega^2}{c^2} \, p_0 \left( \cos \theta \cos \phi \right) e^{-i\omega t} \frac{e^{-i\omega t}}{r}$$

$$H_x = 0$$

$$H_y = \frac{\omega^2}{c^2} \, p_0 \cos \theta \, e^{-i\omega t} \frac{e^{-i\omega t}}{r}$$

$$H_z = -\frac{\omega^2}{c^2} \, p_0 \sin \theta \sin \phi \, e^{-i\omega t} \frac{e^{-i\omega t}}{r}$$
Transforming to polar coordinates by

\[ E_\theta = E_x \frac{\partial \phi}{\partial x} + E_y \frac{\partial \phi}{\partial y} + E_z \frac{\partial \phi}{\partial z} \]  

we obtain

\[ E_\theta = \frac{\omega^2}{c^2} p_0 \cos \theta \cos \phi \frac{e^{-i\omega r}}{r} \]

\[ E_\phi = -\frac{\omega^2}{c^2} p_0 \sin \phi \frac{e^{-i\omega r}}{r} \]

\[ H_\theta = \frac{\omega^2}{c^2} p_0 \sin \phi \frac{e^{-i\omega r}}{r} \]

\[ H_\phi = \frac{\omega^2}{c^2} p_0 \cos \theta \cos \phi \frac{e^{-i\omega r}}{r} \]  

If these equations are compared with the formulae of Capt. 6 Sect. 71 p.289 of Optik it is seen that the first partial electric waves have the same form as the dipole waves given in (9) only in (9) the vibration is in vacuum with a real amplitude while in the other case the vibration is in a medium of dielectric constant \( \varepsilon^{(a)} \) and with a complex amplitude i.e. there is a phase difference with respect to the incident wave. Disregarding this we find by comparison of the maximum amplitude of the equivalent dipole the relation

\[ \frac{\omega^2}{c^2} p_0 = \left| \frac{\alpha^3}{K_2^{(a)} \sqrt{\varepsilon^a}} \cdot \frac{\eta^2 - 1}{\eta^2 + 2} \right| \]  

Using (2) and equations 55c Sect.70 of the above
5.

reference

\[ p_0 = \frac{R^3 \kappa^a}{\eta^2 + 2} = R^3 \kappa^a \left( \frac{\omega^2 (\varepsilon^2 - \varepsilon^2 \kappa^a)^2 + \kappa^a}{\omega^2 (\varepsilon^2 - 2 \varepsilon^2 \kappa^a)^2 + \kappa^a} \right) \]  

(11)

For vanishing conductivity (\( \eta \) real) we obtain

\[ p_0 = \frac{R^3 \kappa^a \eta^2}{\eta^2 + 2} = R^3 \kappa^a \frac{\varepsilon^2 - \varepsilon^2 \kappa^a}{\varepsilon^2 + 2 \varepsilon^2 \kappa^a} \]  

(12)

A refractive index is therefore essential for the scattering of light by a dielectric sphere.

Turning to molecular scattering we are interested in the polarisation of the scattered wave. Let \( \vec{q} \) be a unit vector in the direction of our analyser and therefore perpendicular to the radius vector \( \vec{r} \).

Then \( \vec{q} \cdot \vec{r} = 0 \)  

(13)

and the component of the electric field strength which represents the vector of the light vibration is in the direction of \( \vec{q} \)

\[ \vec{E} \cdot \vec{q} = -\frac{\omega^2}{C^2} \frac{1}{r^3} \vec{q} \cdot \left[ \nabla \times (\nabla \times \vec{P}) \right] = \frac{\omega^2}{C^2} \frac{\vec{P} \cdot \vec{q}}{r} \]  

(14)

The intensity of the scattered wave available for observation from a volume \( V \) is

\[ \left| \Delta \sum \vec{E} \cdot \vec{q} \right|^2 = J \]  

(15)

where \( \Delta \) signifies the fluctuation from the mean value (14) and the summation is over all the molecules within \( V \) contributing to the outgoing waves. Substituting (14) in (15) we have an expression for the intensity of light
scattered from

\[
J = \frac{\omega^2}{C^2} v^2 \left| \Delta \sum_k p_k \cdot q \right|^2 = \frac{(2\pi)^2}{\lambda^3 v^2} \left| \Delta \sum_k p_k \cdot q \right|^2
\]  

(16)

where \( p_k \) is the instantaneous moment of the \( k \)th molecule.

The last factor above is the same as that which arises from the fluctuations of the square of the moment and is independent of the frequency or wavelength of the light. Therefore we can say that the intensity of the scattered radiation is inversely proportional to the fourth power of the wave length.

Now the fluctuation of the quantity \( \sum_k p_k \cdot q \) arises from two causes

1. The number of molecules \( N \) in \( V \) varies

\[
N = \bar{N} + \Delta N
\]  

(17)

2. The individual moments vary

\[
p_k = \bar{p}_k + \Delta p_k
\]  

(18)

and the instantaneous moment in \( V \) is

\[
\sum_k p_k = \sum_{k=1}^N (\bar{p}_k + \Delta p_k) = \bar{p}_k (\bar{N} + \Delta N) + \sum_{k=1}^\bar{N} \Delta p_k
\]  

(19)

\[
\therefore \Delta \sum_k p_k = \bar{p}_k \Delta N + \sum_{k=1}^\bar{N} \Delta p_k
\]  

(20)

Assume that the fluctuations of \( N \) and of the moments
are statistically independent. If we consider the magnitudes \[ |\Delta \sum_k p_k q| \] the product term vanishes

\[
|\Delta \sum_k p_k q|^2 = (\Delta \sum_k p_k q)^2 = |\sum_k \Delta p_k q|^2 (\Delta N)^2 + |\sum_k \Delta p_k q|^2
\]

Therefore the effects can be calculated separately and added. The problem of calculating density fluctuations is solved in statistical mechanics here we confine ourselves to the ideal case where the mutual interaction of molecules is negligible then

\[
(\Delta N)^2 = \overline{N} = \mathcal{N} V
\]

where \( \mathcal{N} \) is the number of molecules in unit volume and it is assumed that \( V \) is small compared with unit volume. Further we will assume that the fluctuations in direction of the molecules are independent so that in

\[
|\sum_{k} \Delta p_k q|^2
\]

the product terms can be omitted and there remains only the squared terms \( \mathcal{N} \) in number all of which can be considered equal to one another so that the sum (23) is

\[
\mathcal{N} |\Delta p \cdot q|^2
\]

where \( \Delta p \) is the fluctuation of the moment of an individual molecule. Equation (21) now becomes

\[
|\Delta \sum_k p_k q|^2 = \mathcal{N} \left[ |p q|^2 + |\Delta p \cdot q|^2 \right]
\]

being further simplified by using

\[
|\Delta p \cdot q|^2 = |(p - \overline{p}) q|^2 = |p q|^2 - |p|^2
\]
Substituting (25) in (24)

\[
\left| \Delta \sum_k p_k \cdot q \right|^2 = \mathbf{N} \left| \mathbf{p} \cdot q \right|^2
\]  

which shows that the intensity of scattering is proportioned to the mean number of scattering particles in \( \mathbf{V} \). The formula of course includes the contributions from both density and moment fluctuations however we will initially assume that the latter do not enter the problem. This is correct if the atoms or molecules are spherically symmetric. This simplified theory then applies and was used by Rayleigh in explaining the blue of the sky as due to scattering in consequence of density fluctuations in the air. It is given by (16) with

\[
\left| \Delta \sum_k p_k \cdot q \right|^2 = \mathbf{N} \left| \mathbf{p} \cdot q \right|^2
\]  

Although this expression is inadequate for air (two atomic molecules) we will calculate the results.

Now (18) can be written

\[
\mathbf{p} = \alpha \mathbf{E}' \quad , \quad \alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

and it follows that

\[
\left| \Delta \sum_k p_k \cdot q \right|^2 = \mathbf{N} \alpha^2 \left| \mathbf{E}' \cdot q \right|^2
\]

For the case of gases we can equate the active field strength \( \mathbf{E}' \) and that of the incident light \( \mathbf{E} \) and from Equation (17) Sect. 76.

\[\text{(1)}\]

Born Optik Sect. 73 Equation 19
If we limit the discussion to the simple case in which the incident light is linearly polarised then \( E \cdot E' \) is real and the scalar product

\[
E' \cdot q = E \cdot q = E \cos \psi
\]

where \( \psi \) is the angle between the direction of vibration of the primary light and that of the analyser. Using this result in (16) and (19) we have for Rayleigh Scattering

\[
\mathbf{J} = A \mathbf{E}^2 \cos \psi
\]

where according to (22) and (30)

\[
A = \frac{N \pi r^2(n^2 - 1)}{N \pi r^2 \lambda^2} = \frac{\sqrt{\pi}}{N} \frac{\pi r^2(n^2 - 1)}{r^2 \lambda^2} \tag{33}
\]

We can interpret this in the following manner. For fixed density i.e. a given \( N \) the strength of scattering is proportional to the number of molecules \( N \) in the volume concerned with scattering and for a fixed scattering volume \( V \) it is proportioned to \( \frac{1}{N} \) or inversely proportional to the density.

We now consider the polarisation relationships. The plane \( H \) (which in Fig. (1) is shown horizontal) is perpendicular to the direction of observation \( \mathbf{V} \) and contains \( \mathbf{q} \), the direction of vibration for the analyser. Let \( \mathbf{s} \) be a vector in the direction of the wave normal, the equatorial plane \( A \) perpendicular to \( \mathbf{s} \) contains the vibration...
direction $E$ of the exciting wave. Planes $A$ and $H$ intersect in a line $k$, the line of nodes, and it is from this line that the directions of $q$ viz. the angle $\psi$ is measured. In the plane $A$ the angle $\chi$ between $E$ and $k$ defines the direction of primary vibration. Finally let the angle between the direction of observation and the wave normal $S$ be $\theta$ then from the spherical triangle $Ekq$ we have

$$\cos \psi = \cos \phi \cos \chi + \sin \phi \sin \chi \cos \theta$$

(34)

There are three special cases:

Case 1. If the primary radiation is unpolarised and $E^2$ signifies the total intensity then the intensity of the radiation scattered in the direction $q$ is

$$\frac{1}{2\pi} \int_0^{2\pi} J d\chi = \frac{AE^2}{2} \left( \cos^2 \phi + \sin^2 \phi \cos^2 \theta \right)$$

$$= \frac{AE^2}{2} \left( 1 - \sin^2 \phi \sin^2 \theta \right)$$

$$= \frac{AE^2}{2} \sin^2 \chi$$

(35)

where $\chi$ satisfies

$$\cos \chi = \sin \phi \sin \theta$$

(36)

If the minus sign is chosen then $\chi$ has a simple geometrical interpretation for it is the angle between the incident ray $S$ and the direction of polarisation of the incident light.

Now if the direction of observation is parallel to the primary ray ($\theta = 0, \chi = \frac{\pi}{2}$) the factor $\frac{AE^2}{2}$ is independent of $\phi$ and has the value $\frac{1}{2}$. The scattered light is unpolarised and its intensity is $AE^2$ (twice as great as
the component along $q \parallel \phi$). However, if the direction of observation is perpendicular to the primary ray ($\theta = \pm \frac{\pi}{2}$), the intensity parallel to $q$ is $\frac{1}{2} AE^2 \cos^2 \phi$ and the secondary radiation is therefore completely polarised. Its direction of vibration is perpendicular to the primary ray.

Case II. If we observe without an analyser the scattered light from a polarised primary ray then the intensity of the scattered radiation is

$$\int_{0}^{2\pi} J d\phi = AE^2 \bar{\Pi} (\cos^2 \chi + \sin^2 \chi \cos^2 \theta) = AE^2 \bar{\Pi} (1 - \sin^2 \chi \sin^2 \theta) = AE^2 \bar{\Pi} \sin^2 \eta$$

(37)

where

$$\pm \cos \eta = \sin \theta \sin \chi$$

(38)

If we take the plus sign then $\eta$ is the angle between the direction of observation $\chi$ and the direction of the field $E$. And if the direction of observation is parallel to the primary ray then the intensity of the scattered light equals $\bar{\Pi} AE^2$ and is thus independent of the direction of polarisation of the primary ray. However, if the direction of observation is perpendicular to the primary ray then the scattered intensity changes as the eye travels around the primary ray according to $AE^2 \bar{\Pi} \cos^2 \chi$ and has a maximum perpendicular to the primary direction of vibration ($\chi = 0$) and vanishes when parallel to it ($\chi = \frac{\pi}{2}$).

Case III. If the primary ray is unpolarised and we observe
the scattered light without an analyser then the intensity is

\[ 2 \cdot \frac{1}{2\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} J \, d\phi \, d\chi = A \pi \theta (1 + \cos^2 \Theta) \]  

(39)

which has a max. parallel to the incident ray and a minimum perpendicular to the ray equal to half of the maximum value. This formula gives the variation in brightness of skylight where \( \Theta \) is the angle between the visual ray to the sun and the direction of observation.

For completeness we include the expression for the total scattered energy arising from an unpolarised primary ray

\[ 2 \cdot \frac{1}{2\pi} \int_{0}^{2\pi} \int_{0}^{2\pi} J \sin \theta \, d\theta \, d\phi \, d\chi = \frac{8\pi}{3} A \pi^2 \]  

(40)

The foregoing theory does not cater for anisotropic molecules with direction fluctuations of electric moment. If we consider the above case where observation is perpendicular to unpolarised light then the scattered light according to our formula must be totally polarised under all circumstances. This must be interpreted as follows. The omission of the fluctuations of the separate molecular moments is equivalent to the assumption of isotropic molecular structure, for the moment produced by the light vector is parallel to it and an observer in the plane perpendicular to the light incident on the molecule considers only those components lying in his plane.
The observation of a poly atomic gas such as air also shows an unpolarised part in the scattered ray. This is explained in the following way.

For an anisotropic molecule the electric moment $\vec{\rho}$ is not parallel to the field vector $\vec{E}'$. Thus in general we have a component of the moment $\vec{\rho}$ perpendicular to the primary vibration vector. If this component is averaged over the molecule the mean value vanishes not however the mean of the square (on which scattering depends). We will show from (26) that there is a term independent of $\Psi$ which produces the unpolarised part.

We write

$$\mathbf{p} = \sum_{x,y} \alpha_{xy} q_x E'_y$$

where $x,y,z$, represents a coordinate system fixed in the molecule in which $\alpha_{xy}$ are constants. Confining the discussion to linearly polarised light ($\mathbf{E'} = 0$) and to gases ($\mathbf{E'} = \mathbf{E}$) we put

$$\mathbf{E} = E \mathbf{e},$$

and $\mathbf{e} = c \mathbf{e}_1 + s \mathbf{e}_2$, with $\mathbf{e}_1 \cdot \mathbf{e}_2 = 0$

($c = \cos \gamma$, $s = \sin \gamma$). We now obtain from (41)

$$|\mathbf{p}|^2 = \sum_{xy} d_{xy} d_{x'y'} (CX_i + SX_i)(CX_i' + SX_i') Y_i' Y_i,$$

$$N \alpha x_i x_i' Y_i Y_i' = x_i x_i' Y_i Y_i' = 0$$

and there remains

$$|\mathbf{p}|^2 = E^2 \left[ c \sum_{xy} \alpha_{xy} \alpha_{x'y'} x_i x_i' Y_i Y_i' + s \sum_{xy} \alpha_{xy} \alpha_{x'y'} x_i x_i' Y_i Y_i' \right]$$
Introducing the abbreviations

\[ A_1 = \alpha_{xx} \alpha_{xx}^{*} + \alpha_{yy} \alpha_{yy}^{*} + \alpha_{zz} \alpha_{zz}^{*} \]

\[ A_2 = \alpha_{yx} \alpha_{yx}^{*} + \alpha_{zy} \alpha_{zy}^{*} + \alpha_{zx} \alpha_{zx}^{*} + \alpha_{xy} \alpha_{xy}^{*} + \alpha_{yx} \alpha_{yx}^{*} + \alpha_{yy} \alpha_{yy}^{*} \]

\[ A_3 = \alpha_{yz} \alpha_{yz}^{*} + \alpha_{zy} \alpha_{zy}^{*} + \alpha_{xz} \alpha_{xz}^{*} + \alpha_{yz} \alpha_{yz}^{*} + \alpha_{xy} \alpha_{xy}^{*} + \alpha_{yx} \alpha_{yx}^{*} \]

\[ A_4 = \alpha_{yz} \alpha_{yz}^{*} + \alpha_{zy} \alpha_{zy}^{*} + \alpha_{zx} \alpha_{zx}^{*} + \alpha_{yz} \alpha_{yz}^{*} + \alpha_{xy} \alpha_{xy}^{*} + \alpha_{yx} \alpha_{yx}^{*} \] (47)

there results

\[
\frac{1}{|pq|^2} = \frac{E^2}{30} \left[ C^2 (GA_1 + 2A_2 + 2A_3 + 2A_4) + \frac{1}{3} (2A_1 - A_2 - A_3 + 4A_4) \right]
\]

or if we set

\[ \Omega_0 = \frac{1}{3} (A_1 + A_2) \]

\[ \Omega_1 = \frac{1}{30} (2A_1 - A_2 + 5A_3 - 6A_4) \]

\[ \Omega_2 = \frac{1}{30} (2A_1 - A_2 - A_3 + 4A_4) \] (49)

then

\[
\frac{1}{|pq|^2} = E^2 \left[ (\Omega_0 + \Omega_1) C^2 + \Omega_2 \right] \]

Of special interest is the case where the frequency of the incident light is far from any absorption line. Then the tensor \( \alpha \) is Hermitean (\( \alpha_{xx} = \alpha_{xx}^{*} \)) and from (47) \( A_3 = A_4 \). Therefore \( \frac{1}{3} \Omega_0 = \Omega_1 = \frac{1}{3} \Omega \) and using equations (43) and (50) we have

\[
\frac{1}{|pq|^2} = \Omega_0 \cos^2 \psi E^2 + \Omega (1 + \cos^2 \psi) E^2 \] (51)
In this formula the Rayleigh part of the scattering appears separated from the part arising from moment fluctuations (It is of interest to note that both are of the same order), and only when the molecule is optically isotropic does the second part vanish. That is when $\Omega = 0$. For all poly atomic molecules this is not the case and it follows that (51) is not appropriate. We will consider polarised and unpolarised parts.

If we write for the intensity of the linearly polarised incident light $E' = \bar{J}_0$ then from (16), (26) and (51) we have for the scattering in an arbitrary direction.

$$\bar{J} = \bar{J}_0 \left( \frac{2\pi}{\lambda^2} \right)^4 N \left[ (\Omega_0 + \frac{\Omega}{3}) \cos^2 \theta + \Omega \right]$$

(52)

The parameters in this case reducing to

$$\Omega_0 = \alpha^2 = \frac{1}{9} \left( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right)^2 = \left( \frac{n^2 - 1}{4 \pi N} \right)^2$$

(53)

(See equation (30)) and

$$\Omega = \frac{1}{15} \left[ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2 - 3 (\alpha_{yy} \alpha_{zz} + \alpha_{zz} \alpha_{xx} + \alpha_{xx} \alpha_{yy}) + 3 (\alpha_{yz} \alpha_{zy} + \alpha_{zx} \alpha_{xz} + \alpha_{xy} \alpha_{yx}) \right]$$

(54)

A further simplification of this last expression occurs if we assume that in the molecule an optical principle axis exists (independent of frequency). This is true of diatomic molecules for example for which a principle axis coincides with the axis of nuclear centres. Thus we put

$$\alpha_{xy} = 0$$

(55)
and then
\[
\Omega = \frac{1}{5\alpha} \left[ (\alpha_x - \alpha_y)^2 + (\alpha_z - \alpha_y)^2 + (\alpha_\lambda - \alpha_y)^2 \right]
\]
\[
= \frac{1}{15} \left[ (\alpha_x^3 + \alpha_y^3 + \alpha_z^3) - (\alpha_x \alpha_z + \alpha_z \alpha_x + \alpha_x \alpha_y) \right]
\]
\[
= \frac{1}{5} \left[ 3 \Omega_0 - (\alpha_y \alpha_x + \alpha_z \alpha_x + \alpha_x \alpha_y) \right]
\]

(56)

where for simplicity $\alpha_{xx} = \alpha_x$ etc.

Since by definition the principle polarisabilities are positive numbers it now follows from (56) that
\[
\Omega \leq \frac{3}{5} \Omega_0
\]

(57)

the equality sign holding only in the case of anisotropy i.e. when the dipole induced by an arbitrary field can only vibrate in a single fixed molecular direction. If this is the case then all components of the tensor $\alpha$ are zero except one called $\alpha_x$ and we have
\[
\Omega = (\frac{\alpha_x}{3})^2 ; \quad \Omega = \frac{1}{15} \alpha_x^3 = \frac{3}{5} \Omega_0
\]

(58)

If there is a fixed principle axis system in the molecule then the static deformation tensor $\alpha_{(s)}$ has the same fixed set of primary axes. For simplification we assume that the frequency dependence of the principle deformabilities $\alpha_x, \alpha_y, \alpha_z$ is essentially the same and that they can differ from the static deformabilities only by constant factors. We can now say
\[
\alpha_{(s)}^{(a)} \neq \alpha_{xy} = \cdots = \Omega
\]
\[
\alpha_{(s)}^{(a)} = \alpha_{(s)}^{(a)} = \alpha_x = \Omega
\]

(59)
where
\[ \Upsilon = \frac{(\eta^2)^2 - 1}{\eta^2 - 1} \]  \hspace{1cm} (60)

For a non-polar substance, the Kerr Effect is determined by the constant \( b_1 \).

\[ b_1 = \frac{5}{45} \left[ (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2 + (\alpha_x - \alpha_y)^2 \right] \]  \hspace{1cm} (61)

which using (56) and (60) becomes

\[ b_1 = \frac{2}{5} \Omega = \frac{2}{5} \left( \frac{(\eta^2)^2 - 1}{\eta^2 - 1} \right) \Omega \]  \hspace{1cm} (62)

Since \( \Omega \) is given by the refractive index only the constant \( \Omega \) occurs in expressions which are determined by absorption. In its place we introduce another variable - the degree of polarisation. The degree of polarisation for linearly polarised incident light is the ratio of the smallest to the largest scattered intensity. In (52) for \( c_{\omega = 0} \gamma = 0 \) and \( c_{\omega = 1} \gamma = 1 \) we therefore obtain the values of \( \Upsilon \) and determine the degree of polarisation

\[ \Delta = \frac{\Omega}{\Omega + \frac{45}{5} \Omega} \]  \hspace{1cm} (63)

The degree of polarisation for natural incident light is different from (63) for in this case \( c_{\omega = \gamma} \) is to be considered as a function of \( \chi, \beta, \phi \) and is to be averaged over \( \chi \). Therefore according to (35) is to be replaced by

\[ \frac{1}{2} \left( c_{\omega = \gamma} \beta + \cos \beta \sin \gamma \right) = \frac{1}{2} \sin \frac{\chi}{2} \frac{\gamma}{2} \] where \( \gamma \) is the angle between the direction of \( \gamma \) of the primary ray and the analyser setting. Therefore

\[ \Delta' = \frac{\Omega}{\Omega + \frac{45}{5} \Omega} \]  \hspace{1cm} (64)

The quantities \( \Delta \) and \( \Delta' \) are both monotone increasing.
functions of $\Omega$. If we substitute for $\Omega$ the maximal value from (57) then it follows

$$\Delta \approx \frac{1}{3}, \quad \Delta' \approx \frac{1}{2}$$

(65)

and these are the values expected for complete anisotropy i.e. for $\Omega_0$ and $\Omega$ given by (58). We can now use the degree of polarisation and obtain

$$\Omega = \Omega_0 \frac{3 \Delta'}{C - \gamma \Delta'}$$

(66)

Then according to (53) and (56)

$$(\alpha_x - \alpha_z)^2 + (\alpha_x - \alpha_z)^2 + (\alpha_x - \alpha_z)^2 = \frac{4 \psi}{8 \pi^2} \frac{\beta^2}{\mathcal{N}'} \frac{\Delta'}{C - \gamma \Delta'}$$

(67)

As well as $\Delta'$ the total scattering is easy to observe or what amounts to the same thing in the case of gases where absorption is small viz. the total light lost from the incident radiation.

We have now to calculate from (52) in the same way the total scattering for a non polarised primary ray as occurs in (40) without consideration of anisotropy. (Averaging over $\chi$, integrating over $\phi$ and $\Theta$ and multiplying by 2; \(\cos^2 \psi\) is to be replaced by $\frac{\beta}{3}$ and the constant multiplied by $\beta$). We have

$$\overline{J} = \overline{J}_0 \frac{(2\pi)^3}{\lambda^2} N \frac{\beta}{3 \pi} \left[ \left( \Omega_0 + \frac{1}{3} \Omega \right) \frac{1}{3} + \Omega \right]$$

(68)

and for the extinction coefficient

$$h = \frac{\overline{J}}{\overline{J}_0} = \frac{8 \pi}{\Theta} \frac{(2\pi)^3}{\lambda^2} N \left( 3 \Omega_0 + 10 \Omega \right)$$

(69)

Further one can easily observe the average intensity
scattered through a right angle i.e. to observe the naturally scattered light for \( \theta = \frac{\pi}{2} \) without analyser. We obtain from (52) for \( \theta = \frac{\pi}{2} \) (by averaging over \( \psi \) and \( \chi \) and multiplying by \( 2 \)).

\[
\begin{aligned}
J_\perp &= J_o \frac{(2\pi)^4}{\lambda^2 r^2} 2 N \left[ (-\Omega_\perp + \frac{1}{3} \Omega) \frac{1}{4} + \Omega \right] \\
&= J_o \frac{(2\pi)^4}{\lambda^2 r^2} \frac{N}{2} \left( \Omega_\perp + \frac{1}{3} \Omega \right)
\end{aligned}
\]  

(70)

Let us now introduce into (69) and (70) the quantity \( \Delta' \) instead of \( \Omega \) (as given in (66)) then with \( N = \mathcal{N} V \) as in (22) the formulae become

\[
\begin{aligned}
\mathcal{B} &= \frac{8\pi (2\pi)^4}{\lambda^2 r^2} N \Omega_\perp \frac{Z + \Delta'}{G - 1 \Delta'} = \frac{8\pi \mathcal{N} V}{\lambda^2 r^2} \left( \frac{n^2-1}{n^2+1} \right)^2 \frac{Z + \Delta'}{G - 1 \Delta'} \\
\end{aligned}
\]  

(71)

and

\[
\begin{aligned}
J_\perp &= J_o \frac{3\mathcal{N} V}{\lambda^2 r^2} \left( \frac{n^2-1}{n^2+1} \right)^2 \frac{1 + \Delta'}{G - 1 \Delta'} \\
\end{aligned}
\]  

(72)

Finally we introduce in (62) (the relation between Kerr constant and scattering) the degree of polarisation according to (66) giving

\[
\begin{aligned}
\mathcal{B}_\perp &= \frac{2 \left( \frac{n^2-1}{n^2+1} \right)^2 \frac{\Delta'}{G - 1 \Delta'}}{4\pi \mathcal{N}^2} \\
\end{aligned}
\]  

(73)

and from this the Kerr constant itself for gases with \( n \approx 1 \) and \( \mathcal{B} = \frac{\mathcal{B}_\perp}{\kappa T} \)

\[
\begin{aligned}
\mathcal{B} = \frac{3}{2} \frac{\mathcal{N} \mathcal{B}_\perp}{\lambda \kappa T} &= \frac{3}{16 \pi^2} \frac{1}{\lambda} \frac{1}{\mathcal{N} \kappa T} \left( \frac{n^2-1}{n^2+1} \right)^2 \frac{\Delta'}{G - 1 \Delta'} \\
\end{aligned}
\]  

(74)

This formula (74) now connects two constants which are obtained in completely different ways. The experimental proof of this relation is an especially noteworthy fulfillment of the theory. The following table 24 gives a quick
resumé. In the first column is given the measured degrees of polarisation $\Delta'$, in the second the electric moment $p$, in the third the Kerr constants calculated from $\Delta'$ using (74) and in the fourth column the directly measured Kerr constants. One sees that in fact non-polar substances give a very good agreement which is not fulfilled for the polar gases. Tables 25 and 26 again give the degrees of polarisation for different gases and vapours. The experimental arrangement is reproduced in Fig. 196.

According to the preceding verification of the theory, outlined in Table 24, for a simple class of substances one can now use it to determine the constants of anisotropy $\alpha_x, \alpha_y, \alpha_z$. This proceeds under the assumption (Stuart, J. Phys. 55, 367, 1929) that the direction of the permanent electric moment coincides with one of the axes of deformation, called the $Z$ axis, which will certainly be approximately fulfilled for many molecules. Then one has $p_x^0 = 0, p_y^0 = p_z^0$ and obtains for the constants of anisotropy the following formulae:

$$\alpha_x + \alpha_y + \alpha_z = 3 \alpha$$
$$2\alpha_z - \alpha_x - \alpha_y = \frac{3}{\beta} = \frac{4s k T (kT b - b)}{b^2}$$
$$= \frac{4s k T (kT b - 2(n^2 - 1)(n^2 - 1))}{(4n^2 \alpha')^2} \frac{\Delta'}{6 - 7 \Delta'}$$

$$[\alpha_x - \alpha_y]^2 + [\alpha_y - \alpha_z]^2 + [\alpha_z - \alpha_x]^2 = 3 \gamma = \frac{4s b}{\alpha} = 80 \left( \frac{n^2 - 1}{4n^2 \alpha'} \right)^2 \frac{\Delta'}{6 - 7 \Delta'}$$

By the solution of these quadratic equations one obtains the constants of anisotropy as functions of the Kerr constants and the depolarisation, namely
\[ \alpha_z = \alpha \beta \]
\[ \alpha_x = \alpha - \beta^2 + \frac{1}{2} \sqrt{2y - 3\beta^2} \]
\[ \alpha_y = \alpha - \beta^2 - \frac{1}{2} \sqrt{2y - 3\beta^2} \]  \hspace{1cm} (75b)

The quantities \( \alpha, \beta, y \) are known by measurements of the refractive index, the degree of depolarisation and the total Kerr constant \( \Delta \) (for a definite temperature).

The duplicity in the ordering of the axis \( X, Y \) to the two solutions \( \alpha_x \) and \( \alpha_y \), which still remain in (75b) can be removed in several cases by other physical considerations as we shall see at once.

For diatomic molecules the formula (75) simplifies itself still further since \( \alpha_x = \alpha_y \).

In this way one obtains for the anisotropy constants of \( \text{HCl}, \text{NH}_3 \), and \( \text{SO}_2 \) the values given in table 27.

Which of the two axis \( X, Y \) corresponds to the greater polarisability can then be estimated, if one knows approximately from other reasons the shape of the molecule, as is the case for \( \text{SO}_2 \) and \( \text{NH}_3 \). Since \( \text{SO}_2 \) possesses a static electric moment the three atoms \( \text{O, S, O} \) cannot lie on a straight line, but must form a triangle. The direction of the moment, called the \( Z \) -axis, coincides with the right bisector through \( S \). If we choose the \( X \)-axis along \( 00 \), then \( Y \) lies at \( \text{r} \) degrees to the plane of the triangle, then \( \alpha_x > \alpha_y \) of necessity, for in a chain of alternately linked dipoles, the one turns itself opposite to the other. This effect is present in the \( X \)-direction, but obviously not in the \( Y \)-direction. There occurs therefore in the \( X \)-direction a strengthening of the external field.
Also for ammonia we investigate a similar relationship. The molecule is a three-sided pyramid, whose case is formed of an equivalent triangle $\text{H}_1, \text{H}_2, \text{H}_3$. The normal to this base is obviously the direction of the electric moment $\boldsymbol{p}$, the $Z$-axis. We choose as $X$-axis the edge $\text{H}_1, \text{H}_2$ of the base then the $Y$-axis is the bisector of the opposite corner. The above mentioned increase arises here in the following way:

Let $\gamma$ be the projection of two atoms on the ray direction, then the increase of the polarisation will be approximately proportional to $\gamma$. The increase for a ray direction parallel to $X$ will then be proportional to the side $a$ of the equilateral triangle for the atom pair $\text{H}_1, \text{H}_2$, for the pair $\text{H}_1, \text{H}_3$, and $\text{H}_2, \text{H}_3$ however only half so great, therefore as $\frac{a}{2}$, altogether therefore $(a + 2\frac{a}{2}) = 2a$. Correspondingly there occurs for the $Y$-direction no strengthening for the atoms $\text{H}_1, \text{H}_2$, for the pairs $\text{H}_1, \text{H}_3$ and $\text{H}_2, \text{H}_3$ however each $h$, altogether $2h$ where $h = a\frac{\sqrt{3}}{2}$ is the height of the triangle. The increase in the $Y$ direction is to that in the $X$-direction approximately as $\frac{\sqrt{3}}{2} : 1 = 0.866$. From our table 27 there however results $\alpha_x : \alpha_y = 0.871$. If however this agreement occurs accidentally, then the sequence of axial directions will still be determined by these considerations in consequence of the magnitudes of the polarisabilities: to the $Z$-axis belongs the magnitude $\alpha$, which we have initially assumed in table 27 without foundation.
Fig. 195

Fig. 197

Fig. 198

Fig. 199

Fig. 200

Fig. 201

To face p. 22 of Appendix
From the optical anisotropy of a molecule determined through the constants of anisotropy the geometry or structure can be determined. One finds for example that the molecule of methyl alcohol $\text{CH}_3\text{OH}$ is not straight but is bent. In the case of a straight molecule where the $\text{H}$ atom lies on the elongation of the CO axis, the moment $\vec{P}$, which arises as the combined moment $\vec{0}\hat{\text{H}}$ and $\hat{\text{A}}$, the Kerr constant is large and positive. Since the Kerr constant is practically zero the molecule must be bent (see Fig. 199). More precise results on the angle at the O atom, the direction of the electric moment and the optical principal axis can be obtained by combining observations of Kerr constant with those of electric moments, molar refraction etc.

In the case of diethyl ether $(\text{C}_2\text{H}_5\text{O})$ the thorough discussion of the polarisation ellipsoid leads uniquely to a definite configuration of the molecule. The axial values show that the molecule has the $Z$-axis approximately as an optical axis of symmetry. (see Fig. 200) according to the rules of stereochemistry this was to be expected, as each of the $\text{C}_2\text{H}_5$ groups can rotate freely about CO. In this case the two positions designated I and II would be equally probable (that is would occur on the average equally often). However this is not compatible with the designation of the $Z$-axis as an optical symmetry axis.

Position I must therefore be privileged and indeed so that it represents a position of stable equilibrium, about
which rotary oscillations finite amplitude take place. Configuration II is on the other hand impossible as a position of stable equilibrium.

For propyl chloride $\text{C}_3\text{H}_7\text{Cl}$ the "cradle I" and "chair II" forms are both incompatible with the observations of the Kerr constants and the degree of depolarisation. These configurations are therefore not especially stable, and we have to consider a strong free-rotation of the terminal $\text{C}_3\text{H}_5$ group, it describes a circle, with the $\text{C}'-\text{C}$" direction a conical envelope about $\text{C}'-\text{C}$" as axis.

The following two tables 28 and 29 give several new measurements of the degree of depolarisation and the Kerr constants for gases with axially symmetric molecules ($\text{C}_2$), indeed (28) of non polar molecules and (29) of polar molecules. In (28) from the measured degree of depolarisation is calculated according to $\delta_0(4)$ the Kerr constant $B$, and from the mean polarisability and the polarisabilities $\alpha_z$ and $\alpha_x - \alpha_y$. Moreover the anisotropy $\alpha_z - \alpha_x$ is given. The degree of depolarisation for highly symmetric molecules like $\text{CH}_4$ and the noble gases are on account of the difficulties of the measurement very uncertain and all too high so that from the measurements of the degrees of depolarisation one cannot decide whether complete spherical symmetry is present or whether a slight anisotropy is present. In the case of $\text{CCl}_4$ the measurement of the Kerr constant, which is here very precise, gives for the anisotropy $\alpha_z - \alpha_x$ the value zero or as upper limit a value
which is calculated about ten times smaller than that from the degree of depolarisation. In (29) the dipole moment \( \rho^0 \) is given in addition to the degree of depolarisation and the Kerr constant \( B = B_1 + B_2 + B_0 \). \( B_0 \) is negligible compared to \( B_1 \) and \( B_2 \) (see \( \Phi.80 \), p.368). Finally there are also presented the three principal polarisabilities calculated from the moment, the degree of depolarisation or the Kerr constant and the molar refraction (mean polarisability \( \alpha \)). These measurements are all reduced to wave length \( \lambda = 5890 \).

For our earlier considerations the knowledge of Loschmidt's number is assumed. One can however also universally obtain the Loschmidt's number \( N \) from absolute determination of the ratio of the scattered light to the incident or also from the extinction coefficient and the degree of depolarisation \( \Delta \). These can be carried out in the Laboratory with the help of the apparatus sketched in Fig. 196, as well as by measurement of the scattering of skylight. Table 30 presents several of the results reduced to one mole. The mean value agrees very well with the values obtained by quite different methods.

As far as the degree of polarisation of skylight is concerned, its maximum lies at about \( 90^0 \) from the sun, corresponding to the theory, as has been found already by Arago in 1809. The degree of polarisation is not complete but is much larger than would be expected on the basis of laboratory measurements. The reason for this is probably that "multiple scattering" takes place, which is not
considered in our theory.

The theory of light scattering can also be developed for fluids and solids. Our general formula (16) then remains correct, except that the simple connection between the fluctuation amplitude of the electric moment and the mean number of particles fails, this arises from the assumption of vanishing interactions between molecules which should only be made for ideal gases. However it is possible theoretically even for fluids to calculate the spontaneous fluctuations of density and state of polarisation. The basic idea, developed by both Smoluchowski and Einstein

\[ S = k - \log W \]  \hspace{1cm} (76)

and calculate the probability of a state differing from that of equilibrium by the formula

\[ \frac{W}{W_0} = e^{\frac{k}{\hbar}(S - S_0)} \]  \hspace{1cm} (77)

In this equation one considers \( S \) as a function of the macroscopic variables, the density and temperature, and expresses the fluctuations \( S - S_0 = \Delta S \) by the fluctuations \( \Delta \rho \) and \( \Delta \gamma \) according to the laws of thermodynamics. If one wishes to consider the fluctuation of the polarisation \( P \),

\[ (Ann. \ der \ Phys. \ 25, \ 205, \ 1908, \ \text{and} \ 33, \ 1275, \ 1910) \]
then one must also know the dependence of the entropy on P and to also include in \( \Delta S \) the term in \( \Delta P \). We do not wish to carry through these complicated considerations (see Gaus: FS:J. Phys. 17, 353, 1923), but only to record that the density fluctuations will be proportional to the compressibility of the substance and the polarisation fluctuations can be immediately connected to the Kerr effect. For the density fluctuations within a given volume \( V \) one obtains the formula

\[
\frac{\langle \Delta \rho \rangle^2}{V} = \frac{k T \rho}{\chi} = \frac{k T \rho \chi}{V}
\]  
(78)

where

\[
\chi = \frac{1}{\rho} \frac{\partial \rho}{\partial P}
\]  
(79)

is the compressibility.

1) We give a short derivation of this formula for the density fluctuation. The first and second laws of thermodynamics may be combined in the expression

\[
TdS = \rho dV + dU
\]

where \( U \) is the internal energy and \( S \) is the entropy. From this it follows that at constant temperature

\[
\frac{\partial S}{\partial V} = \frac{\rho}{T} \quad ; \quad \frac{\partial^2 S}{\partial V^2} = \frac{\chi}{T} \frac{\partial P}{\partial V}
\]

If one looks upon \( S \) as a function of \( V \) while holding fixed all other independent variables and considers the fluctuation for a quantity of fluid \( M \) about its equilibrium weight, then in the development of \( \Delta S \) in powers of \( \frac{1}{\pi} \Delta V \) and the other independent variables the terms of first order do not occur and there remains
Consequently the probability becomes

\[ W = W_0 e^{-\beta \xi^2}, \quad \beta = -\frac{1}{kT} \frac{d\beta}{dV} \]

where for all stable equilibrium states \((\frac{d\beta}{dV} < 0)\) \(\beta\) is positive. From the condition

\[ \int_0^\infty W d\xi = 1 \]

one obtains \(W_0\), and then one obtains

\[ (\Delta V)^2 = \bar{\xi}^2 = \int_0^\infty W \xi^2 d\xi = \frac{1}{2\beta} = -kT \frac{dV}{d\beta} \]

Now \(\bar{V} = \frac{M}{\rho}\) so that

\[ \Delta \rho = -\frac{\bar{\rho}^2}{M} \Delta V \]

so that finally

\[ (\Delta \rho)^2 = \frac{\bar{\rho}^2}{M^2} (\Delta V)^2 = \frac{kT}{\bar{V}} \frac{d\beta}{dV} \]

The above formula agrees with our earlier expression for an ideal gas. In this case one has

\[ \rho = \frac{RT}{U} \rho = \frac{K U}{m} \rho \]

where \(U = Nm\) is the molecular weight (\(m,\) is the molecular mass and \(N\) Avogadro's number).

From this follows

\[ (\Delta \rho)^2 = \frac{\rho m}{\bar{V}} = \frac{\bar{\rho}^2 m^2}{\bar{V}} \]

where \(\bar{\rho} = \frac{\rho}{m}\) is Læschmidt's number of molecules per unit volume. The fluctuations of the number of particles \(\bar{N}\) in the fixed volume \(\bar{V}\) is therefore

\[ (\Delta N)^2 = \frac{\bar{V}}{m^2} (\Delta \rho)^2 = \bar{V} \frac{\rho^2 m^2}{\bar{V}} = N \]

and this formula agrees with (22) derived earlier.
In fluids the compressibility is very small, increasing however as one approaches the critical point, where it theoretically becomes infinite. In the neighbourhood of the critical point therefore the light scattering should be very considerable and indeed one observes there a turbidity of the liquid (called critical opalescence). With modern technique the scattering of the purest fluids (and also of crystals) is perceptible and capable of measurement. (See Gaus. Ann. der Phys. 77, 317, 1925. Leontowitsch Manderstam, Phys. ZS. der U.S.S.R. 1, 317, 1932).
Table 24.

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<th>$\Delta$</th>
<th>$\Delta \cdot 10^6$</th>
<th>$B \cdot \lambda \cdot 10^{-5}$ berechnet</th>
<th>$B \cdot \lambda \cdot 10^{-5}$ beobachtet</th>
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Table 25. $\Delta'$ for Gases.

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<tr>
<td>Xenon .......</td>
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<td>Chlor .....</td>
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<td>-</td>
<td>-</td>
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<td>0,0437</td>
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Table 26.

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<tr>
<th></th>
<th>Rao</th>
<th>Cabannes</th>
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<tr>
<td>Methan</td>
<td>-</td>
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</tr>
<tr>
<td>Athan</td>
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<td>0,016</td>
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<tr>
<td>Propan</td>
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<td>0,016</td>
</tr>
<tr>
<td>Butan</td>
<td>-</td>
<td>0,017</td>
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<tr>
<td>Pentan</td>
<td>0,013</td>
<td>0,012</td>
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<td>Hexan</td>
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<td>0,015</td>
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<tr>
<td>Heptan</td>
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<td>-</td>
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<tr>
<td>Octan</td>
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<td>-</td>
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<tr>
<td>Methylalkohol</td>
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<tr>
<td>Benzol</td>
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<td>Toluol</td>
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<tr>
<td>Chloroform</td>
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<td>0,0167</td>
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<tr>
<td>Schwefelkohlenstoff</td>
<td>0,112</td>
<td>-</td>
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<tr>
<td>Ather</td>
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Table 27.

<table>
<thead>
<tr>
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<th>$\alpha_X = \alpha_Y = 23,9 \cdot 10^{-25}$</th>
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<tbody>
<tr>
<td></td>
<td>$\alpha_Z = 31,6$</td>
</tr>
<tr>
<td>HCl</td>
<td>$\alpha_X = 23,3$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_Y = 20,3$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_Z = 24,2$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$\alpha_X = 55,5$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_Y = 28,0$</td>
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<tr>
<td></td>
<td>$\alpha_Z = 35,1$</td>
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Table 28.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta \cdot 10^4 ) beobachtet</th>
<th>( \Delta \cdot 10^4 ) berechn.</th>
<th>Temp. ( \circ C )</th>
<th>( \kappa \cdot 4 \cdot 10^5 )</th>
<th>( \kappa \cdot 4 \cdot 10^{2r} )</th>
<th>( \kappa \cdot 4 \cdot 10^{2r} )</th>
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<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>2,7</td>
<td>-</td>
<td>0,034</td>
<td>20</td>
<td>8,2</td>
<td>3,77</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>3,6</td>
<td>-</td>
<td>0,23</td>
<td>20</td>
<td>17,6</td>
<td>9,28</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>6,4</td>
<td>-</td>
<td>0,33</td>
<td>20</td>
<td>15,9</td>
<td>11,4</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>4,3</td>
<td>2,30</td>
<td>2,03</td>
<td>20</td>
<td>45,3</td>
<td>26,4</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>9,8</td>
<td>1,43</td>
<td>1,70</td>
<td>18</td>
<td>26,5</td>
<td>24,2</td>
</tr>
<tr>
<td>( \text{CS}_2 )</td>
<td>14,3</td>
<td>21,0</td>
<td>16,4</td>
<td>56,7</td>
<td>87,4</td>
<td>97,0</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>12,5</td>
<td>3,08</td>
<td>2,80</td>
<td>26</td>
<td>29,9</td>
<td>31,4</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>12,0</td>
<td>4,30</td>
<td>6,7</td>
<td>20</td>
<td>50,1</td>
<td>34,5</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 )</td>
<td>12</td>
<td>1,85</td>
<td>3,26</td>
<td>20</td>
<td>33,2</td>
<td>23,5</td>
</tr>
<tr>
<td>( \text{CCl}_4 )</td>
<td>0,52</td>
<td>0,2</td>
<td>0,67</td>
<td>99,4</td>
<td>105</td>
<td>0</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>1,5</td>
<td>-</td>
<td>0,22</td>
<td>20</td>
<td>26,1</td>
<td>(8,84)</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_6 )</td>
<td>1,6</td>
<td>-</td>
<td>0,72</td>
<td>20</td>
<td>45,0</td>
<td>15,6</td>
</tr>
<tr>
<td>( \text{C}_6 \text{H}_6 )</td>
<td>4,2</td>
<td>5,9</td>
<td>5,8</td>
<td>105</td>
<td>107,3</td>
<td>61,0</td>
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<tr>
<td>( \text{C}<em>6 \text{H}</em>{12} )</td>
<td>1,0</td>
<td>-</td>
<td>2,8</td>
<td>18</td>
<td>109</td>
<td>30,0</td>
</tr>
<tr>
<td>A</td>
<td>0,6</td>
<td>-</td>
<td>0,031</td>
<td>18</td>
<td>16,8</td>
<td>(3,6)</td>
</tr>
<tr>
<td>Kr</td>
<td>0,55</td>
<td>-</td>
<td>0,07</td>
<td>18</td>
<td>25,6</td>
<td>(5,2)</td>
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Table 29.

<table>
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<th>Compound</th>
<th>$V_{10^{-9}}$</th>
<th>$\alpha_{10^{-6}}$</th>
<th>$\beta_{10^{-6}}$</th>
<th>$\gamma_{10^{-6}}$</th>
<th>$\delta_{10^{-6}}$</th>
<th>$\eta_{10^{-6}}$</th>
<th>$\zeta_{10^{-6}}$</th>
<th>$\alpha_{10^{-6}}$</th>
<th>$\beta_{10^{-6}}$</th>
<th>$\gamma_{10^{-6}}$</th>
<th>$\delta_{10^{-6}}$</th>
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<tbody>
<tr>
<td>HCl</td>
<td>1.034</td>
<td>2.56</td>
<td>-3.8</td>
<td>0.188</td>
<td>5.56</td>
<td>26.0</td>
<td>31.6</td>
<td>23.9</td>
<td>23.9</td>
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<tr>
<td>$(C_2H_5)_2O$</td>
<td>1.14</td>
<td>0.66</td>
<td>5.75</td>
<td>3.75</td>
<td>-7.55</td>
<td>87.3</td>
<td>112.6</td>
<td>70.7</td>
<td>78.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(C_3H_6)_2$</td>
<td>2.72</td>
<td>1.7</td>
<td>31.2</td>
<td>0.98</td>
<td>30.2</td>
<td>61.8</td>
<td>69.5</td>
<td>46.9</td>
<td>69.1</td>
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<tr>
<td>CH$_3$OH</td>
<td>1.68</td>
<td>1.6</td>
<td>0.4</td>
<td>0.3</td>
<td>36.7</td>
<td>44.3</td>
<td>29.9</td>
<td>35.7</td>
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<tr>
<td>CO</td>
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<td>2.1</td>
<td>-</td>
<td>0.158</td>
<td>10.054</td>
<td>19.7</td>
<td>25.0</td>
<td>17.1</td>
<td>17.1</td>
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<tr>
<td>HCN</td>
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<td>1.08</td>
<td>92.0</td>
<td>25.8</td>
<td>38.9</td>
<td>19.2</td>
<td>19.2</td>
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<tr>
<td>H$_2$S</td>
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<td>1.59</td>
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<td>1.31</td>
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<td>39.3</td>
<td>32.9</td>
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<td>SO$_2$</td>
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<td>-11.6</td>
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<td>35.1</td>
<td>28.0</td>
<td>55.5</td>
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<tr>
<td>NH$_3$</td>
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<td>3.48</td>
<td>-</td>
<td>-</td>
<td>22.6</td>
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<td>23.3</td>
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<td>CH$_3$Cl</td>
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<td>60.0</td>
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<td>45.5</td>
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<tr>
<td>CHCl$_3$</td>
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<td>1.4</td>
<td>-8.9</td>
<td>85.5</td>
<td>66.8</td>
<td>94.8</td>
<td>94.8</td>
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Table 30.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$N_{10^{-23}}$</th>
<th>$N_{10^{-23}}$</th>
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<tr>
<td>Ewing (Ather)</td>
<td>5.95</td>
<td>Fowle ........</td>
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<tr>
<td>(Benzol)</td>
<td>6.05</td>
<td>Dember ........</td>
</tr>
<tr>
<td>(Chloroform)</td>
<td>5.98</td>
<td></td>
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<tr>
<td>(Methylalkohol)</td>
<td>6.24</td>
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<tr>
<td>(Athylalkohol)</td>
<td>6.08</td>
<td></td>
</tr>
<tr>
<td>Daure (Athylchlorid)</td>
<td>6.08</td>
<td></td>
</tr>
<tr>
<td>Mittelwert</td>
<td>6.06</td>
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