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(CONTRIBUTIONS ON THE OPTICS OF TURBID MEDIA, PARTICULARLY COLLOIDAL METAL SOLUTIONS---Translation)

BY: G. Mie

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TRANSLATION

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CONTRIBUTIONS ON THE OPTICS OF TURBID
MEDIA, PARTICULARLY COLLOIDAL METAL SOLUTIONS

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CONTRIBUTIONS ON THE OPTICS OF TURBID
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1. The various colorations of metals in the colloidal state have had different interpretations at different times. Formerly it was assumed that the metals in question (particularly silver) occurred in several differently colored modifications. A later theory was founded on the assumption that the colors were based on optical resonance. The principal proponent of this theory was Ehrenhaft [1]. Recently Maxwell [2] demonstrated that the theory developed by Lorenz [3] for optically inhomogeneous media offers an incontestable explanation for the colors of colloidal metals if the suspended metal particles are very small. For the case of a fine metal suspension in which the particles are very small with respect to the wave lengths and the distance between them, the theory gives a very definite absorption curve from which the optical constants of the metal can be calculated. Although it is very different from the absorption curve of the solid metal, it nevertheless has nothing to do with resonance in the sense in which this term was used by Ehrenhaft, Wood and others. Thus Maxwell-Garnett, for instance, freely derived from Lorenz' theory the red color of many gold solutions which Ehrenhaft

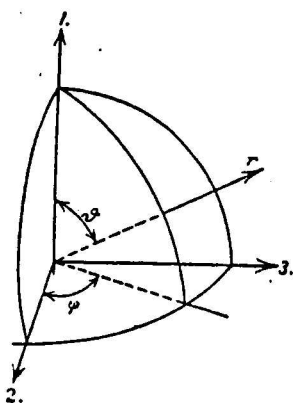
regularly, predominantly in octahedral form, it is nevertheless very possible that upon rapid precipitation from the solution very severely deformed crystals may form and be suspended in the fluid as flakes or rods. On the other hand however, regular crystals may certainly form, as observed, for example, in the beautiful copper octahedrons in the so-called Avanturin glass. In theory it seems permissible to substitute spheres for homogeneously developed crystals such as octahedrons, cubes etc., and flattened or elongated ellipsoids for the flakes and rods. I however would like to mention that the observations made by Mr. Steubing on the polarization of the diffusely scattered light, which I shall refer to again in § 20, suggest that we are really not dealing with spheres or similarly structured bodies.

The present work deals only with the simplest case, in which spherical form may be ascribed to the particles.

Polar Coordinates

2. For the sake of simplicity we shall number the coordinate axes (x, y, z) of a rectangular system of coordinates $(1, 2, 3)$. Let r be the radius vector of a point (x, y, z) , let θ be the angle formed by r with axis 1, and ϕ be the angle made by the projection of r on the $(2, 3)$ plane

with axis 2 (Fig. 1). Then (r, θ, ϕ) are the polar coordinates of the point. Furthermore we want to call the components of the electrical and magnetic field intensities $\mathcal{E}_r, \mathcal{E}_\theta, \mathcal{E}_\phi$ and $\mathcal{H}_r, \mathcal{H}_\theta, \mathcal{H}_\phi$ in this polar coordinate system. Then it can be shown that Maxwell's equations take the following form:



$$\left. \begin{aligned}
 r^2 \cdot \sin \theta \left(k \cdot \frac{\partial \mathcal{E}_r}{\partial t} + \Lambda \cdot \mathcal{E}_r \right) &= \frac{\partial (r \cdot \sin \theta \cdot \mathcal{H}_\phi)}{\partial \theta} - \frac{\partial (r \cdot \mathcal{H}_\theta)}{\partial \phi}, \\
 r \cdot \sin \theta \cdot \left(k \cdot \frac{\partial \mathcal{E}_\theta}{\partial t} + \Lambda \cdot \mathcal{E}_\theta \right) &= \frac{\partial \mathcal{H}_r}{\partial \phi} - \frac{\partial (r \cdot \sin \theta \cdot \mathcal{H}_\phi)}{\partial r}, \\
 r \cdot \left(k \cdot \frac{\partial \mathcal{E}_\phi}{\partial t} + \Lambda \cdot \mathcal{E}_\phi \right) &= \frac{\partial (r \cdot \mathcal{H}_\theta)}{\partial r} - \frac{\partial \mathcal{H}_r}{\partial \theta}, \\
 -r^2 \cdot \sin \theta \cdot \mu \cdot \frac{\partial \mathcal{H}_r}{\partial t} &= \frac{\partial (r \cdot \sin \theta \cdot \mathcal{E}_\phi)}{\partial \theta} - \frac{\partial (r \cdot \mathcal{E}_\theta)}{\partial \phi}, \\
 -r \cdot \sin \theta \cdot \mu \cdot \frac{\partial \mathcal{H}_\theta}{\partial t} &= \frac{\partial \mathcal{E}_r}{\partial \phi} - \frac{\partial (r \cdot \sin \theta \cdot \mathcal{E}_\phi)}{\partial r}, \\
 -r \cdot \mu \cdot \frac{\partial \mathcal{H}_\phi}{\partial t} &= \frac{\partial (r \cdot \mathcal{E}_\theta)}{\partial r} - \frac{\partial \mathcal{E}_r}{\partial \theta}.
 \end{aligned} \right\} (1)$$

Fig. 1. Coordinate system

Here k, Λ, μ stand for dielectricity, conductivity and permeability in the same system. In a nonconducting medium, $k \cdot \mu + 1/v^2$, where v is the velocity of electromagnetic waves in the medium.

By elimination we can arrive at a second order differential equation for \mathcal{E}_r and \mathcal{H}_r that does not contain the other unknowns. This will be done however, only after we have transformed the equations for the problem of regular oscillations.

We set:

$$\mathfrak{E}_r = E_r \cdot e^{2\pi i n t}, \quad \mathfrak{H}_r = H_r \cdot e^{2\pi i n t} \quad \text{etc.} \quad (2)$$

where E_r and H_r only depend on the coordinates and not on time, and n is the number of oscillations per second.

Furthermore:

$$4\pi^2 \cdot n^2 \cdot \mu \cdot k - 2\pi i \cdot n \cdot \mu \cdot A = \frac{4\pi^2 \cdot m^2}{\lambda^2} \quad (3)$$

and here λ indicates the wave lengths of the oscillation in question in vacuum, and m is the complex refraction exponent of the medium for light of wave length λ . In a nonabsorbing medium (e.g. water), m is identical with the usual index of refraction, but in metals $m = \nu \cdot (1 - i \cdot \kappa)$, where ν is the real quantity conventionally called the index of refraction and κ is the absorption coefficient.

Finally we introduce the following notation:

$$- \frac{i \cdot n \cdot \mu \cdot \lambda}{m} \cdot H_r = M_r \quad \text{etc.} \quad (4)$$

$$\frac{2\pi m r}{\lambda} = x. \quad (5)$$

We now arrive at the following equations in which the quantities E and M occur in the same way:

$$\left. \begin{aligned}
x^2 \sin \vartheta \cdot E_r &= \frac{\partial (x \sin \vartheta \cdot M_\varphi)}{\partial \vartheta} - \frac{\partial (x \cdot M_\vartheta)}{\partial \varphi}, \\
x \sin \vartheta \cdot E_\vartheta &= \frac{\partial M_r}{\partial \varphi} - \frac{\partial (x \sin \vartheta \cdot M_\varphi)}{\partial x}, \\
x \cdot E_\varphi &= \frac{\partial (x \cdot M_\vartheta)}{\partial x} - \frac{\partial M_r}{\partial \vartheta}, \\
x^2 \sin \vartheta \cdot M_r &= \frac{\partial (x \sin \vartheta \cdot E_\varphi)}{\partial \vartheta} - \frac{\partial (x E_\vartheta)}{\partial \varphi}, \\
x \sin \vartheta \cdot M_\vartheta &= \frac{\partial E_r}{\partial \varphi} - \frac{\partial (x \sin \vartheta \cdot E_\varphi)}{\partial x}, \\
x \cdot M_\varphi &= \frac{\partial (x \cdot E_\vartheta)}{\partial x} - \frac{\partial E_r}{\partial \vartheta}.
\end{aligned} \right\} (6)$$

Now we consider a spherical particle of radius ρ whose center coincides with the origin and which is surrounded by the solvent (e.g. water). The fields in the sphere and solvent will be designated with the suffixes i and a respectively, the two indices of refraction will be m and m_0 . We assume permeability to be the same inside and outside: $\mu_i = \mu_a$. The variable x has a discontinuity at the surface of the sphere, since

$$x_i = \frac{2\pi m}{\lambda} \cdot r, \quad x_a = \frac{2\pi m_0}{\lambda} \cdot r = \frac{2\pi}{\lambda'} \cdot r,$$

where λ' indicates the wave length in the solvent. The following boundary conditions must hold at the surface of the sphere:

$$\left. \begin{aligned}
E_{\vartheta a} = E_{\vartheta i}, \quad E_{\varphi a} = E_{\varphi i}, \\
(x \cdot M_\vartheta)_a = (x \cdot M_\vartheta)_i, \quad (x \cdot M_\varphi)_a = (x \cdot M_\varphi)_i.
\end{aligned} \right\} (7)$$

Solutions of Maxwell's Equations

3. The methods developed by Rayleigh "Theory of Sound" are used to solve Eq. (6). This has already been done by Hasenöhr [6] for other purposes. In order to have together all the equations required for the discussion, I shall give below a brief derivation of the integrals.

As already mentioned, appropriate eliminations from Eq. (6) provides a second order differential equation for E_r and M_r :

$$\left. \begin{aligned} \frac{\partial^2(x^2 E_r)}{\partial x^2} + \frac{1}{\sin \vartheta} \cdot \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \cdot \frac{\partial E_r}{\partial \vartheta} \right) \\ + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial^2 E_r}{\partial \varphi^2} + x^2 E_r = 0, \\ \frac{\partial^2(x^2 M_r)}{\partial x^2} + \frac{1}{\sin \vartheta} \cdot \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \cdot \frac{\partial M_r}{\partial \vartheta} \right) \\ + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial^2 M_r}{\partial \varphi^2} + x^2 M_r = 0. \end{aligned} \right\} \quad (8)$$

We can now divide all solutions of Eq. (6) into three groups. The first group represents the waves due to electrical oscillations of the sphere; it is characterized by:

$$E_r \neq 0, \quad M_r = 0.$$

The second group represents the waves due to magnetic oscillations of the sphere. For it we have:

$$E_r = 0, \quad M_r \neq 0.$$

The third group contains all integrals of the Maxwell equations that represent regular periodic oscillations. They can be found by adding the integrals of group I to the integrals of group II.

Assuming that we found a solution of the differential equation for E_r , we find the remaining components corresponding to group I very simply by the following procedure: we substitute $M_r = 0$ into the second and third equations of system (6) and then substitute for M_ϕ and M_θ the values from the fifth and sixth equation. We find immediately equations which can be used to calculate E_θ and E_ϕ from the known E_r . Now if we have E_r , E_θ , E_ϕ , we naturally find M_θ and M_ϕ from the two last equations of system (6). This gives us the following system of equations:

$$\left. \begin{aligned} E_r, & & M_r = 0, \\ \frac{\partial^2(x \cdot E_\theta)}{\partial x^2} + x \cdot E_\theta &= \frac{\partial^2 E_r}{\partial \theta \partial x}, & \frac{\partial(x \cdot M_\theta)}{\partial x} = x \cdot E_\phi, \\ \frac{\partial^2(x \cdot \sin \vartheta \cdot E_\phi)}{\partial x^2} + x \sin \vartheta \cdot E_\phi &= \frac{\partial^2 E_r}{\partial \varphi \partial x}, & \frac{\partial(x \cdot M_\phi)}{\partial x} = -x \cdot E_\theta. \end{aligned} \right\} \quad (9)$$

The calculation is the same for group II. Furthermore we can calculate E_r in general as a sum of terms each of which fulfills Eq. (8) individually and is a product of a function of x with the function of the angle θ , ϕ . The v th term is:

$$E_r^{(v)} = \frac{K_v(x)}{x^3} \cdot P_v(\vartheta, \varphi).$$

Then K_ν and P_ν must satisfy the following two equations:

$$\frac{d^2 K_\nu}{dx^2} + \left(1 - \frac{c_\nu}{x^2}\right) K_\nu = 0, \quad (10)$$

$$\frac{1}{\sin \vartheta} \cdot \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \cdot \frac{\partial P_\nu}{\partial \vartheta} \right] + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial^2 P_\nu}{\partial \varphi^2} + c_\nu \cdot P_\nu = 0, \quad (11)$$

where c_ν may be any either real or complex number. We now want to use functions of K_ν and P_ν for which

$$c_\nu = \nu \cdot (\nu + 1). \quad (12)$$

Then P_ν is a spherical function of variables θ, ϕ of whole number order ν , K_ν is a function closely related to the cylindrical function with broken index (denominator 2). Equations (9) now give the following solution of Maxwell's equations:

$$\left. \begin{aligned} E_r^{(\nu)} &= \frac{K_\nu(x)}{x^2} \cdot P_\nu(\vartheta, \varphi), \\ E_\vartheta^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu'(x)}{x} \cdot \frac{\partial P_\nu}{\partial \vartheta}, \\ E_\varphi^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu'(x)}{x \cdot \sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi}, \\ M_r^{(\nu)} &= 0, \\ M_\vartheta^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu(x)}{x \cdot \sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi}, \\ M_\varphi^{(\nu)} &= - \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu(x)}{x} \cdot \frac{\partial P_\nu}{\partial \vartheta}. \end{aligned} \right\} \quad (13)$$

Thus we have found the solutions of the first group ($M_r = 0$). But now because of the symmetry of system (6) with respect to the E and M , we can immediately write the solutions of group II ($E_r = 0$):

$$\left. \begin{aligned}
E_r^{(\nu)} &= 0, \\
E_\vartheta^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu(x)}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_\nu(\vartheta, \varphi)}{\partial \varphi}, \\
E_\varphi^{(\nu)} &= -\frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu(x)}{x} \cdot \frac{\partial \mathfrak{P}_\nu(\vartheta, \varphi)}{\partial \vartheta}, \\
M_r^{(\nu)} &= \frac{K_\nu(x)}{x^2} \cdot \mathfrak{P}_\nu(\vartheta, \varphi), \\
M_\vartheta^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu'(x)}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \vartheta}, \\
M_\varphi^{(\nu)} &= \frac{1}{\nu \cdot (\nu + 1)} \cdot \frac{K_\nu'(x)}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi},
\end{aligned} \right\} \quad (14)$$

where K_ν and \mathfrak{P}_ν are any solutions of Eq. (10) and (11) in which we can set $c = \nu \cdot (\nu + 1)$.

Now we must express a plane wave, namely that which strikes the spherical particle, with the aid of (13) and (14). But first we must know the most important properties of the solutions of (10) and (11).

The Functions K_ν and I_ν

4. Differential equation (10)

$$\frac{d^2 K_\nu}{dx^2} + \left(1 - \frac{\nu \cdot (\nu + 1)}{x^2}\right) \cdot K_\nu = 0$$

can be solved immediately for the case $\nu = 0$. Two particular integrals are:

$$\begin{aligned}
K_0(x) &= e^{ix}, \\
K_0(-x) &= e^{-ix}.
\end{aligned}$$

Furthermore, if we know the ν th solution of the equation, K_ν , then by substitution we can easily demonstrate that the $(\nu + 1)$ th solution of the equation, $K_{\nu+1}$, can be calculated as follows:

$$K_{\nu+1}(x) = i \cdot \left((\nu + 1) \cdot \frac{K_\nu}{x} - \frac{dK_\nu}{dx} \right). \quad (15)$$

If we chose $K_0(x) = e^{ix}$, this recursion equation gives:

$$K_\nu(x) = e^{ix} \cdot \sum_0^\nu \frac{(\nu + \mu)!}{\mu!(\nu - \mu)!} \cdot \frac{i^\mu}{2^\mu \cdot x^\mu}. \quad (16)$$

Differentiating once and eliminating dK_ν/dx and d^2K_ν/dx^2 with the aid of (10), we find from (15):

$$K_{\nu-1}(x) = -i \cdot \left(\nu \cdot \frac{K_\nu}{x} + \frac{dK_\nu}{dx} \right). \quad (17)$$

From Eq. (15) and (17) we find the following often used relationships:

$$\left. \begin{aligned} (2\nu + 1) \cdot \frac{K_\nu(x)}{x} &= i \cdot K_{\nu-1} + \frac{1}{i} \cdot K_{\nu+1} \\ (2\nu + 1) \cdot \frac{dK_\nu}{dx} &= (\nu + 1) \cdot i \cdot K_{\nu-1} - \nu \cdot \frac{1}{i} \cdot K_{\nu+1} \end{aligned} \right\} \quad (18)$$

A second particular solution of (10) is found immediately, since in (10) we have only the second power of x and dx , if we reverse the sign of $K_\nu(-x)$ in the first solution. The general solution is thus:

$$A \cdot K_\nu(x) + B \cdot K_\nu(-x).$$

Since in the following discussion we will use the

solution $K_\nu(-x)$ immediately, it is appropriate to write the relationship that we obtain by reversing the sign of x in (15), (16), (17), (18):

$$K_\nu(-x) = e^{-ix} \cdot \sum_0^{\nu} \frac{(\nu + \mu)!}{\mu!(\nu - \mu)!} \cdot \frac{(-i)^\mu}{2^\mu \cdot x^\mu}, \quad (19)$$

$$\left. \begin{aligned} K_{\nu+1}(-x) &= -i \cdot \left((\nu + 1) \cdot \frac{K_\nu(-x)}{x} - K'_\nu(-x) \right), \\ K_{\nu-1}(-x) &= +i \cdot \left(\nu \cdot \frac{K_\nu(-x)}{x} + K'_\nu(-x) \right). \end{aligned} \right\} \quad (20)$$

$$\left. \begin{aligned} -(2\nu + 1) \cdot \frac{K_\nu(-x)}{x} &= i \cdot K_{\nu-1}(-x) + \frac{1}{i} \cdot K_{\nu+1}(-x), \\ -(2\nu + 1) \cdot K'_\nu(-x) &= i \cdot (\nu + 1) \cdot K_{\nu-1}(-x) - \frac{\nu}{i} \cdot K_{\nu+1}(-x). \end{aligned} \right\} \quad (21)$$

5. If in expressions (16) and (19), we expand e^{ix} and e^{-ix} in power series and then multiply and arrange in order of powers of x , we obtain the power series expansions for $K_\nu(x)$ and $K_\nu(-x)$, which naturally contain a finite number of powers with negative, whole exponents. We find:

$$K_\nu(x) = \sum_{r=-\nu}^{r=+\infty} i^r \cdot x^r \cdot \sum_0^{\nu} \frac{(\nu + \mu)! (-1)^\mu}{(\mu + r)! \mu! (\nu - \mu)! 2^\mu}.$$

Now, however, it can be shown that:

$$\sum_0^{\nu} \frac{(-1)^\mu \cdot (\nu + \mu)!}{2^\mu \cdot (\mu + r)! \mu! (\nu - \mu)!} = \frac{(r - \nu + 1) \cdot (r - \nu + 3) \dots (r + \nu - 1)}{(r + \nu)!}.$$

This expression is remarkable in that it is always different from zero and equal to zero in turn up to $r = \nu$. Up to the power x^ν only terms of the form $x^{-\nu + 2\mu}$ remain in the series. If we substitute $r = -\nu + 2\mu$ into the coefficients

we obtain:

$$\frac{(r-\nu+1)(r-\nu+3)\dots(r+\nu-1)}{(r+\mu)!}$$

$$= (-1)^{\nu+\mu+1} \frac{1 \cdot 3 \cdot 5 \dots (2\nu-2\mu-1) \cdot 1 \cdot 3 \dots (2\mu-1)}{(2\mu)!}$$

Thus:

$$K_\nu(x) = -i^\nu \sum_0^\nu \frac{1 \cdot 3 \dots (2\nu-2\mu-1) \cdot 1 \cdot 3 \dots (2\mu-1)}{(2\mu)!} \cdot x^{-\nu+2\mu} \quad (22)$$

$$+ \sum_{r=\nu+1}^{r+\infty} \frac{(r-\nu+1)(r-\nu+3)\dots(r+\nu-1)}{(r+\nu)!} \cdot i^r \cdot x^r.$$

Likewise:

$$K_\nu(-x)$$

$$= -(-i)^\nu \sum_0^\nu \frac{1 \cdot 3 \dots (2\nu-2\mu-1) \cdot 1 \cdot 3 \dots (2\mu-1)}{(2\mu)!} \cdot x^{-\nu+2\mu} \quad (23)$$

$$+ \sum_{r=\nu+1}^{r+\infty} \frac{(r-\nu+1)(r-\nu+3)\dots(r+\nu-1)}{(r+\nu)!} \cdot (-i)^r \cdot x^r.$$

We see that differential equation (10) also has *one* solution which can be developed around the zero point into a power series without negative powers. We will represent it by I_ν and set:

$$I_\nu(x) = \frac{1}{2i} \cdot \left(\frac{K_\nu(x)}{i^\nu} - \frac{K_\nu(-x)}{(-i)^\nu} \right). \quad (24)$$

The power series for I_ν has only real coefficients:

$$I_\nu(x) = \sum_0^\infty \frac{(-1)^\mu \cdot x^{\nu+2\mu+1}}{(2\mu+1)!(2\mu+3)(2\mu+5)\dots(2\mu+2\nu+1)} \quad (25)$$

From Eqs. (18) and (19) we find two important relationships:

$$\left. \begin{aligned} (2\nu + 1) \cdot \frac{I_\nu}{x} &= I_{\nu-1} + I_{\nu+1}, \\ (2\nu + 1) \cdot \frac{dI_\nu}{dx} &= (\nu + 1) \cdot I_{\nu-1} - \nu \cdot I_{\nu+1}. \end{aligned} \right\} \quad (26)$$

6. To calculate the functions $K_\nu(-x)$, $I_\nu(x)$ and their first derivatives (which alone appear in the final equations), we use the following expressions:

$$(27) \left\{ \begin{aligned} K_1(-x) &= -\frac{i}{x} \cdot e^{-ix} \cdot (1 + ix), \\ K_2(-x) &= -\frac{3}{x^3} \cdot e^{-ix} \cdot \left(\left(1 - \frac{1}{3}x^2\right) + ix \right), \\ K_3(-x) &= +\frac{15 \cdot i}{x^5} \cdot e^{-ix} \cdot \left(\left(1 - \frac{2}{5}x^2\right) + ix \cdot \left(1 - \frac{1}{15}x^2\right) \right), \\ &\dots \\ K_\nu(-x) &= (-i)^\nu \cdot \frac{1 \cdot 3 \dots (2\nu-1)}{x^\nu} \cdot e^{-ix} \\ &\cdot \left\{ \left(1 + \sum_1^{\frac{\nu(-1)}{2}} \frac{(\nu-\sigma)_\sigma (-1)^\sigma}{(2\nu-1)(2\nu-3)\dots(2\nu-2\sigma+1)} \cdot \frac{x^{2\sigma}}{1 \cdot 3 \dots (2\sigma-1)} \right) \right. \\ &\left. + ix \cdot \left(1 + \sum_1^{\frac{\nu(+1)}{2}-1} \frac{(\nu-\sigma-1)_\sigma (-1)^\sigma}{(2\nu-1)(2\nu-3)\dots(2\nu-2\sigma+1)} \cdot \frac{x^{2\sigma}}{1 \cdot 3 \dots (2\sigma+1)} \right) \right\}. \end{aligned} \right.$$

$$(28) \left\{ \begin{aligned} K_1'(-x) &= +\frac{i}{x^3} \cdot e^{-ix} \cdot \left((1-x^2) + ix \right), \\ K_2'(-x) &= +\frac{6}{x^5} \cdot e^{-ix} \cdot \left(\left(1 - \frac{1}{2}x^2\right) + ix \cdot \left(1 - \frac{1}{6}x^2\right) \right), \\ K_3'(-x) &= -\frac{45 \cdot i}{x^7} \cdot e^{-ix} \cdot \left(\left(1 - \frac{7}{15}x^2 + \frac{1}{45}x^4\right) + ix \cdot \left(1 - \frac{2}{15}x^2\right) \right), \\ &\dots \\ K_\nu'(-x) &= -(-i)^\nu \cdot \nu \cdot \frac{1 \cdot 3 \dots (2\nu-1)}{x^{\nu+1}} \cdot e^{-ix} \\ &\cdot \left\{ \left(1 + \sum_1^{\frac{\nu(+1)}{2}} (-1)^\sigma \frac{(\nu-\sigma)_\sigma + \frac{2\sigma-1}{\nu} \cdot (\nu-\sigma)_{\sigma-1}}{(2\nu-1)(2\nu-3)\dots(2\nu-2\sigma+1)} \cdot \frac{x^{2\sigma}}{1 \cdot 3 \dots (2\sigma-1)} \right) \right. \\ &\left. + ix \cdot \left(1 + \sum_1^{\frac{\nu(-1)}{2}} (-1)^\sigma \frac{(\nu-\sigma-1)_\sigma + \frac{2\sigma+1}{\nu} \cdot (\nu-\sigma-1)_{\sigma-1}}{(2\nu-1)(2\nu-3)\dots(2\nu-2\sigma+1)} \cdot \frac{x^{2\sigma}}{1 \cdot 3 \dots (2\sigma+1)} \right) \right\}. \end{aligned} \right.$$

$$(29) \left\{ \begin{aligned} I_1(x) &= \frac{x^3}{3} \cdot \left(1 - \frac{3}{5} \cdot \frac{x^2}{3!} + \frac{3}{7} \cdot \frac{x^4}{5!} - \frac{3}{9} \cdot \frac{x^6}{7!} + \dots \right); \\ I_2(x) &= \frac{x^3}{15} \cdot \left(1 - \frac{3}{7} \cdot \frac{x^2}{3!} + \frac{3 \cdot 5}{7 \cdot 9} \cdot \frac{x^4}{5!} - \frac{3 \cdot 5}{9 \cdot 11} \cdot \frac{x^6}{7!} + \dots \right); \\ I_3(x) &= \frac{x^4}{105} \cdot \left(1 - \frac{3}{9} \cdot \frac{x^2}{3!} + \frac{3 \cdot 5}{9 \cdot 11} \cdot \frac{x^4}{5!} - \frac{3 \cdot 5 \cdot 7}{9 \cdot 11 \cdot 13} \cdot \frac{x^6}{7!} + \dots \right); \\ &\dots \\ I_\nu(x) &= \frac{x^{\nu+1}}{1 \cdot 3 \cdot \dots \cdot (2\nu+1)} \cdot \left(1 - \frac{3}{2\nu+3} \cdot \frac{x^2}{3!} + \frac{3 \cdot 5}{(2\nu+3)(2\nu+5)} \cdot \frac{x^4}{5!} \right. \\ &\quad \left. - \frac{3 \cdot 5 \cdot 7}{(2\nu+3)(2\nu+5)(2\nu+7)} \cdot \frac{x^6}{7!} + \dots \right). \end{aligned} \right.$$

$$(30) \left\{ \begin{aligned} I_1'(x) &= \frac{2 \cdot x}{3} \cdot \left(1 - 2 \cdot \frac{3}{5} \cdot \frac{x^2}{3!} + 3 \cdot \frac{3}{7} \cdot \frac{x^4}{5!} - 4 \cdot \frac{3}{9} \cdot \frac{x^6}{7!} + \dots \right); \\ I_2'(x) &= \frac{3 \cdot x^2}{15} \cdot \left(1 - \frac{5}{7} \cdot \frac{x^2}{3!} + \frac{5}{9} \cdot \frac{x^4}{5!} - \frac{5}{11} \cdot \frac{x^6}{7!} + \dots \right); \\ I_3'(x) &= \frac{4 \cdot x^3}{104} \cdot \left(1 - \frac{3}{2} \cdot \frac{3}{9} \cdot \frac{x^2}{3!} + \frac{4}{2} \cdot \frac{3 \cdot 5}{9 \cdot 11} \cdot \frac{x^4}{5!} \right. \\ &\quad \left. - \frac{5}{2} \cdot \frac{3 \cdot 5 \cdot 7}{9 \cdot 11 \cdot 13} \cdot \frac{x^6}{7!} + \dots \right); \\ &\dots \\ I_\nu'(x) &= \frac{(\nu+1) \cdot x^\nu}{1 \cdot 3 \cdot \dots \cdot (2\nu+1)} \cdot \left(1 - \frac{\nu+3}{\nu+1} \cdot \frac{3}{2\nu+3} \cdot \frac{x^2}{3!} \right. \\ &\quad \left. + \frac{\nu+5}{\nu+1} \cdot \frac{3 \cdot 5}{(2\nu+1)(2\nu+5)} \cdot \frac{x^4}{5!} - \dots \right). \end{aligned} \right.$$

These series are much more adapted to numerical calculations than the finite expressions obtained for I_ν and I_ν' from (24). For other purposes however, we must also know them:

$$(29a) \left\{ \begin{aligned} I_1(x) &= -\cos x + \frac{\sin x}{x}, \\ I_2(x) &= -\sin x - \frac{8 \cdot \cos x}{x} + \frac{9 \cdot \sin x}{x^2}, \\ I_3(x) &= +\cos x - \frac{6 \cdot \sin x}{x} - \frac{15 \cdot \cos x}{x^2} + \frac{15 \cdot \sin x}{x^3}, \\ &\dots \\ I_\nu(x) &= \sin \left(x - \frac{\nu\pi}{2} \right) + \sum_1^\nu \sin \left(x - \frac{(\nu-r)\pi}{2} \right) \\ &\quad \cdot \frac{(\nu+r)!}{(\nu-r)! r!} \cdot \frac{1}{2^r \cdot x^r}. \end{aligned} \right.$$

$$\begin{aligned}
(30a) \quad & I_1'(x) = + \sin x + \frac{\cos x}{x} - \frac{\sin x}{x^2}, \\
& I_2'(x) = - \cos x + \frac{3 \cdot \sin x}{x} + \frac{6 \cdot \cos x}{x^2} - \frac{6 \cdot \sin x}{x^3}, \\
& I_3'(x) = - \sin x - \frac{6 \cdot \cos x}{x} + \frac{21 \cdot \sin x}{x^2} + \frac{45 \cdot \cos x}{x^3} - \frac{45 \cdot \sin x}{x^4}, \\
& \dots \dots \dots \\
& I_r'(x) = \cos \left(x - \frac{r \cdot \pi}{2} \right) + \sum_1^{r+1} r \cos \left(x - \frac{(r-r)\pi}{2} \right) \\
& \qquad \qquad \qquad \frac{(r+r-1)! \cdot (r(r+1) + r(r-1))}{(r-r+1)! \cdot 2^r \cdot x^r}.
\end{aligned}$$

The Spherical Functions

7. The conventional spherical functions, which only depend on one variable (the zonal spherical functions) cannot be used for this problem. We shall see in the next section that functions of the following two forms are required for the solution:

$$P_\nu(\vartheta, \varphi) = \Pi_\nu(\nu) \cdot \cos \vartheta, \tag{31}$$

$$\mathfrak{P}_\nu(\vartheta, \varphi) = \Pi_\nu(\nu) \cdot \sin \vartheta \cdot \cos \varphi, \tag{32}$$

$$v = \sin \vartheta \cdot \sin \varphi. \tag{33}$$

The function Π_ν must, as we can see by substituting the expressions for P_ν and \mathfrak{P}_ν into (11), belong to the following differential equation:

$$\frac{d^2}{dv^2} ((1 - v^2) \cdot \Pi_\nu) + \nu \cdot (\nu + 1) \cdot \Pi_\nu = 0. \tag{34}$$

The geometrical significance of the three angle functions found in (31), (32), and (33),:

$$\cos \vartheta, \sin \vartheta \cdot \sin \varphi, \sin \vartheta \cdot \cos \varphi$$

is immediately evident. If we call the angles formed by the radius vector of the point under discussion with the axes 1, 2, 3 (cf. 2) $\theta_1, \theta_2, \theta_3$, then as we can see immediately from Fig. 2:

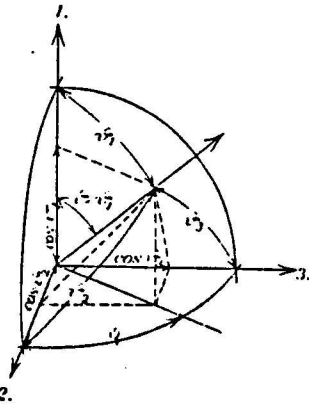


Fig. 2. Trigonometric relationships

$$\begin{aligned} \cos \theta_1 &= \cos \vartheta, \\ \cos \theta_2 &= \sin \vartheta \cdot \cos \varphi, \\ \cos \theta_3 &= \sin \vartheta \cdot \sin \varphi = v. \end{aligned} \quad (35)$$

Now we want to collect the most important equations for functions of Π_ν . Of course one particular solution of the differential equation of the spherical function is rational and whole in the trigonometric functions of the angular

coordinates θ, ϕ . Only this solution is of interest. If we have found it for one index (e.g. $\nu = 1$), we can calculate for all other indices with the aid of the following recursion equation

$$\frac{d \Pi_{\nu+1}}{d \nu} = \nu \cdot \frac{d \Pi_\nu}{d \nu} + (\nu + 2) \cdot \Pi_\nu. \quad (36)$$

This equation can be verified immediately by substitution into (34). A solution of (34) for the case $\nu = 1$ is then:

$$\Pi_1(\nu) = 1. \quad (37)$$

Then using (36) we find:

$$\left. \begin{aligned}
\Pi_0(v) &= 0, & \Pi_1(v) &= 1, \\
\Pi_2 &= 3v, \\
\Pi_3 &= \frac{15}{2} \cdot v^2 - \frac{3}{2}, \\
\Pi_4 &= \frac{35}{2} v^3 - \frac{15}{2} v, \\
\Pi_v &= \frac{1}{2^v} \cdot \sum_0^{\frac{v(+1)}{2} - 1} (-1)^s \cdot \frac{(2v-2s)!}{(v-s)!s!} \cdot \frac{v^{v-2s-1}}{(v-2s-1)!}.
\end{aligned} \right\} \quad (38)$$

Another series expansion for Π_v is the following:

$$\Pi_v = \sum_0^{\frac{v(+1)}{2} - 1} (-1)^s \cdot \frac{(v+1)!}{s!(v+1)!} \cdot \frac{v^{v-2s-1} \cdot (1-r)^s}{(v-2s-1)! 2^{2s+1}}. \quad (39)$$

For the special value $v = 0$, Eq. (38) gives:

$$\begin{aligned}
\Pi_v(0) &= 0, & \text{when } v & \text{ is even,} \\
\Pi_v(0) &= (-1)^{\frac{v-1}{2}} \cdot \frac{(v+1)!}{2^v \left(\frac{v+1}{2}\right)! \left(\frac{v-1}{2}\right)!}, & \text{when } v & \text{ is odd,}
\end{aligned} \quad (40)$$

and for the first derivative:

$$\begin{aligned}
\left(\frac{d\Pi_v}{dv}\right)_{v=0} &= (-1)^{\frac{v}{2}-1} \cdot \frac{(v+1)!}{2^{v-1} \left(\frac{v}{2}\right)! \left(\frac{v}{2}-1\right)!}, & \text{when } v & \text{ is even,} \\
\left(\frac{d\Pi_v}{dv}\right)_{v=0} &= 0, & \text{when } v & \text{ is odd.}
\end{aligned} \quad (41)$$

Similarly from (39) we can calculate the values of Π_v and its derivatives for $v = 1$.

8. Just as for the above mentioned functions K_ν and I_ν , we also have for Π_ν besides the recursion equation (36) a second equation that can be demonstrated as was (36):

$$\frac{d \Pi_{\nu-1}}{d \nu} = \nu \cdot \frac{d \Pi_\nu}{d \nu} - (\nu - 1) \cdot \Pi_\nu. \quad (42)$$

From (36) and (42) we obtain the two often very useful equations:

$$\left. \begin{aligned} (2\nu + 1) \cdot \Pi_\nu &= \frac{d \Pi_{\nu+1}}{d \nu} - \frac{d \Pi_{\nu-1}}{d \nu}, \\ (2\nu + 1) \cdot \nu \cdot \Pi_\nu &= \nu \cdot \Pi_{\nu+1} + (\nu + 1) \cdot \Pi_{\nu-1}. \end{aligned} \right\} \quad (43)$$

9. Finally the differential quotients of P_ν and \mathfrak{P}_ν , appearing in Eqs. (13) and (14) should be noted here.

$$\left. \begin{aligned} P_\nu &= \Pi_\nu \cdot \cos \vartheta, \\ \frac{\partial P_\nu}{\partial \vartheta} &= - \frac{d(\nu \cdot \Pi_\nu)}{d \nu} \cdot \sin \vartheta + \frac{d \Pi_\nu}{d \nu} \cdot \sin \varphi, \\ \frac{1}{\sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi} &= \frac{d \Pi_\nu}{d \nu} \cdot \cos \vartheta \cdot \cos \varphi. \end{aligned} \right\} \quad (44)$$

$$\left. \begin{aligned} \mathfrak{P}_\nu &= \Pi_\nu \cdot \sin \vartheta \cdot \cos \varphi, \\ \frac{\partial \mathfrak{P}_\nu}{\partial \vartheta} &= \frac{d(\nu \cdot \Pi_\nu)}{d \nu} \cdot \cos \vartheta \cdot \cos \varphi, \\ \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} &= - \frac{d(\nu \cdot \Pi_\nu)}{d \nu} \cdot \sin \varphi + \frac{d \Pi_\nu}{d \nu} \cdot \sin \vartheta. \end{aligned} \right\} \quad (45)$$

In particular for the first two ordinal numbers we have:

$$\begin{aligned} P_1 &= \cos \vartheta, & P_2 &= 3 \cdot \sin \vartheta \cdot \cos \vartheta \cdot \sin \varphi, \\ \frac{\partial P_1}{\partial \vartheta} &= - \sin \vartheta, & \frac{\partial P_2}{\partial \vartheta} &= 3 \cdot \cos 2 \vartheta \cdot \sin \varphi, \\ \frac{1}{\sin \vartheta} \cdot \frac{\partial P_1}{\partial \varphi} &= 0, & \frac{1}{\sin \vartheta} \cdot \frac{\partial P_2}{\partial \varphi} &= 3 \cdot \cos \vartheta \cdot \cos \varphi, \\ \mathfrak{P}_1 &= \sin \vartheta \cdot \cos \varphi, & \mathfrak{P}_2 &= 3 \cdot \sin^2 \vartheta \cdot \sin \varphi \cdot \cos \varphi, \\ \frac{\partial \mathfrak{P}_1}{\partial \vartheta} &= \cos \vartheta \cdot \cos \varphi, & \frac{\partial \mathfrak{P}_2}{\partial \vartheta} &= 3 \cdot \sin 2 \vartheta \cdot \sin \varphi \cdot \cos \varphi, \\ \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{P}_1}{\partial \varphi} &= - \sin \varphi, & \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{P}_2}{\partial \varphi} &= 3 \cdot \sin \vartheta \cdot \cos 2 \varphi. \end{aligned}$$

Integral Values of the Spherical Functions

10. Below we must calculate the total radiation reflected by the sphere. We shall see that this problem reduces to finding the contour integrals

$$\int_0^\pi \int_0^{2\pi} P_\nu \cdot P_\mu \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi \quad \text{and} \quad \int_0^\pi \int_0^{2\pi} \mathfrak{P}_\nu \cdot \mathfrak{P}_\mu \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi$$

These integrals can be calculated very easily, for example by a method used in Maxwell's Treatise on Electricity [7].

We find:

$$\left. \begin{aligned} \int_0^\pi \int_0^{2\pi} P_\nu \cdot P_\mu \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi &= \int_0^\pi \int_0^{2\pi} \mathfrak{P}_\nu \cdot \mathfrak{P}_\mu \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi = 0, \\ \int_0^\pi \int_0^{2\pi} P_\nu^2 \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi &= \int_0^\pi \int_0^{2\pi} \mathfrak{P}_\nu^2 \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi = 2\pi \cdot \frac{\nu \cdot (\nu + 1)}{2\nu + 1}. \end{aligned} \right\} \quad (46)$$

Plane Waves

11. The present problem can be considered solved as soon as the plane waves incident on the sphere are resolved into expressions of the form of (13) and (14).

We shall chose axis 3, in the negative direction, as the direction of propagation of the plane waves. We assume the light to be rectilinearly polarized, and axis 1 is the direction of the electrical oscillation, thus axis 2 is the direction of the magnetic oscillation.

If we again call z the coordinate of a point in the direction of axis 3, then according to (35):

$$z = r \cdot \cos \vartheta_3 = r \cdot v.$$

The plane wave is thus represented by the following quantities:

$$\begin{aligned} \mathfrak{E}_1 &= e^{2\pi i n t + \frac{2\pi i z}{\lambda'}}, & \mathfrak{E}_2 &= \mathfrak{E}_3 = 0, \\ \mathfrak{H}_1 &= 0, & \mathfrak{H}_2 &= -\sqrt{\frac{k}{\mu}} \cdot e^{2\pi i n t + \frac{2\pi i z}{\lambda'}}, & \mathfrak{H}_3 &= 0. \end{aligned}$$

Here k and μ are the dielectricity and permeability in the sense used in (1), and we have assumed the conductivity of the medium through which the beam passes (the water) to be zero, λ' is the wave length in the medium (water). Now if we set (cf. (5))

$$\frac{2\pi i z}{\lambda'} = \frac{2\pi i \cdot r \cdot v}{\lambda'} = i \cdot x \cdot v,$$

then the quantities E_r, \dots and M_r, \dots , which were introduced earlier (Eq. (2) and (4)) can immediately be written as:

$$\left. \begin{aligned} E_r &= e^{i \cdot x \cdot v} \cdot \cos \vartheta, & M_r &= i \cdot e^{i \cdot x \cdot v} \cdot \sin \vartheta \cdot \cos \varphi, \\ E_\vartheta &= -e^{i \cdot v \cdot x} \cdot \sin \vartheta, & M_\vartheta &= i \cdot e^{i \cdot x \cdot v} \cdot \cos \vartheta \cdot \cos \varphi, \\ E_\varphi &= 0, & M_\varphi &= -i \cdot e^{i \cdot x \cdot v} \cdot \sin \varphi. \end{aligned} \right\} \quad (47)$$

But now the exponential function can be easily developed into I and Π functions. We have:

$$e^{i x v} = \sum_{\nu=1}^{\nu=\infty} (2\nu+1) \cdot i^{\nu-1} \cdot \frac{I_\nu(x)}{x^\nu} \cdot \Pi_\nu(v). \quad (48)$$

The validity of this equation can be most easily demonstrated by differentiating with respect to x and v . If we first call the series $f(x, v)$, then according to (26) and (43):

$$\begin{aligned}
 \frac{\partial f}{\partial x} &= \frac{1}{x^2} \cdot \left\{ \sum_1^{\infty} i^{\nu-1} \cdot (2\nu+1) \cdot \left(\frac{dI_\nu}{dx} - 2 \cdot \frac{I_\nu}{x} \right) \cdot \Pi_\nu(v) \right\}, \\
 &= \frac{i}{x^2} \cdot \sum_1^{\infty} \nu \cdot ((\nu-1) \cdot i^{\nu-2} \cdot I_{\nu-1} + (\nu+2) \cdot i^\nu \cdot I_{\nu+1}) \cdot \Pi_\nu(v), \\
 &= i \cdot \sum_1^{\infty} i^{\nu-1} \cdot \frac{I_\nu}{x^2} \cdot (\nu \cdot \Pi_{\nu+1} + (\nu+1) \cdot \Pi_{\nu-1}), \\
 &= i \cdot v \cdot \sum_1^{\infty} (2\nu+1) \cdot i^{\nu-1} \cdot \frac{I_\nu}{x^2} \cdot \Pi_\nu(v), \\
 &= i \cdot v \cdot f(x, v).
 \end{aligned}$$

Likewise we can show that:

$$\frac{\partial f}{\partial v} = i \cdot x \cdot f(x, v).$$

And finally:

$$(f(x, v))_{v=0} = 1.$$

Thus

$$f(x, v) = e^{ixv}.$$

Accordingly we have the desired series expansion for E_r and M_r :

$$\begin{aligned}
 E_r &= \sum_1^{\infty} \nu (2\nu+1) \cdot i^{\nu-1} \cdot \frac{I_\nu}{x^2} \cdot P_\nu, \\
 M_r &= \sum_1^{\infty} \nu (2\nu+1) \cdot i^\nu \cdot \frac{I_\nu}{x^2} \cdot \mathfrak{P}_\nu.
 \end{aligned}$$

where P_ν and \mathfrak{P}_ν are the functions defined in (31) and (32).

Now from the values found for E_r using (13) we can find a solution for group I. Furthermore using M_r and (14) we can find a solution of group II; the sum of these two solutions must then be that integral of the Maxwell equations that gives the plane wave. We can easily demonstrate by direct calculations that the resulting series expansions are in fact identical with expressions (47).

Then from (26) and (43), keeping in mind the differential equation (10)

$$\frac{1}{r \cdot (r+1)} \cdot \left(\frac{d^2 J_r}{dx^2} + J_r \right) = \frac{J_r}{x^2}$$

we can derive the following two equations

$$\left. \begin{aligned} \sum_1^\infty \frac{2\nu+1}{r \cdot (r+1)} \cdot \left(i^{r-1} \cdot J_r \cdot \frac{d(\nu H_\nu)}{d\nu} + i^r \cdot \frac{dJ_r}{dx} \cdot \frac{d\Pi_\nu}{d\nu} \right) &= 0, \\ \sum_1^\infty \frac{2\nu+1}{r \cdot (r+1)} \cdot \left(i^{r-1} \cdot J_r \cdot \frac{d\Pi_\nu}{d\nu} + i^r \cdot \frac{dJ_r}{dx} \cdot \frac{d(\nu H_\nu)}{d\nu} \right) & \\ &= \sum_1^\infty (2\nu+1) \cdot i^{r-1} \cdot \frac{J_r}{x^2} \cdot \frac{dH_\nu}{d\nu}, \\ &= \sum_1^\infty (2\nu+1) \cdot i^r \cdot \frac{J_r}{x} \cdot \Pi_\nu, \\ &= i \cdot x \cdot e^{ix\nu}. \end{aligned} \right\} \quad (49)$$

If then according to (13) and (14) we form for example:

$$\begin{aligned} E_\nu &= \sum_1^\infty \frac{2\nu+1}{r \cdot (r+1)} \cdot i^{r-1} \cdot \frac{J_r}{x} \cdot \frac{\partial P_r}{\partial \vartheta} \\ &\quad + \sum_1^\infty \frac{2\nu+1}{r \cdot (r+1)} \cdot i^r \cdot \frac{J_r}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_r}{\partial \varphi} \end{aligned}$$

then using (44), (45) and (49) we find:

$$E_{\theta} = -e^{i\pi\nu} \cdot \sin \theta.$$

Likewise:

$$E_{\varphi} = \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \frac{I_{\nu}}{x \cdot \sin \theta} \cdot \frac{\partial P_{\nu}}{\partial \varphi} - \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \frac{I_{\nu}}{x} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \theta} = 0.$$

The procedure is similar for M_{θ} and M_{ϕ} . Thus for the plane wave, instead of (47), we can use the following:

$$\begin{aligned} E_r &= \sum_1^{\infty} (2\nu+1) \cdot i^{\nu-1} \cdot \frac{I_{\nu}}{x^2} \cdot P_{\nu}, \\ E_{\theta} &= \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \frac{I'_{\nu}}{x} \cdot \frac{\partial P_{\nu}}{\partial \theta} + \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \frac{I_{\nu}}{x \cdot \sin \theta} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \varphi}, \\ E_r &= \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \frac{I'_{\nu}}{x \cdot \sin \theta} \cdot \frac{\partial P_{\nu}}{\partial \varphi} - \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \frac{I_{\nu}}{x} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \theta}, \\ M_r &= \sum_1^{\infty} (2\nu+1) \cdot i^{\nu} \cdot \frac{I_{\nu}}{x^2} \cdot P_{\nu}, \\ M_{\theta} &= \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \frac{I_{\nu}}{x \cdot \sin \theta} \cdot \frac{\partial P_{\nu}}{\partial \varphi} + \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \frac{I'_{\nu}}{x} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \theta}, \\ M_{\varphi} &= -\sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \frac{I_{\nu}}{x} \cdot \frac{\partial P_{\nu}}{\partial \theta} + \sum_1^{\infty} \nu \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \frac{I'_{\nu}}{x \cdot \sin \theta} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \varphi}. \end{aligned} \quad (50)$$

Broken and Reflected Waves

12. If now we want to express the waves in the interior of the sphere and those waves radiated outward from it in the form of (13) and (14), we must take into account: first, that inside the sphere only the integral designated I_{ν} of Eq. (10) can be used, because all other

particular integrals for $x = 0$, i.e. in the center of the sphere, become infinite; second, that outside $K_\nu(-x)$ is to be used because only it has the factor

$$e^{-ix} = e^{-\frac{2\pi i r}{\lambda}}$$

so the components of the electric and magnetic forces contain time only in the combination:

$$e^{2\pi i \left(\pi t - \frac{r}{\lambda} \right)}$$

which is the characteristic of radiation coming from the sphere. The radiation inside the sphere can thus be represented as follows:

$$\left. \begin{aligned} E_{rt} &= \sum_1^{\infty} i \cdot b_\nu \cdot \frac{I_\nu}{x^2} \cdot P_\nu, \\ E_{\theta t} &= \sum_1^{\infty} \left(\frac{b_\nu \cdot i}{\nu \cdot (\nu + 1)} \cdot \frac{I'_\nu}{x} \cdot \frac{\partial P_\nu}{\partial \vartheta} + \frac{q_\nu}{\nu \cdot (\nu + 1)} \cdot \frac{I_\nu}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} \right), \\ E_{\varphi t} &= \sum_1^{\infty} \left(\frac{b_\nu \cdot i}{\nu \cdot (\nu + 1)} \cdot \frac{I'_\nu}{x \cdot \sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi} - \frac{q_\nu}{\nu \cdot (\nu + 1)} \cdot \frac{I_\nu}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \vartheta} \right), \\ M_{rt} &= \sum_1^{\infty} q_\nu \cdot \frac{I_\nu}{x^2} \cdot \mathfrak{P}_\nu, \\ M_{\theta t} &= \sum_1^{\infty} \left(\frac{b_\nu \cdot i}{\nu \cdot (\nu + 1)} \cdot \frac{I_\nu}{x \cdot \sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \vartheta} + \frac{q_\nu}{\nu \cdot (\nu + 1)} \cdot \frac{I'_\nu}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} \right), \\ M_{\varphi t} &= \sum_1^{\infty} \left(-\frac{b_\nu \cdot i}{\nu \cdot (\nu + 1)} \cdot \frac{I_\nu}{x} \cdot \frac{\partial P_\nu}{\partial \vartheta} + \frac{q_\nu}{\nu \cdot (\nu + 1)} \cdot \frac{I'_\nu}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} \right). \end{aligned} \right\} \quad (51)$$

The coefficients b_ν and q_ν , to one of which the factor I is added only to make subsequent equations somewhat more elegant, can, in addition to the factors a_ν and p_ν appearing in the following expressions (52), be determined from the boundary conditions (7).

Outside in addition to the plane wave (50), which appears on the wave, we have in addition the reflected radiation:

$$\begin{aligned}
 E_{r_a} &= \sum_1^{\infty} a_\nu i \cdot \frac{K_\nu(-x)}{x^2} \cdot P_\nu, \\
 E_{\theta_a} &= \sum_1^{\infty} \left(\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K'_\nu(-x)}{x} \cdot \frac{\partial P_\nu}{\partial \theta} + \frac{p_\nu}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x \cdot \sin \theta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} \right), \\
 E_{\varphi_a} &= \sum_1^{\infty} \left(\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K'_\nu(-x)}{x \cdot \sin \theta} \cdot \frac{\partial P_\nu}{\partial \varphi} - \frac{p_\nu}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \theta} \right), \\
 M_{r_a} &= \sum_1^{\infty} p_\nu \cdot \frac{K_\nu(-x)}{x^2} \cdot \mathfrak{P}_\nu, \\
 M_{\theta_a} &= \sum_1^{\infty} \left(\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x \cdot \sin \theta} \cdot \frac{\partial P_\nu}{\partial \varphi} + \frac{p_\nu}{\nu(\nu+1)} \cdot \frac{K'_\nu(-x)}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \theta} \right), \\
 M_{\varphi_a} &= \sum_1^{\infty} \left(-\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x} \cdot \frac{\partial P_\nu}{\partial \theta} + \frac{p_\nu}{\nu(\nu+1)} \cdot \frac{K'_\nu(-x)}{x \cdot \sin \theta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \varphi} \right).
 \end{aligned} \tag{52}$$

Determination of the Coefficients

13. We have called the radius of the small sphere ρ , the index of refraction of the medium (water) m_0 , the complex index of refraction of the material of the sphere

m . Further we use α and β for the quantities x_α and x_i for the special value $r = \rho$, and we use m' for the relative index of refraction m/m_0 :

$$\left. \begin{aligned} \alpha &= \frac{2\pi \cdot m \cdot \rho}{\lambda} = \frac{2\pi \rho}{\lambda'} \\ \beta &= \frac{2\pi \cdot m' \cdot \rho}{\lambda} = \frac{m}{m_0} \cdot \alpha = m' \cdot \alpha. \end{aligned} \right\} \quad (53)$$

Finally we use the abbreviations:

$$\left. \begin{aligned} I_\nu(\alpha) &= A_\nu & I'_\nu(\alpha) &= A'_\nu \\ I_\nu(\beta) &= B_\nu & I'_\nu(\beta) &= B'_\nu \\ K_\nu(-\alpha) &= C_\nu & K'_\nu(-\alpha) &= C'_\nu. \end{aligned} \right\} \quad (54)$$

Now we introduce into the boundary conditions:

$$\begin{aligned} (E_\rho + E_{\rho a})_{r=\rho} &= (E_{\rho i})_{r=\rho}, \\ (E_\varphi + E_{\varphi a})_{r=\rho} &= (E_{\varphi i})_{r=\rho}, \\ \alpha \cdot (M_\rho + M_{\rho a})_{r=\rho} &= \beta \cdot (M_{\rho i})_{r=\rho}, \\ \alpha \cdot (M_\varphi + M_{\varphi a})_{r=\rho} &= \beta \cdot (M_{\varphi i})_{r=\rho}, \end{aligned}$$

the expressions (50), (52), and (51) and find, since two pairs of these equations are identical, for a_ν , b_ν , p_ν , q_ν , the following conditions:

$$\begin{aligned} -(2\nu + 1) \cdot i^\nu \cdot \frac{A'_\nu}{\alpha} + a_\nu \cdot \frac{C'_\nu}{\alpha} &= b_\nu \cdot \frac{B'_\nu}{\beta}, \\ -(2\nu + 1) \cdot i^\nu \cdot A_\nu + a_\nu \cdot C_\nu &= b_\nu \cdot B_\nu, \\ (2\nu + 1) \cdot i^\nu \cdot \frac{A_\nu}{\alpha} + p_\nu \cdot \frac{C_\nu}{\alpha} &= q_\nu \cdot \frac{B_\nu}{\beta}, \\ (2\nu + 1) \cdot i^\nu \cdot A'_\nu + p_\nu \cdot C'_\nu &= q_\nu \cdot B'_\nu. \end{aligned}$$

From this it follows that:

$$\left. \begin{aligned} a_\nu &= + (2\nu + 1) \cdot i^\nu \cdot \frac{A'_\nu \cdot B_\nu \cdot \beta - B'_\nu \cdot A_\nu \cdot \alpha}{C'_\nu \cdot B_\nu \cdot \beta - B'_\nu \cdot C_\nu \cdot \alpha}, \\ p_\nu &= - (2\nu + 1) \cdot i^\nu \cdot \frac{A_\nu \cdot B'_\nu \cdot \beta - B_\nu \cdot A'_\nu \cdot \alpha}{C_\nu \cdot B'_\nu \cdot \beta - B_\nu \cdot C'_\nu \cdot \alpha}. \end{aligned} \right\} \quad (55)$$

Equations for Practical Calculations

14. The equations in (55) at first glance appear to be so simple that it is difficult to discuss them. In the case of a metallic sphere, the problem is complicated by the fact that β and of course B_ν and B'_ν are complex quantities. But even in the case of nonabsorbing spheres, where β is real, there remain two quantities that are always complex, namely C_ν and C'_ν .

If the spheres are not very large, it will always be most comfortable to calculate with (27), (28), (29) and (30). Accordingly we can set:

$$\left. \begin{aligned}
 A_\nu &= \frac{\alpha^{\nu+1}}{1 \cdot 3 \dots (2\nu+1)} \cdot f_\nu, \\
 B_\nu &= \frac{\beta^{\nu+1}}{1 \cdot 3 \dots (2\nu+1)} \cdot g_\nu, \\
 C_\nu &= (-i)^\nu \frac{1 \cdot 3 \dots (2\nu-1)}{\alpha^\nu} \cdot e^{-i\alpha \cdot (h_\nu + i\alpha \cdot k_\nu)}; \\
 A'_\nu &= \frac{(\nu+1) \cdot \alpha^\nu}{1 \cdot 3 \dots (2\nu+1)} \cdot f'_\nu, \\
 B'_\nu &= \frac{(\nu+1) \cdot \beta^\nu}{1 \cdot 3 \dots (2\nu+1)} \cdot g'_\nu, \\
 C'_\nu &= -\nu \cdot (-i)^\nu \frac{1 \cdot 3 \dots (2\nu-1)}{\alpha^{\nu+1}} \cdot e^{-i\alpha \cdot (h'_\nu + i\alpha \cdot k'_\nu)}.
 \end{aligned} \right\} \quad (56)$$

The factors f_ν , f'_ν are rapidly converging power series in α^2 ; g_ν , g'_ν are the same series in β^2 ; h_ν , k_ν , h'_ν , k'_ν are finite power sums in α^2 , thus all expressions which are relatively easy to calculate. They can be obtained directly from Eq. (27) to (30). All these sums f_ν , f'_ν , etc., begin

with term 1, for a sphere whose diameter is small with respect to the wave lengths of the light inside and outside, thus they all are very close to 1, and one obtains very simple expressions for A_{ν} , A'_{ν} etc. If we substitute (56) into (55) and write for brevity:

$$u_{\nu} = e^{i\alpha} \frac{f'_{\nu}}{h'_{\nu} + i\alpha \cdot k'_{\nu}}, \quad v_{\nu} = \frac{f'_{\nu}}{f'_{\nu}} \cdot \frac{g'_{\nu}}{g'_{\nu}}, \quad w_{\nu} = \frac{h_{\nu} + i\alpha \cdot k_{\nu}}{h'_{\nu} + i\alpha \cdot k'_{\nu}} \cdot \frac{g'_{\nu}}{g'_{\nu}}, \quad (57)$$

$$\frac{\beta^2}{\alpha^2} = \frac{m^2}{m_0^2} = m'^2, \quad (58)$$

then we find the following practical equations:

$$\left. \begin{aligned} a_{\nu} &= (-1)^{\nu-1} \cdot \frac{\nu+1}{\nu} \cdot \frac{\alpha^{2\nu+1}}{1^2 \cdot 3^2 \dots (2\nu-1)^2} \cdot u_{\nu} \cdot \frac{m'^2 - r_{\nu}}{m'^2 + \frac{\nu+1}{\nu} \cdot w_{\nu}}, \\ p_{\nu} &= (-1)^{\nu} \cdot \frac{\nu+1}{\nu} \cdot \frac{\alpha^{2\nu+1}}{1^2 \cdot 3^2 \dots (2\nu-1)^2} \cdot u_{\nu} \cdot \frac{1 - r_{\nu}}{1 + \frac{\nu+1}{\nu} \cdot w_{\nu}} \end{aligned} \right\} \quad (59)$$

15. It is not difficult to evaluate approximately how a_{ν} varies with increasing particles size. For small α the f'_{ν} , g'_{ν} etc are all rather precisely equal to 1 and consequently we can use the approximation equation:

$$\left. \begin{aligned} a_{\nu} &\sim \alpha^{2\nu+1} \cdot \frac{\nu+1}{\nu} \cdot \frac{C_{\nu}}{1^2 \cdot 3^2 \dots (2\nu-1)^2}, \\ C_{\nu} &= \frac{m'^2 - 1}{m'^2 + \frac{\nu+1}{\nu}} \cdot (-1)^{\nu-1}. \end{aligned} \right\} \quad (60)$$

Here C_{ν} is a complex number whose absolute magnitude is not very far from 1 [8]. While a_{ν} , as (60) shows, first increases with the $(2\nu + 1)^{\text{th}}$ power of α , for larger values of α the a_{ν} curve bends and never goes below a certain value. This can be seen if we take from (29a) and (19) the values for I_{ν} and K_{ν} for very large arguments. Since α is real

and $\beta = \beta' - I \cdot \beta''$ is complex, we have:

$$\begin{aligned} K_\nu(-\alpha) &\sim e^{-i\alpha}, & K'_\nu(-\alpha) &\sim -i \cdot e^{-i\alpha}, \\ I_\nu(\alpha) &\sim \sin\left(\alpha - \frac{\nu\pi}{2}\right), & I'_\nu(\alpha) &\sim \cos\left(\alpha - \frac{\nu\pi}{2}\right), \\ I_\nu(\beta) &\sim -\frac{i}{2} \cdot e^{\beta''} \cdot e^{i\left(\beta' - \frac{\nu\pi}{2}\right)}, & I'_\nu(\beta) &\sim \frac{1}{2} \cdot e^{\beta''} \cdot e^{i\left(\beta' - \frac{\nu\pi}{2}\right)}. \end{aligned}$$

Thus if we substitute this into (55), then as a limiting value for very large α we find:

$$\left. \begin{aligned} a_\nu &\sim (2\nu + 1) \cdot c_\nu, \\ c_\nu &= \frac{i^\nu \cdot e^{i\alpha}}{1 + m'} \cdot \left(\sin\left(\alpha - \frac{\nu\pi}{2}\right) + i \cdot m' \cdot \cos\left(\alpha - \frac{\nu\pi}{2}\right) \right). \end{aligned} \right\} \quad (61)$$

Here C_ν is a complex quantity varying periodically with α , whose absolute value always remains in the vicinity of 1.

Since the power $\alpha^{2\nu+1}$ appears in (60), but in addition the denominator increases rapidly with ν , a_1 must first far exceed all other coefficients. But as a_1 approaches its

limit (61), a_2 becomes significant, while all others still remain small. Later a_3 joins the other two, etc. It can be seen from the equations for f_ν , g_ν etc., that Eq. (60) remains approximately valid for the subsequent coefficients.

From this discussion it follows that, no matter how large α , beginning with a given ν , all coefficients remain so small with respect to the first that they can be completely neglected.

The radiation reflected from a small sphere essentially comprises a finite number of partial waves, but the number of partial waves increases as the sphere becomes larger.

This statement is first proven only for the "electrical oscillations" of the particle which correspond to the coefficients a_ν ; it will also be confirmed for the "magnetic oscillations," which the incident wave excites, i.e. the coefficients ρ_n , which we shall discuss in 17.

In the numerical example shown below, I shall take a diameter $2\rho = 180\mu\mu$, in order to show the optical properties of colloidal metal solutions in more detail. This value is within the range of microscopic resolution, thus it corresponds to the extreme particle sizes of colloidal solutions. *Even for the large diameter $2\rho = 180\mu\mu$, beginning with $\nu = 3$ all higher "electrical particle oscillations" are vanishingly small with respect to the first two, so we only need to calculate a_1 and a_2 .*

On the other hand, e.g. in the rainbow problem, which can be considered with the method used here, a rather large number of partial waves would have to be taken into account and would result in considerable difficulties in calculation.

The first two coefficients are:

$$\left. \begin{aligned} a_1 &= 2 \cdot \alpha^3 \cdot u_1 \cdot \frac{m'^2 - v_1}{m'^2 + 2v_1}, \\ a_2 &= -\frac{1}{6} \cdot \alpha^5 \cdot u_2 \cdot \frac{m'^2 - v_2}{m'^2 + \frac{3}{2}v_2}. \end{aligned} \right\} \quad (62)$$

If α becomes very small, then the u , v , w can be taken equal to 1 and we find:

$$\left. \begin{aligned} a_1 &= 2 \cdot \alpha^3 \frac{m'^2 - 1}{m'^2 + 2}, \\ a_2 &= -\frac{1}{6} \alpha^5 \frac{m'^2 - 1}{m'^2 + \frac{3}{2}}. \end{aligned} \right\} \quad (63)$$

For small α , naturally, a_2 is vanishingly small with respect to a_1 , and only that first partial wave remains whose existence was first demonstrated theoretically by Rayleigh, and which I shall consequently call the Rayleigh radiation for short.

16. We shall also consider briefly the special case in which the sphere consists of a completely conducting material. This case was first discussed by Thomson, and Ehrenhaft thought that the theory developed by Thomson could be applied to the optics of colloidal solutions. Although this does not follow for reasons discussed in §1, the case does have a certain historical and theoretical interest. We set:

$$m'^2 = -i \cdot \infty \quad (\text{cf. (3)}),$$

and accordingly neglect in (55) the terms in a with respect

to those in β . Then we find:

$$a_\nu = (2\nu + 1) \cdot i^\nu \cdot \frac{A_\nu'}{C_\nu'}$$

Then for small α :

$$a_\nu = (-1)^{\nu-1} \cdot \frac{\nu+1}{\nu} \cdot \frac{\alpha^{2\nu+1}}{1^2 \cdot 3^2 \dots (2\nu-1)^2} \cdot e^{i\alpha} \cdot \frac{f_\nu'}{h_\nu' + i\alpha \cdot k_\nu'}$$

For large α , (19) and (30a) give:

$$a_\nu = (2\nu + 1) \cdot i^{\nu+1} \cdot e^{i\alpha} \cdot \sin\left(\alpha - \frac{\nu-1}{2} \pi\right)$$

The absolute magnitude of this quantity oscillates regularly and periodically between zero and $(2\nu + 1)$.

The Rayleigh wave is of special interest here. The exact value of a_1 is:

$$a_1 = 3 \cdot e^{i\alpha} \frac{\alpha \cdot \cos \alpha - (1 - \alpha^2) \cdot \sin \alpha}{i\alpha + (1 - \alpha^2)} \quad (64)$$

For infinitely small α we find:

$$a_1 = 2 \cdot \alpha^3 \quad (65)$$

The characteristic difference between this equation and (63) is that the factor $(m'^2 - 1)/(m'^2 + 2)$ appears which, as we shall see, can be set approximately equal to 1 in metals and which in any case varies severely with wave length. Another very important difference is that in (65) a_1 is a purely real number, while the a_1 calculated correctly from (63) has a substantial imaginary component.

This component, as we shall see, determines absorption in the colloidal metal solutions.

17. We now discuss the "magnetic oscillations," i.e. the coefficients p_ν . For the smallest particles equation (59) cannot be used, since $(1 - v_\nu)$ then approaches zero. According to (57), (29) and (30) we have:

$$\begin{aligned}
 1 - v_\nu &= \frac{1}{f'_\nu \cdot g_\nu} \cdot (f'_\nu \cdot g_\nu - f_\nu \cdot g'_\nu), \\
 1 - v_\nu &= \frac{\beta^2 - \alpha^2}{(\nu + 1)(2\nu + 3)} \cdot \frac{1}{f'_\nu \cdot g_\nu} \cdot \left(1 - \frac{1}{2\nu + 5} \cdot \frac{\alpha^2 + \beta^2}{2!} \right. \\
 &\quad \left. + \frac{1 \cdot 3}{(2\nu + 5)(2\nu + 7)} \cdot \frac{\alpha^4 + 2 \frac{2\nu + 5}{2\nu + 3} \alpha^2 \beta^2 + \beta^4}{4!} + \dots \right) \\
 &= \frac{\beta^2 - \alpha^2}{(\nu + 1)(2\nu + 3)} \cdot \frac{l_\nu}{f'_\nu \cdot g_\nu}.
 \end{aligned} \tag{66}$$

Here l_ν , as did the f_ν , f'_ν etc, indicates a rapidly converging power series in α^2 and β^2 , which for small particle dimension is equal to 1. Furthermore we set:

$$s_\nu = e^{i\alpha} \cdot \frac{l_\nu}{g_\nu} \cdot \frac{1}{h'_\nu + i u k'_\nu} = u_\nu \cdot \frac{l_\nu}{f'_\nu \cdot g_\nu}, \tag{67}$$

and Eq. (59) gives for p_ν :

$$p_\nu = \frac{(-1)^\nu}{\nu \cdot (2\nu + 3)} \cdot \frac{\alpha^{2\nu+3}}{1^2 \cdot 3^2 \cdot \dots \cdot (2\nu - 1)^2} \cdot \frac{m'^2 - 1}{1 + \frac{\nu + 1}{\nu} \cdot u_\nu}. \tag{68}$$

For very small diameters we can set approximately:

$$p_\nu = \frac{(-1)^\nu}{(2\nu + 1)(2\nu + 3)} \cdot \frac{\alpha^{2\nu+3}}{1^2 \cdot 3^2 \cdot \dots \cdot (2\nu - 1)^2} \cdot (m'^2 - 1). \tag{69}$$

For large diameters, when the quantities A_ν , A'_ν etc. (54) are calculated according to (39a) and (19), (55) gives:

$$p_\nu \sim (2\nu + 1) \cdot i^\nu \cdot e^{i\alpha} \cdot \frac{m' \cdot \sin\left(\alpha - \frac{\nu\pi}{2}\right) + i \cdot \cos\left(\alpha - \frac{\nu\pi}{2}\right)}{m' + 1} \quad (70)$$

Thus the curve of p_ν can be described just as was done in (15) with the α_ν .

For small particles p_ν increases with increasing particle size approximately:

$$\left. \begin{aligned} p_\nu &\sim \alpha^{2\nu+3} \cdot \frac{C'_\nu}{1^2 \cdot 3^2 \cdot \dots \cdot (2\nu-1)^2 \cdot (2\nu+1) \cdot (2\nu+3)^2} \\ C'_\nu &= (m'^2 - 1) \cdot (-1)^\nu. \end{aligned} \right\} \quad (71)$$

The absolute value of C'_ν is very far from 1. For larger values of α , the p_ν curve bends and varies periodically for very large α with further increase in particle diameter:

$$p_\nu \sim (2\nu + 1) \cdot C'_\nu \quad (72)$$

C'_ν is a complex, periodically varying number whose amplitude is not far from 1.

The same statements are valid for the magnetic partial oscillations as for the electrical, and indeed the ν th magnetic oscillation runs approximately parallel to the $(\nu + 1)$ th electrical oscillation.

By comparing Eqs. (59) and (70) with (60) and (61) we see that the absolute value of p_ν in general lies somewhat below that of $\alpha_{\nu+1}$.

The first magnetic partial oscillation is, for example, always of the same order of magnitude for all particle

sizes, as is the second electrical.

Very small particles always radiate sideways only the Rayleigh wave, for the very coarse particles in a colloidal solution the second electrical and first magnetic partial oscillation are also of concern.

Thus I shall have to take into account in the numerical example to be discussed below only three coefficients in all, namely: a_1 , a_2 and p_1 . And indeed I shall calculate p_1 for coarser particles according to the following equation:

$$p_1 = -2 \cdot a^3 \cdot u_1 \frac{1 - \epsilon_1}{1 + 2\epsilon_1}, \quad (73)$$

where u_1 , v_1 , w_1 are the same quantities as in (62). For small particles the approximation equation

$$p_1 = -\frac{a^3}{15} \cdot (m^2 - 1). \quad (74)$$

is valid.

18. While the assumption of complete conductivity in the electrical partial oscillation lead to results very comparable with theoretical predictions, for the magnetic oscillations it produces completely deviant results. If in (55) we assume β infinitely large, we find:

$$p_r = -(2r + 1) \cdot i r \cdot \frac{A_r}{C_r}.$$

Thus according to (27) and (29) for small diameters:

$$p_r = (-1)^{r-1} \cdot \frac{a^{2r+1}}{1^2 \cdot 3^2 \cdot \dots \cdot (2r-1)^2} \cdot e^{i\alpha} \cdot \frac{f_r}{h_r + i a \cdot k_r},$$

a value which is of the same order of magnitude as the value of a_v found under the same assumption.

If we assume that the spheres suspended in the medium are perfect conductors, we come to the opposite result that the magnetic partial oscillation of the v^{th} order goes parallel to the electrical partial oscillation of the same ordinal number (instead of the next higher ordinal number). In particular for very fine particles we thus come to the false result that, besides the Rayleigh wave, the first magnetic oscillation appears approximately in the same order of magnitude.

Thomson, who first proved the last part of this theorem, has of course shown that the study of polarization of the light scattered laterally by colloidal metal solutions demonstrates that the result is erroneous. The characteristic polarization phenomena observed by Ehrenhaft [9] and Müller [10] are no proof of the partial validity of the assumption of perfect conductivity. We shall see below that the phenomena are clearly explained by the exact theory.

For the sake of the following numerical discussion, we note the value of p_1 :

$$p_1 = 3 \cdot e^{i\alpha} \frac{\sin \alpha - \alpha \cdot \cos \alpha}{1 + i\alpha}. \quad (75)$$

For small α :

$$p_1 = \alpha^3. \quad (76)$$

If we compare (76) with (65), we see that the amplitude of the magnetic oscillation must be exactly half that of the electrical for very small, perfectly conducting particles.

Partial Waves

19. For the following it will be useful to have an idea of how intensity and oscillation direction of the individual partial waves (particularly the first) vary from point to point on a large sphere in whose center is found the particle under discussion.

The components \mathcal{E}_r and \mathcal{E}_θ must not be taken into account, because they do not participate in energy transfer outside, according to the Poynting theorem. Thus on the surface of the sphere there are only tangential components. But now according to (13) and (14) we have for each partial wave:

$$E_\theta \cdot M_\theta + E_\varphi \cdot M_\varphi = 0,$$

i.e. the magnetic lines of force on the surface of the sphere are always normal to the electrical. Consequently to obtain a clear representation of the radiation it is sufficient to define the electrical lines of force on the surface of the sphere.

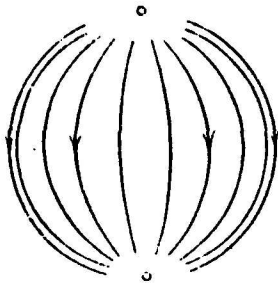


Fig. 3. First electrical partial oscillation

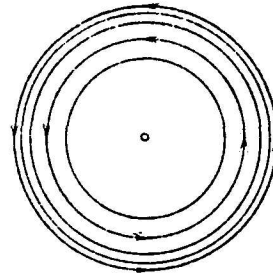


Fig. 4. First magnetic partial oscillation

Figures 3 - 10 show the electrical field lines on a surface of the sphere surrounding the particle for the first four electrical and the first four magnetic particle oscillations. The plane of the diagram is the (1.3.) plane, i.e. the plane of oscillation of the light beam generating the waves. It is the only plane of symmetry involved, and the planes behind the plane of the figure can be easily added to the hemispheres in front of those shown in the figure, since the curves on both are congruent. For the magnetic oscillations $E_r = 0$, so the lines describe closed, spherical curves, and on each of the two hemispheres at the equator ($\theta = \pi/2$) there are ν central points in which the force is zero and about which the field lines curve in ν different groups. In the electrical oscillations, on the

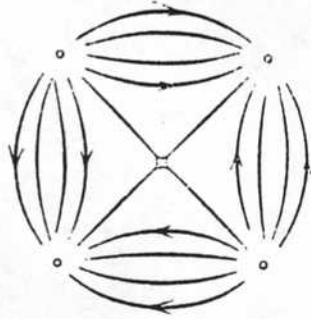


Fig. 5. Second electrical partial oscillation

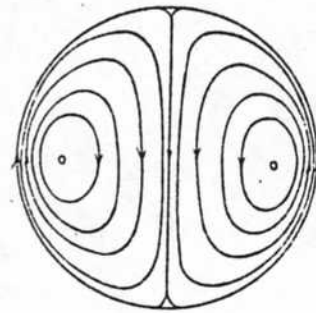


Fig. 6. Second magnetic partial oscillation

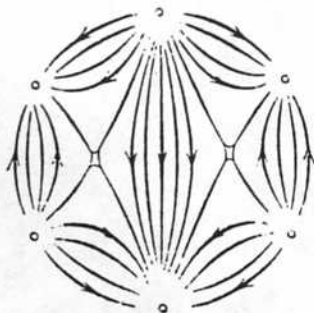


Fig. 7. Third electrical partial oscillation

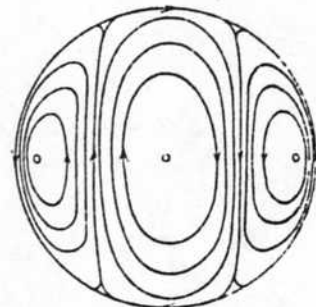


Fig. 8. Third magnetic partial oscillation

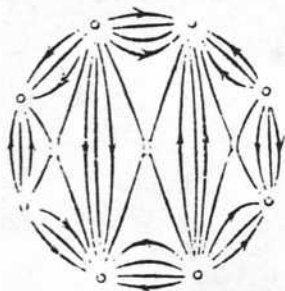


Fig. 9. Fourth electrical partial oscillation

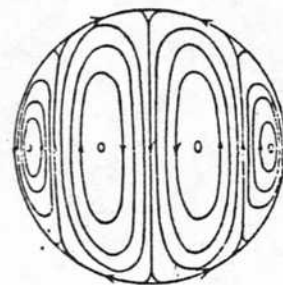


Fig. 10. Fourth magnetic partial oscillation

other hand, the lines of force lie on certain conical surfaces which all pass through ν conical diameters lying in the plane of the drawing. The indicated curves are the intersections of these conical surfaces on the sphere. These curves all spread towards the ν poles cut through the ν diameters. In reality the lines of force bend out of the spherical surface in order to be included in the interior or the exterior, depending on the phase of the oscillation, since they naturally can have neither beginning nor end (with the exception of the lines directly on the radiating particles).

We can now easily construct a picture of the magnetic lines of force. The figures of group I immediately show the magnetic lines of force of group II and vice versa, if they are rotated 90° , i.e. axes 1 and 2 are interchanged.

Diffuse Lateral Radiation

20. If we observe at an infinite distance away from the particle, then we must substitute into (52)

$$K_\nu(-x) = e^{-ix},$$

as follows from Eq. (19). Furthermore:

$$K'_\nu(-x) = -i \cdot e^{-ix},$$

thus:

$$\left. \begin{aligned}
 H_{\theta a} = +i.M_{\varphi a} &= -i \cdot \frac{k'}{2\pi} \cdot \frac{e^{-\frac{2\pi i r}{\lambda'}}}{r} \\
 &\cdot \sum_1^{\infty} \nu \left(\frac{a_\nu}{r \cdot (\nu+1)} \cdot \frac{\partial P_\nu}{\partial \vartheta} + \frac{p_\nu}{r \cdot (\nu+1)} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial \Psi_\nu}{\partial \varphi} \right), \\
 E_{\varphi a} = -i.M_{\theta a} &= -i \cdot \frac{k'}{2\pi} \cdot \frac{e^{-\frac{2\pi i r}{\lambda'}}}{r} \\
 &\cdot \sum_1^{\infty} \nu \left(\frac{a_\nu}{r \cdot (\nu+1)} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi} - \frac{p_\nu}{r \cdot (\nu+1)} \cdot \frac{\partial \Psi_\nu}{\partial \vartheta} \right).
 \end{aligned} \right\} \quad (77)$$

Here it is assumed that the light passing through the solution is rectilinearly polarized, and that the electrical oscillation direction forms axis 1. According to (47):

$$E_1 = -i.M_2 = e \frac{2\pi i r}{\lambda'}.$$

Referring to the intensity of the transmitted light as unity, the intensity of the diffusely scattered light is:

$$\left. \begin{aligned}
 J_\theta &= \frac{k'^2}{4\pi^2 \cdot r^2} \cdot \left| \sum_1^{\infty} \nu \left(\frac{a_\nu}{r \cdot (\nu+1)} \cdot \frac{\partial P_\nu}{\partial \vartheta} + \frac{p_\nu}{r \cdot (\nu+1)} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial \Psi_\nu}{\partial \varphi} \right) \right|^2, \\
 J_\varphi &= \frac{k'^2}{4\pi^2 \cdot r^2} \cdot \left| \sum_1^{\infty} \nu \left(\frac{a_\nu}{r \cdot (\nu+1)} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi} - \frac{p_\nu}{r \cdot (\nu+1)} \cdot \frac{\partial \Psi_\nu}{\partial \vartheta} \right) \right|^2.
 \end{aligned} \right\} \quad (78)$$

In these equations the straight lines indicate that the complex quantities enclosed within them should be considered as absolute values. We recognize from (78), which was already clear, that the intensity is inversely proportional to the square of the distance r . The two intensities J_θ and J_ϕ indicate the components oscillating parallel to

the meridian (J_θ) and to the circle of latitude (J_ϕ). Both components in general have a distinct phase difference which can be found by calculating the phases of the two complex quantities in Eq. (77). Thus if one observes at an arbitrarily oblique angle to the beam passing through the solution, one will obtain in general elliptically polarized light, assuming that the transmitted beam is rectilinearly polarized and that the suspended particles are so large that in addition to the (rectilinearly polarized for itself alone) Rayleigh radiation, higher partial waves are also significant.

We must exclude however all directions that lie in the two planes of symmetry 1.3. and 2.3. From the figures of §19 we can immediately conclude:

If the colloidal solution is illuminated with rectilinearly polarized light and observed in a direction that is normal to its electrical oscillation, the laterally scattered light is rectilinearly polarized, and indeed its electrical oscillation direction is parallel to that of the beam passing through the solution. If the direction of sight is unchanged and the oscillation direction of the transmitted beam is rotated about 90° , we again obtain rectilinearly polarized light, but its oscillation direction has also been rotated about 90° with respect to its previous direction.

The first case will be characterized in our equation by $\theta = \pi/2$, the second by $\phi = \pm\pi/2$.

The simpler the theorem above appears to be, the more important it may nevertheless turn out to be. Observations made by Steubing (cf. §1) of polarization of laterally scattered light showed that even if completely rectilinearly polarized light is used in this way, the lateral radiation will still contain a very small component of unpolarized light in addition to the predominantly linearly polarized light. I am very inclined to conclude from this, *that the particles suspended in colloidal solutions cannot be spheres, even if the other optical properties may agree with this assumption.*

The case where unpolarized light is used for illumination can be rapidly taken care of. We can imagine the unpolarized light divided simply into two incoherent beams of equal intensity that are rectilinearly polarized, the one so that its electrical oscillation direction is normal to the plane determined by the beam direction and the radius of vision, the other so that its electrical oscillation lies in this plane. We then obtain in the radiated light two incoherent, mutually perpendicular linearly polarized components, but in general of different intensity. This means that the radiated light is in part linearly polarized.

If an unpolarized light beam passes through the colloidal solution, the laterally scattered light is always in part linearly polarized (never elliptically). And indeed the electrical oscillation direction of the polarized component is either normal to the plane determined by the direction of the beam and the radius of vision, or it lies in this plane, depending on the size of the particle and the direction of sight.

This theorem is of course proven only under the assumption of spherical particles, but it is not doubted that it is always valid in case of amorphous (thus not dichroic) colloidal solutions.

In solutions with very small particles only the first mentioned polarization direction is of course observed, but for coarse particles, as we shall see, the second may also appear.

Intensity of the Light Scattered
Normal to the Transmitted Beam

21. Since in general we observe with unpolarized light, we are only interested in the two major cases:
I. $\theta = \pi/2$, II. $\phi = \pm\pi/2$. In both cases $E_\phi = M_\theta = 0$, thus there remains only J_θ , which we will distinguish in the

two cases as J_I and J_{II} . J_I is the intensity of the radiation whose oscillation direction is normal to the plane of vision, as we shall say briefly. J_{II} is the intensity of the beam oscillating in the plane of vision. Initially (44) and (45) give for the two cases:

$$\left. \begin{aligned} \text{I. } \theta &= \frac{\pi}{2}, \quad \sin \varphi = v, \\ \frac{\partial P_v}{\partial \vartheta} &= -\Pi_v(v), \quad \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{B}_v}{\partial \vartheta} = (1-v^2) \cdot \Pi_v'(v) - v \cdot \Pi_v(v). \end{aligned} \right\} \quad (79)$$

$$\left. \begin{aligned} \text{II. } \varphi &= \pm \frac{\pi}{2}, \quad \sin \theta = \pm v, \\ \frac{\partial P_v}{\partial \vartheta} &= \pm [(1-v^2) \cdot \Pi_v'(v) - v \cdot \Pi_v(v)], \quad \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{B}_v}{\partial \vartheta} = \mp \Pi_v(v). \end{aligned} \right\} \quad (80)$$

This must be substituted into (78). First we want to limit ourselves further to the case where we observe only normal to the beam. Thus we set $v = 0$ and now use Eqs. (40) and (41). We find:

$$\left. \begin{aligned} J_I &= \frac{\lambda'^2}{4\pi^2 r^2} \cdot \left[-\frac{a_1}{2} + \sum_1^{\infty} (-1)^{\sigma+1} \cdot \frac{(2\sigma)_a}{2^{2\sigma}} \cdot \left(\frac{a_{2\sigma+1}}{2(\sigma+1)} + p_{2\sigma} \right) \right], \\ J_{II} &= \frac{\lambda'^2}{4\pi^2 r^2} \cdot \left[\sum_1^{\infty} (-1)^{\nu+1} \cdot \frac{(2\nu)_a}{2^{2\nu}} \cdot \left(a_{2\nu} - \frac{p_{2\nu-1}}{2\nu-1} \right) \right]. \end{aligned} \right\} \quad (81)$$

These equations are written so that two coefficients of the same order of magnitude appear in each summand (cf. §17). In the numerical example, as frequently mentioned, I can limit myself to the coefficients a_1, a_2, p_1 . I shall calculate with the following equations:

$$\left. \begin{aligned} J_I &= \frac{\lambda'^2}{4\pi^2 r^2} \cdot \left[\frac{a_1}{2} \right], \\ J_{II} &= \frac{\lambda'^2}{4\pi^2 r^2} \cdot \left[a_2 - \frac{p_1}{2} \right]. \end{aligned} \right\} \quad (82)$$

J_{II} now has a significant value only for the very largest particles, and even there J_I predominates. Its value is that of the Rayleigh radiation intensity, and it is at a right angle to the electrical oscillation producing it that it has its maximum. Under other angles its intensity is:

$$J = J_1 \cdot \sin^2 \vartheta$$

and its total radiation is accordingly:

$$R = J_1 \cdot 2\pi r^2 \cdot \int_0^\pi \sin^3 \vartheta \cdot d\vartheta = \frac{8\pi}{3} \cdot r^2 \cdot J_1.$$

Accordingly if the Rayleigh radiation is measured in the principal direction, J_1 , we can find its total, i.e. the loss experienced by the light beam passing through it.

Below we shall always give the quantity:

$$R = \frac{2}{3\pi} \cdot \lambda'^2 \cdot \left| \frac{a_1}{2} \right|^2 \quad (83)$$

which at the same time is the measure for J_I :

$$J_1 = \frac{3}{8\pi} \cdot \frac{R}{r^2}. \quad (84)$$

We shall see in §26 how to find the total contribution of radiation II.

Radiation of Many Particles

22. Previously we have always restricted ourselves to calculating the light diffusely scattered by a single particle. Now we want to consider the case where very many particles are finely distributed in the medium, all of the same diameter 2ρ and with the same optical property m' . Then each individual particle is impacted not only by the directly transmitted beam, but also by the light scattered diffusely by the other spheres. The effect of this second ether oscillation on the events in each sphere and the resulting change in the total lateral radiation has been studied experimentally for the smallest particles by Lorenz ; and Maxwell-Garnett has calculated the consequences of the Lorenz theory for the optics of colloidal metal solutions (cf. §1). It is found there that the suspended particles must be closely packed in order that the reaction of the lateral radiation should have a noticeable effect on the radiation itself.

We shall consider aqueous colloidal metal solutions as optically infinitely dilute, and the total lateral irradiation will be calculated simply by multiplying the radiation that would be scattered diffusely by a single particle by the number of particles.

If any doubts remain about the validity of this assumption, they can be tested experimentally very easily by diluting the solution a bit further. If our assumption is correct, the color of the solution will remain unchanged, absorption in all parts of the spectrum being proportional to concentration. If on the other hand the assumption is false, the color must change, as Kirchner and Zsigmondy observed in concentrated gold solutions in gelatin (cf. §1). So far as I know, no one has yet succeeded in obtaining concentrated aqueous solutions of this type. In any case I shall limit the discussion to conventional dilute solutions.

In the following the concentration of the solution will be given in cubic millimeters of metal per cubic millimeter of water. If the number of particles in a cubic millimeter is N , their diameter 2ρ , thus the volume $V = 4\pi\rho^3/3$, then the concentration:

$$C = N \cdot V = \frac{4\pi}{3} \cdot N \cdot \rho^3. \quad (85)$$

On the other hand, according to (83) the total Rayleigh radiation is:

$$R = N \cdot \frac{2}{3\pi} \cdot \lambda'^2 \cdot \left| \frac{a_1}{2} \right|^2,$$

thus:

$$R = F_1 \cdot C, \quad (86)$$

where F_1 indicates a quantity that is independent of

concentration but dependent on particle size and wave length. We shall use two different equations for this quantity F_1 , depending on whether the particles are small or large:

$$F_1 = \frac{24 \pi^3}{\lambda^4} \cdot I \cdot \left| \frac{a_1}{2 a^3} \right|^2, \quad (87)$$

$$F_1 = \frac{4 \pi}{\lambda^4} \cdot \frac{1}{a^3} \cdot \left| \frac{a_1}{2} \right|^2. \quad (88)$$

For this reason the first equation is especially convenient for small particles, because, as we shall see, a_1 increases in proportion as α^3 for very small spheres. According to (62):

$$\frac{a_1}{2 a^3} = u_1 \frac{m'^2 - v_1}{m'^2 + 2 w_1},$$

where u_1, v_1, w_1 take the value 1 for very small particle diameter. Thus:

$$F_1 = \frac{24 \pi^3}{\lambda^4} \cdot I \cdot \left| u_1 \frac{m'^2 - v_1}{m'^2 + 2 w_1} \right|^2 \quad (89)$$

and for the smallest particles:

$$F_1 = \frac{24 \pi^3}{\lambda^4} \cdot I \cdot \left| \frac{m'^2 - 1}{m'^2 + 2} \right|^2. \quad (90)$$

This equation (90) is none other than the well-known Rayleigh equation [11]. It says that, for constant concentration, the radiation of a solution is the greater, the larger the particles. Indeed the intensity of the radiation is directly proportional to the particle volume. Furthermore in general the short wave beams predominate, *when the factor $(m'^2 - 1)/(m'^2 + 2)$, which depends on the optical properties of the spheres, does not vary much with the color of the*

light. But the latter presupposition does not apply in the case of metals; the light which is diffusely dispersed by colloidal metal solutions with very fine particles is generally not blue, as is true of other turbid solutions, but has the color characteristic of the metal. If $(m'^2 - 1)/(m'^2 + 2)$ is constant, the well-known Rayleigh law holds, which says that the radiation is proportional to λ'^{-4} for various colors, all other conditions being equal.

Equation (88) allows us to apply the law for Rayleigh radiation in the range for very coarse particles. As we have seen (§15), a_1 for very large particles varies as a periodic function of particle diameter with constant amplitude. Accordingly from (88) it follows that for constant concentration Rayleigh radiation decreases with increasing particle diameter, so long as the particles are large. Indeed the Rayleigh radiation is finally inversely proportional to particle volume, with the exception of periodic oscillation.

I. *Given constant concentration and a very fine distribution, the Rayleigh radiation increases as particle diameter increases, approximately in proportion as the particle volume; however when the particles have become quite large, it reaches a maximum and then decreases rapidly if the distribution becomes increasingly coarser; weaker and weaker maxima may still appear periodically.*

II. *If the small spheres consist of perfectly conducting*

or perfectly white material, the particle diameter for which the radiation maximum occurs is proportional to the wave length, and the maximum value of the radiation itself is inversely proportional to the wave length.

The second theorem, which follows directly from Eq. (88), is naturally not valid for colloidal metal solutions.

With some reservations, the appearance of this radiation maximum, which must also occur in turbid solutions of nonconductors (mastic, steam, etc.), although at a different position than for conductors, can be considered as *optical resonance*. We must however keep in mind that this "optical resonance" is only accompanied by very flat maxima, and that accordingly the energy spectrum of the diffuse radiation, even when all particles are exactly the same size, will exhibit only slight increases above an average value, if the particles have become large. The radiated light will therefore be almost white in turbid material with non-conducting particles (stea, mastic), with only a very weakly evident color nuance. The colloidal metal solutions behave similarly; as we shall see, for gold, for example, the yellow color is generally evident, corresponding to the intrinsic yellow color.

Rayleigh Radiation of Gold Solutions

23. I now begin to calculate the optical properties of a suspension of minute gold spheres in water, beginning with the Rayleigh radiation. I base my calculation on the following numbers, which are found by drawing the flattest curve possible through the experimental data found by Hagen and Rubens [12]. I have only changed the reflection coefficient in the violet, which Hagen and Rubens have certainly given as too small [13].

λ	R (H. u. R.)	$\nu \cdot x$ (H. u. R.)	R ang.	$\nu \cdot x$ ang.	m	m'^2	λ'
420	0,293	1,72	0,332	1,70	$1,70 - i \cdot 1,70$	$0,00 - i \cdot 3,20$	313
450	0,331	1,73	0,338	1,72	$1,73 - i \cdot 1,72$	$-0,017 - i \cdot 3,32$	336
500	0,470	2,07	0,480	2,02	$1,10 - i \cdot 2,02$	$-1,60 - i \cdot 2,49$	374
525	—	—	0,613	2,23	$0,79 - i \cdot 2,23$	$-2,45 - i \cdot 1,98$	393
550	0,740	2,32	0,730	2,45	$0,57 - i \cdot 2,45$	$-3,20 - i \cdot 1,57$	412
600	0,844	2,91	0,850	2,96	$0,38 - i \cdot 2,96$	$-4,84 - i \cdot 1,26$	450
650	0,889	3,58	0,888	3,54	$0,41 - i \cdot 3,54$	$-6,97 - i \cdot 1,63$	487

In this table the first column shows the wave length of the given color in vacuum, the two following columns give the reflection and absorption coefficient from Hagen and Rubens, the third and fourth columns the numbers that I used for the calculation, m is the calculated complex index of refraction of gold referred to vacuum, m'^2 is the square

of the complex index of refraction, referred to water ($m'^2 = m^2/m_0^2$) and finally λ' is the wave length in water.

Further I shall introduce another practical abbreviation:

$$\frac{a_1}{2\alpha^2} = a_1 \quad (91)$$

Then the Rayleigh radiation is calculated from (87) as:

$$\left. \begin{aligned} R_1 &= \frac{24\pi^3}{\lambda'^4} \cdot \mathcal{V} \cdot |a_1|^2, \\ a_1 &= u_1 \cdot \frac{m'^2 - v_1}{m'^2 + 2w_1} \end{aligned} \right\} \quad (92)$$

The radiation for infinitely small particles is found by setting u_1, v_1, w_1 all equal to 1. For gold the following values are found for $(a_1)_0 = (m'^2 - 1)/(m'^2 + 2)$:

$\lambda =$	420	450	500	525
	0,579 - i. 0,675	0,802 - i. 0,666	0,807 - i. 1,180	1,330 - i. 1,440
$\lambda =$	550	600	650	
	1,925 - i. 1,211	1,880 - i. 0,391	1,545 - i. 0,180	

thus in any case very different from what one would find for infinitely high conductivity. For perfect conductors we find from Eq. (65):

$$(a_1)_0 = 1$$

completely independent of wave length. In general for metals a_1 has the form:

$$a_1 = a_1' - i \cdot a_1''$$

and $|a_1|^2 = a_1'^2 + a_1''^2$. In order to clearly demonstrate the difference with respect to perfect conductors, for which $|a_1|^2 = 1$, I shall cite the values of $|a_1|^2$ for gold:

420	450	500	525	550	600	650
0,790	0,805	2,05	3,84	5,18	3,70	2,42

We can now picture the energy spectrum of the lateral radiation from very small particles, since it is equal to the product of concentration, particle volume and the quantity $24\pi^3 \cdot |a_1|^2 / \lambda^4$. The following table gives these values for both perfectly conducting spheres and for gold spheres:

	420	450	500	525
$\frac{24\pi^3}{\lambda^4} \cdot 1$	7,76 · 10 ¹⁶	5,85 · 10 ¹⁶	3,81 · 10 ¹⁶	3,13 · 10 ¹⁶
$\frac{24\pi^3}{\lambda^4} \cdot a_1 ^2$	6,12 · 10 ¹⁶	4,71 · 10 ¹⁶	7,77 · 10 ¹⁵	11,95 · 10 ¹⁵
	550	600	650	
$\frac{24\pi^3}{\lambda^4} \cdot 1$	2,59 · 10 ¹⁶	1,82 · 10 ¹⁶	1,315 · 10 ¹⁶	
$\frac{24\pi^3}{\lambda^4} \cdot a_1 ^2$	13,37 · 10 ¹⁶	6,70 · 10 ¹⁶	3,17 · 10 ¹⁶	

Here I have chosen the millimeter as the unit of length, and I will continue to do so below.

With the exception of the extreme blue and the violet, the radiation of the gold spheres is stronger than that of the perfectly conducting sphere would be.

One can thus perhaps say that the gold atoms resonate on the light waves and best in the green-yellow. We must therefore assume that in larger particles they are better coupled with the vibrating ether than in small particles, because the radiation increases with particle volume.

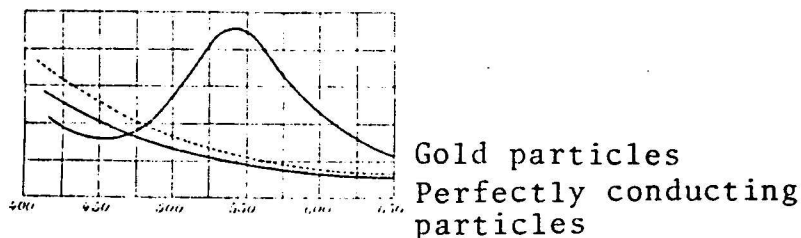


Fig. 11. Radiation of an infinitely fine suspension

Figure 11 shows a graphical representation of the radiation of small gold particles and small perfectly conducting particles. (The dotted line shows the radiation of the latter when the first magnetic vibration has been added (cf. §18).). The last mentioned radiation precisely follows the Rayleigh law (proportional to λ'^{-4}).

To find the radiation for coarser distributions, I had to calculate u_1, v_1, w_1 , which consists of series in α^2 ($\beta^2 = m'^2 \cdot \alpha^2$). I calculated for the values of α^2 given in the first column of the following Table I, and at the same time I calculated a_1 for the case of a perfect conductor for the same α^2 .

Then I calculated the radiation (87):

$$R_1 = \frac{24 \cdot \pi^3}{\lambda'^4} \cdot I \cdot \frac{|a_1|^2}{2 \alpha^3} = \frac{4 \pi}{\lambda'} \cdot \alpha^3 \cdot |a_1|^2.$$

The particle diameter belonging to each value of α^2 :

$$2 \rho = \frac{\lambda'}{\pi} \cdot \sqrt{\alpha^2}$$

Table I. Values of the Coefficients $\alpha_i = \alpha_i/2\alpha^2$.

α^2	Perfect conductor	Gold			
		420	450	500	525
0	1,00	0,579 - <i>i</i> . 0,675	0,602 - <i>i</i> . 0,666	0,807 - <i>i</i> . 1,180	1,330 - <i>i</i> . 1,440
0,2	1,04 - <i>i</i> . 0,065	0,484 - <i>i</i> . 0,755	0,505 - <i>i</i> . 0,743	0,528 - <i>i</i> . 1,312	0,850 - <i>i</i> . 1,823
0,4	1,04 - <i>i</i> . 0,188	0,343 - <i>i</i> . 0,750	0,368 - <i>i</i> . 0,757	0,216 - <i>i</i> . 1,211	0,263 - <i>i</i> . 1,640
0,6	0,961 - <i>i</i> . 0,318	0,224 - <i>i</i> . 0,699	0,244 - <i>i</i> . 0,706	0,042 - <i>i</i> . 1,029	-0,028 - <i>i</i> . 1,347
0,8	0,831 - <i>i</i> . 0,410	0,145 - <i>i</i> . 0,632	0,156 - <i>i</i> . 0,640	-0,047 - <i>i</i> . 0,849	-0,114 - <i>i</i> . 1,061
1,0	0,638 - <i>i</i> . 0,437	0,094 - <i>i</i> . 0,559	0,100 - <i>i</i> . 0,566	-0,056 - <i>i</i> . 0,715	-0,126 - <i>i</i> . 0,855
1,5	0,405 - <i>i</i> . 0,366	0,038 - <i>i</i> . 0,401	0,043 - <i>i</i> . 0,406	-0,044 - <i>i</i> . 0,480	-0,075 - <i>i</i> . 0,554
2,0	0,265 - <i>i</i> . 0,256	0,028 - <i>i</i> . 0,297	0,031 - <i>i</i> . 0,299	-0,015 - <i>i</i> . 0,349	-0,029 - <i>i</i> . 0,395
2,6	0,190 - <i>i</i> . 0,176	0,026 - <i>i</i> . 0,225	—	—	—

α^2	Gold		
	550	600	650
0	1,925 - <i>i</i> . 1,211	1,880 - <i>i</i> . 0,391	1,545 - <i>i</i> . 0,180
0,2	1,602 - <i>i</i> . 2,050	2,190 - <i>i</i> . 0,977	1,920 - <i>i</i> . 0,515
0,4	0,975 - <i>i</i> . 2,040	1,750 - <i>i</i> . 1,874	1,767 - <i>i</i> . 1,080
0,6	0,057 - <i>i</i> . 1,719	0,807 - <i>i</i> . 1,980	1,233 - <i>i</i> . 1,492
0,8	-0,107 - <i>i</i> . 1,306	0,160 - <i>i</i> . 1,612	0,673 - <i>i</i> . 1,431
1,0	-0,134 - <i>i</i> . 1,014	0,095 - <i>i</i> . 1,240	0,353 - <i>i</i> . 1,191
1,5	-0,079 - <i>i</i> . 0,627	0,009 - <i>i</i> . 0,721	0,124 - <i>i</i> . 0,718
2,0	-0,022 - <i>i</i> . 0,435	0,032 - <i>i</i> . 0,479	0,096 - <i>i</i> . 0,471
2,5	—	—	—

can be found from the following table:

α^2	$\lambda = 420$	450	500	525	550	600	650
0,2	44,6	47,8	53,2	55,9	58,6	64,0	69,3
0,4	63,1	67,6	75,2	79,1	82,9	90,5	98,1
0,6	77,3	82,9	92,2	96,8	101,5	110,8	120,1
0,8	89,3	95,8	106,5	111,8	117,2	128,0	138,7
1,0	99,8	107,0	119,0	125,0	131,0	143,0	155,0
1,5	122,2	131,1	145,8	153,1	160,5	175,2	190,0
,0	141,1	151,3	168,3	176,8	185,3	202,2	219,2
2,5	157,7	169,1					

Particle diameter in mm

Curves showing radiation as a function of particle diameter are shown in Fig. 12.

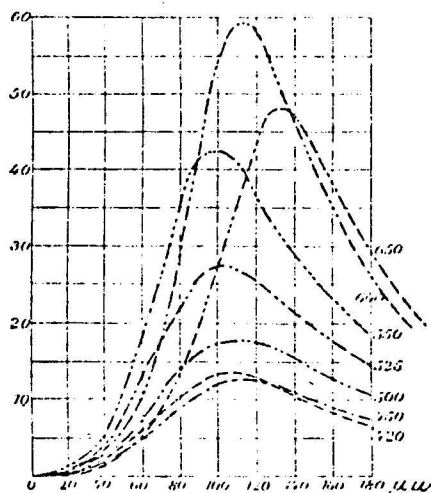


Fig. 12. "Optical resonance" of small gold spheres

The abscissa shows particle diameter in μ , the ordinate shows total radiation intensity R coming from a cubic millimeter of a solution with a concentration 10^{-6} (1 cbmm gold per liter water), in thousandths of the intensity of the light beam passing through a square millimeter.

The quantity F_1 can thus be found from the numbers on the ordinate by multiplying them by 10^3 . For comparison I have shown the corresponding curves (only the Rayleigh radiation) in the same scale for spheres of a perfect conductor. The diameters at which the radiation maximum occurs are here proportional to wave length λ' :

$$2 \varrho_{\text{Max.}} = 0,324 \cdot \lambda'.$$

The maxima decrease with increasing wave length as $1/\lambda$.

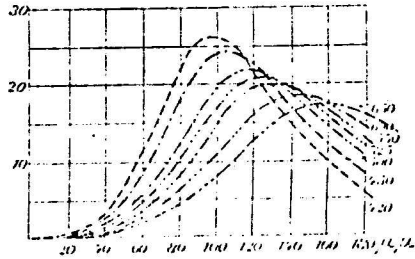


Fig. 13. "Optical resonance" of perfectly conducting spheres

With the exception of blue and violet, the radiation of the gold particles is always considerably greater than that of the perfectly conducting particles. It is, as we said above, as though the resonance of the gold atoms in the yellow were added to the "resonance" of the particles. The curve is highest at 600 $\mu\mu$ (orange-yellow). The diameters of the most intensely radiating particles are:

	420	450	500	525	550	600	650
$2 \rho_{\text{Max.}}$	105	111	110	100	96	113	131
λ'	113	336	374	393	412	450	487
$\frac{2 \rho_{\text{Max.}}}{\lambda'}$	0,336	0,331	0,294	0,255	0,233	0,252	0,269

Thus $2\rho_{\text{max}}$ in general lies between $\lambda'/4$ and $\lambda'/3$.

The energy spectra of the radiations for given particle sizes can be found easily from the curves of Fig. 12.

The following numbers can be taken from the figure:

2ρ	420	450	500	525	550	600	650
20	0,262	0,199	0,338	0,546	0,637	0,299	0,139
40	2,10	1,60	2,72	4,62	5,90	2,92	1,35
60	6,2	5,0	8,0	13,7	19,7	12,3	5,9
80	10,4	9,1	14,1	22,9	37,8	33,0	14,7
100	13,2	12,0	17,2	27,1	42,3	55,5	29,0
120	12,5	12,0	17,1	25,0	36,0	57,5	45,0
140	10,0	10,5	15,0	20,8	27,9	44,5	46,2
160	7,9	8,5	12,4	17,1	22,5	33,3	36,8
180	6,3	7,2	10,4	13,8	17,7	25,0	28,0

The curves of Fig. 14 are constructed with these numbers. We see then that:

Small spherical gold particles must appear yellow-green in the ultra microscope. The larger they become, the more their color changes towards yellow and red-yellow. Given a constant concentration, solutions whose particle diameter lies between 100 and 140 $\mu\mu$ radiate the most intensely; their particles send out primarily orange colored light. The most intensely radiating solutions are consequently brown in incident light.

Constructing the corresponding radiation curves from the "resonance curve" of perfectly conducting spheres clearly reveals that these color phenomena are due to the special optical properties of gold. I have demonstrated this in Fig. 15 for particle sizes $2\rho = 100, 120, 140, 160$ and $180 \mu\mu$. These are already rather coarse turbidities. While for $2\rho = 100$ the curve increases quite sharply towards violet, it flattens out increasingly with increasing particle

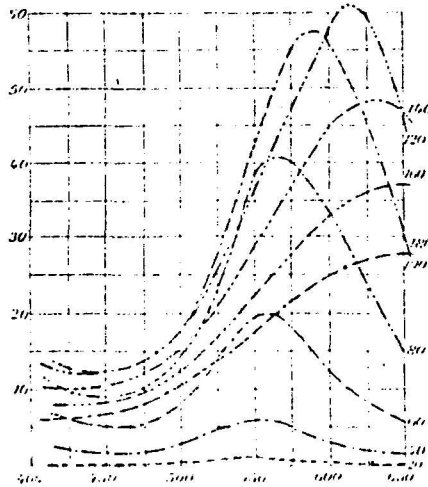


Fig. 14. Radiation of colloidal gold solutions

size and shows a very weak maximum which at 180 $\mu\mu$ lies at a wave length that is greater than 650 $\mu\mu$. The radiated light from particles larger than 100 $\mu\mu$ is in fact rather white with a dark tone which, depending on particle size, can be blue, green, yellow or red. According to Fig. 15 however, at 180 $\mu\mu$ orange must be rather clearly pronounced; this is associated with the fact that we have limited the problem to Raleigh radiation. If the subsequent partial waves were to be taken into account, all curves and particularly the last would be even more flattened, as an easy calculation will show.

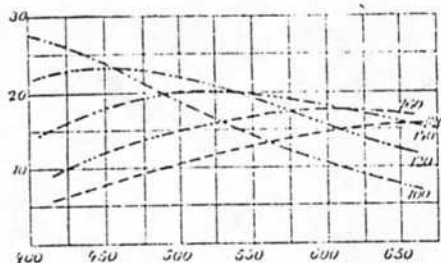


Fig. 15. Radiation from coarse, perfectly conducting spheres

Colors very similar to those associated with the imaginary perfectly conducting particles will be obtained with colorless particles. Using the equations that I used, one can easily calculate the phenomena, for example, of colored steam; the curves obtained will be similar to those in Fig. 15, but with different particle sizes.

Polarization of Diffusely Scattered Light from Gold Solutions

24. Now we proceed to calculate coefficients a_2 and p_1 . For convenience we shall introduce new notations:

$$a_2 = -\frac{a_2}{2a^3}, \quad p_1 = \frac{p_1}{2a^2}. \quad (93)$$

From (62), (73), and (74) it follows that:

$$a_2 = \frac{a^2}{12} \cdot n_2 \frac{m'^2 - r_2}{m'^2 + 1,5 \cdot r_2}, \quad p_1 = n_1 \cdot \frac{r_1 - 1}{1 + 2r_1}, \quad (94)$$

and for small values of α :

$$a_2 = \frac{a^2}{12} \cdot \frac{m'^2 - 1}{m'^2 + 1,5}, \quad p_1 = \frac{a^2}{30} \cdot (1 - m'^2). \quad (95)$$

Here u_1, v_1, w_1 are the functions of α^2 already used to calculate a_1 ; u_2, v_2, w_2 are taken from Eq. (57) and (27) to (30).

From the values of a_2 and p_1 shown in Tables II and III we see that the second electrical and first magnetic partial waves are significant with respect to the Rayleigh radiation only for very coarse distribution. They appear most strongly at approximately $550 \mu\mu$. If we calculate from (82) for $550 \mu\mu$ the ratio J_{II}/J_I for the radiation normal to the transmitted beam:

$$\frac{J_{II}}{J_I} = \frac{a_2 - p_1^2}{a_1^2} = \frac{|a_2 + p_1^2|}{a_1^2}, \quad (96)$$

then we find:

α^2	small	1	2
$\frac{J_{II}}{J_I}$	$0,016 \cdot \alpha^2$	0,059	0,642
$2q$	—	131 $\mu\mu$	185,3 $\mu\mu$

One of the curves in Fig. 16 is constructed with these numbers. Now as customary we can give the amount of polarized light in the radiation in percent:

$$P = \frac{J_I - J_{II}}{J_I + J_{II}}$$

In our example:

α^2	1	2
P	0,885	0,22
$2q$	131 $\mu\mu$	185,3 $\mu\mu$

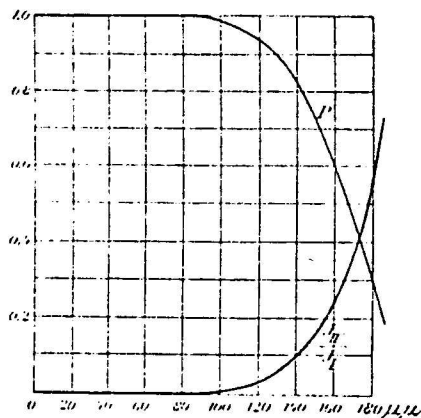


Fig. 16. Polarization of light radiated under 90° at the $550 \mu\mu$ wave length

The quantity P is shown as the second curve in Fig. 16.

If the radiation of a colloidal gold solution is not completely polarized at an angle of 90° to the transmitted beam, then it follows that the solution contains particles whose diameter is much greater than $100 \mu\mu$. Given a particle size of $130 \mu\mu$, the polarization amounts to approximately 90%.

Table II. Values of $a_1 = -\frac{a_2}{2 \cdot a^3}$.

a^3	420	450	500	525	550	600	650
klein	$a^3 \times$ 0,058 - i.0,053	$a^3 \times$ 0,060 - i.0,052	$a^3 \times$ 0,087 - i.0,081	$a^3 \times$ 0,121 - i.0,085	$a^3 \times$ 0,149 - i.0,061	$a^3 \times$ 0,138 - i.0,021	$a^3 \times$ 0,118 - i.0,010
1	0,047 - i.0,059	0,049 - i.0,058	0,063 - i.0,101	0,102 - i.0,124	0,152 - i.0,114	0,157 - i.0,043	0,132 - i.0,023
2	0,053 - i.0,118	0,057 - i.0,119	0,038 - i.0,188	0,052 - i.0,258	0,108 - i.0,322	0,264 - i.0,261	0,260 - i.0,151
2,5	0,039 - i.0,140						

Table III. Values of $p_1 = \frac{p_1}{2 \cdot \alpha^2}$.

α^2	420	450	500	525	550	600	650
klein	$\alpha^2 \times$ 0,033 + i.0,107	$\alpha^2 \times$ 0,034 + i.0,111	$\alpha^2 \times$ 0,087 + i.0,083	$\alpha^2 \times$ 0,115 + i.0,066	$\alpha^2 \times$ 0,140 + i.0,052	$\alpha^2 \times$ 0,195 + i.0,042	$\alpha^2 \times$ 0,266 + i.0,054
1	0,045 + i.0,065	0,045 + i.0,066	0,063 + i.0,042	0,072 + i.0,031	0,081 + i.0,025	0,100 + i.0,020	0,117 + i.0,021
2	0,064 + i.0,072	0,065 + i.0,073	0,078 + i.0,051	0,087 + i.0,042	0,094 + i.0,037	0,110 + i.0,036	0,123 + i.0,041
1,5	0,065 + i.0,071						

Solutions with particles larger than 100 $\mu\mu$ are now those that radiate primarily yellow and red. We will see below that they are always blue transparent.

Only the particles of blue gold solutions radiate light that is only slightly polarized at an angle of 90° with respect to the transmitted beam.

This theorem can only be stated with a reservation, since it is derived under the assumption of spherical particles. There are in any case blue solutions that radiate almost completely polarized light at an angle of 90°. But certainly one can say that there can be no red solutions that do not give completely polarized light at an angle of 90°. If observations give a different result (14), then it follows that the solutions were inhomogeneous, that they contained many weakly radiating but strongly absorbing red particles and relatively few strongly radiating blue particles.

25. We now want to calculate the polarization of the light at various angles with respect to the transmitted beam. We shall call λ the angle measured with respect to the direction from which the beam comes. In the two major cases I and II (§21):

$$\begin{aligned} \text{I. } \vartheta &= \frac{\pi}{2}, \quad \varphi = \frac{\pi}{2} - \gamma, \quad v = \cos \gamma \\ J_{\text{I}} &= \frac{\lambda^2}{4\pi^2 r^2} \cdot \left| \sum_1^{\infty} \left\{ \frac{a_\nu}{\nu(\nu+1)} \cdot H_\nu + \frac{b_\nu}{\nu(\nu+1)} \cdot (v \cdot H_\nu - (1-v^2) \cdot H'_\nu) \right\} \right|^2 \\ \text{II. } \varphi &= \frac{\pi}{2}, \quad \vartheta = \frac{\pi}{2} - \gamma, \quad v = \cos \gamma \\ J_{\text{II}} &= \frac{\lambda^2}{4\pi^2 r^2} \cdot \left| \sum_1^{\infty} \left\{ \frac{a_\nu}{\nu(\nu+1)} \cdot (v \cdot H_\nu - (1-v^2) \cdot H'_\nu) + \frac{b_\nu}{\nu(\nu+1)} \cdot H_\nu \right\} \right|^2 \end{aligned}$$

Since we will deal only with the relative value $J_{\text{II}}:J_{\text{I}}$ we shall calculate only the quantities:

$$\mathfrak{S}_{\text{I}} = \frac{4\pi^2 r^2}{\lambda^2} \cdot \frac{J_{\text{I}}}{a_0^2}, \quad \mathfrak{S}_{\text{II}} = \frac{4\pi^2 r^2}{\lambda^2} \cdot \frac{J_{\text{II}}}{a_0^2}$$

Furthermore we limit ourselves as always to the first terms. We find

$$\begin{cases} \mathfrak{S}_{\text{I}} = |a_1 - (a_2 - v_1) \cdot \cos \gamma|^2, \\ \mathfrak{S}_{\text{II}} = |a_1 \cdot \cos \gamma - a_2 \cdot \cos 2\gamma + v_1|^2. \end{cases} \quad (97)$$

Here a_1, a_2, v_1 are the quantities whose values can be taken from Tables I, II and III. By graphical interpolation we find from these tables:

$2\vartheta = 160 \mu\mu$	$180 \mu\mu$
$a_1 = -0,08 - i \cdot 0,63$	$-0,03 - i \cdot 0,47$
$a_2 = 0,15 - i \cdot 0,22$	$0,12 - i \cdot 0,30$
$v_1 = 0,09 + i \cdot 0,03$	$0,09 + i \cdot 0,03$

for $\lambda = 550 \mu\mu$

If this is substituted into (97), then $\mathfrak{S}_I + \mathfrak{S}_{II}$ gives the total radiation as a function of the angle γ , $\mathfrak{S}_I - \mathfrak{S}_{II}$ gives the excess of polarized light over unpolarized, $P = (\mathfrak{S}_I - \mathfrak{S}_{II}) / (\mathfrak{S}_I + \mathfrak{S}_{II})$ is the percent content of polarized light. Since we are dealing only with a relative value, I divided the individual values of \mathfrak{S} by $(\mathfrak{S}_I + \mathfrak{S}_{II})_{90^\circ}$; i.e. I referred everything to the radiation taking place under an angle $\gamma = 90^\circ$ as unity. The calculated values are:

		$2\rho = 160 \mu\mu.$					
		0°	20°	40°	60°	80°	90°
Total radiation	} 0,64	0,67	0,75	0,88	0,97	1,00	
	Polarized	0	0,02	0,06	0,13	0,44	0,62
P		0	0,03	0,09	0,21	0,46	0,62
		100°	120°	140°	160°	180°	
Total radiation	} 1,06	1,35	2,01	2,76	3,17		
	Polarized	0,80	0,97	0,72	0,29	0	
P		0,76	0,72	0,36	0,10	0	
		$2\rho = 180 \mu\mu.$					
		0°	20°	40°	60°	80°	90°
Total radiation	} 0,12	0,17	0,37	0,68	0,95	1,00	
	Polarized	0	-0,02	-0,10	-0,15	+0,06	0,31
P		0	-0,11	-0,27	-0,22	+0,06	0,31
		100°	120°	140°	160°	180°	
Total radiation	} 1,04	1,33	2,16	3,30	3,85		
	Polarized	0,62	1,10	0,65	0,35	0	
P		0,60	0,82	0,30	0,10	0	

In both cases the polarization maximum is thus shifted 90° towards increasing q and in one case ($2\rho = 160 \mu\mu$) towards $\gamma = 110^\circ$, in the other case ($180 \mu\mu$) towards $\gamma = 120^\circ$. The fact that these are the angles is apparently due to the

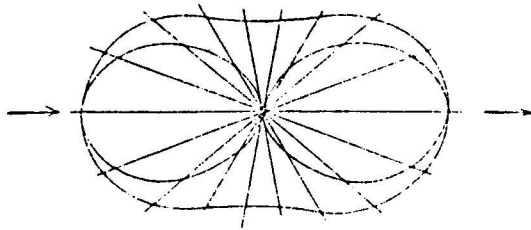


Fig. 17. Radiation diagram of an infinitely small gold sphere

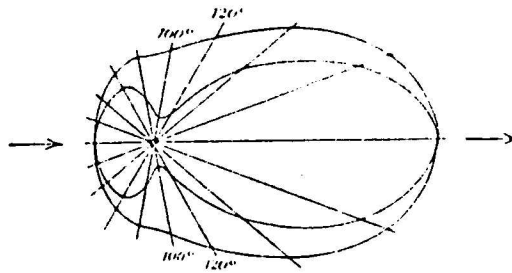


Fig. 18. Radiation diagram of a gold sphere 160 μ in diameter

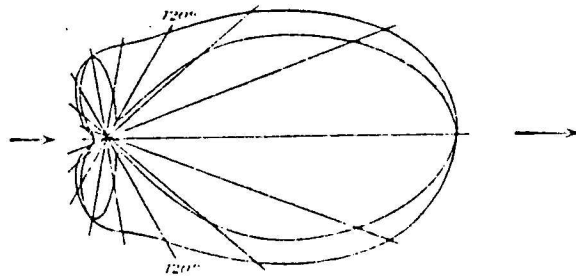


Fig. 19. Radiation diagram of a gold sphere 180 μ diameter

special optical nature of gold, since for other metals generally smaller angles were found experimentally. The negative sign in front of some numbers in the case of $2\rho = 180 \mu$ means that here there is an excess of polarized light that oscillates *normal to the Rayleigh radiation*.

The most striking of these numbers is however the high variability of the values with radiation angle. Given large particles, the radiation toward the side toward which the transmitted beam is pointed is extraordinarily predominant. I have tried to make this behavior clear by means of several radiation diagrams in which I indicated the intensity of the radiation by the length of the radius vectors emanating from the particle. The outer curves in Figs. 17-20 cut off pieces of the radii which are proportional to the intensity of the total radiation, likewise the inner curves indicate unpolarized radiation, the intermediate piece of the radius vector is thus proportional to the polarized radiation.

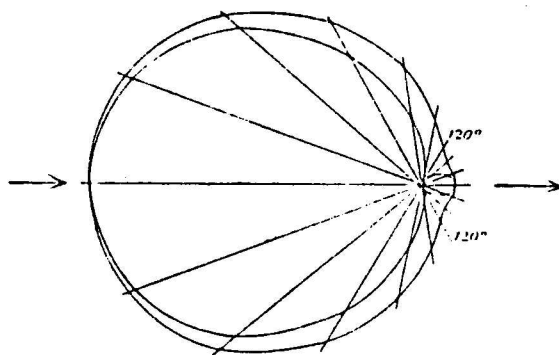


Fig. 20. Radiation diagram of an imaginary, perfectly conducting, infinitely small sphere.

In conclusion we can say:

If the polarization maximum of the laterally scattered light of a turbid solution is shifted 90° towards increasing

γ , this is a sure indication that the solution contains very large particles. At the same time the lateral radiation must then be extraordinarily much more intensive towards the side towards which the exciting light beam passes ($\gamma > 90^\circ$) than towards the other side ($\gamma < 90^\circ$).

For comparison I have also constructed the radiation diagram for very fine particles and one for very fine particles of an imaginary perfect conductor (Figs. 17, 20). It can be seen from the latter that the intensities are just the reverse from the large gold particles. Should there still remain any doubt that the explanation of the polarization phenomena observed by Ehrenhaft and Muller is correct, the question can be resolved very easily by comparing the intensities scattered under different angles; this can probably be done with the naked eye.

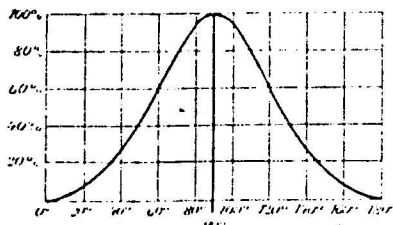


Fig. 21. Polarization of the diffusely scattered light given infinitely fine particles

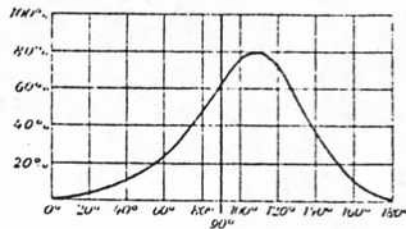


Fig. 22. Polarization of the diffusely scattered light for 160 $\mu\mu$ particles

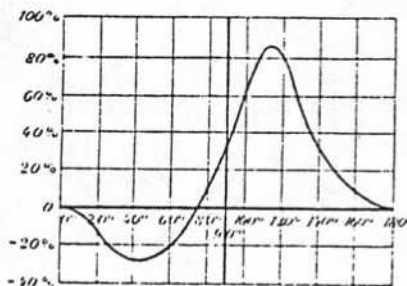


Fig. 23. Polarization of the diffusely scattered light for 180 $\mu\mu$ particles

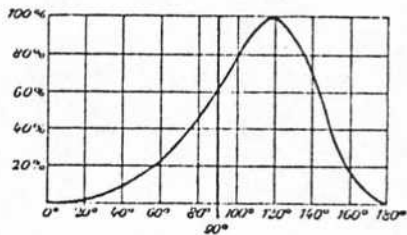


Fig. 24. Polarization of the diffusely scattered light from imaginary, perfectly conducting, infinitely small particles

Curves of P (Figs. 21 - 24) require no further explanation.

Absorption of Turbid Media

26. To calculate absorption we shall determine how much energy would be consumed by a particle if it alone were present. The absorption coefficients of the solution are found by multiplying by the number of particles in a cubic millimeter.

We imagine a spherical surface of radius r drawn about the center of the sphere, and let $x = 2\pi r/\lambda'$ be a very large number. The current density of the energy flow through this spherical surface towards the outside is at any moment:

$$\mathcal{E}_\rho \cdot \mathfrak{H}_\varphi - \mathcal{E}_\varphi \cdot \mathfrak{H}_\rho.$$

We must now integrate this instantaneous energy flow over one second to arrive at the intensity of the light. But according to (2):

$$\mathcal{E}_\rho = \Re [E_\rho \cdot e^{2\pi i n t}], \quad \mathfrak{H}_\rho = \Re [H_\rho \cdot e^{2\pi i n t}] \quad \text{etc.}$$

[] means "real part of." If this is substituted, then we find the desired time integral:

$$\int_{t=0}^{t=1} (\mathcal{E}_\rho \cdot \mathfrak{H}_\varphi - \mathcal{E}_\varphi \cdot \mathfrak{H}_\rho) \cdot dt = \frac{1}{2} [(E_\rho \cdot H_\varphi) - (E_\varphi \cdot H_\rho)].$$

Here the parentheses mean that the "scalar product" of the two complex factors is to be formed, i. e. the product of the two absolute values with the

cosine of the phase difference. If:

$$E_{\theta} = E'_{\theta} + i \cdot E''_{\theta}, \quad H_{\phi} = H'_{\phi} + i \cdot H''_{\phi},$$

where E'_{θ} , E''_{θ} etc. indicate real quantities, then:

$$(E_{\theta} \cdot H_{\phi}) = E'_{\theta} \cdot H'_{\phi} + E''_{\theta} \cdot H''_{\phi}.$$

Since the same rules are valid for the scalar multiplication of two quantities as for conventional multiplication, we shall simply omit the parentheses from the following discussion. Where two complex quantities E and H are to be multiplied, the scalar product will always be implied. According to (4) we can replace the complex quantities H_{θ} and H_{ϕ} by $i \cdot M_{\theta}$ and $i \cdot M_{\phi}$. The intensity of the normal components of the lights passing through the spherical surface is then some factor times:

$$E_{\theta} \cdot i M_{\phi} - E_{\phi} \cdot i M_{\theta}.$$

This factor is chosen so that the intensity of the beam passing through the solution is equal to 1. We must substitute for E_{θ} , M_{ϕ} etc from (51) and (52) the values $E_{\theta}^E + E_{\theta a}$, $M_{\phi} + M_{\phi a}$. Then the integral over the spherical surface that represents the total amount of light passing through the spherical surface towards the outside divides into three components:

$$\begin{aligned}
I &= \int_0^\pi \int_0^{2\pi} (E_\vartheta \cdot iM_\varphi - E_\varphi \cdot iM_\vartheta) \cdot r^2 \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi, \\
II &= \int_0^\pi \int_0^{2\pi} (E_{\vartheta a} \cdot iM_\varphi + E_\vartheta \cdot iM_{\varphi a} - E_{\varphi a} \cdot iM_\vartheta - E_\varphi \cdot iM_{\vartheta a}) r^2 \sin \vartheta d\vartheta d\varphi, \\
III &= \int_0^\pi \int_0^{2\pi} (E_{\vartheta a} \cdot iM_{\varphi a} - E_{\varphi a} \cdot iM_{\vartheta a}) r^2 \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi.
\end{aligned}$$

Component I contains the energy flow of the transmitted light beam. If it were not at all affected by the particle, it is immediately obvious that component I would be zero. Component III is a positive quantity, namely the total laterally radiated energy; thus it also gives the component of the absorption coefficient which is used to calculate diffuse radiation. Component II is negative, representing the total energy loss of the transmitted beam. Thus it gives the total absorption coefficient which is determined both by the diffuse radiation and the actual absorption of radiant energy in the particle.

Since we assumed that $x = 2\pi r/\lambda'$ is infinitely large with respect to 1, then according to (29a) and (19) we can set:

$$\begin{aligned}
J_\nu(x) &= \sin\left(x - \frac{\nu\pi}{2}\right), & I'_\nu(x) &= \cos\left(x - \frac{\nu\pi}{2}\right); \\
K_\nu(-x) &= e^{-ix}, & K'_\nu(-x) &= -i \cdot e^{-ix}.
\end{aligned}$$

Furthermore if we introduce the following abbreviations:

$$A_r = \frac{\kappa'}{2\pi} \cdot \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu-1} \cdot \cos\left(x - \frac{\nu\pi}{2}\right),$$

$$B_r = \frac{\kappa'}{2\pi} \cdot \frac{2\nu+1}{\nu(\nu+1)} \cdot i^{\nu} \cdot \sin\left(x - \frac{\nu\pi}{2}\right),$$

$$C_r = \frac{\kappa'}{2\pi} \cdot \frac{a_{\nu}}{\nu(\nu+1)} \cdot e^{-ix},$$

$$D_r = \frac{\kappa'}{2\pi} \cdot \frac{b_{\nu}}{\nu(\nu+1)} \cdot e^{-ix},$$

then for the factors of the scalar products to be calculated we find:

$$\begin{aligned} E_{\theta} + E_{\theta a} &= \sum_1^{\infty} \frac{A_r + C_r}{r} \cdot \frac{\partial P_{\nu}}{\partial \vartheta} - \sum_1^{\infty} \frac{B_r + D_r}{r} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{F}_{\nu}}{\partial \varphi}, \\ E_{\varphi} + E_{\varphi a} &= \sum_1^{\infty} \frac{A_r + C_r}{r} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial P_{\nu}}{\partial \varphi} + \sum_1^{\infty} \frac{B_r + D_r}{r} \cdot \frac{\partial \mathfrak{F}_{\nu}}{\partial \vartheta}, \\ -i(M_{\theta} + M_{\theta a}) &= \sum_1^{\infty} \frac{B_r + C_r}{r} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial P_{\nu}}{\partial \varphi} + \sum_1^{\infty} \frac{A_r + D_r}{r} \cdot \frac{\partial \mathfrak{F}_{\nu}}{\partial \vartheta}, \\ i(M_{\varphi} + M_{\varphi a}) &= \sum_1^{\infty} \frac{B_r + C_r}{r} \cdot \frac{\partial P_{\nu}}{\partial \vartheta} - \sum_1^{\infty} \frac{A_r + D_r}{r} \cdot \frac{1}{\sin \vartheta} \cdot \frac{\partial \mathfrak{F}_{\nu}}{\partial \varphi}. \end{aligned}$$

The light intensity itself is now calculated from:

$$\begin{aligned} &(E_{\theta} + E_{\theta a}) \cdot i(M_{\varphi} + M_{\varphi a}) - (E_{\varphi} + E_{\varphi a}) \cdot i(M_{\theta} + M_{\theta a}) \\ &= \sum_1^{\infty} \sum_1^{\infty} \frac{(A_r + C_r)(B_{\mu} + D_{\mu})}{r^2} \cdot \left(\frac{\partial P_r}{\partial \vartheta} \cdot \frac{\partial P_{\mu}}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial P_r}{\partial \varphi} \cdot \frac{\partial P_{\mu}}{\partial \varphi} \right) \\ &- \sum_1^{\infty} \sum_1^{\infty} \frac{(A_r + C_r)(A_{\mu} + D_{\mu}) + (B_r + C_r)(B_{\mu} + D_{\mu})}{r^2} \cdot \frac{1}{\sin \vartheta} \cdot \left(\frac{\partial P_r}{\partial \vartheta} \cdot \frac{\partial \mathfrak{F}_{\mu}}{\partial \varphi} - \frac{\partial P_r}{\partial \varphi} \cdot \frac{\partial \mathfrak{F}_{\mu}}{\partial \vartheta} \right) \\ &+ \sum_1^{\infty} \sum_1^{\infty} \frac{(B_r + D_r)(A_{\mu} + D_{\mu})}{r^2} \cdot \left(\frac{\partial \mathfrak{F}_r}{\partial \vartheta} \cdot \frac{\partial \mathfrak{F}_{\mu}}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial \mathfrak{F}_r}{\partial \varphi} \cdot \frac{\partial \mathfrak{F}_{\mu}}{\partial \varphi} \right). \end{aligned}$$

We can now integrate over the spherical surface as follows:

$$\int_0^{2\pi} \int_0^\pi \frac{\partial P_\nu}{\partial \vartheta} \cdot \frac{\partial P_\mu}{\partial \vartheta} \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi = - \int_0^{2\pi} \int_0^\pi P_\nu \cdot \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \cdot \frac{\partial P_\mu}{\partial \vartheta} \right) \cdot d\vartheta \cdot d\varphi$$

$$\int_0^{2\pi} \int_0^\pi \frac{\partial P_\nu}{\partial \varphi} \cdot \frac{\partial P_\mu}{\partial \varphi} \cdot \frac{d\vartheta \cdot d\varphi}{\sin \vartheta} = - \int_0^{2\pi} \int_0^\pi P_\nu \cdot \frac{\partial^2 P_\mu}{\partial \varphi^2} \cdot \frac{d\vartheta \cdot d\varphi}{\sin \vartheta}$$

Using Eq. (11) we find:

$$\int_0^{2\pi} \int_0^\pi \left(\frac{\partial P_\nu}{\partial \vartheta} \cdot \frac{\partial P_\mu}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \cdot \frac{\partial P_\nu}{\partial \varphi} \cdot \frac{\partial P_\mu}{\partial \varphi} \right) \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi$$

$$= \mu \cdot (\mu + 1) \int_0^{2\pi} \int_0^\pi P_\nu \cdot P_\mu \cdot \sin \vartheta \cdot d\vartheta \cdot d\varphi.$$

Thus according to (46):

$$= 0, \quad \nu \neq \mu$$

$$= 2\pi \cdot \frac{\nu^2 \cdot (\nu + 1)^2}{2\nu + 1}, \quad \nu = \mu.$$

We arrive at the same conclusion if we substitute

$\mathfrak{P}_\nu, \mathfrak{P}_\mu$ for P_ν, P_μ . Finally:

$$\int_0^{2\pi} \int_0^\pi \left(\frac{\partial P_\nu}{\partial \vartheta} \cdot \frac{\partial \mathfrak{P}_\mu}{\partial \varphi} - \frac{\partial P_\nu}{\partial \varphi} \cdot \frac{\partial \mathfrak{P}_\mu}{\partial \vartheta} \right) \cdot d\vartheta \cdot d\varphi$$

$$= \int_0^{2\pi} \left[P_\nu \cdot \frac{\partial \mathfrak{P}_\mu}{\partial \varphi} \right]_{\vartheta=0}^{\vartheta=\pi} \cdot d\varphi - \int_0^\pi \left[P_\nu \cdot \frac{\partial \mathfrak{P}_\mu}{\partial \vartheta} \right]_{\varphi=0}^{\varphi=2\pi} \cdot d\vartheta = 0.$$

The energy flow out of the spherical surface is accordingly:

$$2\pi \cdot \sum_1^\infty ((A_\nu + C_\nu) \cdot (B_\nu + D_\nu) + (A_\nu + D_\nu) \cdot (B_\nu + C_\nu)) \cdot \frac{\nu^2 \cdot (\nu + 1)^2}{2\nu + 1}.$$

This expression is now decomposed into the above-mentioned three parts:

$$I = 4\pi \cdot \sum_1^\infty (A_\nu \cdot B_\nu) \cdot \frac{\nu^2 \cdot (\nu + 1)^2}{2\nu + 1} = 0,$$

$$II = 2\pi \cdot \sum_1^\infty (A_\nu + B_\nu) \cdot (C_\nu + D_\nu) \cdot \frac{\nu^2 \cdot (\nu + 1)^2}{2\nu + 1}$$

$$= \frac{\lambda'^2}{2\pi} \cdot \sum_1^\infty (-1)^{\nu-1} \cdot (i e^{-i\pi} \times (a_\nu - p_\nu) e^{-i\pi})$$

$$= \frac{\lambda'^2}{2\pi} \cdot \Im \left(\sum_1^\infty (-1)^{\nu-1} \cdot (a_\nu - p_\nu) \right).$$

$$\text{III} = 2\pi \cdot \sum_1^{\infty} (C_v^2 + D_v^2) \cdot \frac{v^2 \cdot (v+1)^2}{2v+1} = \frac{k^2}{2\pi} \cdot \sum_1^{\infty} \frac{a_v^2 + p_v^2}{2v+1}$$

If the number of particles per cubic millimeter is N , then II gives as the absorption coefficient of the solution per millimeter:

$$k = N \cdot \frac{k^2}{2\pi} \cdot \Im m \left(\sum_1^{\infty} (-1)^v \cdot (a_v - ip_v) \right). \quad (98)$$

According to III, radiation loss alone per millimeter amounts to:

$$k' = N \cdot \frac{k^2}{2\pi} \cdot \sum_1^{\infty} \frac{a_v^2 + |p_v|^2}{2v+1}. \quad (99)$$

The symbol $\Im m()$ in (98) indicates that the imaginary part of the complex number inside the parentheses is to be taken. The vertical lines in Eq. (99) indicate that the absolute value of the quantities enclosed within them is to be formed.

Absorption of Colloidal Gold Solutions

27. We can limit ourselves to the coefficients a_1, a_2, p_1 for the colloidal solutions. Furthermore as above we want to introduce the three quantities

$$a_1 = \frac{a_1}{2a^3}, \quad a_2 = -\frac{a_2}{2a^3}, \quad p_1 = \frac{p_1}{2a^3}$$

Since further the concentration of the solution is

$$C = N \cdot V, \quad V = \frac{4\pi a^3}{3} = \frac{a^3 \cdot \lambda'^3}{6\pi^2},$$

we find:

$$\left. \begin{aligned} k &= C \cdot K, \\ K &= \frac{6\pi}{\lambda'} \cdot \text{Im}(-a_1 - a_2 + v_1). \end{aligned} \right\} \quad (100)$$

For very small particle diameters, the quantity K varies only slowly as the particles become larger.

Given a very fine distribution of the metal in solution, the color is independent of particle size, absorption coefficient is simply proportional to the concentration of the solution.

This theory can of course be valid only up to a certain lower limit on the smallness of the particles, since the gold atoms behave differently in the optical sense than do small gold spheres. It would therefore be no doubt very interesting to study the absorption of solutions with the smallest amicroscopic particles and somehow to follow optically the processes by which the gold particles are constructed from the atoms.

If the gold particles become greater than about $10 \mu\mu$, the theorem is no longer valid. I have taken the values a_1, a_2, v_1 from Tables I, II, III, and constructed the curve

for each color which represents absorption as a function of particle diameter (similar to the radiation curves in Fig. 12). From this diagram I then read off the absorption coefficients for the particle diameters listed in the following tables. The numbers are given in the same units as the radiated energy above. Thus they signify the light loss on a 1 mm path through a solution with concentration 10^{-6} (1 cbmm gold in 1 liter of water) in units per thousand. The quantity K is thus found by multiplying by 10^3 .

Absorption of Colloidal Gold Solutions

$2q$	420	450	500	525	550	600	650
0	40,5	37,4	59,6	69,0	55,5	16,4	7,0
20 $\mu\mu$	42,7	38,8	62,2	76,6	61,6	18,5	8,0
40 "	46,5	42,0	66,0	86,5	77,7	25,0	11,3
60 "	48,8	45,4	67,4	88,4	96,1	37,3	16,4
80 "	46,5	44,8	62,5	81,0	97,0	65,0	27,1
100 "	41,0	41,0	52,2	66,3	82,2	85,0	44,5
120 "	34,6	34,8	42,8	51,2	61,0	77,5	58,7
140 "	29,4	29,7	35,9	41,9	48,6	57,0	56,1
160 "	25,7	26,1	30,8	36,0	41,2	45,1	45,6
180 "	21,0	21,8	28,0	33,0	37,0	37,7	36,5

These numbers are shown graphically in Fig. 25 as the absorption spectra for various particle sizes.

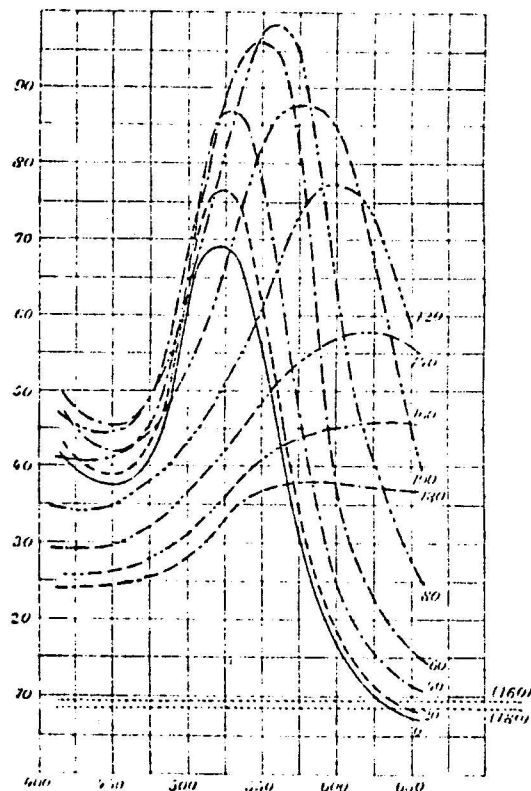


Fig. 25. Absorption of colloidal gold solutions

Thus we see for fine distribution the well-known steep absorption maximum of the ruby red gold solution in the green at about $525 \mu\mu$ wave length. If particle size increases, then for a constant concentration, absorption first increases in the entire spectrum, color changes a little, gradually shifts towards the blue, and the maximum is always bent towards the right. A severe change is first observed when the particle diameter is about $100 \mu\mu$. For this particle size, the solution is violet. At 120 and 140 we

already see the characteristic spectra of deep blue gold solutions, at 160 that of an indigo blue, at 180 that of a greenish blue. Thus in fact we obtain all the colors observed in colloidal gold solutions as particle size changes.

28. It is already clear that the color of gold solutions is primarily based on the absorption of light in the gold particles themselves. They would never be observed with perfectly conducting particles. Here the light loss would be entirely due to transverse light scattering alone, and the absorption curves would therefore be identical with the radiation curves shown earlier in Fig. 15. (if the next higher partial wave, thus the coefficients P_2 of the corresponding losses were added). These curves appear quite different, like the absorption curves of gold solutions; they would always represent only very flat colors, and for infinitely fine distribution the absorption would be zero.

For larger particle sizes the light loss through lateral radiation also determines the color of the gold solutions. Blue solutions are those that show a strong red-yellow radiation. It is in any case of interest to calculate both summands of the absorption coefficient. For a practical calculation we find from (99) the equations:

$$\begin{aligned}
 k &= C \cdot K', \\
 K' &= \frac{4\pi}{\lambda} \cdot a^3 \cdot \left(a_1^2 + v_1^2 + \frac{3}{5} \cdot a_2^2 \right) \\
 &= \frac{24\pi^2}{\lambda^4} \cdot J \cdot \left(a_1^2 + v_1^2 + \frac{3}{5} \cdot a_2^2 \right).
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} K' &= \frac{4\pi}{\lambda} \cdot a^3 \cdot \left(a_1^2 + v_1^2 + \frac{3}{5} \cdot a_2^2 \right) \\ &= \frac{24\pi^2}{\lambda^4} \cdot J \cdot \left(a_1^2 + v_1^2 + \frac{3}{5} \cdot a_2^2 \right). \end{aligned}} \right\} \quad (101)$$

Up to about $2\rho = 100 \text{ mm}$, K' is identical with the quantity F_1 calculated in §23 (Fig. 14). For larger particle diameters, coefficients ν_1 and α_2 are significant, although Rayleigh radiation continues to predominate up to $180 \mu\mu$. I found the quantities ν_1 and α_2 for coarser particles by graphical interpolation from Table II and III, and calculated K' for the same particle sizes for which we already know K . Then

$$K'' = K - K' \quad (102)$$

is the measure for the fraction of the light lost in the particles themselves. The following table shows the calculated values of K'' , again neglecting a factor of 10^3 .

Coefficients of Pure Absorption

2ρ	420	450	500	525	550	600	650
0	40,5	37,4	59,6	69,0	55,5	16,4	7,0
20 $\mu\mu$	42,4	38,6	61,9	76,1	61,0	18,2	7,9
40 "	44,4	40,4	63,3	81,9	71,8	22,1	9,9
60 "	42,6	40,4	59,4	74,7	76,4	25,0	10,5
80 "	35,9	35,6	48,3	58,1	59,2	32,0	12,4
100 "	27,4	28,7	34,9	39,0	39,8	29,5	25,5
120 "	21,1	22,0	25,2	25,6	24,5	19,7	13,6
140 "	17,2	18,0	20,1	19,9	19,1	11,9	9,6
160 "	14,0	14,8	16,4	16,1	15,2	10,0	8,1
180 "	11,9	12,9	14,1	14,3	13,3	8,8	6,5

These numbers are shown graphically in Fig. 26. These pure absorptions curves always have their maximum in the

green between $\lambda = 525$ and $\lambda = 550$. If we compare Fig. 26 with Fig. 14, we see no parallel between absorption and irradiation. Thus for small particles, where irradiation is still at a maximum in the green-yellow, the irradiation increases very rapidly with increasing particle size, while at the same time absorption exhibits a weak decrease. Then while the irradiation maximum moves towards the right, the pure absorption maximum also moves a little to the right, although it remains always in the green. But in addition to these relatively slight variations, we observe another, which apparently does not depend on the special nature of gold and which finally predominates over all others: the larger the particles become, the lower and flatter are the curves. This is also obvious; for when the particles are to a certain extent thick, they are finally opaque for all colors, and the thicker they become, the smaller the sum of the cross section casting a shadow.

If the bending effect is neglected, thus only geometric shadows are involved, the absorption coefficient would be $k_0 = N \cdot q$, where at a concentration of 10^6 :

$$N = \frac{10^{-6}}{\frac{4}{3} \pi \rho^3}, \quad q = \pi \cdot \rho^2.$$

thus:

$$k_0 = N \cdot q = \frac{3}{4} \cdot 10^{-6}.$$

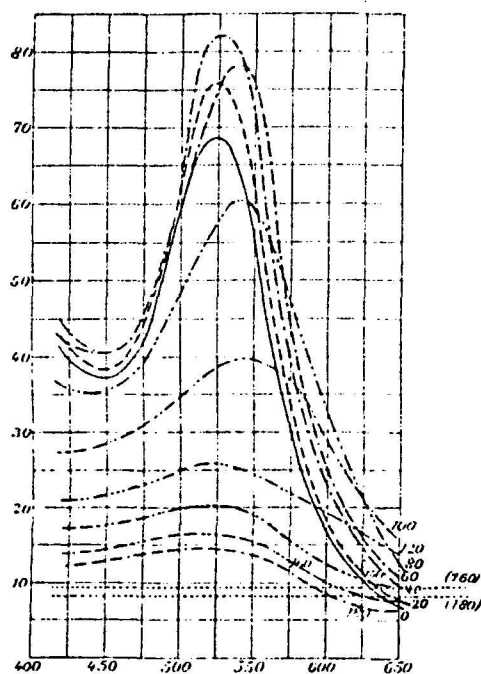


Fig. 26. "Pure absorption" in colloidal gold solutions

Then we can calculate for $2\rho = 180$: $k_0 = 8.3/1000$,
for $2\rho = 160$: $k_0 = 9.4/1000$. I have likewise entered
these values of k_0 in Fig. 25 and 26, naturally, as straight
lines, because k_0 does not depend on color. We see that
diffraction makes absorption considerably greater. Further-
more in the yellow and red by far the greatest part of the
light is removed by the particles through reflection, while
in the left half of the spectrum approximately half of the
lost light is absorbed in the particles.

The colors of colloidal gold solutions are explained

by the interaction of two properties of gold particles. The gold particles have in fact a very sharp maximum in the absorption capability in the green, and secondly a maximum in reflection capability in the yellow-red. Very small particles reflect weakly and absorb strongly, consequently they make the solution ruby red. Large particles reflect strongly, at the same time the pure absorption curve for them becomes lower and flatter, so they make the solution blue. The color of the coarsest solution is alone determined by the property of the gold to reflect strongly the red-yellow part of the spectrum, this results in its less saturated blue-green color.

Of course this theorem can only be demonstrated under the assumption of spherical particles. But even for flake and rod shaped particles, we must distinguish similarly between absorption capability and reflection capability of the particles.

The comparison of the theoretical results found in this work with the measurement results will be left for Mr. Steubing. However it should be pointed out here that these measurements indicate that in fact the known optical properties of gold are retained for the ultramicroscopic particles and are completely sufficient to explain the optical properties of the colloidal solution, but on the

other hand the theory needs to be extended in order to explain everything, and should probably be developed further for ellipsoidal particles (flakes or rods).

Results

1. The problem of calculating the optical properties of turbid media has been solved under two simplifying assumptions: first that the particles may be considered spherical, second, that the turbidity is infinitely dilute in the optical sense. The second assumption is certainly appropriate for the conventional colloidal solutions.

2. The light irradiated by the small particles can be calculated as a series of "partial waves," and indeed there are two groups of partial waves corresponding to the electrical and magnetic oscillations of the particles. Only a finite number of these partial waves needs to be considered for large particles, and the $(v-1)^{\text{th}}$ magnetic oscillation is parallel to the v^{th} electrical oscillation.

In colloidal solutions with very fine particles only the first electrical oscillation, which corresponds to the "Rayleigh radiation" is of significance. For coarser colloidal solutions, the second electrical and the first magnetic oscillation are of significance.

3. The assumption that the spheres are perfect..... conductors, which results in improper simplification of the equations, leads to another result, namely that the v^{th} magnetic oscillation is parallel with the v^{th} electrical oscillation. Accordingly even in the finest turbidities, the first magnetic oscillation must be noticeable in addition to the Rayleigh radiation, and this would give the Thomson theorem of the polarization maximum at 120° . Since the assumption is false, the result cannot be confirmed empirically.

4. If an unpolarized light beam is passed through the turbid solution, the laterally irradiated light is wholly or partially linearly polarized (never elliptically polarized).

Up to a particle size of about $100 \mu\mu$, the light scattered laterally by the gold spheres is almost solely Rayleigh radiation, which has its polarization maximum (100 %) at 90° . If the particles become larger, then the contribution of the unpolarized light at 90° increases very rapidly, and the polarization maximum shifts forward; at particle sizes 160 and $180 \mu\mu$, it lies at 110° and 120° . At the same time the initial symmetry of the Rayleigh radiation is disturbed by interference of the partial waves with each other; by far the greatest part of the diffuse

radiation goes towards the side to which the exciting light beam is directed. In the latter regard, the light reflected by imaginary, very small, perfectly conducting spheres would behave exactly opposite. The large gold spheres, which exhibit this anomalous polarization behavior, have a red-yellow diffuse radiation and color the solution blue. There can be no red particles that behave in this way.

6. Given a constant concentration, the diffuse radiation of very fine turbidities is proportional to the volume of a particle. In coarser turbidities it increases with increasing particle size more slowly and finally reaches a maximum whose position depends on the wave length. In a turbidity of imaginary, perfectly conducting spheres, the particle diameter corresponding to maximum radiation is proportional to the wave length ($0.324\lambda'$); for gold spheres there is no law so simple, yet the particle diameters concerned are always between $\lambda'/4$ and $\lambda'/3$.

The color of the diffusely scattered light, both for the imaginary, perfectly conducting spheres and for completely white spheres, provided they are very small, is blue-violet, corresponding to the Rayleigh law (radiation proportional to λ'^{-4}). Coarser spheres would send out an approximately white light with a weak, dull hue, which depends on the particle size. An optical resonance, which would vigorously

generate a given color, is excluded, at least for spherical particles, and it is not possible to explain the vigorous coloring of the colloidal solutions by means of resonance.

8. The diffuse radiation of gold particles is in general much stronger than that of equally large, perfectly conducting spheres. Furthermore, for the finest distribution, it exhibits a very sharp maximum in the green-yellow. Later the radiation maximum increases especially high in the red-yellow. To speak of resonance, we must first speak of a resonance of the gold atoms in the yellow, which is superimposed on the phenomenon to be expected in colorless conducting particles.

9. Infinitely fine turbidities involving gold particles show (in sharpest contrast to what would be expected of perfectly conducting particles) a characteristic absorption that depends only on the quantity of suspended metal (concentration) and not on the degree of finess. It would be interesting to study experimentally the way in which this may change in the case of minute particles which contain only a few atoms.

10. Generally absorption of colloidal gold solutions depends on two properties of the metallic gold: the absorption capability and reflection capability. Solutions in which the diffuse reflection opposes absorption show the

absorption maximum of the gold particles, which lies in the green; they are consequently ruby red. Solutions that show strong diffuse reflection are on the other hand blue-transparent, because gold reflects mainly the red-yellow light.

11. To complete the theory it is absolutely necessary to study the behavior of ellipsoidal particles.

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FOOTNOTES

1. F. Ehrenhaft, Wiener Sitzungsber. IIa, 112, 181 (1903); 114, 1115 (1905).
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5. Cf. the discussion between F. Pockels and F. Ehrenhaft in Physik. Zeitschrift, 5, 152, 387, 460 (1904).
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7. Vol. I, p. 200 of the German translation.
8. In gold spheres, for example, the absolute magnitude of C_1 is between 0.9 and 2.5, depending on the color of the light.
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13. Cf. E. Hagen and H. Rubens, loc. cit., p. 453.
14. Cf. for example, E. Müller, Ann. d. Phys., 24, 13, 16 (1907).
15. F. Ehrenhaft, Ann. d. Phys., 11, 489 (1903).
16. E. Müller, Ann. d. Phys., 24, 1 (1907).