Molecular theory of the reflection and refraction of light*

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Abstract

The object of this paper is to investigate theoretically the reasons for observed deviations from the Fresnel formula for the reflection of light from a "clean" surface. In the first part, formulas are derived based on quasi-microscopic considerations for the reflection of light from an optically isotropic medium with a transition layer on its surface, whose thickness is small compared to the wavelength of the light. The formulas are valid for macroscopic as well as for molecular (in particular, monomolecular) layers.

In the second part we consider the reflection of light from an optically isotropic cubic crystalline array made up of isotropic point atoms. The author supplements the well-known calculation of Ewald by terms of order a/λ and shows that the reflection of light from the array is the same as if there were a continuous medium with a continuous transition layer on its surface. A calculation of the parameters γ_x, γ_y and γ_z of the array is carried out, and the effect of distortion of the array near the boundary is considered as well.

Part I
Quasi-Microscopic Theory

1 Introduction

1. The application of the phenomenological theory of the transition layer based on the macroscopic Maxwell equations becomes questionable when dealing with reflection of light from clean surfaces. Rayleigh [1] and later Raman and Ramdas [2] found deviations from the Fresnel formula for the reflection of light from the

*English translation with corrections by E. F. Kuester, University of Colorado at Boulder, USA. The notations $\mathbf{fg}$ for the scalar or dot product, $[\mathbf{fg}]$ for the vector or cross product between two vectors $\mathbf{f}$ and $\mathbf{g}$ and rot for the curl ($\nabla\times$) have been retained from the original.

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extremely smooth surface of a liquid. If we estimate the thickness of a transition layer using a phenomenological theory based on these deviations, then it turns out that this thickness is of the same order as the intermolecular distances [3, 4]. Application of the macroscopic Maxwell equations to this layer violates the conditions for the validity of these equations.

2. In one of his 1940 lectures, the late academician L. I. Mandel'shtam indicated three possible reasons for the discrepancy with the Fresnel formula for reflection from a clean liquid surface. Due to thermal molecular motion, the surface of the liquid is always wavy; surface scattering of the light results from this. Could this waviness be the reason for deviations from the Fresnel formula? In Section 3 we will show that the answer to this question must be in the negative, at least if we consider the reflection of light from the wavy surface macroscopically.

In order to understand the other two reasons suggested by L. I. Mandel'shtam, we turn to the well-known interpretation of the Brewster phenomenon from the molecular point of view. Let a light wave polarized parallel to the plane of incidence be incident at the boundary of a body at the Brewster angle. Because of the transverse nature of light waves, we conclude that the electric field in the second medium is oriented parallel to the reflected ray. The oscillating dipole moments thereby induced in the molecules of this medium will be aligned in the same direction. And since an oscillating dipole does not radiate in the direction of oscillation of its electric moment, none of the molecules of the medium will radiate in the direction of the reflected ray, and this ray does not arise at all.

There are two inaccuracies in this argument.

First, only for isotropic molecules will the directions of the induced dipole moments of the molecules be the same as that of the field acting on them. If an isotropic medium is made up of anisotropic molecules, then these molecules will radiate in the direction of the reflected ray. However, this is not yet sufficient for a reflected ray to arise. It is also necessary that the radiation of the molecules be coherent, or at least partially coherent. For anisotropic molecules in an isotropic medium this condition is not observed since in order to have an isotropic medium it is necessary that its anisotropic molecules be randomly oriented. But this can be observed to a certain extent in molecules near the boundary of a region, in which case the possibility of their being oriented preponderantly in some direction cannot be ruled out. If this does happen, then the radiation from the molecules near the interface will be partially coherent, and as a result their interference will create a reflected wave. This could be a second reason for the deviations from the Fresnel formulas.

In the second place, the direction of the dipole moment of a molecule is determined by the field acting on it, and not by the average Maxwell field. For a molecule located far from an interface, the direction of both fields is the same. But the average field according to phenomenological theory is perpendicular to the refracted ray. The physical interpretation of Brewster's law is based on the use of this result. However, the phenomenological theory cannot say anything about the direction of the field acting on a molecule near the boundary, since the ordinary phenomenological Maxwell equations are not applicable near the

boundary, if only because the very concept of an average field or a dielectric permittivity is devoid of meaning. If it happens that the electric field acting on a molecule near the boundary is not perpendicular to the refracted ray, then in spite of Brewster's law, a reflected ray must appear. In Part II we will show that for the example of an optically isotropic cubic crystalline array, this is indeed the case. This constitutes the third reason for the discrepancy with Fresnel's formulas.

To these three possible reasons indicated by L. I. Mandel'shtam should be added a fourth: the change in the nature of molecular structure of a body near its surface. That is, the average distance between molecules near the surface is different than it is far away from the surface.

3. All of these reasons lead to the formation of a thin transition layer at the surface of a reflecting body within which the dipole moments of the molecules are oriented differently than they are within the medium. Since the thickness of this layer can be on the order of the intermolecular distances, a complete theory of it must be constructed on a molecular basis. However the construction of a molecular theory must proceed from a definite simplified model of the reflecting medium. Thus, in order to obtain our formulas in a general form, independent of the peculiarities of one model or another, in Part I we will apply a quasi-microscopic approach. It will be characterized by taking the dipole moment of a molecule of the medium excited by a light wave to be averaged over a physically infinitely small volume, as in the macroscopic theory. The radiating centers are considered to be not the molecules of the medium, but volume elements of the medium, for which the dipole moment of a volume element dV is given by the expression $\mathbf{P}\,dV$, where $\mathbf{P}$ is the polarization vector in the medium. But in contrast to the phenomenological theory, in the quasi-microscopic approach, just as in the molecular theory, it is assumed that waves radiating from an arbitrary volume element dV propagate not in the material medium, but in vacuum with velocity c.

2 Derivation of the general formulas

1. We consider a transparent isotropic medium bounded above by a plane. Near the boundary of the medium there can be an isotropic or anisotropic transition layer. The upper boundary of this layer will be taken to lie in the XY-plane of a rectangular coordinate system; the Z-axis will be directed downwards, towards the side the medium is on. If a plane monochromatic light wave of angular frequency ω is incident from vacuum to the medium, then the polarization vector $\mathbf{P}$ in the medium must have the form

$$\mathbf{P} = \mathbf{P}_0(z)e^{i(\mathbf{kr}-\omega t)} \tag{1}$$

The components of the wave vector $\mathbf{k}$ parallel to the interface must be identically equal to the components of the wave vector $\mathbf{f}$ of the incident wave. Otherwise the polarization wave (1) would excite a boundary wave in the medium, propagating with a velocity c in a different direction than the incident wave.

Such a boundary wave could not cancel the incident wave, and the stationary state (1) of polarization in the medium could not exist. On the contrary, the z-component of the wave vector $\mathbf{k}$ might be chosen arbitrarily, since a change in this component is tantamount to a change in the complex amplitude $\mathbf{P}_0(z)$. We demand that $k = \omega n/c = k_0 n$, where $k_0 = \omega/c$ is the wavenumber in vacuum, where n is the refractive index of the medium (not the layer!). Moreover, in order that the wave (1) be propagating away from the interface, we must require that the component k_z of $\mathbf{k}$ is positive. This wave vector $\mathbf{k}$ is determined uniquely. The vector $\mathbf{k}$ does not depend on z. But the amplitude $\mathbf{P}_0(z)$ will not depend on z if z is large enough. Regardless of how the transition layer originated, we will define it to be the region in which the amplitude $\mathbf{P}_0(z)$ varies with z.

Each volume element dV of the medium and the layer, possessing a time-varying dipole moment $\mathbf{P}\,dV$, is regarded as a source of light waves propagating in vacuum with velocity c. Our problem is to find the total radiation field inside and outside the medium. This problem is easy to solve for the case when the layer is entirely absent, i. e., when $\mathbf{P}_0(z)$ does not depend on z. Here we can, for example, apply the method of Ewald [5] which, although not characterized by mathematical rigor, nevertheless leads to correct results. The general case when $\mathbf{P}_0$ depends on z can easily be reduced to this special case. To do this we divide the entire medium into plane layers of thickness Δz parallel to the XY-plane, and in each of these layers we will assume that the amplitude $\mathbf{P}_0(z)$ in each layer can be taken to be constant. Thus inside the first layer there will propagate a wave of constant amplitude: $\mathbf{P}_1 = \mathbf{P}_{01}e^{i(\mathbf{kr}-\omega t)}$, inside the second $\mathbf{P}_2 = \mathbf{P}_{02}e^{i(\mathbf{kr}-\omega t)}$ and so on. These waves can be replaced by the following system of waves of constant amplitude, propagating towards the depths of the entire medium, but from the boundaries of the various layers:

1st wave: $\mathbf{P}_{01}e^{i(\mathbf{kr}-\omega t)}$, propagating from plane I;
2nd wave: $(\mathbf{P}_{02} - \mathbf{P}_{01})e^{i(\mathbf{kr}-\omega t)}$, propagating from plane II;
3rd wave: $(\mathbf{P}_{03} - \mathbf{P}_{02})e^{i(\mathbf{kr}-\omega t)}$, propagating from plane III, and so on.

This problem of calculating the radiation field of wave (I) reduces to that of the radiation field of a constant-amplitude polarization. The radiation field inside or near the transition layer does not concern us for the time being. To derive the general formulas it is sufficient to know the radiation field only at points far from the boundary of the medium. It can be expressed in terms of a Hertz vector $\mathbf{Z}$. Calculations carried out as indicated above lead to the following results.

The radiation field in the medium far from its boundary is the sum of a refracted wave:

$$\mathbf{Z}_d = \frac{4\pi}{k^2 - k_0^2}\mathbf{P}_0(\infty)e^{i(\mathbf{kr}-\omega t)}\,, \tag{2}$$

and a boundary wave:

$$\mathbf{Z}_c = \frac{2\pi}{f_z(f_z - k_z)}\left\{\mathbf{P}_0(0) + \int_0^\infty e^{i(k_z - f_z)\zeta}\,d\mathbf{P}_0(\zeta)\right\}e^{i(\mathbf{fr}-\omega t)}\,. \tag{3}$$

Outside the medium, the reflected wave is expressed as:

$$\mathbf{Z}_r = -\frac{2\pi}{f_z(f_z+k_z)}\left\{\mathbf{P}_0(0)+\int_0^\infty e^{i(k_z+f_z)\zeta}\,d\mathbf{P}_0(\zeta)\right\}e^{i(\mathbf{f}'\mathbf{r}-\omega t)}\,. \qquad (4)$$

The components of the wave vectors $\mathbf{f}$ and $\mathbf{f}'$ are determined by the following equations:

$$f_x = f'_x = k_x, \qquad f_y = f'_y = k_y, \qquad f_z = -f'_z = +\sqrt{k_0^2-k_x^2-k_y^2}\,. \qquad (5)$$

We recall that in the radiation field of the medium, the incident field is necessarily present. Otherwise, the polarization wave (1) would not exist. The role of the incident wave, according to the Oseen [6]-Ewald [5] extinction theorem consists in canceling out the boundary wave inside the medium. On this basis, we can write the Hertz vector of the incident wave as $\mathbf{Z}_e = -\mathbf{Z}_c$.

The integrations from 0 to ∞ can clearly be replaced by integrals from 0 to l, where l is the thickness of the transition layer, since only inside the layer is $d\mathbf{P}_0(\zeta) \neq 0$. If the thickness of the layer is small compared to the wavelength of the light, then the exponential functions in (3) and (4) can be expanded in a power series, neglecting all terms starting with the quadratic. In this approximation,

$$\begin{aligned}
\mathbf{Z}_e &= -\mathbf{Z}_c = -\frac{2\pi}{f_z(f_z-k_z)}\left\{\mathbf{P}_0(\infty)-i(f_z-k_z)\int_0^\infty \zeta\,d\mathbf{P}_0(\zeta)\right\}e^{i(\mathbf{f}\mathbf{r}-\omega t)}\,,\\
\mathbf{Z}_r &= -\frac{2\pi}{f_z(f_z+k_z)}\left\{\mathbf{P}_0(\infty)+i(f_z+k_z)\int_0^\infty \zeta\,d\mathbf{P}_0(\zeta)\right\}e^{i(\mathbf{f}'\mathbf{r}-\omega t)}\,. \qquad (6)
\end{aligned}$$

The calculation of the integral appearing here is a purely electrostatic problem. In fact, if the integral is expanded in a power series in k, then linear terms will show up in equations (6) only as terms of second order. Therefore in the expansion of the integral it is sufficient to keep only the zero-order term. This zeroth term does not depend on the wavelength, and consequently can be found using methods of electrostatics. Furthermore, the components of the vectors $\mathbf{P}_0(\infty)$ and $\int_0^\infty \zeta\,d\mathbf{P}_0(\zeta)$ are clearly proportional to the corresponding components of the electric field of the incident wave. As a result, if we introduce the three parameters

$$\gamma_i = [P_{0i}(\infty)]^{-1}\int_0^\infty z\,dP_{0i}(z), \qquad i = x, y, z\,, \qquad (7)$$

and evaluate them in the zeroth approximation, then these parameters will depend neither on the wavelength of the light[1] nor on the strength of the externally impressed field. These parameters of the first-order theory are dependent

[1]Strictly speaking, they depend on the light wavelength to the extent that the refractive index n of the medium depends on λ. Indeed, when solving the electrostatic problem one should take not the static, but the dynamic permittivity which is a function of the wavelength λ.

on the properties of the transition layer. We will be interested only in layers whose properties are the same in all directions parallel to the XY-plane. For such layers, $\gamma_x = \gamma_y$.

Passing from the Hertz vector to the electric and magnetic field strengths presents no difficulty. We denote by $\mathcal{E}_s$, $\mathcal{E}_p$, R_s and R_p the complex amplitudes of the electric fields of the principal components of the incident and reflected waves, polarized parallel to and perpendicular to the plane of incidence respectively. In the case of the s-components, we take the positive direction of the electric field to be along the positive Y-axis. For the case of p-components, the positive directions are shown in Fig. 1. Then

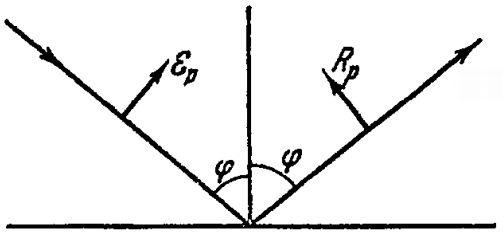

Figure 1:

$$\begin{aligned} \frac{R_s}{\mathcal{E}_s} &= -\frac{\tan(\varphi-\psi)}{\sin(\varphi+\psi)}\{1+2ik_0\gamma_y\cos\varphi\}\,, \\ \frac{R_p}{\mathcal{E}_p} &= -\frac{\tan(\varphi-\psi)}{\sin(\varphi+\psi)}\left\{1+2ik_0\cos\varphi\frac{\gamma_x\cos^2\psi-\gamma_z\sin^2\varphi}{\cos^2\psi+\sin^2\varphi}\right\}, \end{aligned} \tag{8}$$

where φ is the angle of incidence and ψ the angle of refraction.

2. If the transition layer is macroscopic, then formula (8) reduces to the known formula of Drude. In this case, the optical properties of the transition layer can be characterized by the principal refractive indices n_x, n_y and n_z as functions of z. Here, due to symmetry, $n_x = n_y$. To determine the parameters γ_x, γ_y and γ_z, we should imagine that the medium is immersed in an electrostatic field that is uniform at infinity. The strength of this field can depend only on z. Since the static field is irrotational, we have $\partial E_x/\partial z = 0$, i. e., E_x is independent of z. Therefore,

$$\int_0^\infty z\,dP_x(z) = \int_0^l \frac{d}{dz}\left(\frac{n_x^2-1}{4\pi}E_x\right)dz = \frac{E_x}{4\pi}\int_0^l z\frac{dn_x^2}{dz}\,dz\,.$$

Integration by parts leads to expressing the integral in terms of the integral

$$p = \int_0^l n_x^2(z)\,dz \tag{9}$$

We obtain at last

$$\gamma_x = \frac{p-ln^2}{1-n^2}\,. \tag{10}$$

Analogously, using the solenoidal character of the induction vector $\mathbf{D}$, we show that D_z is independent of z. From this we obtain easily that:

$$\gamma_z = \frac{l - qn^2}{1 - n^2}\,, \tag{11}$$

$$q = \int_0^l \frac{dz}{n_z^2(z)} \tag{12}$$

Upon substituting (10) and (11) into (8), we obtain the formulas of Drude [7, 9].

3. Although formulas (8) agree in form with those of Drude, they are more general. In point of fact, Drude's formulas make sense only for sufficiently thin transition layers whose optical properties can be characterized macroscopically by a refractive index. On the contrary, in deriving equation (8), we did not introduce any macroscopic characteristics of the transition layer. It is true that we averaged the dipole moments of the molecules of the medium and layer over a physically small volume and introduced the polarization vector $\mathbf{P}$, which characterizes the polarization of the medium and the layer macroscopically. However, this was done in order to calculate the radiation field not inside the transition layer, but far away from it. For this purpose, the averaging is permissible. As far as the transition layer is concerned, we made absolutely no use of the field strength inside the layer, and furthermore did not assume any dependence of the polarization vector on this field either. Thus formula (8) is also valid for monomolecular layers. Finally, the quasi-microscopic theory does not permit the calculation of the layer parameters γ_x and γ_z. It only reduces their calculation to an electrostatic problem. This electrostatic problem can only be solved with knowledge of the structure of the layer. For monomolecular layers the calculation of the parameters γ_x and γ_z can only be carried out on the basis of molecular theory.

4. We have carried out our calculations with an accuracy of up to first order terms, omitting terms containing k_0 in powers 2 or higher. This is permissible when investigating those properties of light reflection which depend linearly on the field strength. This is the case for the polarization properties of the reflected light. On the contrary, when calculating the intensity of the reflected light, which depends quadratically on the field strength, we must carry out our calculations at least to second-order accuracy. Thus the first-order theory is useful only for studying the effect of the transition layer on the polarization of the reflected light. As is known, the polarization properties of the reflected light are completely determined by the complex ratio R_p/R_s. If the incident light is linearly polarized at an angle of 45° to the plane of incidence, i. e., if $\mathcal{E}_s = \mathcal{E}_p$, then this ratio is equal to

$$\frac{R_p}{R_s} = \rho e^{-i\delta} = -\frac{\cos(\varphi - \psi)}{\cos(\varphi + \psi)} - 2ik_0 \cos\varphi \sin^2\varphi \frac{\gamma_x - \gamma_z}{\cos^2(\varphi - \psi)} \tag{13}$$

In particular, for reflection at the Brewster angle $\delta = \pi/2$, and at this angle of incidence we obtain the following expression for the ellipticity coefficient:

$$\rho = \frac{1}{3} k_0 \sqrt{n^2 + 1}(\gamma_x - \gamma_z) \tag{14}$$

Therefore the polarization of the light depends only on the difference between the parameters γ_x and γ_z, and not on their separate values. Thus in the first-order theory we can replace the parameters γ_x and γ_z by any other two which differ from the originals by the same arbitrary constant. In other words, the parameters γ_x and γ_z can be determined to within an accuracy of a common arbitrary constant.

Integrating by parts we find:

$$\gamma_x = \frac{1}{P_{0x}(\infty)} \int_0^l z \, dP_{0x}(z) = l - \frac{1}{P_{0x}(\infty)} \int_0^l P_{0x}(z) \, dz$$

Thus, neglecting the constant l common to the expressions for all of the parameters γ_x, γ_y and γ_z, we could define these parameters by the relations:

$$\gamma_x = -\frac{1}{P_{0x}(\infty)} \int_0^l P_{0x}(z) \, dz \tag{15}$$

and so forth. Hence it is clear that the manner in which $\mathbf{P}_0$ varies within the transition layer plays no role. The only essential thing is the value of the integral $\int_0^l P_{0x}(z) \, dz$. The layer could be regarded as infinitely thin, having no thickness in the limit, as was done for example by Strachan [8].

Evidently, the integral $\int_0^l P_{0x}(z) \, dz$ is none other than the sum $\sum \mathbf{p}_0$ of all the dipole moments of the molecules in the transition layer per unit area of its surface. By the same token, this establishes a molecular interpretation of the parameters γ_x, γ_y and γ_z.

3 The effect of reflecting surface roughness

1. Roughness of the reflecting surface can be considered as a transition layer whose properties vary with x and y. We will assume that the thickness of the layer is small compared to the wavelength of the light, and the properties of the layer vary periodically with the (x, y) variables. The periods of these variations are denoted a and b. If a monochromatic plane wave is incident on the medium, then the polarization vector $\mathbf{P}$ will have the form:

$$\mathbf{P} = \mathbf{P}_0(x, y, z) e^{i(\mathbf{kr} - \omega t)} \tag{16}$$

where $\mathbf{P}_0(x, y, z)$ is a periodic function in (x, y) with periods (a, b). We expand it in a Fourier series:

$$\mathbf{P}_0(x, y, z) = \sum_l \sum_m \mathbf{A}_{lm}(z) e^{i(\mathbf{q}_{lm}\mathbf{r} - \omega t)}$$

The vectors $\mathbf{q}_{lm}$ must satisfy the conditions:

$$(q_{lm})_x = \frac{2\pi l}{a}, \qquad (q_{lm})_y = \frac{2\pi m}{b}. \tag{17}$$

Therefore

$$\mathbf{P} = \sum_l \sum_m \mathbf{A}_{lm}(z) e^{i(\mathbf{k}_{lm}\mathbf{r} - \omega t)} \tag{18}$$

where $\mathbf{k}_{lm} = \mathbf{k} + \mathbf{q}_{lm}$.

We require that

$$k_{lm}^2 = k^2 = \frac{n^2\omega^2}{c^2}\,. \tag{19}$$

This determines the z-component of the vector $\mathbf{q}_{lm}$. We require that the inhomogeneous waves appearing in (18) decay with distance from the interface. Only homogeneous waves radiating away from the interface with constant amplitudes $\mathbf{A}_{lm}(z) = \mathbf{A}_{lm}(\infty)$ should remain.

Each wave appearing in (18) has the form (1). This problem reduces to the one considered in Section 2. Neglecting terms containing second and higher powers of k, we find that the radiation field outside the medium at large distances far from the reflecting surface is

$$\mathbf{Z}_a = -\sum_l \sum_m \frac{2\pi}{f_{lmz}(f_{lmz} + k_{lmz})} \left\{ \mathbf{A}_{lm}(\infty) + i(f_{lmz} + k_{lmz}) \int_0^\infty \zeta \, d\mathbf{A}_{lm}(\zeta) \right\} \times$$

$$\times e^{i(\mathbf{f}'_{lm}\mathbf{r} - \omega t)}\,, \tag{20}$$

where

$$f_{lmx} = f'_{lmx} = k_{lmx}; \qquad f_{lmy} = f'_{lmy} = k_{lmy};$$
$$f_{lmz} = -f'_{lmz} = +\sqrt{k_0^2 - k_{lmx}^2 - k_{lmy}^2}\,, \tag{21}$$

and the sign $\sum$ denotes summation over the homogeneous waves. The boundary wave far from the reflecting surface will have the form

$$\mathbf{Z}_c = \sum_l \sum_m \frac{2\pi}{f_{lmz}(f_{lmz} - k_{lmz})} \left\{ \mathbf{A}_{lm}(\infty) - i(f_{lmz} - k_{lmz}) \int_0^\infty \zeta \, d\mathbf{A}_{lm}(\zeta) \right\} \times$$

$$\times e^{i(\mathbf{f}_{lm}\mathbf{r} - \omega t)}\,. \tag{22}$$

The component of this wave with $l = m = 0$ must be canceled by the incident wave:

$$\mathbf{Z}_e = -\frac{2\pi}{f_z(f_z - k_z)} \left\{ \mathbf{A}_{00}(\infty) - i(f_z - k_z) \int_0^\infty \zeta \, d\mathbf{A}_{00}(\zeta) \right\} e^{i(\mathbf{fr} - \omega t)}\,. \tag{23}$$

Each of the other components of the vector $\mathbf{Z}_c$ must correspond to a field that vanishes. This is possible if the (lm) component of the Hertz vector is parallel to $\mathbf{f}_{lm}$, i. e., if

$$[\mathbf{f}_{lm}\mathbf{A}_{00}(\infty)] - i(f_z - k_z) \int_0^\infty \zeta \, [\mathbf{f}_{lm} \, d\mathbf{A}_{00}(\zeta)] = 0\,.$$

With no loss of generality, we can require that $\mathbf{f}'_{lm}\mathbf{A}_{00}(\infty) = 0$. This gives

$$\mathbf{A}_{lm}(\infty) =$$

$$= i(f_{lmz} - k_{lmz}) \int_0^\infty \zeta \, d\mathbf{A}_{lm}(\zeta) - i\mathbf{f}_{lm} \frac{f_{lmz} - k_{lmz}}{(\mathbf{f}_{lm}\mathbf{f}'_{lm})} \int_0^\infty \mathbf{f}'_{lm} \zeta \, d\mathbf{A}_{lm}(\zeta) \, .$$

This calculation of $\mathbf{A}_{lm}(\infty)$ has been reduced to an electrostatic problem.

We obtain the reflected wave by putting $l = m = 0$ in (20). The remaining components relate to the scattered light (a diffraction array!). So for the reflected wave we have

$$\mathbf{Z}_r = -\frac{2\pi}{f_z(f_z + k_z)} \left\{ \mathbf{A}_{00}(\infty) + i(f_z + k_z) \int_0^\infty \zeta \, d\mathbf{A}_{00}(\zeta) \right\} e^{i(\mathbf{f}'\mathbf{r} - \omega t)} \, . \qquad (24)$$

Expressions (23) and (24) are identical with expressions (6) if we put $\mathbf{A}_{00}(z) = \mathbf{P}_0(z)$. But $\mathbf{A}_{00}(z)$ is the static polarization vector averaged over the x and y coordinates. Therefore, in spite of the presence of diffracted waves, the results of the preceding paragraph are valid even for the case of light reflection from a rough surface if only we understand by $\mathbf{P}_0(z)$ the static polarization vector, averaged over the x and y coordinates. Of course, in this case the results of the quasi-microscopic investigation are identical with those obtained with the molecular theory below.

2. As an example, we consider a one-dimensional reflecting array with symmetrical rulings, i. e., we assume that the surface of a homogeneous medium with refractive index n is rough and is given by an equation of the form $z = f(x)$, where $f(x)$ is an even periodic function of period a. The cross section of this surface in the XZ-plane is shown in Fig. 2. To determine the parameters γ_x, γ_y

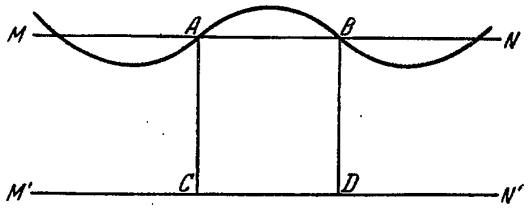

Figure 2:

and γ_z we postulate that an electrostatic field, uniform at infinity, is introduced into the medium. We draw straight lines MN and $M'N'$ parallel to the X-axis, such that MN intersects the curve $z = f(x)$, while $M'N'$ is taken sufficiently far from the boundary of the medium that the field $\mathbf{E}$ can be reckoned constant on it. At the points of intersection A and B of MN with the curve $z = f(x)$ we draw the perpendiculars AC and DB. Since the static field $\mathbf{E}$ is conservative,

$$\oint_{ABDCA} E_s \, ds = 0 \, .$$

Furthermore, by symmetry we have

$$\oint_{CA} E_s\,ds = \oint_{DB} E_s\,ds\,.$$

Therefore,

$$\int_{AB} E_x\,dx = \int_{CD} E_x\,dx = CD\,E_X(\infty)\,.$$

Hence it follows that the average value of E_x on AB is equal to $E_x(\infty)$. Analogously, because the vector $\mathbf{E}$ is divergenceless, it can be shown that the average value of E_z on AB is equal to $E_z(\infty)$. Consequently, the average of $\mathbf{E}$ over AB is $\mathbf{E}(\infty)$, and therefore by reason of the homogeneity of the medium the average of the vector $\mathbf{P} = \alpha\mathbf{E}$ over AB is $\mathbf{P}(\infty)$ as well. On a segment BE that passes through the vacuum, $\mathbf{P} = 0$. Thus, after we average the vector $\mathbf{P}$ over the x-coordinate, we get a vector parallel to $\mathbf{P}(\infty)$. Hence it follows that the parameters γ_x, γ_y and γ_z are all equal. Inasmuch as they are determined within an arbitrary constant, we can put $\gamma_x = \gamma_y = \gamma_z = 0$. Thus, to first order the reflection of light follows Fresnel's formulas accurately. We obtained this result by describing the properties of the layer macroscopically—by its index of refraction. Thus it could have been obtained from the macroscopic Maxwell equations, and could, as is well known, be obtained *ab initio* by such a method. However, in proceeding this way, we must make the assumption that the roughness of the reflecting surface is gentle, i. e., $|dz/dx| = |df(x)/dx| \ll 1$. We see that this result remains valid also in the case of steep roughness, provided there is symmetry expressed by the relation $f(x) = f(-x)$. Of course, all of the above are also valid for two-dimensional arrays.

3. The results obtained can also be extended to the case when the form of the reflecting surface is completely irregular. Such a form is taken, for example, by the surface of any liquid thanks to thermal agitation of the molecules. We once again draw the lines MN and $M'N'$ parallel to the X-axis (Fig. 3). Because $\mathbf{E}$

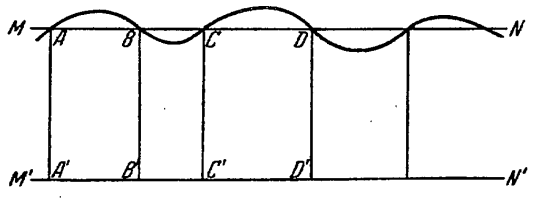

Figure 3:

is a conservative vector, we can write

$$\oint_{ABB'A'A} E_s\,ds = 0; \qquad \oint_{CDD'C'C} E_s\,ds = 0 \quad \text{and so on.}$$

Putting these equalities together, we obtain:

$$\int_{AB} E_x\,dx + \int_{CD} E_x\,dx + \ldots = \int_{A'B'} E_x\,dx + \int_{C'D'} E_x\,dx + \ldots$$
$$\ldots + \left(\int_{AA'} - \int_{BB'} + \int_{CC'} - \int_{DD'} + \ldots\right).$$

Thanks to the irregularity of the reflecting surface, the average value of the sum of the integrals inside the parentheses is equal to zero. As a result, the average value of E_x on the segments AB, CD, EF, ... will be equal to $E_x(\infty)$. Analogously, using the divergencelessness of the vector $\mathbf{E}$ we show that the average value of E_z over these segments will be equal to $E_z(\infty)$. Hence, as in Paragraph 2, we conclude that $\gamma_x = \gamma_y = \gamma_z$, i. e., to first order the roughness of the reflecting surface does not manifest itself in the reflected light.

Part II
Reflection from a Crystalline Array

4 Reflection of light from an optically isotropic cubic crystalline array

1. As a model of an optically isotropic medium we take a cubic crystalline array made up of isotropic point atoms. The position of each atom of the array can be defined by the position vector $\mathbf{r}_{lmn}$ with coordinates

$$x_{lmn} \equiv x_l = la, \qquad y_{lmn} \equiv y_m = ma, \qquad z_{lmn} \equiv z_n = na, \tag{25}$$

where a is the lattice constant, while l, m and n are integers that for an unbounded array take on all values from $-\infty$ to $+\infty$. Our development will be based on the following two results of Ewald [5, 10]:

a) In an unbounded array, there can propagate a transverse dipole wave of constant amplitude:

$$\mathbf{p}_{lmn} = \mathbf{p}e^{i(\mathbf{k}\mathbf{r}_{lmn} - \omega t)} \tag{26}$$

provided the wavenumber k is equal to $k_0 n = \omega n/c$, where n is the refractive index of the array. This means that the radiation field from the atoms of the array is maintained by the dipole wave (26); i. e., there is a dynamic balance between the dipole oscillations (26) and the radiation field of the atoms of the array. The Hertz vector of the radiation field of the atoms of an unbounded array is thus:

$$\mathbf{Z}_d = -4\pi\mathbf{p}a^{-3}e^{i(\mathbf{k}\mathbf{r}-\omega t)} \sum_{l,m,n} \left[k_0^2 - (\mathbf{k} + \mathbf{q}_{lmn})^2\right]^{-1} e^{i(\mathbf{q}_{lmn}\mathbf{r})} \tag{27}$$

where the components of the vector $\mathbf{q}_{lmn}$ are defined as:

$$(q_{lmn})_x = 2\pi l/a\,; \qquad (q_{lmn})_y = 2\pi m/a\,; \qquad (q_{lmn})_z = 2\pi n/a\,. \quad (28)$$

b) If the array is bounded above by the XY-plane, then in (25) the values of the integers l and m run from $-\infty$ to $+\infty$, while n runs from 0 to $+\infty$. We assume for the moment that the dipole oscillations of such an array are determined by the wave (26). We direct the Z-axis into the array. Ewald showed that the radiation field of all the atoms of such an array is determined inside it by the Hertz vector $\mathbf{Z}_d + \mathbf{Z}_c$, where[2]

$$\mathbf{Z}_c = -\frac{2\pi \mathbf{p} i}{a^2} \sum_{l,m} \frac{e^{i(\mathbf{f}_{lm}\mathbf{r}-\omega t)}}{f_{lmz}\left[e^{i(k_z - f_{lmz})a} - 1\right]}\,, \quad (29)$$

and outside the array by the Hertz vector

$$\mathbf{Z}_r = -\frac{2\pi \mathbf{p} i}{a^2} \sum_{l,m} \frac{e^{i(\mathbf{f}_{lm}\mathbf{r}-\omega t)}}{f_{lmz}\left[e^{i(k_z + f_{lmz})a} - 1\right]}\,. \quad (30)$$

Here we have introduced the notations

$$f_{lmx} = f'_{lmx} = k_x + (2\pi/a)l\,, \qquad f_{lmy} = f'_{lmy} = k_y + (2\pi/a)m\,,$$
$$f_{lmz} = -f'_{lmz} = +\sqrt{k_0^2 + (k_x + (2\pi l/a))^2 + (k_y + (2\pi m/a))^2}\,. \quad (31)$$

The + sign in front of the square root is there so that all homogeneous waves appearing in (29) and (30) should be moving away from the boundary of the array. If the expression under the square root becomes negative, then the imaginary part should also be given a + sign so that the corresponding homogeneous waves decay with distance from the boundary of the array.

In his treatment of the problem of light reflection, Ewald neglected in expression (29) for the boundary wave $\mathbf{Z}_c$ all inhomogeneous components. In this approximation, the dipole oscillations (25) of the atoms of the array are found by dynamic balance of the radiation field of the array and the field of the incident wave. In this way, Ewald arrived at the classical Fresnel formulas. If on the other hand we do not neglect the inhomogeneous components in (29), then it must be recognized that in the presence of only one incident monochromatic plane wave, a dipole wave of the form (26) in the crystalline array is impossible. Therefore, we will solve the problem of the reflection of light from a crystalline array more accurately, i. e., without neglecting the inhomogeneous components in expression (29).

2. We consider a two-dimensional square grid of atoms located in the XY-plane. The coordinates of the atoms are given by the expressions $x_{lm} = la$,

[2] A typographical error in this equation has been corrected [Translator's note].

$y_{lm} = ma$. A two-dimensional homogeneous dipole wave $\mathbf{p}_{lm} = \mathbf{p}e^{i(\mathbf{k}\mathbf{r}_{lm}-\omega t)}$ moves along the grid. It is required to compute the radiation field of all the atoms of our grid. We imagine a cubic array filling the half-space bounded by the XY-plane, through which the dipole wave (26) passes. Our grid can be considered as the first layer of atoms in such an array. The radiation field of the atoms of the grid will be equal to the difference between the radiation fields of two arrays, one of which is bounded by the XY-plane and the other of which is obtained from the first by removing the first layer of atoms. Applying (27), (29) and (30) to both arrays, we obtain for the Hertz vector of the radiation field of the layer the expression

$$\mathbf{Z}(\mathbf{r}) = 2\pi\mathbf{p}a^{-2}i\sum_{l,m} e^{i(\mathbf{f}_{lm}\mathbf{r}-\omega t)}/f_{lmz}\,, \tag{32}$$

for $z > 0$, and

$$\mathbf{Z}(\mathbf{r}) = 2\pi\mathbf{p}a^{-2}i\sum_{l,m} e^{i(\mathbf{f}'_{lm}\mathbf{r}-\omega t)}/f_{lmz}\,, \tag{33}$$

for $z < 0$. These expressions can also be obtained by applying Ewald's summation method [5] to our grid.

3. Now we can turn to the problem of the reflection of light from a crystalline array. In order to account for the effect of possible distortions in the structure of the array near its surface, we assume that the array is made up of grids of atoms, but that the distances between the grids near the boundary can be different from a. Furthermore, we assume that the atoms in grids near the boundary of the array can be anisotropic. The atoms within a single grid are assumed to be identical. All atoms located far from the boundary of the array are similarly assumed to be identical, and in addition isotropic. Finally, the thickness of the transition layer is assumed to be very small in comparison with the wavelength of the light.

Therefore the coordinates of each atom can be expressed as follows:

$$x_{lmn} \equiv x_l = la, \qquad y_{lmn} \equiv y_m = ma, \qquad z_{lmn} \equiv z_n = a_1 + a_2 + \ldots + a_n\,, \tag{34}$$

in which $a_n \to a$ as $n \to \infty$.

If a plane monochromatic light wave is incident at the surface of the array, then the dipole oscillations of the atoms of the array must have the form:

$$\mathbf{p}_{lmn} = \mathbf{p}_n e^{i(\mathbf{k}\mathbf{r}_{lmn}-\omega t)} \tag{35}$$

The components of the wave vector $\mathbf{k}$ parallel to the boundary of the array must be equal to the corresponding components of the wave vector of the incident wave. If this were not so, then the dipole oscillations excited would be homogeneous waves propagating into the depths of the array with a velocity c, along a direction different than that of the incident wave. Such a wave could not extinguish the incident wave, and a condition of dynamic balance between the field of the incident wave, the radiation field of the atoms of the array and its dipole oscillations would be impossible. On the other hand, the z-component of

the wave vector $\mathbf{k}$ might be chosen arbitrarily, since a change in this component could be considered as a change in the amplitudes $\mathbf{p}_n$. As in Section 2, we put $k = k_0 n$, where n is an index of refraction, and will take k_z to be positive. Then at infinite distances from the boundary of the array the amplitude $\mathbf{p}_n$ approaches a constant amplitude $\mathbf{p}_\infty$.

The radiation field of the entire array is easily computed if we analyze it for a square grid parallel to the boundary of the array and use formulas (32) and (33). The superposition of homogeneous waves radiated towards the depths of the array by all the grids of atoms gives the boundary wave at infinity:

$$\mathbf{Z}_c = \frac{2\pi i}{f_z a^2} e^{i(\mathbf{fr}-\omega t)} \sum_{n=0}^{\infty} \mathbf{p}_n e^{i(k_z - f_z)(a_1+a_2+\ldots+a_n)} . \tag{36}$$

The superposition of the very same homogeneous waves propagating outwards from all the atomic grids of the array gives the reflected wave:

$$\mathbf{Z}_r = \frac{2\pi i}{f_z a^2} e^{i(\mathbf{f'r}-\omega t)} \sum_{n=0}^{\infty} \mathbf{p}_n e^{i(k_z + f_z)(a_1+a_2+\ldots+a_n)} , \tag{37}$$

Here the wave vectors $\mathbf{f} = \mathbf{f}_{00}$ and $\mathbf{f}' = \mathbf{f}'_{00}$ are determined by expressions (5). According to the Oseen-Ewald extinction theorem, the boundary wave $\mathbf{Z}_c$ must be canceled by the incident wave. This gives:

$$\mathbf{Z}_e = -\frac{2\pi i}{f_z a^2} e^{i(\mathbf{fr}-\omega t)} \sum_{n=0}^{\infty} \mathbf{A}_n e^{i(k_z - f_z)na} . \tag{38}$$

where we have introduced the notation

$$\mathbf{A}_n = \mathbf{p}_n e^{i(k_z - f_z)(a_1+a_2+\ldots+a_n - na)} .$$

We rewrite (38) in the form

$$\mathbf{Z}_e = -\frac{2\pi i}{f_z a^2} e^{i(\mathbf{fr}-\omega t)} \left\{ \mathbf{A}_0 \sum_{n=0}^{\infty} e^{i(k_z - f_z)na} + \right.$$
$$\left. + (\mathbf{A}_1 - \mathbf{A}_0) \sum_{n=1}^{\infty} e^{i(k_z - f_z)na} + (\mathbf{A}_2 - \mathbf{A}_1) \sum_{n=2}^{\infty} e^{i(k_z - f_z)na} + \ldots \right\} .$$

Clearly

$$\sum_{n=0}^{\infty} e^{i(k_z - f_z)na} = \lim_{N\to\infty} \frac{1 - e^{i(k_z - f_z)Na}}{1 - e^{i(k_z - f_z)a}}$$

For k_z real, this expression does not tend to any definite limit. In order to avoid the indefiniteness that would result from this, we note that a true homogeneous wave cannot exist, strictly speaking; all waves attenuate. Attenuation can be

introduced if the component k_z is taken to be complex with positive imaginary part, though this imaginary part can be as small as desired. Then in the limit

$$\sum_{n=0}^{\infty} e^{i(k_z-f_z)na} = \left[1 - e^{i(k_z-f_z)a}\right]^{-1}$$

which still makes sense when k_z becomes real. Using the foregoing formulas, we obtain

$$\mathbf{Z}_e = -\frac{2\pi i}{f_z a^2} \frac{e^{i(\mathbf{fr}-\omega t)}}{1 - e^{i(k_z-f_z)a}} \left\{ \mathbf{A}_0 + \sum_{n=1}^{\infty} (\mathbf{A}_n - \mathbf{A}_{n-1})\, e^{i(k_z-f_z)na} \right\}.$$

Since we supposed that the thickness of the transition layer is very small compared to the wavelength of the light, the differences $\mathbf{A}_n - \mathbf{A}_{n-1}$ will be significantly different from zero only for small values of n. Therefore, the exponential function inside the summation can be expanded in a power series and truncated after the linear term (it is then necessary to keep quadratic terms when expanding the exponential function in the denominator). This gives

$$\mathbf{Z}_e = -\frac{2\pi}{f_z(f_z - k_z)a^3} \left\{ \mathbf{A}_\infty + i(k_z - f_z)a \left[\sum_{n=1}^{\infty} n\,(\mathbf{A}_n - \mathbf{A}_{n-1}) - \frac{\mathbf{A}_\infty}{2} \right] \right\} e^{i(\mathbf{fr}-\omega t)}.$$

Furthermore, to the same accuracy,

$$\mathbf{A}_\infty - \mathbf{p}_\infty \left\{ 1 + i(k_z - f_z) \sum_{n=1}^{\infty} (a_n - a) \right\}.$$

As far as the sum $\sum n\,(\mathbf{A}_n - \mathbf{A}_{n-1})$ is concerned, it is sufficient to compute it to the zeroth approximation. To this order,

$$\sum_{n=1}^{\infty} n\,(\mathbf{A}_n - \mathbf{A}_{n-1}) = \sum_{n=1}^{\infty} n\,(\mathbf{p}_n - \mathbf{p}_{n-1}) = \sum_{n=0}^{\infty} (\mathbf{p}_\infty - \mathbf{p}_n)\,.$$

Thus,

$$\begin{aligned}
\mathbf{Z}_e &= -\frac{2\pi}{f_z(f_z - k_z)a^3} \{\mathbf{p}_\infty - i(f_z - k_z)\times \\
&\times \left[a \sum_{n=0}^{\infty} (\mathbf{p}_\infty - \mathbf{p}_n) + \mathbf{p}_\infty \sum_{n=1}^{\infty} (a_n - a) - \frac{a}{2}\mathbf{p}_\infty \right] \Bigg\} e^{i(\mathbf{fr}-\omega t)}, \qquad (39) \\
\mathbf{Z}_r &= -\frac{2\pi}{f_z(f_z + k_z)a^3} \{\mathbf{p}_\infty + i(f_z + k_z)\times \\
&\times \left[a \sum_{n=0}^{\infty} (\mathbf{p}_\infty - \mathbf{p}_n) + \mathbf{p}_\infty \sum_{n=1}^{\infty} (a_n - a) - \frac{a}{2}\mathbf{p}_\infty \right] \Bigg\} e^{i(\mathbf{f'r}-\omega t)}.
\end{aligned}$$

These expressions reduce to (6) if we put

$$\mathbf{p}_\infty = a^3 \mathbf{P}(\infty), \qquad a \sum_{n=0}^{\infty} (\mathbf{p}_\infty - \mathbf{p}_n) + \mathbf{p}_\infty \sum_{n=1}^{\infty} (a_n - a) - \frac{a}{2}\mathbf{p}_\infty = a^3 \int \zeta\, d\mathbf{P}_0(\zeta)\,.$$

Thus we arrive at formulas (8) and we obtain the following theorem: the reflection of light from a crystalline array behaves as if the array were a continuous medium with a continuous transition layer at its surface. The parameters of this layer are determined by the formula

$$\gamma_x = \frac{a}{p_{\infty x}} \sum_{n=0}^{\infty} (p_{\infty x} - p_{nx}) \tag{40}$$

and similarly for γ_y and γ_z. Inasmuch as the parameters γ_x, γ_y and γ_z are determined to first order only to within one and the same arbitrary constant in this theory, we have neglected the constant $\sum_{n=1}^{\infty}(a_n - a) - \frac{a}{2}$ in these expressions. These parameters should be calculated in the electrostatic approximation. Therefore they depend on the structure of the array, but not on the wavelength of the light (if dispersion is neglected).

This theorem was proved by the author in 1941 [11] by a somewhat different method for an array of less general structure. The quasi-microscopic theory laid out in Section 2 shows that this theorem is valid for an arbitrary thin transition layer on the surface of a transparent isotropic medium. Taking into account that the parameters γ_x, γ_y and γ_z can be altered by the same arbitrary constant, it is not difficult to show that our systematic solution of the molecular problem leading to formulas (8) confirms the molecular interpretation of the parameters γ_x, γ_y and γ_z that we gave in Section 2 for an arbitrary transition layer.

5 Electrostatic field of a square grid of dipoles

1. To calculate the parameters γ_x, γ_y and γ_z we need the solution of the following electrostatic problem. Consider a square grid of identical and identically oriented point dipoles of moment $\mathbf{p}$, laid out in the XY coordinate plane. It is required to determine the electric field acting on the dipole located at the origin produced by all the remaining dipoles.

The static field produced by a dipole of moment $\mathbf{p}$ is given by the expression:

$$3(\mathbf{pr})\mathbf{r}r^{-5} - \mathbf{p}r^{-3}$$

where $\mathbf{r}$ is the position vector directed from the dipole to a given observation point. Summing over all the dipoles except the one at the origin that has been excluded, and denoting the position vector of an atom of the grid by $\mathbf{r}_{lm}$, we obtain for the desired acting field

$$\mathbf{E}'_{\text{grid}} = \sum_{l,m}{}' \left\{ 3(\mathbf{pr}_{l,m})\mathbf{r}_{l,m} r_{l,m}^{-5} - \mathbf{p} r_{l,m}^{-3} \right\}$$

(the prime on the summation sign indicates that the term with $l = m = 0$ should be omitted). Hence

$$(E'_x)_{\text{grid}} = \frac{p_x A}{2a^3}; \qquad (E'_y)_{\text{grid}} = \frac{p_y A}{2a^3}; \qquad (E'_z)_{\text{grid}} = -\frac{p_z A}{a^3}, \tag{41}$$

where

$$A = \sum_{l,m}{}' (l^2+m^2)^{-3/2} = 4\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}(l^2+m^2)^{-3/2} \tag{42}$$

2. The series (42) converges slowly and is thus not convenient for calculating the constant A. We will transform it into a more rapidly converging one. If a low-frequency electromagnetic wave propagates in an unbounded cubic array, then, as is well known, the field $\mathbf{E}'$ acting on an atom of the array is given by the expression

$$\mathbf{E}' = \mathbf{E} + \frac{4\pi}{3}\mathbf{P} = \frac{4\pi\mathbf{p}}{a^3[(n^2-1)+\frac{1}{3}]} \tag{43}$$

On the other hand, the field acting on the atom located at the origin can be calculated in the following way. We split our unbounded array into three parts: 1) a part consisting of the atoms lying above the XY-plane, 2) a part consisting of the atoms lying below this plane, and 3) a part consisting of the atoms lying in the XY-plane. The radiation field of the first part is an external field with respect to the other two parts of the array, and must cancel ("extinguish") the boundary wave in these two parts. Therefore, on the basis of (29) we can write the following expression for the Hertz vector $\mathbf{Z}_1$ of the radiation field of this part (at points outside of it)

$$\mathbf{Z}_1 = -\mathbf{Z}_c = \frac{2\mathbf{p}i}{a^2}\sum_{l,m}\frac{e^{i(\mathbf{f}_{lm}\mathbf{r}-\omega t)}}{f_{lmz}\left[e^{i(k_z-f_{lmz})a}-1\right]}\,.$$

Hence for the field $\mathbf{E}_1$ produced by the first part of the array at the origin we obtain

$$\mathbf{E}_1 = \operatorname{rot}\operatorname{rot}\mathbf{Z}_1 = -\frac{2\pi i}{a^2}\sum_{l,m}\frac{[\mathbf{f}_{lm}[\mathbf{f}_{lm}\mathbf{p}]]e^{-i\omega t}}{f_{lmz}\left[e^{i(k_z-f_{lmz})a}-1\right]}\,.$$

We take the electrostatic limit where $k \to 0$ and consequently $\mathbf{f}_{lm}^2 \to 0$. We obtain

$$\mathbf{E}_1 = \frac{2\pi}{a^2}\frac{(\mathbf{pf})\mathbf{f}-f^2\mathbf{p}}{f_z(k_z-f_z)} - \frac{2\pi i}{a^2}\sum{}'\frac{(\mathbf{pf}_{lm})}{f_{lmz}\left[e^{-if_{lmz}a}-1\right]}\mathbf{f}_{lm}\,.$$

To simplify the calculation we assume that the wave propagates along the X direction and the dipole moments are oriented along the Z-axis. Then the previous expression gives:

$$E_{1z} = \left[\frac{2\pi n^2}{n^2-1}+B\right]\frac{p_z}{a^3}$$

where B is a constant defined by the series:

$$B = -2\pi a i\sum{}'\frac{f_{lmz}}{e^{-if_{lmz}a}-1} = 16\pi^2\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}\frac{\sqrt{l^2+m^2}}{e^{2\pi\sqrt{l^2+m^2}}-1} \tag{44}$$

The exact same field is clearly created by the second part of the array at the origin. The field due to the atoms lying in the XY-plane acting on the atom at the origin is given by (41). Therefore the total acting field is equal to

$$E'_z = \left[\frac{4\pi n^2}{n^2-1} + 2B - A\right]\frac{p_z}{a^3} \tag{45}$$

Comparing this expression with (43) gives

$$A - 2B = \frac{8\pi}{3} \tag{46}$$

The series (44) converges extremely rapidly and is therefore well suited for computations. With the help of this series and relation (46) we obtain[3]

$$A = 9.035; \qquad B = 0.329 \tag{47}$$

3. In order to calculate the parameters γ_x, γ_y and γ_z, we will also need to know the field strength acting on an arbitrary atom of an unbounded array due to a homogeneous wave radiated by all the rows of atoms of the array except for the one in which the atom under consideration is located. We denote this field by $\mathbf{E}_{\text{hom}}$. From the derivation of formula (45), it follows that the first term on the right side of this formula is $(E_z)_{\text{hom}}$ and is the electric induction for the case when the wave is propagating along the X-axis while the dipole moments are directed along the Z-axis. This was to be expected. Indeed, if we consider only a single homogeneous wave, then this corresponds to the average field over a physically infinitely small volume. Moreover, if in order to calculate the field we exclude from consideration the layer of atoms lying in the XY-plane, then this corresponds to removing from the medium a thin slot perpendicular to the direction of the field. As is well known, the field strength in such a slot is equal to the induction field of the medium. If the wave propagates along the Z-axis with dipole moments directed along the X-axis, then clearly our slot will be parallel to the field strength, and consequently the vector $\mathbf{E}_{\text{hom}}$ will be equal to the average Maxwell field $\mathbf{E}$ in the medium for this case. Finally, for this situation it is again easy to verify calculations analogous to those used in deriving formula (45). Therefore it follows from formulas (43) for the two cases considered that

$$E'_x = E_x + \frac{4\pi}{3}P_x = (E_x)_{\text{hom}} + \frac{4\pi}{3}\frac{p_x}{a^3}$$

$$E'_z = E_z + \frac{4\pi}{3}P_z = \frac{D_z}{n^2} + \frac{4\pi}{3}P_z = \frac{(E_z)_{\text{hom}}}{n^2} + \frac{4\pi}{3}\frac{p_x}{a^3}$$

[3]These results are not quite correct to the number of significant digits displayed. Modern computational software gives

$$A = 9.033622; \qquad B = 0.328021$$

See also, e. g.:

J. Topping, "On the mutual potential energy of a plane network of doublets," *Proc. Roy. Soc. London A*, **114**, 67-72, 1927.

[Translator's note].

In view of the fact that in electrostatics each component of the fields $\mathbf{E}'$ and $\mathbf{E}_{\rm hom}$ can be expressed solely in terms of the corresponding component of the vector $\mathbf{p}$, these expressions are also valid for arbitrary directions of $\mathbf{p}$. If β is the polarizability of an atom, then $\mathbf{p} = \beta\mathbf{E}'$. Thus from the previous formulas we obtain

$$\begin{aligned} (E_x)_{\rm hom} &= \left(\frac{1}{\beta} - \frac{4\pi}{3a^3}\right) p_x \qquad (48) \\ (E_z)_{\rm hom} &= n^2 \left(\frac{1}{\beta} - \frac{4\pi}{3a^3}\right) p_z = \left(\frac{1}{\beta} + \frac{8\pi}{3a^3}\right) p_z \end{aligned}$$

6 Calculation of the parameters γ_x, γ_y and γ_z

1. To determine the parameters γ_x, γ_y and γ_z we must evaluate in the electrostatic approximation the electric field acting on the atom located at the point $\mathbf{r}_{00n}$. To this end we separate this field into the following parts:

a) The field $\mathbf{E}_{\rm hom}$, through which the incident light wave and the homogeneous wave radiated by all the rows of atoms except the row containing the atom under consideration act on this atom.

b) The field $\mathbf{E}'_{\rm grid}$ through which all the remaining atoms of the grid act on the atom under consideration. This field is determined by expression (41) if we replace $\mathbf{p}$ by $\mathbf{p}_n$ in it.

c) The field $\mathbf{E}_{\rm inhom}$ through which the inhomogeneous wave arising from all the rows of the array except the one in which the atom under consideration lies acts on this atom.

The Hertz vector $\mathbf{Z}_{\rm hom}$ is assembled first from the Hertz vector of the incident wave:

$$-\frac{2\pi i}{f_z a^2} e^{i(\mathbf{fr})} \sum_{n'=0}^{\infty} \mathbf{A}_{n'} e^{i(k_z - f_z)n'a}\,.$$

Secondly, from the Hertz vector of the homogeneous wave radiated by the first n rows of atoms of the array:

$$\frac{2\pi i}{f_z a^2} e^{i(\mathbf{fr})} \sum_{n'=0}^{n-1} \mathbf{A}_{n'} e^{i(k_z - f_z)n'a}\,.$$

Thirdly, from the Hertz vector of the homogeneous wave radiated by all the rows of atoms lying below the one under consideration:

$$\frac{2\pi i}{f_z a^2} e^{i(\mathbf{f}'\mathbf{r})} \sum_{n'=n+1}^{\infty} \mathbf{A}'_{n'} e^{i(k_z + f_z)n'a}\,.$$

where

$$\mathbf{A}'_n = \mathbf{p}_n e^{i(k_z + f_z)(a_1 + a_2 + \ldots + a_n - na)}\,.$$

Adding these expressions and taking the electrostatic limit, we obtain

$$\mathbf{Z}_{\rm hom} = -\frac{2\pi\mathbf{p}}{f_z(f_z-k_z)a^3}e^{i\mathbf{fr}} - \frac{2\pi\mathbf{p}_\infty}{f_z(f_z+k_z)a^3}e^{i\mathbf{f}'\mathbf{r}}\,.$$

Thus, in the electrostatic approximation the field of this homogeneous wave is just the same as the field of a homogeneous wave in an unbounded array by a dipole wave of constant amplitude $\mathbf{p}_\infty$. This result is almost self-evident. In fact, the influence of the transition layer of the array on the formation of the homogeneous wave is smaller, the smaller is the thickness of the transition layer with respect to a wavelength. In the limit of infinite wavelength, this influence disappears completely. Thus, the field $\mathbf{E}_{\rm hom}$ can be calculated from formula (48) if we replace $\mathbf{p}$ by $\mathbf{p}_\infty$ in it.

We denote by $\mathbf{E}_{nn'}$ the field through which the inhomogeneous components of the dipole waves $\mathbf{p}_{lmn'} = \mathbf{p}_{n'}e^{i\mathbf{kr}_{lmn'}}$ propagating in the $(n'+1)$st layer of atoms act on the atom under consideration. This field is easily calculated with the help of (32) and (33). We obtain

$$E_{nn'x} = -\frac{B_{nn'}p_{n'x}}{2a^3}, \qquad E_{nn'z} = -\frac{B_{nn'}p_{n'z}}{a^3}\,, \tag{49}$$

where

$$B_{nn'} \equiv B_{n'n} = 16\pi^2\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}\sqrt{l^2+m^2}e^{-\frac{2\pi}{a}(a_{n'+1}+a_{n'+2}+\ldots+a_n)\sqrt{l^2+m^2}}\,. \tag{50}$$

If $n=n'$, then we will put $B_{nn'} \equiv B_{n'n} = 0$ by convention.

Summing $\mathbf{E}_{nn'}$ over n' gives $\mathbf{E}_{\rm inhom}$. If β_n is the polarizability tensor of our atom under consideration, then

$$\mathbf{p}_n = \beta_n\left(\mathbf{E}_{\rm hom} + \mathbf{E}'_{\rm grid} + \mathbf{E}_{\rm inhom}\right)\,.$$

As a result of this we can write

$$p_{nx} = \beta_{nx}\left[\left(\frac{1}{\beta} - \frac{4\pi}{3a^3}\right)p_{\infty x} + \frac{p_{nx}}{2a^3}A - \frac{1}{2a^3}\sum_{n'=0}^{\infty}B_{nn'}p_{n'x}\right]\,,$$

$$p_{nz} = \beta_{nz}\left[\left(\frac{1}{\beta} + \frac{8\pi}{3a^3}\right)p_{\infty z} - \frac{p_{nx}}{a^3}A + \frac{1}{a^3}\sum_{n'=0}^{\infty}B_{nn'}p_{n'z}\right]\,.$$

We have assumed here that the principal axes of the tensor β_n are parallel to

the coordinate axes. The preceding equations can be written in the form

$$\begin{aligned} p_{nx} - p_{\infty x} &= \frac{\beta_n - \beta}{\beta} p_{\infty x} + \frac{\beta_{nx}}{2a^3} \{ b_n p_{\infty x} + A(p_{nx} - p_{\infty x}) \\ &\quad - \sum_{n'=0}^{\infty} B_{nn'}(p_{n'x} - p_{\infty x}) \Big\} , \qquad (51) \\ p_{nx} - p_{\infty x} &= \frac{\beta_n - \beta}{\beta} p_{\infty x} + \frac{\beta_{nx}}{2a^3} \{ b_n p_{\infty x} + A(p_{nx} - p_{\infty x}) \\ &\quad - \sum_{n'=0}^{\infty} B_{nn'}(p_{n'x} - p_{\infty x}) \Big\} , \end{aligned}$$

where

$$b_n = 2B - \sum_{n'=0}^{\infty} B_{nn'} \qquad (52)$$

From the infinite systems (51) of equations one can determine the unknowns $p_{nx} - p_{\infty x}$ and $p_{nz} - p_{\infty z}$ for any n. Upon substituting these values into (40) we find the parameters γ_x and γ_z. These unknowns can be calculated as accurately as desired by truncating the infinite system of equations (51) to a finite number of equations. Indeed, we can put all $\mathbf{p}_n - \mathbf{p}_\infty$ equal to zero for $n > N$, where N can be chosen at will. Then we obtain a system of $N + 1$ linear equations with $N + 1$ unknowns. For the sake of simplicity we limit ourselves to the case when $N = 0$, i. e., the transition layer is monatomic. In this approximation we obtain:

$$\begin{aligned} \gamma_x &= \frac{\beta - \beta_{0x}}{\beta(1 - \frac{A\beta_{0x}}{2a^3})} a - \frac{\beta_{0x}}{2a^3} \frac{b_0}{1 - \frac{A\beta_{0x}}{2a^3}} a \, , \qquad (53) \\ \gamma_z &= \frac{\beta - \beta_{0z}}{\beta(1 + \frac{A\beta_{0x}}{a^3})} a - \frac{\beta_{0z}}{a^3} \frac{b_0}{1 + \frac{A\beta_{0z}}{a^3}} a \, . \end{aligned}$$

Hence we can express the ellipticity coefficient of light reflected at the Brewster angle as:

$$\rho = \frac{\pi}{\lambda} \sqrt{n^2 + 1} (\gamma_x - \gamma_z) \, . \qquad (54)$$

2. We see that ρ does not vanish even when the structure of the array near the surface has no distortion at all. In this case,[4]

$$\beta_n = \beta, \qquad a_n = a, \qquad b_0 = 2B - \sum_{n=1}^{\infty} B_{0n} \simeq B = 0.329.$$

The polarizability β can be calculated from the formula

$$\beta = \frac{3a^3}{4\pi} \frac{n^2 - 1}{n^2 + 2} \, .$$

[4]See footnote[3] [Translator's note].

Substituting this into (54), and using (53) and (47), we obtain the approximate formula:

$$\rho = -\frac{3}{2}(n^2-1)\sqrt{n^2+1}\frac{a}{\lambda}\left[\frac{1}{39-n^2}+\frac{1}{20n^2-1}\right]. \tag{55}$$

For a hypothetical crystal with the same refractive index as water ($n = 1.33$), this formula gives $\rho = -0.11(a/\lambda)$. Taking $\lambda = 5500$ Å and $a = 3$ Å, i. e., reckoning that the lattice constant is equal to the average distance between water molecules in the absence of coordination, we find $\rho = -0.00006$. In his experiments, Rayleigh [1] found the value $\rho = +0.00042$. Although our formulas for γ_x and γ_z were derived for a crystal, while for liquids at least they have not been validated, we can imagine that they give at least the correct order of magnitude for γ_x and γ_z in the case of a liquid. Hence we can conclude that the molecular structure of matter, even in the absence of distortion in the structure of a body near its surface, produces a deviation from the Fresnel formulas that is observed experimentally. However, this deviation is smaller than that observed by Rayleigh for water, and by Raman and Ramdas for organic liquids. Moreover, we find a discrepancy between the signs of the theoretical and experimental ellipticity coefficients.

3. This disagreement can be ascribed to the compacting of the matter near the surface of the body. In our model with a monatomic layer this means that $a_1 < a$. Then the numerical value of b_0 entering into (53) changes, while in (55) there appears a factor equal to the ratio of the new value of b_0 to its old one. In the following table the constant b_0 is shown for various values of the ratio a_1/a.

a_1/a	b_0	ρ
1.0	+0.33	−0.00006
0.9	+0.02	−0.00000
0.8	−0.65	+0.00012
0.7	−1.8	+0.00033
0.6	−4.3	+0.00078
0.5	−9.8	+0.00178

The constants are calculated from formula (52). In the preceding table are shown theoretical values of ρ for a hypothetical crystalline array with refractive index $n = 1.33$ and lattice constant $a = 3$ Å.

4. For liquids made up of anisotropic molecules, the disagreement can also be partly attributed to the orientation of the axis of largest polarizability of molecules near the boundary being predominantly perpendicular to the boundary of the medium. In this case we should understand β_n in our formulas to mean the average polarizability tensor of the molecules. When the layer is monatomic, β_n reduces to a scalar for all n except $n = 0$. Furthermore, $\beta_{0x}+\beta_{0y}+\beta_{0z} = 3\beta$, and since $\beta_{0x} = \beta_{oy}$, then $2\beta_{0x}+\beta_{0z} = 3\beta$. Based on this, formulas (53) can be

written in the form:

$$\gamma_x = \frac{a}{1-\frac{A\beta_{0x}}{2a^3}}\left\{\frac{\beta_{0z}-\beta_{0x}}{3\beta}-b_0\frac{\beta_{0x}}{2a^3}\right\}, \tag{56}$$

$$\gamma_z = -\frac{2a}{1+\frac{A\beta_{0z}}{a^3}}\left\{\frac{\beta_{0z}-\beta_{0x}}{3\beta}-b_0\frac{\beta_{0z}}{2a^3}\right\}.$$

If $\beta_{0z}-\beta_{0x}=\frac{1}{10}\beta$, then for a hypothetical array with $n=1.33$ and $a=a_1=3$ Å we obtain $\rho=+0.00018$; if $\beta_{0z}-\beta_{0x}=\frac{1}{5}\beta$, then we obtain $\rho=+0.00046$.

When comparing theory with experiment, it should be kept in mind that the foundation of our calculation of the parameters γ_x, γ_y and γ_z relies on a very unrealistic model of the reflecting medium. Therefore the computations carried out here can give only the orders of magnitude of these parameters; their accurate calculation entails much more difficulty and requires knowledge of the molecular structure of the body and of the transition layer.

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