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ABSORPTION SPECTROSCOPY OF DISPERSED MATERIALS

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Part I

THEORETICAL FOUNDATIONS

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1. INTRODUCTION

AGAINST the background of the brilliant successes of spectroscopy, which has long since become a powerful and, for the time being, indispensable means of scientific research and manufacturing control, a serious gap has been all the more noticeable in recent years. The existing methods of spectral analysis are shown to be of little fruitfulness, if not completely powerless, when applied to light-scattering objects. The classic example of this is the phenomenon of the self-reversal of spectral lines, which at the present time lend themselves only to comparatively rough, semiquantitative estimates. The situation is still worse with the region, very broad in the variety of objects and extremely important in practical use, of spectral analysis of materials in a dispersed state. Either because of their nature or because of the character of the analytical problems, these substances permit only the application of absorption methods. The importance of such a type of problem can be judged if only by a simple enumeration of some of the objects that are treated therein. These include in first degree all kinds of pigments, powders, colloids, polymers, aero-and hydrosols, emulsions, adsorbates, mineral formations, ceramics, polycrystalline and fibrous materials, and, finally, the majority of biological objects — blood, chloroplasts and tissues. Furthermore, it happens frequently, especially in infrared spectroscopy, that one has recourse to artificial dispersion of materials under study if their absorption capability is too great for the use of traditional methods; below we shall see that it is reasonable to turn to this approach even in the case of very weak absorption. Virtually all the same problems arise also in connection with luminescent powders.

Up to the present time, there have been thousands of researches devoted in this or that measure to the spectroscopy of dispersed materials. However, if one considers them from the methodological point of view, then it is easy to find that in the overwhelming majority of cases the specific nature of object either was not considered at all, or was considered in very primitive fashion. This frequently not only limited the amount of information and lowered its reliability, but also led to direct mistakes. Yet, in recent years, a fairly large number of theoretical and experimental works have appeared which, if they do not permit us to solve the fundamental methodological problems, do in

every case state them clearly. Therefore, it seems opportune to review the present state of spectroscopy of dispersed materials, and to mark out those problems whose experimental and theoretical study is most essential from the viewpoint of the development of methods of spectral analysis. We shall consider below the theoretical foundations of spectral analysis of dispersed materials — the experimental data will be discussed in Part 2.

The specific difficulties, which we mentioned above and which stand in the way of the development of the spectroanalysis of dispersed materials, are connected in the final analysis with the necessity of separating absorption effects from scattering effects. Even in the case of individual particles of rather small dimensions, this problem requires special investigation.

On the other hand, the transition to an aggregate of many particles, that is, to a dispersive medium, is associated with a qualitative complication of the character of the analytical problem itself, since here various effects of the mutual irradiation of the particles inevitably begin to manifest themselves; these distort the picture materially. In other words, in going from single particles to their aggregate (and in the great majority of practical problems we must deal with the dispersive medium and not with individual particles), we enter into the region of the optics of scattering media. Therefore, the development of spectral analytical methods must be based first on an understanding of the laws of scattering and the propagation of light in a dispersive medium. We shall attack the problem under consideration from just this point of view. However, inasmuch as the optics of scattering media possesses a number of specific peculiarities, and inasmuch as the fundamental representations referring to this region are burdened, for reasons of historical character, by widespread errors, it is appropriate to begin a discussion of the questions of interest to us from basic principles. It is necessary above all to make some general observations.

Until comparatively recently the possibilities of a theoretical investigation of the interaction of radiation with matter within the framework of optics were restricted essentially to two limiting cases. On the one hand, there is the propagation of radiation in quasi-homogeneous media, where the parameters of the radiation field changed smoothly and comparatively slowly as functions of the spatial coordinates. On the other hand, there are the phenomena of emission, absorption and scattering of radiation by single particles, or by inhomogeneities interspersed in a homogeneous medium; in this case the object of study becomes the act of a sharp local transformation of the radiation field under the action of the material. Bordering directly on the latter circle of problems are questions connected with local transformations experienced by radiation at sharp single boundaries of quasi-homogeneous media (reflection, refraction, etc.).

The intermediate case of the propagation of radiation in media which do not satisfy the condition of quasi-homogeneity (including turbid scattering media) remained, and indeed still remains, little studied with the exception of a comparatively small number of special cases. It would appear that, under the pressure of numerous practical needs, this circle of problems forms, in ever increasing degree, one of the fundamental directions of development of contemporary physical optics. One need only recall the recent successes of the optics of thin films, i.e., of essentially inhomogeneous systems, or the vigorous development of the theory of radiation transfer. Moreover one must mention the inadequate attention given to these problems by a wide variety of physicists which must be attributed to the complicated nature and originality of these problems and a certain alienation of them from the traditional directions of development of contemporary physics.

The restriction of the theory of propagation to quasi-homogeneous or, in the best case, regularly inhomogeneous media is dictated by the desire to preserve the applicability of Maxwell's phenomenological equations, which permit us to separate the theory of propagation from the theory of scattering and the theory of dispersion phenomena. The appearance of molecular (both classical and quantum) optics did not change the state of affairs essentially because its contribution was limited precisely to the region of scattering theory and dispersion (determination of material constants) in quasi-homogeneous (molecular) media.

Turning to scattering media, we are at once deprived of this possibility. The decisive factor that determines the specific nature of the conditions for the propagation of radiation in a statistically inhomogeneous medium is the mutual exposure of the light-scattering inhomogeneities. Therefore, even if one succeeds in keeping scattering theory and propagation theory strictly separate, the latter deals essentially with the determination of the effective field in which the separate inhomogeneities are located and with the interference of waves scattered by them. Inasmuch as the outstanding peculiarity of turbid media is the irregularity of their construction, we are confronted with statistical problems which do not allow us to make use of the

equations of phenomenological electrodynamics, nor to separate dispersion theory from the theory of propagation.

However, a closer examination indicates[1] that the corresponding statistical problem admits of important simplification. It is shown that the mutual influence of the inhomogeneities breaks down essentially into two parts — coherent and incoherent. The coherent part, for which only the immediate vicinity of this or that scattering inhomogeneity is actually responsible, is manifest here exclusively in two effects: 1) dispersion phenomena, i.e., a change of the effective complex index (generally a matrix) of refraction of the medium, and 2) in the difference of the effective function (generally a matrix) of the scattering from the medium for an isolated particle. At the same time the incoherent part of the interaction, which owes its origin to the whole volume of the scattering medium, enters in the form of multiple scattering and therefore can (with known reservations) form the subject of an independent investigation.

Inasmuch as all three factors — optical properties of the isolated particle, coherent cooperative effects, and multiple scattering — are important for the solution of spectroscopic problems, we shall consider each of them separately.

2. OPTICAL PROPERTIES OF AN ISOLATED PARTICLE

The immediate problem of an absorption spectro-analytic experiment is the determination of the spectral dependence of the absorption coefficient κ and (or) the index of refraction n of the substance forming a particular body. If the body is homogeneous and rather large in comparison with the optical wavelength, then diffraction and surface effects can be eliminated with the help of traditional methods; hence, no difficulties in principle arise in the realization of the spectro-analytical experiment. However, if the dimensions of the body are comparable with the wavelength of light, then both diffraction and surface effects begin to play the dominant role and it is not possible to separate them. In this case the particle no longer enters as an individual entity characterized by certain optical properties, and the basic problem of the theory of scattering by small particles consists indeed of the establishment of the connection between these properties, the geometric parameters of the particle, and the optical parameters of the material of which the particle is composed. By way of example, we note that the absorbing property of a particle depends essentially on what part

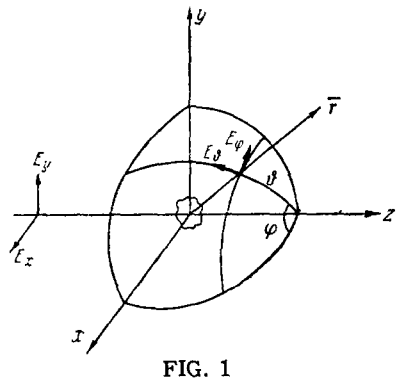

FIG. 1

of the radiation incident upon it can penetrate to the interior of the particle, i.e., on the condition of the diffraction of light on its surface, and in turn on its dimensions and shape. Another example is the important effect of the surface (for example, adsorbed) layer on the optical properties of a particle, especially the effect due to a sharp increase in the specific area of the interphase boundaries in the case of dispersion.

In what way should we characterize the optical properties of the particle as a whole? Obviously, these properties must first find their expression in the character of the radiation field scattered by the particle, including the character of its polarization. We assume that a completely (generally elliptically) polarized plane light wave is incident along the z axis on a particle located at the origin of the coordinates (Fig. 1); the components of the electric field intensity of this wave are E_x and E_y, and we observe the light waves scattered in the direction **r**, which is defined by a polar angle ϑ (scattering angle) and azimuth φ. Then, as a consequence of the linearity of the equations of electrodynamics, the meridional and the latitudinal components E_ϑ and E_φ of the electric field of the scattered wave at a distance r from the particle (sufficiently large so that the point of observation is in the wave region) will be equal to

$$\begin{pmatrix} E_\vartheta \\ E_\varphi \end{pmatrix} = \frac{1}{r}\begin{pmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{pmatrix}\begin{pmatrix} E_x \\ E_y \end{pmatrix}, \qquad (2.1)$$

where the components of the matrix μ_{ik} depend upon the angles ϑ and φ, and naturally on the wavelength. Thus the amplitude scattering matrix μ_{ik} completely characterizes the scattering properties of the particle.

On the other hand, for reasons which will be explained below, the radiation field must be characterized, within the framework of the optics of scattering media, not by the field intensities, but by certain statistical parameters that are additive for incoherent light fluxes. Among such parameters are the so-called Stokes parameters, which entirely

characterize the state of the radiant flux from the viewpoint both of its intensity and its polarization, and which are genetically connected with the quantum-mechanical density matrix.* In generalized form, the Stokes parameters S_i are defined by the relation

$$S_i = \mathbf{E}\sigma_i \mathbf{E}^* \qquad (i = 1, 2, 3, 4) \tag{2.2}$$

and can be incorporated in the single four-dimensional Stokes vector-parameter $\vec{S}$. Here, σ_1 is a unitary matrix of second rank, while σ_2, σ_3 and σ_4 are Pauli matrices which permute in cyclic order, beginning with the third. For clarification we recall that

$$S_1 = I,\ S_2 = Ip\cos 2\psi,\quad S_3 = Ip\sin 2\psi,\quad S_4 = Iq, \tag{2.3}$$

where I is the intensity of the light beam, p is the degree of its polarization, ψ is the angle between the direction of the principal polarization and some arbitrarily chosen reference plane that includes the direction of the light beam, and q is the so-called degree of ellipticity, equal to the product of the angular frequency of the radiation and the flux density of the spin angular momentum of the light wave divided by its power.

Again, as a result of the linearity of the equations of electrodynamics, the vector-parameter of the light wave scattered by the particle is connected with the vector-parameter of the light wave irradiating the particle by the linear relation

$$\vec{S}^{\,\mathrm{scat}} = \frac{1}{r^2} D\vec{S}^{\,\mathrm{inc}}, \tag{2.4}$$

where the energy scattering matrix D is of fourth rank and is directly related to the matrix μ_{ik}: the components of D are real bilinear functions of the components D_{ik} and their conjugates (for details, see reference 2).

Furthermore, it is reasonable to characterize the scattering particle by the transverse scattering cross section $\tilde{\sigma}^0$, i.e., by the fraction of the light power carried away by the particle from the wave irradiating it and scattered in various directions. However, it immediately follows from (2.3) and (2.4) that the transverse scattering cross section depends on the character of the polarization of the incident wave. Therefore, it is advantageous in a number of cases to introduce the transverse scattering cross section σ^0 for a completely unpolarized incident wave ($S_2^{\mathrm{inc}} = S_3^{\mathrm{inc}} = S_4^{\mathrm{inc}} = 0$). We can then set

$$D_{ik} = \frac{\sigma^0}{4\pi} d_{ik}, \tag{2.5}$$

which corresponds to the normalization condition

$$\frac{1}{4\pi}\oint d_{11}\sin\vartheta\, d\vartheta\, d\varphi, \tag{2.6}$$

where the component d_{11} coincides with the so-called scattering function or scattering indicatrix, which is widely used in the literature on light scattering.

But not all the energy carried away by the particle from the incident wave is scattered; part of it is absorbed by the particle. Therefore, the optical properties of the particle are also described in terms of the attenuation (extinction) cross section $\tilde{f}^0$, i.e., the fraction of the power carried away by the particle independent of the way in which this power is consumed. To determine $\tilde{f}^0$, one must consider the energy flux through a closed surface surrounding the particle, with allowance for the interference of the incident and scattered waves. For this purpose, in particular, one can expand the scattered wave field in a set of coherent plane waves of different directions, and take two infinite planes in front of and behind the scattering particle as the enclosing surfaces.[1] Completing such an expansion, and denoting by $E_1(\vartheta, \varphi)$ and $E_2(\vartheta, \varphi)$ the components of the electric field of the plane wave of direction (ϑ, φ), we again obtain a relation of the form (2.1) with replacement of the matrix $\frac{1}{r}\mu_{ik}(\vartheta, \varphi)$ by the matrix $g_{ik}(\vartheta, \varphi)$. Further, computing the energy flux through the enclosing planes and taking it into account that

$$\int_{-\infty}^{+\infty}\int e^{-i(k_x x + k_y y)}\,dx\,dy = \frac{2\pi}{k^2}\delta(k_x)\delta(k_y), \tag{2.7}$$

where $\mathbf{k} = \mathbf{k}_0 n_0$ is the wave vector in the medium surrounding the particle, n_0 the index of refraction of the medium, $k_0 = 2\pi/\lambda$, and δ is the Dirac delta function, we find readily that the transverse cross section of attenuation is equal to

$$\tilde{f}^0 = -\frac{2\pi}{k_0^2 n_0^2}\left\{\mathrm{Re}\,[g_{11}(0) + g_{22}(0)] + \mathrm{Re}\,[g_{11}(0) - g_{22}(0)]\frac{S_2^{\mathrm{inc}}}{S_1^{\mathrm{inc}}} + \mathrm{Re}\,[g_{12}(0) + g_{21}(0)]\frac{S_3^{\mathrm{inc}}}{S_1^{\mathrm{inc}}} + \mathrm{Im}\,[g_{12}(0) - g_{21}(0)]\frac{S_4^{\mathrm{inc}}}{S_1^{\mathrm{inc}}}\right\}, \tag{2.8}$$

where the zero in the parentheses means that the values of g_{ik} are those corresponding to plane waves traveling along the z axis parallel to the incident wave ($\vartheta = 0$). It is seen from (2.8) that $\tilde{f}^0$ depends essentially on the polarization of the incident wave and that this dependence disappears only in the case of isotropic particles.

Finally, to describe the particles, we introduce also the transverse absorption cross section $\tilde{\alpha}^0$, which is defined as the difference between the at-

*For further details on the Stokes parameters and their properties, see reference 2.

tenuation and scattering cross sections:

$$\tilde{\mathfrak{t}} = \tilde{\alpha}^0 + \tilde{\sigma}^0, \tag{2.9}$$

where by $\tilde{\sigma}^0$ is understood the quantity

$$\tilde{\sigma}^0 = \frac{\sigma_0}{4\pi} \oint \left(d_{11} + d_{12} \frac{S_2^{\text{inc}}}{S_1^{\text{inc}}} + d_{13} \frac{S_3^{\text{inc}}}{S_1^{\text{inc}}} + d_{14} \frac{S_4^{\text{inc}}}{S_1^{\text{inc}}} \right) \sin\vartheta \, d\vartheta \, d\varphi, \tag{2.10}$$

which depends on the polarization of the incident wave; the integration is carried out over all the scattering angles [see (2.4)].

In a number of cases, it is reasonable to introduce the attenuation cross section $\mathfrak{t}^0$ and the absorption cross section α^0 for a completely unpolarized incident wave ($S_2^{\text{inc}} = S_3^{\text{inc}} = S_4^{\text{inc}} = 0$), carrying out the corresponding renormalization of the matrix g_{ik}. In this case, an expression of the form (2.9) remains in force for $\mathfrak{t}^0$, α^0, and σ^0.

It should be noted that all the quantities mentioned, which characterize the optical properties of the particle, depend on the orientation of the latter relative to the direction of incidence. Only in the case of isotropic particles does this dependence, and also the dependence of $\mathfrak{t}^0$, $\tilde{\alpha}^0$, and $\tilde{\sigma}^0$ on the polarization of the incident beam vanish and the latter quantities can be considered as the actual characteristics of the scattering particle, which do not depend on the conditions of its irradiation. With certain reservations, the latter statement can be extended to an ensemble of non-isotropic, randomly oriented and non-interacting particles, wherein the quantities $\mathfrak{t}^0$, α^0, and σ^0 will have the meaning of averaged statistical characteristics.

We now turn our attention to the consequences that follow from what was said relative to spectro-analytical problems. First, a transition from the rather numerous optical characteristics of the particle as a whole to the few (for a given wavelength) parameters that characterize the material of which it is composed (n and κ), its dimensions and, in the worst case, its shape and orientation, requires a well-developed theory of light scattering by small particles. The contemporary state of scattering theory (see, for example, references 3 and 4) is very far from being able to serve reliably in problems of this type. In fact, the diffraction problem has been solved only for particles of very simple shape, and essentially only in principle at that. The solutions obtained, with few exceptions, are expressed in the form of complicated series, in which it is necessary to take into account an enormous number of terms of the expansion. In practice, this reduces to the situation that the solution can be obtained only by numerical calculations on mathematical machines. Therefore, at the present time, we do not have at our disposal even a sufficient set of detailed partial solutions, which could serve as a more or less reliable set of basic laws suitable for the interpretation of the experimental data. The existing tables are modest in scope, as a rule, ignore polarization effects, and refer almost exclusively to nonabsorbing particles.

We have discussed above the direct problem of scattering theory — the determination of the optical characteristics of a particle from its given properties. The situation is still worse for the solution of the inverse problem, which is necessary for spectro-analytical purposes. Here, essentially nothing has been done, and one can hardly hope to obtain any sort of rigorous solution in the near future. Therefore, it is of great importance to try such approximate methods of solution of the inverse problem of scattering theory as would guarantee a semi-quantitative or even qualitative approximation, and would permit us to determine the extent of experimental information on the optical properties of particles necessary for analytical purposes. In such a state of the theory, the empirical and semi-empirical methods of investigation of basic dependencies acquire a special importance; unfortunately, experimental researches in this direction have been practically nonexistent to date.

Further, it should be borne in mind that the spectral dependences of α^0, σ^0, and $\mathfrak{t}^0$ for particles of a given size do not correspond at all to the spectral dependences of n and κ of the material forming them, and reflect them only in very indirect form. Thus, for particles whose dimensions are appreciably greater than the wavelength of the light, $\mathfrak{t}^0$ is virtually independent of λ, and is equal to twice the geometric cross section of the particle,[3] while the absorption inside the particle affects essentially the amount of light scattered in the rear hemisphere. The latter circumstance, in particular, frequently prevents us from obtaining even qualitative information on the actual absorption spectrum of dispersive material by measuring the attenuation of a parallel light beam by a thin layer of scattering particles. This was decisively shown in the experiments of É. V. Shpol'skiĭ and A. A. Il'ina with erythrocytes.[5,6] It was shown by the same experiments that the character of pure absorption of the hemoglobin contained in the erythrocytes is much more reliably determined in scattered than in transmitted light. We shall see below that just this circumstance permits the realization of those specific possibilities which are connected with the use of the effects of multiple scattering.

Another effect, which appreciably distorts the spectrum of the attenuation of light by a particle

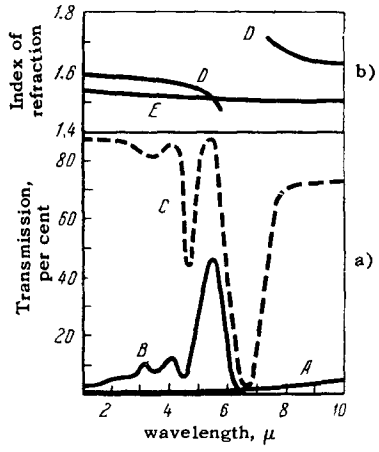

FIG. 2. a – transmission curves of Christiansen filters; b – dispersion curves. A – dry rock-salt powder; B – sodium chloride powder suspended in carbon bisulfide; C – pure carbon bisulfide; E – rock salt; D – carbon bisulfide.[17]

(or by a thin layer of particles) in comparison with the absorption spectrum of the material composing it, is the sharp dependence of the scattering cross section on the ratio of the index of refraction of the particle to that of the surrounding medium. This effect, the operating principle of the well-known Christiansen optical filter* (which consists of a layer of a suitably chosen dispersive medium), is illustrated in Fig. 2, in which the sharp increase in transmission as the index of refraction of the particles approaches that of the immersion liquid, is clearly evident.[17] A unique variant of this effect (Fig. 3) is the transmission of a disperse medium in the region of a resonance absorption band of the dispersive material, connected with the decrease in the index of refraction of the latter in the region of anomalous dispersion; this effect is frequently observed when matter is dispersed in air (powder, water, fog, etc).[18,19] We note that the decrease in the extinction cross section takes place in the given case chiefly as the result of the decrease in the scattering ability of the particles, i.e., σ^0. Naturally, this suggests the possibility of the elimination of scattering effects by immersing the scattering particles in suitably selected immersant. However, the effects of scattering can disappear completely only if the real and imaginary indices of refraction of the particles and of the medium surrounding them coincide (see, for example, references 3 and 16). Therefore, application of the immersion method, for all its undoubted attraction, requires precautions and special preliminary investigations.

We point out one more significant effect of the

*In addition to the effect described, the cooperative effects considered in the next section (see references 7-16) also play an important role in the Christiansen filter.

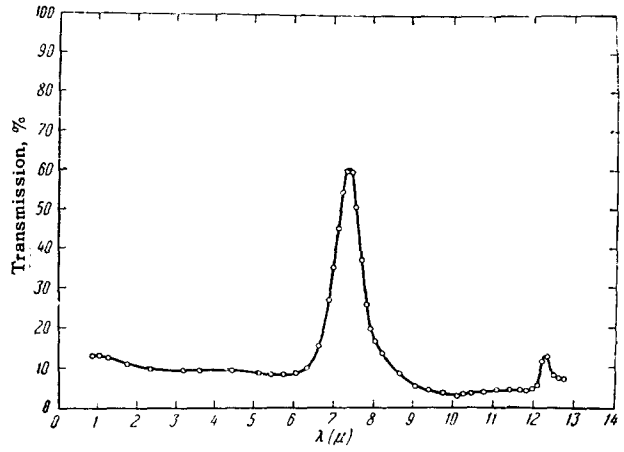

FIG. 3a. Transparency of a layer of powdered quartz with particle dimension 28.1 μ. Thickness of equivalent solid layer of quartz, 7.8 μ.[19]

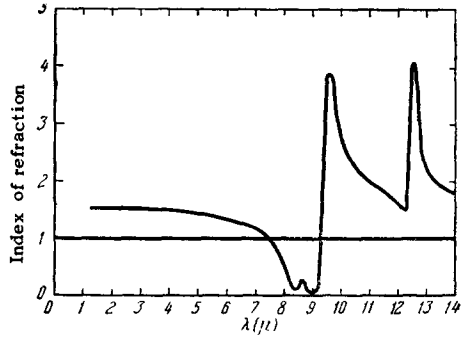

FIG. 3b. Dispersion of quartz (ordinary ray).

dependence of the extinction cross section on the wavelength. It follows from Mie's theory[3,4] that for definite relations beween the dimensions of the particle, the optical wavelength, and the indices of refraction of the particle and the medium surrounding it, a sharp resonance increase in scattering sets in, which is manifest, in particular, in the appearance of corresponding minima of transmission, i.e., pseudo-absorption bands. An example of this rather well-studied effect is shown in Fig. 4.[20]

Thus, we see that by measuring the transmission of a thin layer of a dispersive medium (so far, we neglect effects of multiple scattering), we can essentially determine only the spectral variation of the extinction cross section, and the question of how much this variation is responsible for the spectral dependence of the absorbing ability of the material of the particle requires a special study each time.

We are in a somewhat better position when the dimensions of a sufficiently transparent particle are so large that we can make use of microspectroscopic methods, in which only that light is used for the analysis which travels through the studied particle. In this case, it is true, we are usually

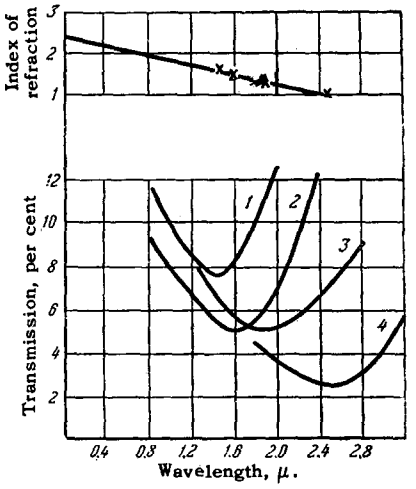

FIG. 4. Transmission minimum caused by Mie resonance in powdered zinc sulfide suspended in different media,[20] 1 – α-chloronaphthalene; 2 – benzene; 3 – methyl alcohol; 4 – air.

deprived of the possibility of determining the real thickness of the material traversed by the light, and we must limit ourselves only to the determination of the location of the absorption bands and to qualitative judgments on their intensities.

Finally, in principle, the absorption cross section α^0 of an isolated, we emphasize, isotropic particle can be determined by placing the latter in a photometric sphere. However, because of the smallness of the effect, this is realizable only for sufficiently large particles. But if we attempt to increase this effect by increasing the number of simultaneously irradiated particles, then we inevitably encounter noise due to multiple scattering. Thus, we see that the methods of direct determination of the extinction or absorption cross sections are not among the best or most suitable ones, and, in any case, do not guarantee the separation of the effects of absorption and scattering.

A great deal of information, at least in principle, can be extracted by studying the angular dependence of the scattering matrix. By itself, measurement of the angular dependence of the scattering matrix of a single particle, especially for very small and very large scattering angles, is a very complicated and sensitive experimental problem, in which one of the fundamental obstacles is the extreme weakness of the scattered light. To be sure, there is some possibility of increasing the measured effect by accumulation (for example, photographic) in the successive viewing of many particles.[21] But here we come against the necessity of guaranteeing the strict identity of the measured particles; furthermore, we do not reduce in the least the demands as regards the signal-to-noise ratio, which, in the last analysis, determines the minimum size of particles accessible to measurement. The number of simultaneously irradiated particles can be increased within very narrow (and not yet sufficiently clear) limits because of the noise created by multiple scattering. It must be noted that experimental investigations of a detailed character are still extremely few in number.

One finds in the literature a whole series of attempts at determining the scattering cross section σ^0 by integrating the experimentally-observed curve of the angular dependence of the intensity of scattered light (including the use of various nephelometers). However, as a consequence of the difficulty of measuring the latter at very small scattering angles, especially in the region of the diffraction aureole, the results so obtained are very unreliable.

In addition, there are grounds for assuming that the development of procedures for interpretation of the angular and spectral dependence of the scattering matrix will allow, in the future, a direct determination of the spectral characteristics of the material forming the particle. A guarantee of this is the success in the development of procedures for determining particle dimensions from the structure of the corona (for particles commensurate with the optical wavelength) or aureoles (for much larger particles).

3. COOPERATIVE EFFECTS

While the theory of light scattering (diffraction) by small particles, in spite of all its inherent difficulties, exists and is successfully developed, the first rough steps have scarcely been made towards an investigation of coherent cooperative effects. Therefore, we must limit ourselves to the general outlines of the phenomena that occur in this area. We shall speak of closely interrelated phenomena of two kinds – the dependence of the effective field in which the particles are located on their concentration, and the interference of waves scattered by neighboring particles. We emphasize that, as a consequence of the random nature of the spatial distribution of particles and of their mobilities, the problem possesses an essentially statistical character. In particular, the light field, which is formed as the result of the interference of scattered waves, will be inhomogeneous in space and fluctuating in time. However, if the detecting apparatus has dimensions large in comparison with the scale of the interference picture (i.e., the scale of the distances between particles) and has a sufficient inertia, then we should be interested only in the picture averaged over all possible positions and orientations of the particles. We shall

begin with a discussion of interference effects, in which, taking into account the specific characteristics of the dispersion (non-molecular) of the medium, we shall modify somewhat[1] the well-known discussions of L. I. Mandel'shtam.[22]

Let us represent the radiation scattered by the particle in the form of a set of plane waves in different directions, and consider first waves propagating along the z axis parallel to the incident wave. Because of the coherence of the scattered and incident waves, all the plane scattered waves that we have selected are strictly in phase, independent of the positions of the scattering particles. Therefore, the total intensity of the field scattered forward by a layer of thickness dl is proportional to the concentration N of the scattering particles and, by virtue of (2.7), is equal to

$$dE_i^{\text{scat}} = \frac{2\pi N}{k_i^2} \sum_j g_{ij}(0) E_j \, dl, \tag{3.1}$$

where i, j = x, y, $\mathbf{E} = \mathbf{E}^{\text{inc}} + \mathbf{E}^{\text{scat}}$ is the total field in which the scattering particles lie, $k_i = k_0 n_i$ is the wave number in the scattering medium (which differs from $k = k_0 n_0$, the wave number in the medium in which the particles are immersed),* and $g_{ij}(0)$ are the components of the matrix g_{ij} (defined above) for the scattering angle $\vartheta = 0$. If the particles are not identical, then by g_{ij} we must understand the corresponding statistical average. Since the wave incident on the layer changes in the path dl (in the absence of scattering particles) by an amount $-ik\mathbf{E}\,dl$, then we have, in the presence of scattering particles,[1,2] (see also references 4, 23, and 24)

$$dE_i = -\sum_j \nu_{ij} E_j \, dl, \tag{3.2}$$

where the components of the dispersion matrix ν_{ij} are

$$\nu_{ij} = ik\delta_{ij} - \frac{2\pi N}{k_i^2} g_{ij}(0). \tag{3.3}$$

If the matrix $g_{ij}(0)$ is diagonalized, then for a turbid medium, one can introduce the concept of an effective complex index of refraction n_i for each of the alternately polarized components of the field E_i:

$$n_i = -\frac{i\nu_{ii}}{k_0} = n_0 + i\frac{2\pi N}{k_0 k_i^2} g_{ii}(0) \tag{3.4}$$

or

$$n_i = n_0 - \frac{2\pi N}{k_0 k_i^2} \operatorname{Im} g_{ii}(0) + i\frac{2\pi N}{k_0 k_i^2} \operatorname{Re} g_{ii}(0). \tag{3.5}$$

*Because of the smallness of $n_i - n_0$, one can usually neglect this difference. As is seen from what follows, the introduction of k_i is permissible only if the matrix ν_{ij} is diagonalized.

Thus in the general case of anisotropic particles, the scattering medium is seen to be doubly refracting (or optically active) and dichroic.[1,2] For the isotropic case, the scattering matrix ν_{ij} degenerates into a scalar [$g_{11}(0) = g_{22}(0) = g(0)$]. the real part of which is seen to be equal to [compare (2.8)]

$$\operatorname{Re} g(0) = -\frac{k^2}{4\pi} \mathfrak{k}^0, \tag{3.6}$$

whence

$$n = n_0 + \frac{N\mathfrak{k}^0}{2k_0} \frac{\operatorname{Im} g(0)}{\operatorname{Re} g(0)} - i\frac{N\mathfrak{k}^0}{2k_0}. \tag{3.7}$$

We note that while the determination of the imaginary part of the index of refraction, that is, the extinction exponent $\mathfrak{k}^0$, is usually burdened by the effect of multiple scattering and by difficulties connected with noise due to the diffraction aureole, the determination of the phase shift due to the presence of scattering particles is free of this noise and in a number of cases can be shown to be more expedient from the point of view of spectroscopic problems.

The dispersive medium as a whole must no longer be characterized by the single-particle cross sections α^0, σ^0, and $\mathfrak{k}^0$ but by the transverse cross sections (or coefficients) of absorption α, of scattering σ, and of extinction $\mathfrak{k}$ of the medium referred to unit volume (with dimensions cm^{-1}) or to unit mass (with dimensions cm^2/g). It immediately follows from (3.7) that

$$\mathfrak{k} = N\mathfrak{k}^0 \tag{3.8}$$

and, correspondingly,

$$\sigma = N\sigma^0, \quad \alpha = N\alpha^0, \tag{3.9}$$

i.e., Bouguer's law (the additivity of the cross sections) holds for monochromatic light. If we now identify our particles with non-absorbing molecules, i.e., we set

$$g(0) = -ik^3\alpha - \frac{k^6\alpha^2}{3} + \ldots \tag{3.10}$$

(compare reference 3), where α is the polarizability of the molecule, then we immediately obtain from (3.5) the classical expression for the index of refraction and the scattering ability of a rarefied gas, not taking into account the difference of the effective field from the field of the incident wave. In other words, the relations obtained are valid only if the distance between scattering particles is so great that the coherent effects of self-radiation vanish. If the distances between particles are comparable with the wavelength, then these effects cease to be negligible and the matrix $g_{ij}(0)$ acquires an additional factor, which takes these effects into account, as it is done in the case of a molecular

medium by means of the Lorentz-Lorenz formula. We shall return to this problem. For the moment we only note that in this case the additivity of the cross sections is violated and Eqs. (3.8) and (3.9) lose their validity.

In addition to the general theory stated above, a number of authors[7-16] have considered cooperative effects in scattering media (especially in connection with the theory of the Christiansen optical filter), by starting out from various model representations of the structure of the medium.

In light flux penetrating a medium described by the Stokes vector-parameter, Eq. (3.2) must be replaced by the equivalent relation

$$dS_i = -\sum_j \varkappa_{ij} S_j \, d\tilde{l}, \tag{3.11}$$

where κ_{ij} are the real components of the energy dispersion matrix κ and are expressed linearly in terms of the matrix components ν_{ij}.[1,2]

We now consider the fate of plane waves scattered in other directions. As soon as the direction of the scattered wave ceases to coincide with the direction of the incident wave, its phase begins to depend upon the position of the scattering particle, i.e., plane waves scattered by particles are no longer in phase and it is desirable to investigate the results of their interference. If the distance between the particles is much less than the wavelength then, as L. I. Mandel'shtam[22] has shown, in the absence of fluctuations whose dimensions are comparable or greater than the wavelength of light, the scattered waves are completely canceled out in all directions.* In the opposite case of extremely rarefied particles, the waves scattered by them will be completely incoherent with respect to each other, and the vector-parameter of the light scattered in any given direction will be expressed by the relation [see (2.4)]

$$S_i^{\text{scat}} = \frac{NV}{r^2} \sum_j D_{ij} S_j^{\text{inc}}, \tag{3.12}$$

where V is the scattering volume and the matrix D_{ij}/r^2 can be expressed in terms of the matrix g_{ij} (we have not taken the effect of multiple scattering into account). We note that what has been said is also completely applicable to fluctuations which we can consider as inhomogeneities of appropriate scale imbedded in the medium; this emerges most clearly in the case of critical opalescence.

But as soon as the distances between particles become comparable with the wavelength, the situation changes radically. Now the waves scattered by neighboring particles are only partially coherent, and the degree of coherence depends essentially on the scattering angle and wavelength. While the coherence can be preserved completely at small angles, i.e., the scattered waves will completely cancel one another, at large angles (backward scattering) it may be completely destroyed, and the particles will scatter independently. Thus the cooperative scattering matrix (which we shall denote by $\frac{1}{4\pi} f_{ij}$ in what follows) can differ greatly from the scattering matrix $\frac{1}{4\pi} d_{ij}$ of the individual particle (in particular the scattering function f_{11} can be extended backward), and can depend essentially on the particle concentration. Similar effects were observed by Oster and his coworkers[25] in the case of colloids and also, evidently, by A. I. Kolyadin and N. A. Voĭshvillo[26] on sodium-borosilicate glasses.* It should be emphasized that in this case the very characteristic spectral dependence of the form of the indicatrix (matrix) and of the absorption coefficient should be observed.†

From the theoretical point of view, the result of the interference of scattered waves is determined by the form of the so-called structure function $\rho(\mathbf{r}-\mathbf{r}_0)$, which describes the conditional probability of finding neighboring particles at the distance $\mathbf{r}-\mathbf{r}_0$ from the point $\mathbf{r}_0$, where an arbitrary fixed particle is already located. A theoretical consideration of a similar nature, which bears, it is true, a highly tentative character, is contained in reference 27 (see also the bibliography therein), and from a somewhat different stand in reference 1.

It is worthy of attention that the gradual decrease of scattering (that is, the decrease of σ and consequently of $\tilde{l}$) with increasing particle concentration is in no way shown in the relations (3.1) — (3.7), in clear contradiction of the law of conservation of energy. Actually, however, the change in the effective field in which the particle is located is unavoidably associated with the appearance of cooperative effects, that is, the factor for $g_{ij}(0)$, which depends upon the concentration, and which has

*This follows directly from Maxwell's equations, inasmuch as in this case the medium can be regarded as quasi-homogeneous and its properties (and consequently the field intensities) do not depend on the coordinates x and y. Under these conditions, the periodic solutions of Maxwell's equations will be plane waves which propagate in directions satisfying Snell's law.

*The explanation advanced by Kolyadin[26] is quite similar to the above, but has little basis as a whole, because it assumes, without sufficient justification, the formation of stable and identical quadrupoles in the glass.

†See also Sec. 13.

already been mentioned above, should appear in relations given (for two-dimensional colloids see references 1, 28, and 29).

The problem of the determination of the effective field in a dispersive medium is one of the difficult problems of the optics of scattering media, and to date, so far as we know, no satisfactory solution has been found. In fact, only the case of a medium with dipole (Rayleigh) scattering particles has been considered. As is well known, the Lorentz-Lorenz formula is obtained in the case of a molecular medium, which is amenable to a quasistatic approximation, (see, for example, reference 30); this has been generalized by Maxwell-Garnett[31] to include volume colloids. The case of a two-dimensional colloid with dipole-scattering particles was considered by the author.[1,28,29] In particular, for normal incidence of light on a layer, the effective field E^{ef} is connected with the field E of the incident wave by the relation

$$E^{ef} = \frac{E}{1-\gamma\eta C}, \qquad (3.13)$$

where $\eta = \frac{2\pi N'}{k^2}$, N′ is the number of particles per unit surface of the layer,

$$\gamma \cong 1 + i\left(\frac{\sqrt{\pi N'}}{2k} - \frac{k}{4\sqrt{\pi N'}}\right) - \frac{k^2}{3\pi N'} \qquad (3.14)$$

and C is the coefficient of dipole scattering of the particle, which is found from the solution of the Mie problem (see, for example, reference 3). One can show[1,28,29] that in the transition to a three-dimensional medium these expressions lead to the Maxwell-Garnett formula for colloids, and to the Lorentz-Lorenz formula for molecular media (see also reference 23). We note that in the case of a two-dimensional colloid the most important role is played by the reflection of light from the underlying surface, which can also be taken into account.[1,28,29]

For colloidal complexes and high-polymer molecules, the calculations of the internal effective field were carried out by Debye.[32]

Of fundamental interest is the completely disregarded case of the dense packing of scattering particles, which occurs, for example, in powders, minerals, biological objects, and also under the conditions of critical opalescence. The singularity of this case is that the particles are in a strongly inhomogeneous field (in the non-wave zone) and one must take into account the longitudinal component of the field of the scattered waves, and also the very important effects of mutual screening of the particles. We note that the expansion of the scattered wave in the non-wave zone in terms of plane waves leads to the necessity of considering the so-called inhomogeneous waves (see reference 28), i.e., to the necessity of generalization of the problem of Mie. The latter is of independent interest from the point of view of the analysis of the phenomenon of scattering under conditions of total internal reflection, in particular, in connection with problems of ultramicrospectroscopy (the dark-field variant).

Returning to the general case, it must be borne in mind that the mutual irradiation of the particles, which creates the effective field, also consists of coherent and incoherent components. In this case the effective field proper, which influences the magnitude of the effective index of refraction, is formed exclusively of the coherent component that owes its existence only to nearest neighbors. The incoherent component is what we isolate as multiple scattering, for which the volume element of the medium must be regarded as a whole, together with its own cooperative matrices of extinction κ_{ij} and scattering $\frac{\sigma}{4\pi} f_{ij}$, which take into account not only the optical characteristics of the scattering particles but also the properties of the medium in which these particles are located.

4. MULTIPLE SCATTERING

Separation of the coherent component of the mutual irradiation of particles allows us, as we have seen, to characterize the properties of the scattering medium by a set of two wavelength-dependent matrices, extinction κ_{ij} and scattering $\frac{\sigma}{4\pi} f_{ij}$, where the latter also depends upon the angle of scattering. Then, account of multiple scattering can be accomplished even in the approximation of ray optics, which at once permits a formulation of the fundamental equation of propagation theory, namely, the equation of radiation transfer in the scattering medium.

As is well known, this equation was first formulated more than a half century ago by O. D. Khvol'son and later by Schwartzschild, who started out from rather evident intuitive considerations and formulated it only as the law of conservation of energy. The physical meaning of this equation is very simple. It states that the change in the intensity of the light beam over an element of its length is composed of the attenuation brought about by absorption and scattering and of the amplification, by scattering into this same direction, of the light that strikes this volume element from all other directions. In this case it is important that the light beams scattered by various elements of the vol-

ume are incoherent with respect to each other, that is, that their intensities are additive. As we have seen, this statement is inherent in the definition of multiple scattering. But we have also seen that scattering phenomena are described not by a coefficient, but by a matrix of scattering, that is, that the fate of the radiant flux depends essentially on the character of its polarization. But since the character of the polarization inevitably changes in each scattering act, and is therefore different for different scattering angles, then, in formulating the equation of transfer, we can no longer ignore this difference. This implies essentially the requirement that the system of ray optics include all the dynamic characteristics of the photon flux (its energy, momentum, spin) and that we take into consideration not only the law of conservation of energy but also the remaining laws of conservation, inasmuch as the latter predetermine the form of the scattering matrix. Furthermore, since the incoherent light beams propagating in the scattering medium have very different past histories and are mixed in very different proportions or, in other words, since the process of light propagation in a scattering medium is statistical in nature, we cannot retain the description of a light wave by means of field intensities, we are therefore obliged to turn to statistical parameters, which are additive for incoherent waves. It was pointed out that the components of the Stokes vector-parameter are such parameters. Therefore, taking into account what was given in Secs. 2 and 3, the equation of transfer can be formulated in the form[1,2]

$$\frac{dS_i(\vartheta, \varphi)}{dl} = \sum_j \left\{ -\varkappa_{ij} S_j(\vartheta, \varphi) + \frac{\sigma}{4\pi} \oint f_{ij}(\vartheta, \varphi, \vartheta' \varphi') S_j(\vartheta', \varphi') \sin \vartheta' \, d\vartheta' \, d\varphi' \right\} + S_i^0(\vartheta, \varphi), \quad (4.1)$$

where the integration is carried out over all directions ϑ' and φ' of the beams incident on a given scattering volume, while the extinction and scattering matrices are referred to unit volume of the medium. The component $S_i^0(\vartheta, \varphi)$ takes into account the possible self radiation of the volume element, of importance for example in the infrared region or in luminescent media. It should be noted that in this form the equation assumes a strict monochromatic character and there are no frequency transformations in the radiation, that is, the equation is not applicable to luminescence problems or to problems of self-reversal of spectral lines, since in the latter the shape of the absorption line is important. The corresponding generalization is carried out without special difficulty, but we cannot dwell on it. We also note that Eq. (4.1) is valid not only for light but also for currents of arbitrary particles with spin $\frac{1}{2}$.

Many terms of this equation, or more precisely of the set of four integro-differential equations, which take into account polarization effects, have generally the same order of magnitude as those contining only $\varkappa_{11}$ and f_{11}, which form the classical transfer equation without consideration of polarization effects. This leads immediately, as pointed out above, to the inadmissibility of ignoring polarization effects even in those problems in which at first glance they do not seem to play a serious role. Examples of this will be given below.

Equation (4.1) permits us to solve, at least in principle, all problems of the optics of anisotropic scattering media, including the theory of electro- and magneto-optical phenomena in colloids. However, excluding such specific cases, we usually encounter isotropic media, especially in spectroanalytical problems, although the isotropy is commonly the result of a random distribution of orientations of anisotropic particles. In this case, the extinction matrix $\varkappa_{ij}$ degenerates into the extinction coefficient $\varkappa = \alpha + \sigma$, and the equation takes on the form in which it was first obtained independently by Chandrasekhar,[33] the author,[34] and somewhat earlier, for the special case of Rayleigh scattering, by V. V. Sobolev.[35] It is in this form that we shall consider it further.

In conclusion, we point out that the essential premise in the derivation of Eq. (4.1) was, as rightly noted by B. I. Stepanov (see, for example, reference 36), the assumption that the dimensions of the scattering particles are much smaller than the mean free path of the photon in the scattering medium. From this Stepanov drew the conclusion that this equation is invalid, for example, in strongly absorbing powders. However, it should be noted that the transfer equation has an essentially probabilistic character. Therefore it is possible, by replacement of local probabilities by some mean probabilities, to preserve the equation in unchanged form even in this case, at least for certain problems. In particular, in the problem of the reflection of light from the surface of the scattering medium, one can evidently speak about the mean probability of transition of the photon from one depth to another in a given direction, about the mean intensity of light at a given depth, and about the intensity of the reflected light averaged over the surface. It would seem here that the connection between the parameters of the medium averaged in such fashion (α, σ, f_{ik}) and the parameters of the individual particles making up the medium needs special consideration, and that the valid-

ity of the above hypothesis needs a most searching verification.

5. GENERAL FORMULATION OF THE PROBLEM OF THE SPECTROSCOPY OF DISPERSED MATERIALS

Turning aside from the numerous gaps in the present-day theory, which were partially noted above, and which seriously complicate practical application of the theory, we see that the spectroanalytical interpretation of experimental data for scattering materials is incomparably more difficult than in the case of quasi-homogeneous bodies, and requires much more information about their properties. In addition, the experimental possibilities of obtaining this information are much broader and more varied. The radiation field can be measured not only in transmitted and reflected light but also within the scattering material and in very different directions. There are also possibilities available to the experimenter of varying the dimensions and shape of the specimen, the conditions of its irradiation, and also its properties. Examples of such changes are dilution (with scattering or non-scattering impurities), which has an effect on cooperative effects, the introduction of immersion, which changes the optical characteristics of the individual particles and, in a number of cases, a change in the degree of dispersiveness of the material. Therefore, to plan the experiment reasonably, one needs to know how the different factors affect the result of the experiment. Furthermore, the multiplicity of experimental possibilities demands a careful and skillful selection of the minimum amount of experimental information which will guarantee the success of the analytical investigation, and which is essentially determined by the character of the analytical problem. At the present time, there is still no possibility of obtaining well based answers to all the questions arising here, but many of them have already been subjected to some degree of investigation; their consideration forms the basic content of what follows. Here we shall attempt to formulate only certain general situations which follow from what has been said.

In all cases, direct experiment gives evidence on the character of the radiation field at the boundaries or inside the specimen as a function of the geometric characteristics of the latter, and the conditions of its irradiation. From these data, we can in principle extract the cooperative optical characteristics of the medium — the coefficients of attenuation and scattering (the medium is assumed to be isotropic) and the scattering matrix.

However, the possibility of extracting such detailed information hinges by the solvability of the transfer equation (4.1) relative to quantities of interest to us.

Up to the present time the development of the theory of propagation of radiation in scattering media has followed two principal paths. The establishment of a more precise formulation of the transfer equation itself has led to the development of mathematical methods of its solution for various models of the turbid medium, as a result of which a large, independent branch of mathematical physics was developed (see references 33 and 35). However, the crudeness of the corresponding mathematical apparatus materially encumbered the possibilities of its application, and dictated a restriction to extremely schematized cases. It is true, the application of mathematical machines permits us to solve a wide circle of straight-forward problems of propagation theory, but the inverse problems, which are of special interest from the viewpoint of spectroscopy, still remain practically untouched and not even propounded, with a few exceptions about which we shall speak below.

As a consequence, it appears that a great deal of effort has been made to obtain methods based on replacement of Eq. (4.1) by very crude representations the validity of which remains unestablished. They are frequently doubtful from the theoretical viewpoint and, in the great majority of cases, they have not been subjected to serious experimental test. Sometimes this course has led to more or less satisfactory (at least at first glance) results, which represent an essential step forward. But the reasons for such (generally surprising) success, and also the limits of applicability of the corresponding simplified expressions, remain undiscovered.

Therefore, giving their due to both the paths mentioned, one can hardly consider them as a reliable basis for the development of spectral analysis of dispersive materials. It seems that the only correct path is as rigorous and general a formulation of the transfer equation as possible and a subsequent search for such experimental conditions for which there is a possibility of obtaining approximate solutions of the inverse problem in comparatively simple analytical form, and with a sufficient degree of accuracy. By approximate solutions we mean primarily the establishment of connections among the different types of experimentally-measured characteristics of the light field, without far-reaching a priori assumptions regarding the form of the scattering matrix.

The latter requirement has a fundamental character, since, under actual conditions, the scattering matrix is unknown, and all indicatrix and polarization effects would be hidden in experimentally determined parameters. It should be especially noted that a certain stylization of the transfer equation, based on empirical and theoretical investigation of the character of the light field in the scattering medium, should accompany this search for such "permissible" experimental conditions. The possibilities of such stylization undoubtedly exist, because the transfer equation (4.1) permits us to obtain a much more detailed picture of the light field than is usually required for purposes of spectral analysis, one that corresponds to the essentials of the physical problem as a consequence of the non-monodisperse character of the material and the incomplete monochromaticity of the light. The well-known low sensitivity of the form of the solution to a variation of certain parameters of the medium, and the success of the rough-model representation already mentioned bears convincing witness to this. However, there is still not enough of either experimental or theoretical investigations of the character of the light field in the scattering medium, which could serve as a basis in the search of means of such stylization. Yet they are essential also for an explanation of the amount of information actually obtainable about the optical properties of the medium, with account of its inherent statistical nature (including the unavoidable fact that the particles are not identical) and of the completeness and reliability of the experimental data obtained in practice.

Thus, under favorable (that is, "solvable") experimental conditions, a certain set of measurements permits us, at least in principle, to obtain the effective optical characteristics of the medium as such. It is evident that the next stage should be the elimination of complications brought about by the cooperative effects. The simplest from this point of view is the case of strong dilution, where the cooperative effects vanish. If the character of the object does not allow such a strong dilution, then the cooperative effects must be subjected to a special investigation, the concrete character of which it is difficult to discuss because of the inadequacy of the theory of these effects. We note only that the experimental criterion of their absence is the satisfaction of the conditions (3.8) and (3.9) and the independence of the form of the scattering matrix of the concentration.

Finally, the transition from optical and geometrical characteristics of the scattering particles to the optical characteristics of the material of which they are composed is an entirely separate problem, lying, as we have seen, outside of the framework of the theory of propagation and dispersion, and representing the inverse problem of scattering theory. Inasmuch as the latter still does not guarantee any possibility for the existence of a similar transition, the establishment of the empirical rules by means of a study of artificially dispersed materials is of great importance. We note that in industrial control of dispersed materials, control of the optical and geometrical characteristics of the particles as such is usually adequate and there is no need for dealing with the characteristics of the material of the particles.

The marked differences of the three spectroanalytical problems described above, namely the determination of the optical characteristics of the scattering medium, the transition from these characteristics to the individual characteristics of the particles and, further the transition to the optical properties of the material of the particles, has in our view fundamental importance. Not only the theoretical treatment, but also the methods of experimental investigations and the practical problems to be solved are entirely different. Yet, by tradition, these three problems are frequently confused, which, naturally, holds back their solution. In what follows we shall deal essentially with the first of these problems.

6. SUBSURFACE CONDITIONS AND THE SPECTROSCOPY OF WEAKLY ABSORBING MATERIALS

A detailed experimental study of the conditions of light in the interior of colored scattering media was made by V. A. Timofeeva.[37-39] It led her to the discovery of a number of empirical laws, which were confirmed by other experiments, for example in the optics of the sea,[40] and also led to the theoretical studies of V. A. Ambartsumyan,[41] V. V. Sobolev,[42] Chandrasekhar,[33] M. V. Maslennikov[43] and S. G. Slyusarev.[44] In addition to the direct applicability of these laws to the solution of many problems of the optics of scattering media, they were shown to be noteworthy in that they disclosed certain new, rather original possibilities of absorption spectroscopy. However, the theoretical investigations mentioned above, which brought about the solution of the direct problem of the theory of propagation and which assume the scattering function to be known, cannot serve as the basis for the solution of analytical problems.

In addition, it has been shown[45,46] that the conditions of light in a semi-infinite scattering medium

illuminated from the surface belongs among those situations which yield an approximate solution of the transfer equation in a form suitable for spectro-analytical purposes.

It follows from very general physical considerations, which have been confirmed by rigorous mathematical analysis,[43] that at a sufficient distance from the boundary, where there is no longer any direct light, there should be established certain stationary forms of the attributes characterizing the angular dependence of the quantities S_i (including the brightness) for the scattered light. These forms, which are determined by the optical properties of the same scattering medium, do not depend either on the depth or on the character of the light flux incident on the external boundary of the medium. Moreover, in the case of an isotropic medium and with properties independent of the horizontal coordinates, the amplitude dependence of the values of S_i must also disappear. Consequently, at a sufficient distance z we can write

$$S_i(z, \mu, \varphi) = S_i(\mu) R(z), \tag{6.1}$$

where $\mu = \cos\vartheta$, and ϑ is the angle between the direction of the light beam and the normal to the irradiated surface of the medium. Substituting (6.1) in (4.1) and integrating over z, we obtain

$$R(z) = e^{-\mathfrak{k}'(z-z_0)}, \tag{6.2}$$

where z_0 is a constant depending essentially on the boundary conditions, while $\mathfrak{k}'$ is determined from the condition of solvability of the equation

$$(1+\beta)(1-\gamma\mu) S_i(\mu) = \frac{1}{2}\sum_j F_{ij}(\mu, \mu') s_j(\mu')\, d\mu', \tag{6.3}$$

in which it is assumed that

$$\beta = \frac{\alpha}{\sigma} \tag{6.4}$$

is the specific absorbing ability of the medium,

$$\gamma = \frac{\mathfrak{k}'}{\mathfrak{k}} \tag{6.5}$$

and

$$F_{ij}(\mu, \mu') = \frac{1}{2\pi}\int_0^{2\pi} f_{ik}(\mu, \mu', \varphi - \varphi')\, d(\varphi - \varphi'). \tag{6.6}$$

Thus, at sufficiently large distances, a decrease in the intensity of the radiation S_1 with depth takes place according to the exponential law (6.2) with a damping coefficient $\mathfrak{k}' = \gamma\mathfrak{k}$ which does not depend on the direction of the ray and which differs from the coefficient of extinction k. We note that, generally speaking, Eq. (6.3) yields a series of values γ, but at a sufficiently great depth z, all solutions are damped out with the exception of that corresponding to the smallest value of γ, which will indeed contribute to the establishment of a stationary mode.

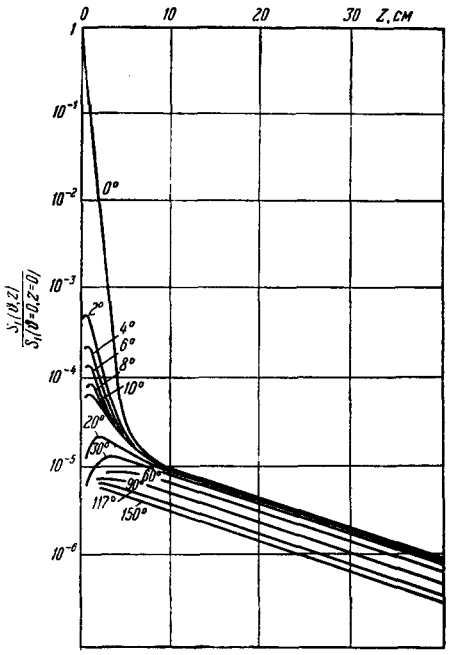

FIG. 5. General picture of the angular and subsurface distribution of intensities in a milky medium with a small specific absorption β ($\mathfrak{k} = 1.9$ cm^{-1}).[37] The numbers on the curves refer to the angle ϑ.

This analysis was confirmed by direct experiments of V. A. Timofeeva[34] and Lenoble[40] (Fig. 5). Integrating Eq. (6.3) with respect to μ, and considering the properties of the scattering matrix for an isotropic medium[45] [in particular, the normalization condition (2.1)], we obtain

$$\beta = \gamma(1+\beta)\bar{\mu}, \tag{6.7}$$

where

$$\bar{\mu} = \frac{\Phi_v}{\Phi_s} \tag{6.8}$$

is the mean cosine of the angle of inclination of the light beams,

$$\Phi_v = \int_{-1}^{+1} \mu S_1(\mu)\, d\mu \tag{6.9}$$

is the density of the light flux across a horizontal area, i.e., the difference of the densities of the incoming and outgoing fluxes, and

$$\Phi_s = \int_{-1}^{+1} S_1(\mu)\, d\mu \tag{6.10}$$

is the so-called volume density of the radiation field, i.e., the radiant flux incident on a spherical surface of unit area. Taking (6.4) and (6.5) into account, along with (2.9) which is valid for an isotropic medium, we can rewrite (6.7) in the form

$$\alpha = \mathfrak{k}'\bar{\mu}. \tag{6.11}$$

Thus, by measuring the $\varkappa$, Φ_V, and Φ_S in the interior of the scattering medium, we can, making use of (6.11), find α directly, i.e., the actual absorption coefficient of the scattering medium; furthermore, knowing the coefficient of extinction $\varkappa$ (see Sec. 9), we can find the scattering coefficient σ.

It is important to note that in addition to the isotropy of the medium, the only important condition that predetermines the satisfaction of the relation (6.11) is the assurance of the subsurface conditions. The depth of establishment of the latter in a homogeneous medium is determined by the quantity β, by the form of the scattering function, and by the character of the illumination of the surface. For directed radiation, it can be significant, but if the radiation is diffuse and close to the state of the subsurface conditions, then it is not large. Therefore, the relation (6.11) retains its force also for media which are inhomogeneous in depth (say, for the sea), when the scale of the inhomogeneity is sufficiently large in comparison with the depth of establishment of a changed stationary mode.

In the case of a weak specific absorption ($\beta \ll 1$), both theory[45,46] and experiment[37,38] lead to the approximate relation

$$\varkappa' \cong \sqrt{\frac{\alpha\varkappa}{q}}, \qquad (6.12)$$

where q is a constant dependent on the form of the scattering function. The constant can be determined either from the relation

$$q = \frac{\varkappa}{\varkappa'}\bar{\mu}, \qquad (6.13)$$

(if the coefficient of extinction $\varkappa$ is known) or (by artificially coloring the medium with a non-scattering dye of known α) from the dependence of $\frac{\varkappa'^2}{\varkappa}$ on the concentration of the dye. Extrapolation of the corresponding straight lines to zero should give the values of the coefficient of absorption α_0 of the undyed medium. The situation is illustrated in Fig. 6, taken from reference 38. It is extremely significant that in a highly scattering medium ($\varkappa \gg 1$) even very small absorption produces a significant change of $\varkappa'$ (see references 6 and 12) — the scattering medium here plays the role of a multi-channel cuvette. Therefore the dispersion of weakly absorbing materials, and also the introduction of a disperse, non-absorbing phase in the weakly absorbing liquid, must produce a large shift, by approximately two orders of magnitude, of the lower boundary of absorption coefficients accessible to measurement.[37,38,45,46]

Finally, changes of the angular distribution and polarization of the scattered light in the interior

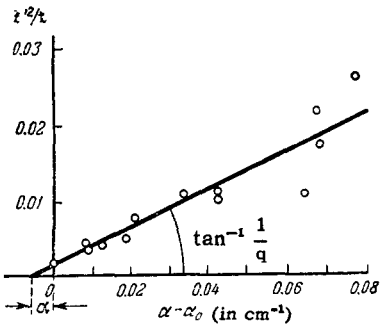

FIG. 6. Dependence of $\frac{\varkappa'^2}{\varkappa}$ on $(\alpha - \alpha_0)$ for a dyed milky medium; α_0 is the coefficient of absorption of the undyed medium.[38]

of the scattering medium,[37,39,45,46] where polarization effects are shown to be occasionally very significant, especially upon increase in the absorption,[46] can also be used for spectral analysis purposes. However, the interpretation of the laws[45] obtained here entails certain difficulties and requires additional investigation. On the other hand, the character of the radiation field in the interior of the scattering medium contains abundant information about the scattering matrix.[45] This information, as we have seen, is of independent interest and must be the object of a special study.

In conclusion let us point out that under considerable absorption, the establishment of the subsurface condition is connected with a very strong attenuation of the light, which makes experiments of this nature impractical. Another obstacle in this case is that the measuring apparatus must be small in comparison with the mean free path of the photon. Therefore, in practice, the method described here is applicable only to weakly absorbing media ($\beta \ll 1$). However, the latter is connected with the requirement of a sufficiently large amount of volume filled with the medium which, together with the necessity of immersion of the apparatus in the medium under study, is a serious limitation. However, in a number of cases (certain biological objects, emulsions and hydrosols, the sea and other natural waters, clouds, smokes and fogs, snow and snowy masses, etc.), these limitations do not play a serious role.

7. REFLECTION FROM THE SURFACE OF A SCATTERING MEDIUM IN THE CASE OF VERY STRONG ABSORPTION

The second case which permits an approximate solution of Eq. (4.1) in a form suitable for spectral-analysis purposes is the reflection of light from the surface of a scattering medium that possesses a high specific absorption.

Inasmuch as the depth of penetration of the radiation is small in this case, the conditions that correspond to reflection from an unbounded, semi-infinite half-space, filled by the scattering medium, the optical characteristics of which do not depend on the coordinates (the Milne problem), can be realized experimentally without difficulty. In this case we assume that the regular interphase boundary is absent, that is, that the binding medium, in which the disperse phase is immersed, is identical with the medium which extends over the surface of the scattering medium.

Inasmuch as the absorption is large, it is reasonable to make use of the method of solution of the transfer equation (4.1) developed in detail by E. S. Kuznetsov[47] in connection with problems of the theory of visibility, of necessity modifying its form somewhat to take into account polarization effects.[1,6,48] Without going into mathematical details, we shall show only that the method consists in the successive calculation of the contribution introduced in the reflectivity of the medium by scatterings of different multiplicity, and that their successive application in the case of an isotropic medium leads to the expressions

$$S_i^{\text{ref}}(\vartheta, \varphi) = S_1^0 \sum_{n=1}^{\infty} \frac{a_{in}(\vartheta, \varphi)}{(1+\beta)^n}, \tag{7.1}$$

for the components of the Stokes vector parameter S_i of the light reflected from the medium. Here ϑ and φ are the coordinate angles that determine the direction of the reflected ray (the normal to the surface of the medium directed into the interior of the latter is taken as the polar axis; the corresponding meridional cross sections are taken as reference planes both for the reflected and for the incident rays), S_1^0 is the intensity of the light beam irradiating the medium, $\beta = \alpha/\sigma$ is the specific absorptivity of the medium, n is the multiplicity of scattering, and

$$a_{in}(\vartheta, \varphi) = \sum_{j=1}^{4} a_{ijn}(\vartheta, \varphi, \vartheta_0, \varphi_0)\, c_j^0. \tag{7.2}$$

Here $c_j^0 = S_j^0/S_1^0$ are the polarization characteristics of the incident beam [cf. (2.3)] and a_{ijn} are coefficients that depend only on the direction of the incident (ϑ_0, φ_0) and observed reflected (ϑ, φ) light rays and on the form of the scattering matrix. In particular,

$$\left.\begin{aligned} a_{ij1} &= \frac{1}{4\pi}\frac{\mu}{\mu+\mu_0} f_{ij}(\mu, \varphi, \mu_0, \varphi_0), \\ a_{ij2} &= \frac{1}{16\pi^2}\frac{\mu}{\mu_0-\mu}\sum_{l=1}^{4}\Bigg[\int_0^1\int_0^{2\pi} f_{il}(\mu,\varphi,\mu',\varphi') f_{lj}(\mu',\varphi',\mu_0,\varphi_0)\frac{\mu}{\mu'-\mu}\,d\mu'd\varphi' \\ &\quad + \int_{-1}^{0}\int_0^{2\pi} f_{il}(\mu, \varphi, \mu', \varphi') f_{lj}(\mu', \varphi', \mu_0, \varphi_0)\frac{\mu_0}{\mu_0-\mu'}\,d\mu'\,d\varphi'\Bigg], \end{aligned}\right\} \tag{7.3}$$

where, as before, $\mu = \cos\vartheta$. Denoting the energy reflectivity by

$$R = \frac{S_1^{\text{ref}}}{S_1^0} \tag{7.4}$$

and introducing the coefficients $c_i = S_i/S_1$, which characterize the polarization of the light reflected from the medium, we find

$$c_i R = \sum_{n=1}^{\infty}\left(\frac{a_{in}}{1+\beta^n}\right). \tag{7.5}$$

It is then immediately evident that as β increases, the role of scattering of higher multiplicity quickly dies out, in which connection the intensity, spectral composition, and polarization of the reflected light must change. This change of the relative role of scattering of different multiplicity with changing β is a fundamental effect that determines the spectral and polarization characteristics of the light reflected from the scattering medium.

As Ambartsumyan[49] has shown, the average multiplicity of the scattering in the case of reflection from a semi-infinite scattering medium (for diffuse illumination and spherical scattering function) is equal to $\sqrt{1+1/\beta}$ (see also Sec. 8), i.e., it is less than two for $\beta \gtrsim 1/3$. In other words, for $\beta \gtrsim 1/3$, one can with a sufficient degree of accuracy restrict oneself to the third or even the second approximation. Besides, for a strongly elongated scattering function and indirect illumination, the convergence of the series (7.5) must be somewhat worse for certain angles of observation.

Inasmuch as the coefficients a_{in} depend on the form of the scattering matrix, and also on the angles of incidence and observation and the character of the polarization of the incident light beam, and inasmuch as the form of the scattering matrix entering into Eq. (7.3) is usually unknown, their determination must be made experimentally. The latter is possible, in particular, by means of artificially coloring the specimen (that is, by

means of a specified change of β), but under the condition that the scattering matrix remain constant. This can be brought about, for example, by adding a non-scattering dye to the binding medium.

Furthermore, in the case of polydisperse media with sufficiently large particles, one can with certain reservations assume that the scattering matrix depends weakly on their absorptivity. In particular, this should be expected in the mixing of different polydisperse materials (for example, pigments) with different α and σ. If this assumption is valid, a hypothesis that requires a special experimental test, then the scattering material itself can be used as a dye (or diluent). If the scattering matrix remains unchanged, the coefficients a_{in} in the expansion (7.5) will be identical for colored and uncolored specimens. Then, limiting ourselves to the first two terms of the series (7.5) for strongly colored specimens, and making use of the entire series for weakly colored specimens, we obtain the following result after simple transformations[1,6,48]

$$\frac{R_0}{R(\beta)} = \frac{(1+\beta)^2}{1+\frac{\beta}{Q}}, \tag{7.6}$$

where R_0 is the reflectivity of the weakly colored specimen (for $\beta = \beta_0 \ll 1$) and

$$Q = 1 + \sum_{n=1}^{\infty} \frac{a_{1,\,n+1}}{a_{11}(1+\beta_0)^n} \tag{7.7}$$

takes into account the relative contribution of the scattering of higher multiplicities for $\beta = \beta_0$.

The quantities R_0 and Q depend upon the angles of incidence and observation and on the form of the scattering matrix, but cannot depend on either the degree of dilution of the medium (this follows from the similarity theorem) or on the nature of the dye, as long as the dye has no effect on the form of the scattering matrix. Thus, Eq. (7.7), like (7.5), describes the variation of the angular dependence of the reflection coefficient of dispersive materials on the concentration of the dye. In this sense the equation can serve as the basis, for example, for solving problems in illumination engineering, and also problems connected with the use of dyes in the textile, polygraphic and lacquer industry, architecture, color photography, painting, etc.

If now the structure of the disperse medium permits us to neglect cooperative effects, then for a mixture of two components with volume concentrations C_1 and C_2, we can use Bouguer's law, i.e., from (3.9) we can write

$$\left.\begin{aligned} \alpha &= C_1\alpha_1^0 + C_2\alpha_2^0, \\ \sigma &= C_1\sigma_1^0 + C_2\sigma_2^0. \end{aligned}\right\} \tag{7.8}$$

Then, varying the relative concentration of the components C_1/C_2, and measuring the ratio $R_0/R(\beta)$, we find Q and at the same time have the possibility of a separate determination of the absorption coefficients α and the scattering coefficients σ of both components, expressed as fractions of the scattering coefficient of one of them. This circumstance can be used as the basis of spectral analysis of strongly absorbing polydisperse materials to the extent to which we are concerned with the determination of the mean optical characteristics of the scattering parficles (see, for example, reference 96).

We note that the mixing procedure that we have described, i.e., the coloring or dilution by scattering additions, is in principle analogous to the artificial coloring by a non-scattering dye in the case of the relation (7.5). While guaranteeing wider experimental possibilities, the procedure requires in this case greater rigor as regard the constancy of the scattering matrix.

The relations (7.5) also permit us to find the degree of polarization p of the reflected light. According to (2.3),

$$p = \frac{\sqrt{S_2^2 + S_3^2}}{S_1} = \sqrt{c_2^2 + c_3^2} \tag{7.9}$$

or, transforming the reference plane for the reflected light[2] so that $S_3 = 0$, we can set $p = c_2$. Then, making use of (7.5) and limiting ourselves (in the case of strong absorption) to the first two terms of the series, we find

$$p = \frac{a_{21}(1+\beta) + a_{22}}{a_{11}(1+\beta) + a_{12}} \tag{7.10}$$

(we recall that the coefficients a_{in} depend on the polarization of the incident light beam). Therefore it is not difficult to obtain an expression for the polarization of the light reflected by the colored material:

$$p = \frac{p_0 + p_\infty \frac{\beta - \beta_0}{(1+\beta_0)\,Q}}{1 + \frac{\beta - \beta_0}{(1+\beta_0)\,Q}}, \tag{7.11}$$

where p_0 and p_∞ are the degrees of polarization of the reflected light for $\beta = \beta_0 \ll 1$ and $\beta \to \infty$, respectively, which also depend on the polarization of the incident light.

The dependence thus determined of the degree of polarization of the reflected light on β is essentially the well-known Umov effect.[50] Umov first made use of it indeed for spectral analysis purposes — for the determination of the absorption spectrum of a dye from the spectrum of the polarization of diffusely reflected light. We note that, together with the effect described, which owes its origin to the change in the relation between the intensities of the scatterings of different multiplici-

ties, another effect, considered by A. S. Toporets,[51] can exist in the presence of interphase boundaries. It consists of a change in the relation between the intensities of light directly reflected from the interphase boundary and the light scattered by the dispersive medium (see also Sec. 13).

We shall show that as $\beta \to \infty$, that is, for very high absorption, only single scattering is maintained. This gives a direct possibility of determining the scattering function, free from obstacles created by multiple scattering [see (7.3)]. The advantage of this method lies not only in that in dealing with a great number of scattering particles, we obtain a significant gain in the intensity of the scattered light, but also that by such means we can make cooperative effects apparent (for example, in powders).

8. ALBEDO OF A SCATTERING MEDIUM AT WEAK ABSORPTION

The relation (7.5) permits us to find the albedo of the surface of a scattering medium that fills the half-space. By definition, the albedo $\mathcal{R}$ of the surface is equal to the ratio of the light flux Φ_{ref} reflected from the surface to the light flux Φ_{inc} incident on the surface,

$$\mathcal{R} = \frac{\Phi_{ref}}{\Phi_{inc}}. \tag{8.1}$$

Inasmuch as

$$\Phi_{inc} = \int_0^1 \int_0^{2\pi} I_{inc}(\mu', \varphi')\, \mu'\, d\mu'\, d\varphi', \tag{8.2}$$

where I_{inc} is the intensity of the incident light rays; similarly, for Φ_{ref}, we obtain, by taking into account (7.4):

$$\mathcal{R} = \frac{\int_0^{-1}\int_0^{2\pi}\int_0^{1}\int_0^{2\pi} \mu R(\mu, \varphi, \mu' \varphi')\, I_{inc}(\mu', \varphi')\, d\mu\, d\varphi\, d\mu'\, d\varphi'}{\int_0^1 \int_0^{2\pi} I_{inc}(\mu', \varphi')\, \mu'\, d\mu'\, d\varphi'}, \tag{8.3}$$

or, substituting the value R from (7.5), where we set $i = 1$ ($c_1 = 1$), we find (see also reference 52)

$$\mathcal{R} = \sum_{n=1}^{\infty} \frac{A_n}{(1+\beta)^n}, \tag{8.4}$$

where

$$A_n = \frac{\int_0^{-1}\int_0^{2\pi}\int_0^{1}\int_0^{2\pi} \mu a_{1n}(\mu, \varphi, \mu', \varphi')\, I_{inc}(\mu', \varphi')\, d\mu\, d\varphi\, d\mu'\, d\varphi'}{\int_0^1 \int_0^{2\pi} I_{inc}(\mu', \varphi')\, d\mu'\, d\varphi'}. \tag{8.5}$$

Thus, the value of the albedo in general depends strongly on the angular structure of the incident light beam.

If we recall that the index n corresponds to the multiplicity of the scattering, it is not difficult to find the average multiplicity of scattering from (8.4):

$$\bar{n} = \frac{\sum_{n=1}^{\infty} n \frac{A_n}{(1+\beta)^n}}{\sum_{n=1}^{\infty} \frac{A_n}{(1+\beta)^n}}. \tag{8.6}$$

Indeed, by differentiating $\mathcal{R}$ with respect to β, we have[49]

$$\bar{n} = -\frac{1+\beta}{\mathcal{R}} \frac{d\mathcal{R}}{d\beta} \tag{8.7}$$

and from (7.5) we get similar expressions (which are different for the different components of the Stokes vector-parameter) for the average multiplicity of the radiation in the case of steady incident and observed radiation fluxes.

For the case of weak absorption, $\bar{n}$ is large and it is necessary in (8.4) to take into account the very large number of terms (for $\beta \to 0$, $\bar{n} \to \infty$). Therefore, it is more reasonable here to expand the solution of Eq. (4.1) in a series of not the scattering multiplicities, but of the small parameter β or the parameter γ connected with it, as we saw in Sec. 6; this parameter characterizes the attenuation of the radiant flux in the interior of the scattering medium (6.5). It has not yet been possible to carry out the similar expansion in the general case. However, this is possible if the structure of the incident beam corresponds to the subsurface mode considered in Sec. 7. In this case, for weak absorption,

$$I(\mu) = I_0 [1 + a(\mu)\gamma + b(\mu)\gamma^2 + \ldots], \tag{8.8}$$

where $a(\mu)$ and $b(\mu)$ . . . are determined only by the form of the scattering matrix.[45] Expanding $\mathcal{R}$ in a series in γ,

$$\mathcal{R} = \mathcal{R}_0 + \mathcal{R}_1\gamma + \mathcal{R}_2\gamma^2 + \ldots, \tag{8.9}$$

substituting (8.8) and (8.9) in (8.1) and (8.2), and equating terms with equal powers of γ, we find

$$\left.\begin{aligned} &\mathcal{R}_0 = 1, \quad \mathcal{R}_1 = -2\int_0^1 \mu\,[a(\mu) - a(-\mu)]\, d\mu, \\ &\mathcal{R}_2 = -2\int_0^1 \mu\,[b(\mu) - b(-\mu)]\, d\mu - 2\mathcal{R}_1 \int_0^1 \mu a(\mu)\, d\mu. \end{aligned}\right\} \tag{8.10}$$

In particular, for a spherical scattering function we get from (6.3)

$$I = \frac{I_0(\gamma)}{1 - \gamma\mu} \simeq I_0(\gamma)(1 + \gamma\mu + \gamma^2\mu^2 + \ldots), \tag{8.11}$$

That is, $a(\mu) = \mu$, $b(\mu) = \mu^2$, whence

$$\mathcal{R}_1 = -\frac{4}{3}, \qquad \mathcal{R}_2 = \frac{8}{9}. \tag{8.12}$$

Thus for a small specific absorption β, the albedo of the surface of the dispersive medium is equal to

$$\mathscr{R} = 1 + \mathscr{R}_1\gamma + \mathscr{R}_2\gamma^2 + \ldots, \qquad (8.13)$$

where $\mathscr{R}_1$ and $\mathscr{R}_2$ depend only on the form of the scattering matrix. Taking it into account[45] that for small specific absorption

$$\gamma \cong \sqrt{\frac{\beta}{\int_0^1 \mu\,[a(\mu)+a(-\mu)]\,d\mu}} \qquad (8.14)$$

and that $\mathscr{R}_1 = \dfrac{d\mathscr{R}}{d\gamma}$, we get from (8.7) and (8.10)

$$n \cong \frac{1+\beta}{\gamma}\frac{\int_0^1 \mu\,[a(\mu)-a(-\mu)]\,d\mu}{\int_0^1 \mu\,[a(\mu)+a(-\mu)]\,d\mu} \cong \frac{\int_0^1 \mu\,[a(u)-a(-\mu)]\,d\mu}{\int_0^1 [a(\mu)+a(-\mu)]\,d\mu}\,\beta^{-\frac{1}{2}}, \qquad (8.15)$$

which, with accuracy to within a multiplicative factor (which depends only on the form of the scattering matrix), coincides with the expression obtained by Ambartsumyan[49] for diffuse illumination and a spherical scattering function when $\beta \ll 1$.

It is not difficult to see that the relations (8.9) and (8.14) can serve as the fundamental method of determination of the specific absorption coefficient of the reflecting medium. In this case, however, it is necessary to keep in mind that the change in β (and consequently in γ) brings about, as a consequence of (8.8), a change in the structure of the incident light beam. How significant these effects are is not yet clear.

Inasmuch as the character of irradiation of the surface influences only the coefficients A_n of the series (8.4), and inasmuch as these coefficients, as well as the coefficients of the series (7.2), do not depend upon β [in accord with (7.3) and (8.5)], a relation similar to (8.9) is retained for the direct-reflection coefficients R:

$$R = R_0 + R_1(\gamma) + R_2\gamma^2 + \ldots, \qquad (8.16)$$

where γ has the previous value of (8.14). Here the coefficients of the expansion R_0, R_1, R_2, ... will depend only on the direction of the incident and observed reflected rays and on the character of the polarization of the incident beam. Therefore, in spectroscopic situations, these parameters will vary with the conditions of the experimental arrangement and require experimental determination. In particular, the angular dependence of these parameters forms a correction to Lambert's law which is never obeyed in practice. Moreover, in the range of angles that insure an approximate satisfaction of Lambert's law, R_0, and possibly also R_1, will be virtually independent both of the conditions of observation and, what is especially important, of the form of the scattering matrix.

9. TRANSMISSION OF AN OPTICALLY THIN LAYER AND THE MEASUREMENT OF THE EXTINCTION COEFFICIENT

An infinite optically thin layer is another case that permits solution of the transfer equation (4.1) in the form of a series with a small number of terms. In fact, if the optical thickness $\varkappa t$ of the layer (t is its geometrical thickness) is small, then the effects of multiple scattering will be greatly weakened, and more so the larger the specific absorption coefficient β. This permits us to resort to the same method of solution of the transfer equation (4.1) by successive approximations as was employed in Sec. 7, and again to limit the series to scatterings of low multiplicity. In particular, for the case in which an unpolarized light beam of intensity I_0 is incident on the layer (in the direction μ_0, φ_0), we obtain[1] the result that the intensity of the light which has passed through the layer in the direction μ, φ is equal in second approximation to

$$I(\mu, \varphi) = I_0\, e^{-\frac{\varkappa t}{\mu_0}}\left[\delta(\mu-\mu_0)\,\delta(\varphi-\varphi_0) + \left(1-e^{-\frac{\mu_0-\mu}{\mu_0\mu}\varkappa t}\right)\frac{A}{1+\beta} + \frac{B}{(1+\beta)^2}\right], \qquad (9.1)$$

where A depends only on μ, φ, μ_0, and φ_0 while B also depends on t and $\varkappa$. The first term in the square bracket takes into account the attenuation of the direct beam, while the others take into account the additional light transmitted in different directions as the result of single and double scattering.

Thus, the spectral composition of the direct and scattered light which penetrates a layer will be entirely different. If only the factor $\varkappa$ (i.e., extinction) acts on the intensity of the direct light, then the spectrum of the scattered light will, in addition to the change of the effective path of the light rays in the medium, be distorted by the effect of a factor containing β. Therefore, the result of the measurement will depend essentially both on the thickness of the layer and on the way in which the scattered light is collected by the receiver.

This effect was already illustrated in the experiments of É. V. Shpol'skiĭ[5] mentioned above, in which the distance between a cell with a suspension of erythrocytes and the light detector was varied; this led to a significant change in the form of the transmitted spectrum.

Keeping this circumstance in mind, M. M. Gure-

vich and L. Chokhrov[53] attempted to reserve the term "transparency" only for direct light, in contrast to the term "transmission" for the scattered component. Experimental division of these quantities is possible up to rather large optical thicknesses of the layer by means of apparatus developed by the same authors and shown schematically in Fig. 7. A parallel light beam penetrating the layer C passes through the lens L_2, in the focal plane of which is placed the diaphragm D_2, which removes either the scattered or the direct beam. In the first case the transparency of the layer, i.e., the coefficient of extinction of the medium, is measured directly; in the second, the transition is measured. However, as is clear from (9.1), this method is effective only under the condition that the role of multiple scattering remains small, which indeed limits the permissible thickness of the layer. Moreover, in the case of a strongly disperse medium, the receiver inevitably picks up a major part of the light diffracted by the particles, i.e., in the region of small angles the measured value of $\varkappa$ is reduced by a factor equal to the scattering coefficient.

We note that a reduction of the transverse dimensions of the layer, i.e., the conversion of the layer into a column, leads to a reduction of the effects of multiple scattering and to an improvement in the conditions of measurement of $\varkappa$. However, this case has not yet been considered theoretically. Besides, the effect of multiple scattering leads to a violation of the exponential dependence of the transparency on the thickness of the layer (the length of the column), which can also serve as an experimental criterion of the reliability of the measurement.

We now assume that the layer is irradiated not by a parallel beam but by a diffuse one, with a structure close to the subsurface conditions (see Sec. 6). Then the transmission of the layer will, by (6.2), be equal to

$$\frac{I_{\text{trans}}}{I_0} = \frac{\Phi_{\text{trans}}}{\Phi_0} = e^{-\varkappa' l}, \qquad (9.2)$$

where, in the case of weak absorption, $\varkappa'$ is determined by (6.12). Incidentally, the relation (9.2) will be satisfied very approximately, since, in contrast to the subsurface conditions, the lower surface of the layer is not illuminated. Nevertheless, comparison of (9.2) and (9.1) clearly illustrates the essential dependence of the transmission of the layer on the angle of its irradiation, use of which can generally be made for an independent determination of $\varkappa$ and $\varkappa'$, i.e., α and σ.

Frequently, especially in experiments with strongly absorbing materials, such thin layers are used that the particles are arranged in a single layer on the supporting surface thus forming a two-dimensional colloid. Then, if the particles are sufficiently bulky or sufficiently thinned out, one can regard them as isolated, and it is necessary to consider only interference phenomena brought about by the presence of the underlying surface. If their dimensions are smaller than or of the order of the wavelength, then cooperative effects become of paramount importance (Sec. 3). The connection of the optical properties of such two-dimensional layers with the optical characteristics of the particles forming them is considered in detail in references 1, 28, 29, and 54; see also the literature cited there.

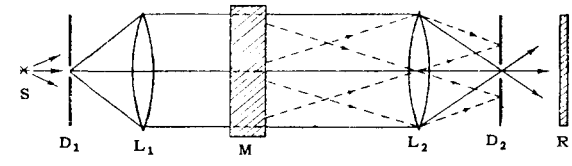

FIG. 7. Schematic arrangement for the measurement of the transparency of a layer of scattering material. S = source of light, L_1 and L_2 = lenses, M = layer, D_1 and D_2 = diaphragms, R = light receiver.

10. DIFFERENTIAL EQUATIONS

An approximate solution of the integro-differential equation (4.1), even in a general form suitable for the solution of analytical problems, i.e., for an arbitrary (unknown) scattering matrix, have been found only for exceptional cases, some of which were discussed above. In this connection, naturally, attempts were made of a simplified approach to the problem by going (in the one-dimensional problem) from intensities to radiation flux, to be able to replace (4.1) by a certain differential equation. Inasmuch as this method is widely used in a number of physical investigations, it is necessary to explain its basic premises and the limits of its applicability. In this case, we shall follow the work of E. S. Kuznetsov,[55] in which polarization effects were not considered (the considerations given here can be suitably generalized without special difficulty). Thus, we assume that a scattering medium, infinite in horizontal directions whose properties do not depend on the horizontal coordinates, is illuminated from the side of the upper or lower boundary. Then the intensities of the light beams in different directions will be functions of a single coordinate — the depth z — and (4.1) (without consideration of polarization effects) takes the form

$$\mu \frac{dI(z, \mathbf{r})}{dz} = -\varkappa I(z, \mathbf{r}) + \frac{\sigma}{4\pi} \oint f(\mathbf{r}, \mathbf{r}') I(z, \mathbf{r}') d\omega', \qquad (10.1)$$

where $d\omega = d\mu\, d\varphi$ is an element of solid angle in the direction $\mathbf{r}$ and f denotes the component f_{11} of the scattering matrix.

The density of radiant flux through the horizontal area is

$$\Phi_j = (-1)^{j+1} \int_0^1 \mu I_j\, d\omega, \qquad (10.2)$$

where integration is carried out within the upper or lower hemisphere; the index $j = 1$ corresponds to the downward direction and the index $j = 2$ to the upward direction. Integrating (10.1) over ω within these same limits, and taking into account the sign of μ, we obtain

$$(-1)^{j+1} \frac{d\Phi_j}{dz} = -\mathfrak{k} I_j + \frac{\sigma}{4\pi} \sum_{l=1}^{2} \int\int f_{jl} I_l\, d\omega\, d\omega', \qquad (10.3)$$

where

$$\left.\begin{aligned} f_{11}(\mathbf{r}, \mathbf{r}') &= f(\mathbf{r}, \mathbf{r}'), \quad & f_{12}(\mathbf{r}, \mathbf{r}') &= f(-\mathbf{r}, \mathbf{r}'), \\ f_{21}(\mathbf{r}, \mathbf{r}') &= f(\mathbf{r}, -\mathbf{r}'), \quad & f_{22}(\mathbf{r}, \mathbf{r}') &= f(-\mathbf{r}, -\mathbf{r}') \end{aligned}\right\} \qquad (10.4)$$

and μ ranges from 0 to +1.

Let us introduce the auxiliary quantity

$$\bar{\mu}_j = \frac{\int \mu I_j d\omega}{I_j d\omega} \qquad (10.5)$$

—the average of the cosines of the angles of inclination of the light beam in the descending and ascending fluxes, and

$$\bar{\nu}_j = \frac{1}{4\pi} \frac{\int\int f_{jj}(\mathbf{r}, \mathbf{r}') I_j(\mathbf{r}')\, d\omega\, d\omega'}{\int I_j(\mathbf{r}')\, d\omega'} \qquad (10.6)$$

—the energy of the descending flux scattered downward (j = 1), or the ascending flux scattered upward (j = 2), with the integration carried out everywhere over the hemisphere.

Then the equations of (10.3) take the form:

$$\left.\begin{aligned} \frac{d\Phi_1}{dz} &= -\frac{\mathfrak{k} - \sigma\bar{\nu}_1}{\bar{\mu}_1} \Phi_1 + \frac{\sigma(1-\bar{\nu}_1)}{\bar{\mu}_2} \Phi_2, \\ \frac{d\Phi_2}{dz} &= -\frac{\sigma(1-\bar{\nu}_2)}{\bar{\mu}_1} \Phi_1 + \frac{\mathfrak{k} - \sigma\bar{\nu}_2}{\bar{\mu}_2} \Phi_2. \end{aligned}\right\} \qquad (10.7)$$

As long as $\bar{\mu}_j$ and $\bar{\nu}_j$ remain constant, we obtain a set of two differential equations which are identical in form with the equations obtained from general physical considerations by G. A. Gamburtsev.[56] If, furthermore, $\bar{\nu}_1 = \bar{\nu}_2 = \frac{1}{2}$, the equations derived by Mecke,[57] Ryde,[58] Kastrov,[59] Gordov,[60] and also by Kubelka[61] are obtained. Finally, if we additionally set $\bar{\mu}_1 = \bar{\mu}_2 = \frac{1}{2}$, we obtain the equations formulated by Schuster[62] and later by Kubelka and Munk[63] (in the absence of absorption or scattering, these reduce to the Schwarzschild equations[64] for a spherical scattering function).

The latter equations are most frequently employed in physical literature devoted to the interpretation of experimental data on the reflectivity and transmission of layers of scattering material. Therefore, it is necessary to highlight the assumptions that determine the region of their application (see also references 65 and 66).

It follows from (10.5) that the constancy of $\bar{\mu}_j$ with depth implies the constancy of the angular dependence of the radiant flux, i.e., the invariance of the brightness (which also guarantees the constancy of $\bar{\nu}_j$). At the surface, as was shown theoretically by E. S. Kuznetsov,[55] the $\bar{\mu}_j$ depend substantially on the boundary conditions, i.e., on the character of the illumination of the surface. Experimentally this dependence was studied by V. A. Timofeev[37] and is shown for two cases in Figs. 8 and 9. Thus the equations in (10.7) are valid only when both boundaries of the medium are illuminated by light rays, the structures and intensity ratios of which correspond to the subsurface mode for a medium with given coefficients of absorption and scattering and a given scattering matrix. We recall that the form of the brightness pattern depends essentially on γ (that is, on β), and differs strongly from spherical for some particular specific absorption coefficient of the medium β (Fig. 10). Consequently, the complete diffusivity of the illumination is known to violate the condition of independence of the brightness pattern (i.e., $\bar{\mu}_j$ and $\bar{\nu}_j$) of the depth.

Furthermore, the assumption $\bar{\nu}_1 = \bar{\nu}_2 = \frac{1}{2}$ can be satisfied only for a strictly fixed relation between the form of the scattering function and the angular dependence of the luminous fluxes I_j. In particular, this assumption will be satisfied for the never-to-be-realized spherical scattering function or for a symmetric (in relation to the forward and backward directions) function of the Rayleigh type, but under the condition of a homogeneous angular dependence of the fluxes I_1 and I_2 (for example, for a spherical brightness diagram), i.e., in practice, only in the absence of absorption. Finally, the assumption $\bar{\mu}_1 = \bar{\mu}_2 = \frac{1}{2}$ corresponds to a spherical brightness diagram, i.e., to the absence of absorption.[45] We shall illustrate these remarks by the example of an infinitely thick layer, the external boundary of which is illuminated in correspondence with the requirements of the subsurface mode. We introduce the notation

$$\left.\begin{aligned} a_{11} &= -\frac{\mathfrak{k} - \sigma\bar{\nu}_1}{\bar{\mu}_1}, \quad & a_{12} &= \frac{\sigma(1-\bar{\nu}_1)}{\bar{\mu}_2}, \\ a_{21} &= -\frac{\sigma(1-\bar{\nu}_2)}{\bar{\mu}_1}, \quad & a_{22} &= \frac{\mathfrak{k} - \sigma\bar{\nu}_2}{\bar{\mu}_2}. \end{aligned}\right\} \qquad (10.8)$$

Then the solution of (10.7) takes the form

$$\left.\begin{aligned} \Phi_1(z) &= \Phi_1(0)\, e^{-lz}, \\ \Phi_2(z) &= \mathscr{R}_\infty \Phi_1(0)\, e^{-lz}, \end{aligned}\right\} \qquad (10.9)$$

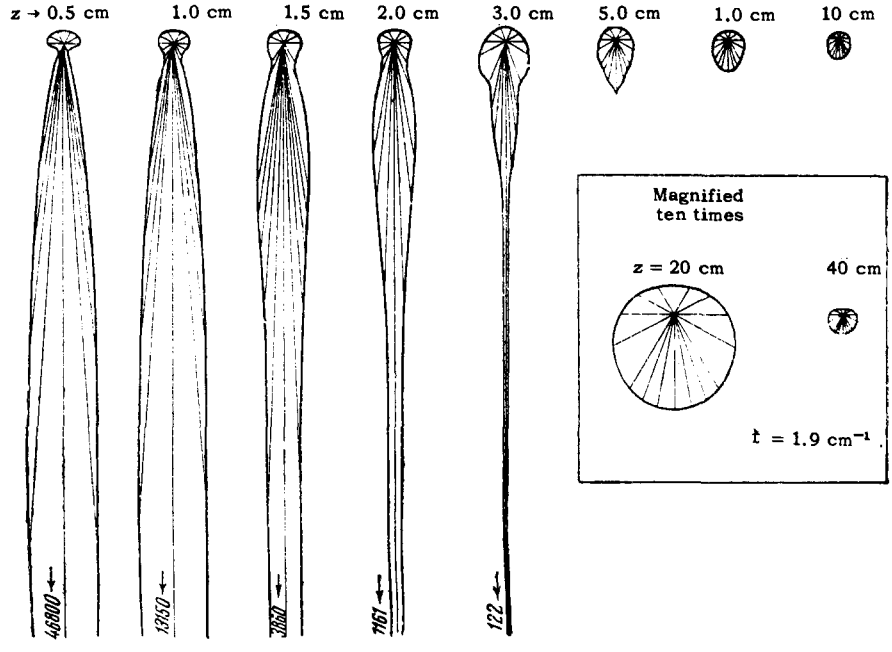

FIG. 8. Polar diagrams of the brightness of a turbid medium at different depths l (milky medium; $t = 1.9\ cm^{-1}$). The illumination is from above with normal incidence.[17]

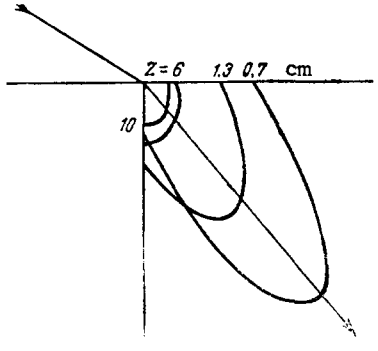

FIG. 9. Change of the polar diagram and of the direction of maximum brightness with depth in the case of illumination by oblique rays of the sun (milky medium; $t \approx 9\ cm^{-1}$).[37]

where the albedo of the infinitely thick layer is

$$\mathcal{R}_\infty = -\frac{a_{11}+L}{a_{12}} = -\frac{a_{21}}{a_{22}+L}, \qquad (10.10)$$

while L is determined from the equation

$$L^2 + (a_{11}+a_{22})L + (a_{11}a_{22} - a_{12}a_{21}) = 0. \qquad (10.11)$$

In particular, for a spherical scattering function $f_{jj} = 1$ and for small β, it is easy to verify from (8.11), (10.5), and (10.6) that

$$\bar{\nu}_1 = \bar{\nu}_2 = \frac{1}{2}, \ \bar{\mu}_1 \cong \frac{1}{2}\left(1+\frac{\gamma}{6}\right), \ \bar{\mu}_2 \cong \frac{1}{2}\left(1-\frac{\gamma}{6}\right), \qquad (10.12)$$

whence $\gamma \cong \sqrt{3\frac{\alpha}{\sigma}}$ [compare (8.14)]. Correspondingly, we obtain:

$$\left.\begin{aligned} a_{11}+a_{22} &\cong \frac{1}{3}\sigma\gamma, \\ a_{11}a_{22} - a_{12}a_{21} &\cong 4\alpha\sigma, \end{aligned}\right\} \qquad (10.13)$$

i.e.,

$$L \cong \sqrt{3\,\alpha\sigma}, \qquad (10.14)$$

which coincides in value with the subsurface coefficient of attenuation t' [Eq. (6.12)] for the corresponding spherical scattering function of value $q = 1/3$ [compare (8.11) and (8.14)].

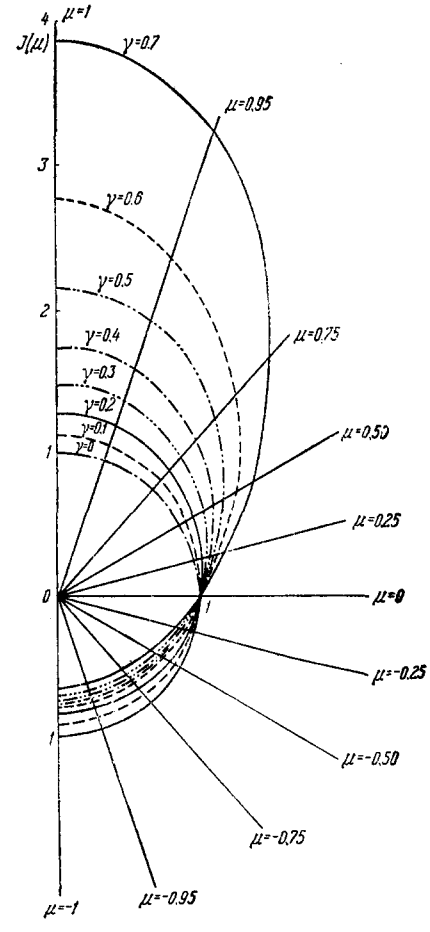

FIG. 10. Form of the brightness in the depth of a medium with Rayleigh scattering as a function of the factor γ.[46]

However, if we neglect the effect of γ on the parameter $\bar{\mu}_j$, and set $\bar{\mu}_1 = \bar{\mu}_2 = \frac{1}{2}$, we get L

$\cong \sqrt{4\alpha\sigma}$, i.e., approximately 15% higher.

Furthermore, with account of the dependence of $\bar{\mu}_j$ on γ we get for $\mathcal{R}_\infty$ the value

$$\mathcal{R}_\infty = 1 - \frac{4}{3}\gamma \qquad (10.15)$$

from (10.10), in correspondence with (8.11) — (8.13). Without consideration of this dependence we get

$$\mathcal{R}_\infty = 1 - \sqrt{\frac{4}{3}\gamma}, \qquad (10.16)$$

i.e., the error in the correction that is dependent on γ amounts to 20%. We note that with increasing β, the error due to neglect of the deviation of $\bar{\mu}_j$ from $\frac{1}{2}$ must increase rapidly.

Thus, Eqs. (10.7), in the form formulated by Schuster and Kubelka and Munk, are valid only in diffuse illumination for an unbounded (or identically illuminated from both sides) non-absorbing medium, and, consequently, they cannot, strictly speaking, be used for spectral analysis problems. Even the artificial separation of a certain "directed component," suggested by Ryde[58] and Silberstein,[67] is of no avail in this connection. The problem as to within what limits the solution of these equations remains little sensitive to violation of the initial assumptions needs special consideration (see, for example, reference 68). From this viewpoint there is needed an experimental study of the dependence of $\bar{\mu}_j$ and the form of the brightness diagram on z for different β and different structures of the incident beam, along with a theoretical study of the dependence of $\bar{\nu}_j$ on the form of the scattering matrix and on the form of the brightness diagram. It can be expected that under certain conditions the corresponding dependences of $\bar{\mu}_j$ and $\bar{\nu}_j$ can be approximated sufficiently well by general empirical formulas with a small number of parameters, which would permit us safely to make use of (10.7) in spectral analysis problems. In conclusion, we emphasize that frequently in experimental research one uses (10.7) or its solution not for fluxes, but for the intensities of the incident and reflected (or transmitted) light beams, which is already utterly inadmissible.

11. THE CONNECTION BETWEEN THE TRANSMISSIVITY AND THE REFLECTIVITY OF A LAYER

The transfer equation (4.1) permits us to find in general form the connection between the transmissivity and the reflectivity of a layer of finite thickness. For this purpose it is convenient to make use of the principles of invariance, rigorously formulated by Ambartsumyan,[69] which reduces to the statement that the transmissivity and reflectivity of a pair of consecutive layers of identical material coincide with the corresponding properties of a single unified layer. As a result, we obtain two nonlinear integral matrix equations, which connect the transmissivity and the reflectivity of the layer in given (arbitrary) directions with the scattering matrix, the extinction and scattering coefficients, and the thickness of the layer. We shall not write out these equations because of their cumbersome nature (see reference 33). It immediately follows from a consideration of these equations that if the angular dependence of the radiant field remains unchanged throughout the thickness of the layer and on its boundaries, and only in this case, the reflectivity R and the transmission coefficient T of the combined layer are connected with the corresponding characteristics of the pair of successive layers which make it up by the simple relations

$$R(t_1+t_2) = R(t_1) + R(t_2)\frac{T^2(t_1)}{1-R(t_1)R(t_2)}, \qquad (11.1)$$

$$T(t_1+t_2) = \frac{T(t_1)T(t_2)}{1-R(t_1)R(t_2)}, \qquad (11.2)$$

where t_1 and t_2 are the thicknesses of the layers.* Thus, it is not possible to agree with B. I. Stepanov, who emphasizes that these formulas are exact and applicable to an arbitrary light-scattering layer under the condition of complete homogeneity of the medium and complete diffusion of the light.[36] In fact, we have seen in Sec. 6 that invariance of the angular dependence of the light field is achieved only in the subsurface mode, that the character of this structure depends strongly on the value of the specific reflectivity of the medium and on the form of the scattering matrix,[45,46] and that complete diffusivity of the light is obtained only in the absence of absorption (see Fig. 10). Moreover, in a layer of finite thickness, subsurface conditions are reached only when the layer is illuminated from both sides, while the illuminating beams must have different intensities and different angular dependences, the relations between which depend on the properties of the medium. If these requirements are not met (for example, as the result of advance along the spectrum, i.e., change of β) changes in the angular dependence of the light field with depth inevitably take place (even in the case of a spherical scattering function). Also, as a consequence of the essential dependence of R and T on this structure (see Sec. 9), Eqs. (11.1) become inconsistent. They become all the more inapplicable to systems of layers with different optical proper-

*The relations (11.1) are derived under these assumptions from the principles of invariance by an elementary method both for fluxes and for direct beams.

ties, because the passage through the boundary inevitably causes structural changes in the light field. We emphasize this point especially inasmuch as Eqs. (11.1) are widely used in theoretical and experimental investigations of the optical properties of layered materials (see, for example, references 61 and 70).

Thus, in investigations, under experimentally reliable conditions, of the optical properties of layers that are composed of scattering materials, Eqs. (11.1) are never strictly applicable, and the basic question is how stringent are the conditions of their applicability, i.e., in what measure does departure from these conditions violate Eqs. (11.1). At the present time, we still do not have a complete answer to this question, but the experimental data which will be considered in the second part of the paper permit us to think that the region of applicability of (11.1) is rather wide, but only as far as tentative, semi-quantitative estimates are concerned. In other words, the practical application of the relations (11.1) and their consequences in the case of scattering media, a practice quite widespread in experimental investigations, remains weakly based at present and requires great care.

The same remarks also apply to the much more detailed consideration of the problem of the relations between R, T, and t in the researches of M. M. Gurevich,[71] A. A. Gershun[72] and Shannon et al.[73] Starting out from Eqs. (11.1) and allowing the thickness of one of the layers (t_2) to approach zero, Gurevich assumed that the albedo $\mathcal{R}$ and the transmission of the diffuse flux $\mathcal{T}$ of an infinitely thick layer are equal, respectively, to

$$\mathcal{R}(dt) = K_1 dt, \quad \mathcal{T}(dt) = 1 - K_2 dt, \tag{11.3}$$

where K_1 and K_2 are certain constants, directly connected with α, σ, and the form of the scattering matrix. This immediately leads to a system of differential equations

$$\left.\begin{aligned} \frac{d\mathcal{R}}{dt} &= K_1 \mathcal{T}^2, \\ \frac{d\mathcal{T}}{dt} &= -\mathcal{T}(K_2 - K_1 \mathcal{R}), \end{aligned}\right\} \tag{11.4}$$

which are completely equivalent to (10.7) if $\bar{\nu}_1 = \bar{\nu}_2$ and $\bar{\mu}_1 = \bar{\mu}_2$, and if these constants are independent of the depth and magnitude of the absorption, a consequence of the identity of the initial assumptions. In this case,

$$K_1 = \frac{\sigma(1-\bar{\nu})}{\bar{\mu}}, \quad K_2 = \frac{1-\sigma\nu}{\bar{\mu}} \tag{11.5}$$

in contrast, in particular, with the values given by A. A. Gershun.[72] The solution of these equations has the form:

$$\left.\begin{aligned} \mathcal{R}(t) &= \frac{1-e^{-2Lt}}{1-\mathcal{R}_\infty^2 e^{-2Lt}}, \\ \mathcal{T}(t) &= \frac{(1-\mathcal{R}_\infty^2)\,e^{-Lt}}{1-\mathcal{R}_\infty^2 e^{-2Lt}}, \end{aligned}\right\} \tag{11.6}$$

where, in correspondence with (10.10) and (10.11),

$$L = \sqrt{K_2^2 - K_1^2} \tag{11.7}$$

and

$$\mathcal{R}_\infty = \frac{K_2}{K_1} - \sqrt{\frac{K_2^2}{K_1^2} - 1}. \tag{11.8}$$

Thus the optical properties of the layer as a whole are defined here by the two parameters, L and $\mathcal{R}_\infty$ or K_1 and K_2, which are connected by the relations

$$K_1 = \frac{2\mathcal{R}_\infty L}{1-\mathcal{R}_\infty^2}, \quad K_2 = \frac{1+\mathcal{R}_\infty^2}{1-\mathcal{R}_\infty^2}, \tag{11.9}$$

whereupon the corresponding theory has obtained the name "two-parameter" in contrast to "four-parameter," in which $\bar{\mu}_1$ is different from $\bar{\mu}_2$ and $\bar{\nu}_1$ from $\bar{\nu}_2$.

Equations (11.8) and (11.5) immediately reduce to a form which is very convenient in practice:

$$\frac{(1-\mathcal{R}_\infty)^2}{2\mathcal{R}_\infty} = \frac{\alpha}{(1-\bar{\nu})\,\sigma}, \tag{11.10}$$

which also serves as the basis for the interpretation of the experimental data in most researches dealing with the spectroscopy of scattering materials (dyes, dusts, etc.), in which it is customary* to assume $\bar{\nu} = \frac{1}{2}$ (spherical scattering). However, this simple equation is immediately violated as soon as the necessity arises of distinguishing $\bar{\mu}_1$ from $\bar{\mu}_2$, or $\bar{\nu}_1$ from $\bar{\nu}_2$, i.e., in all cases in which $\alpha \neq 0$. In other words, Eq. (11.10) can never be strictly satisfied, and the question of the degree of its correspondence to reality requires special investigation, the more so that in a real experiment one usually measures not the albedo $\mathcal{R}_\infty$ under conditions of illumination corresponding to the subsurface mode, but the reflectivity R_∞ in a given direction for diffuse or directed illumination. In this connection, we return to the results of Secs. 7 and 8.

We have seen that in the case of a weakly absorbing medium ($\beta \ll 1$) the relation (8.16) holds for R, from which, with the aid of (6.5) and (6.12), it follows that

$$\frac{\left(1-\frac{R}{R_0}\right)^2}{2\frac{R}{R_0}} \simeq \frac{1}{2q}\left(\frac{R_1}{R_0}\right)^2 \beta \left[1 + \left(2\frac{R_2}{R_1} - \frac{R_1}{R_0}\right)\sqrt{\frac{\beta}{q}} + \ldots\right]. \tag{11.11}$$

*In a number of researches, it has been erroneously assumed that $\bar{\nu} = 0$

In the opposite case of very strongly absorbing media, we can use the relations (7.5) or (7.6) (that is, expansion of R in terms of $1/\beta$), from which we obtain, respectively,

$$R \cong \frac{a_{11}}{\beta}, \quad \frac{R_0}{R} \cong Q_0\beta, \tag{11.12}$$

$$\frac{\left(1-\frac{R}{R_0}\right)^2}{2\frac{R}{R_0}} \cong \frac{1}{2}\frac{R_0}{a_{11}}\beta\left[1+\left(1-2\frac{a_{11}}{R_0}-\frac{a_{12}}{a_{11}}\right)\frac{1}{\beta}+\dots\right] \tag{11.13}$$

and

$$\frac{\left(1-\frac{R}{R_0}\right)^2}{2\frac{R}{R_0}} \cong \frac{1}{2}Q_0\beta\left[1+\left(2-\frac{1+Q_0^2}{Q_0}\right)\frac{1}{\beta}+\dots\right], \tag{11.14}$$

where [see (7.7)]

$$Q_0 \cong \frac{R_0}{a_{11}}. \tag{11.15}$$

In Eqs. (11.12) — (11.15) the zero subscript denotes the value of R and Q corresponding to $\beta = 0$ (i.e., to the absence of absorption) for a medium with the same scattering matrix and under the same conditions of illumination and observation. In a real experiment, R_0 is determined by substituting a white standard for the specimen and, since the conditions of illumination and observation remain unchanged, the difficulty consists only in the necessity of eliminating effects brought about by the difference of the scattering matrix for absorbing and non-absorbing materials. If the absorption is brought about exclusively by the binding medium and the scattering particles themselves in the specimen and the standard are identical, then this difficulty does not arise. If the particles themselves are the absorbing agent in the specimen, then it is necessary either to choose a particular standard of nearly the same scattering matrix (which is scarcely possible in practice), or to carry out the measurements under conditions for which the indicatrix effects are of little importance. We can assume that this takes place for not too large angles of observation and incidence outside the zone of specular reflection, where, as is well known, the departures from Lambert's law for colorless media are not large (see Part II).

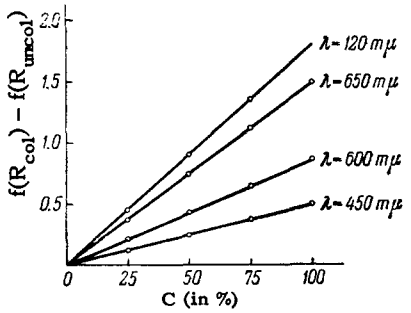

FIG. 11. Dependence of the difference function

$$f(R) \equiv \frac{\left(1-\frac{R}{R_0}\right)^2}{2\frac{R}{R_0}}$$

on the concentration of the mixture of colored and uncolored glass powders. If the coefficients of scattering of both powders are identical then, in agreement with (11.16), (7.8), and (6.4), $f(R_{col}) - f(R_{uncol}) \sim C_{col}$.

Finally, the experimental data (for example, references 97, 98; for details see Part II) show that even in the region of moderate absorption the condition

$$\frac{\left(1-\frac{R}{R_0}\right)^2}{2\frac{R}{R_0}} = C\beta, \tag{11.16}$$

is sufficiently well satisfied, where C remains constant over a rather wide interval of variation of β (Fig. 11); this is still without a theoretical foundation. Thus we can assume that for the experimental conditions chosen, the value of C will depend rather weakly on β, and one of the most important problems lying in the path of the development of practical methods of the spectroscopy of dispersive materials is the investigation of the character of the dependence of $C(\beta)$, and also the explanation of the connection of this quantity with the properties of the medium. In each case, there is today no basis for the assumption that C = 1.

In conclusion we give a table[74] of values of the function $\frac{2x}{(1-x)^2}$.

Values of the function $\frac{2x}{(1-x)^2}$

x	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.000	0.020	0.042	0.064	0.087	0.111	0.136	0.162	0.189	0.217
0.1	0.247	0.278	0.310	0.343	0.379	0.414	0.453	0.493	0.535	0.578
0.2	0.63	0.67	0.72	0.78	0.83	0.89	0.95	1.01	1.08	1.15
0.3	1.23	1.30	1.38	1.47	1.56	1.66	1.76	1.86	1.98	2.10
0.4	2.22	2.36	2.50	2.65	2.81	2.97	3.16	3.35	3.55	3.77
0.5	4.00	4.25	4.51	4.80	5.10	5.44	5.79	6.2	6.6	7.0
0.6	7.5	8.0	8.6	9.2	9.9	10.6	11.4	12.3	13.3	14.4
0.7	15.5	16.7	18.4	20.0	21.9	24.0	26.4	29.1	32.3	35.8
0.8	40.0	44.8	50.7	57.5	66	76	88	103	122	147
0.9	180	224	287	379	522	760	1200	2160	4950	19800
1.0	∞	—	—	—	—	—	—	—	—	—

12. MODEL REPRESENTATIONS AND FINITE-DIFFERENCE EQUATIONS

To counter the concepts put forward above, which stem from a representation of the continuity of the scattering medium, a number of authors,[36,75-80] have advanced a model representation of its structure. Basic here is the assertion that in the case of strongly absorbing or strongly scattering particles, when their dimensions are comparable with or exceed the mean free path of the photon, separation of the medium into layers whose thickness is less than the dimensions of the particles[36] is inadmissible. Therefore the light-scattering medium is represented in the form of a set of elementary layers of thickness l (l is the average dimension of the particles), wherein each layer is characterized by the coefficients of reflection r and transmission t. If we assume that the coefficients of reflection of all layers are identical, i.e., that they do not depend upon the depth of the layer, then the problem reduces to the classical problem of a pile of thick plates, treated in detail by Stokes[81] and Vasicek.[82] From the mathematical point of view this is equivalent to replacing the differential equations (11.5) by finite differences. If the number of layers in the pile is equal to $m = d/l$, where d is the thickness of the pile, then

$$\frac{R_m}{b^m - b^{-m}} = \frac{T_m}{\frac{1}{R_\infty} - R_\infty} = \frac{1}{\frac{b^m}{R_\infty} - R_\infty b^{-m}}, \qquad (12.1)$$

where

$$R_\infty = \frac{2r}{1+r^2-t^2+\Delta}, \quad b = \frac{1+t^2-r^2+\Delta}{2t}, \quad \Delta = \sqrt{(1+r+t)(1+r-t)(1-r+t)(1-r-t)}. \qquad (12.2)$$

We note that (12.1) coincides with (11.6), if we assume $\ln b = Ll$, which is natural, since in both cases it has been assumed that the structure of the radiation field is independent of the depth. Thus, all remarks made in connection with the theories considered in Secs. 10 and 11 retain their force in this case, too.

We have pointed out above that as long as we are concerned with the reflectivity or the transmissivity of a single layer, which is infinite in the transverse directions, we are interested not in the local probabilities of absorption or scattering of the photon and in the probability of its transition from one elementary layer to another in the given direction, but in the average value of these quantities over the entire extension of the layer. Furthermore, inasmuch as the particles are considered not to be in layers but arranged at random, these probabilities cannot be referred to an infinitesimally thin layer, independently of the individual properties of the particles. However, if the particles are sufficiently large and in the shape of platelets, which is not at all uncommon, then the concept of a layered structure of the scattering medium can be pretty well substantiated. In this case, the equivalence of (12.1) and (11.6) is completely retained, and the advantage of the model treatment is the explicit introduction of the mean diameter of the particles into the formula. But, if the particles have an entirely irregular shape, and do not form any clearly expressed (even if local) layers, then the quantity $m = d/l$ in Eqs. (12.1) loses its direct physical significance, and it is no longer possible to take the parameter l as the mean dimension of the particle.

The greatest difficulty in model theories lies in the determination of the parameters r and t of the elementary layer, which is natural, since the problem of the relation of r and t with the individual properties of the medium already lies outside the theory of propagation, and belongs to scattering theory. In correspondence with the general picture of a plate-like structure of the scattering medium, which lies at the basis of the model, all the authors mentioned[36,75-79] assume the elementary layers to be continuous and to consist of the same material as the particle. It is not difficult to see that even in the case of dense packing of the particles, such an assumption is far from correct if the specific area of the gaps between particles is in any way comparable with the specific area of the particles themselves.* Thus this assumption can be valid only for dense packing of rather thick plates. The next assumption is that Fresnel reflection takes place on the surfaces of the plates (as a consequence of the roughness of the surface this reflection can be diffuse), but scattering does not, i.e., once again the dimensions of the plates are assumed to be much larger than the wavelength of the light. Then, if r_0 is the coefficient of Fresnel reflection from the surface of the plate, while κ is the index of refraction of the material composing it, then

$$\bar{r} = \bar{r}_0 + \frac{(1-\bar{r}_0)^2 \bar{r}_0 e^{-2\kappa\bar{l}}}{1-\bar{r}_0^2 e^{-2\kappa\bar{l}}}, \quad \bar{t} = \frac{(1-\bar{r}_0)^2 e^{-\kappa\bar{l}}}{1-\bar{r}_0^2 e^{-2\kappa\bar{l}}}, \qquad (12.3)$$

where the bars denote values corresponding to the statistical average over the directions of the plate and the direction of the light ray [in the lat-

*As A. P. Prishivalko[15] has shown, cooperative effects play an important role in such a model and must be taken into account, in particular in the interpretation of data not only on transmission but also the reflectivity of the layer (see also reference 52 and Sec. 13).

ter case, the effective thickness of the plate $\bar{l}$ also does not coincide with l (see reference 28)]. Thus r and t, generally speaking, depend on the angular dependence of the light rays in the scattering medium.

Now the problem reduces to the determination of $\bar{r}_0$ and $\bar{l}$. In references 75, 77, and 78 it is assumed that r_0 corresponds to the Fresnel coefficient of reflection for normal incidence of light, independently of the angle of incidence, while $\bar{l} = l$. Johnson[76] assumed the radiation field to be completely diffuse and that, in the mean, $\bar{r}_0$ corresponded to the value of r_0 at an angle of incidence of 30° (i.e., approximately 1.5 times larger than in the case of normal incidence). In both cases the coefficient of reflection, which is directly connected with the index of refraction of the material composing the particle, takes the place of the scattering coefficient. A similar consideration is substantially based on the representation that at all depths the radiation field remains completely diffuse, and that the plates are randomly oriented, which, as we have seen, contradicts the conditions for the validity of the model. We also note that in the case in which the pile is formed of plates oriented parallel to one another, the angular dependence of r_0 leads to a stretching, which increases with depth, of the indicatrix of the illumination along the normal to the surface of the pile.[82] However, in plate-like scattering media, the stratification can bear only a local character and it must be concluded that this effect does not play an essential role.

V. V. Antonov-Romanovskiĭ,[80] considering an aggregate of particles of irregular shape, also replaced the scattering by surface reflection, but introduced in addition a correction to the total internal reflection of light within the scattering particle, and estimated this correction within the framework of geometric optics, which is valid for sufficiently large particles.[3]

Thus, while the problem of the propagation of light in a scattering medium is solved correctly in the model theories that have been considered, at least within the framework of the same (unrealizable, as we have seen) assumptions as in the case of differential equations, the problem of the scattering of light by particles is solved extremely primitively and without consideration of what has already been accomplished by scattering theory. Furthermore, cooperative effects are completely ignored. Therefore it appears to us that it is essential to segregate clearly, in the analysis of the experimental data, the effects connected with the various facets of model theory and that an experimental investigation of the degree of reliability of each of the assumptions separately is most important at the present time.

In this connection we note that references 77 — 79 contain detailed tables that simplify the analysis of experimental data on the basis of model theories and permit us to display the sensitivity of the result to variations of the parameters that enter into these theories. In particular, A. P. Ivanov[83] has shown that model theories guarantee satisfactory fulfillment of conditions (11.16) in a very wide range of the dimensions of the particles and their optical characteristics, and has considered the problem of the sensitivity of the corresponding methods in the absorption coefficient.[84] It should be pointed out that the experimental data in many cases are in excellent agreement, both qualitatively and quantitatively, with the conclusions of the model theory (see Part II), a fact deserving of intensive analysis (in particular, the comparison of these data with the conclusions of the other theories).

13. THE ROLE OF THE BOUNDARY OF A SCATTERING MEDIUM

Nowhere in Secs. 7 — 12 did we take into consideration the phenomena of reflection and refraction of light at the boundary of the scattering surface. Therefore, it is essential to make clear in what cases these phenomena take place and to what extent they can affect the results of measurements, the more so that discussions of this problem in the literature are insufficiently clear.

We first assume that the binding medium (for example, air or liquid) in which the scattering particles are immersed is identical with the medium located over the surface of the scattering volume.

We have seen in Sec. 3 that if the mean dimensions of the particles or the distance between them is large in comparison with the optical wavelength, then the light waves scattered by the particles are mutually incoherent in all directions except the direction coinciding with that of the radiating wave. However, there is also one direction in which the light waves scattered by the particles are in phase, independently of the relative positions of the particles — this is the direction of specular reflection from the boundary, in conformity with Snell's law.[1] To be sure, this occurs only within a layer the thickness of which is of the order $\lambda/4\mu$.

In order to find the intensity of the specularly reflected wave, we must consider the result of the interference of waves scattered in the corresponding direction by all the particles, taking it into account that the waves are propagated in a

medium with a complex effective index of refraction, $n = A + iB$, determined by the relation (3.5). If the medium is irradiated by a plane wave, then the refracted and specularly reflected waves will be inhomogeneous inside the medium, i.e., their amplitudes will vary with the depth z as $e^{-k_0(iA\mu' + B)z}$, where μ' is the cosine of the angle ϑ' that determines the direction of the wave normal to the refracted wave (for details see reference 28). Expanding the scattered wave in a set of plane waves of different direction (see Sec. 2), we can make use of Eq. (2.7) in which, if we take into account the inhomogeneity of the refracted wave and its inclination to the layer parallel to the outside boundary, we must replace k^2 by $k_0^2 \frac{(A\mu' + iB)^2}{\mu'}$. Then we get for the components of the intensity of the specularly reflected wave

$$E_i^{\text{ref}} = \frac{2\pi N\mu'}{k_0^2 (A_i\mu' + iB_i)^2} \int_0^\infty e^{-2k_0(iA_i\mu' + B_i)z} dz \sum_j g_{ij\,\text{spec}} E_j^{\text{inc}} = \frac{\pi N\mu'}{k_0^2 (iA_i\mu' + B_i)^3} \sum_j g_{ij\,\text{spec}} E_j^{\text{inc}} = C \sum_j g_{ij\,\text{spec}} E_j^{\text{inc}}. \quad (13.1)$$

Here E_j^{inc} is the component of the field intensity of the incident wave, N = concentration of particles, and $g_{ij\,\text{spec}}$ are the components of the cooperative scattering matrix corresponding to a plane scattered wave whose direction satisfies the conditions of specular reflection and, in accordance with (3.5) and (3.6),

$$\left.\begin{aligned} A_i &= n_0 - \frac{2\pi N}{k_0 k_i^2} \operatorname{Im} g_{ii}(0), \\ B_i &= \frac{N f_i^0}{2k_0}. \end{aligned}\right\} \quad (13.2)$$

If we form the Stokes vector-parameter for the reflected wave according to the general rule (2.2), we find that the intensity of the specularly reflected light in an isotropic medium is proportional to

$$CC^* \cong \frac{\pi^2 N^2 \mu'^2}{k_0^6 (A^2\mu'^2 + B^2)^3} \quad (13.3)$$

and depends, like the polarization, on the form of the matrix $g_{ij\,\text{spec}}$, which in turn depends on the scattering angle, equal to $2\vartheta'$. It would appear that the resulting formulas are valid only for small effective index of refraction. If μ' is not too small, then, as a consequence of the smallness of $A - n_0$ and B, we obtain

$$CC^* \cong \frac{\pi N^2}{k_0^6 n_0^6 \mu'^4}. \quad (13.4)$$

In other words, the coefficient of specular reflection is in general very small, and increases rapidly with increase in the angle of incidence, which explains the generally well-known phenomenon of the clearly pronounced specular reflection from scattering surfaces at grazing angles of incidence.

For $\mu' \ll 1$, (13.3) reduces to the form

$$CC^* \cong \frac{\pi^2 N^2 \mu'^2}{k_0^6 B^6}, \quad (13.5)$$

that is, the specular reflection should disappear. However, as a result of the extreme smallness of B, this effect becomes apparent only for very small grazing angles, when the mutual screening of the particles forming the rough surface of the medium begins to have an effect.

Thus, as the result of cooperative effects, regular specular refraction and reflection of light waves takes place on the statistically smooth boundary of the scattering medium as though the medium possessed a certain effective index of refraction. However, as a result of the departure of the scattering function for large particles from the Rayleigh scattering also under the action of the cooperative effects considered in Sec. 3, the effective indices of refraction for the phenomena of reflection and refraction are shown to be different and to depend essentially on the angle of incidence.[1] The Fresnel formulas are obtained only as a limiting case in the transition to a quasi-homogeneous molecular medium with Rayleigh scattering function (here our treatment is seen to be similar to the treatment of Oseen and Ewald[85-87]), but also for the case of a small index of refraction of the medium $n = 1 + \epsilon$ ($\epsilon \ll 1$). In this case, as is not difficult to show, our formulas reduce to expressions identical with those resulting from the Fresnel formula:

$$R_s \cong \frac{\varepsilon^2}{16\mu^4}, \quad R_p \cong \frac{(1 - 2\mu'^2)^2 \varepsilon^2}{16\mu^4}, \quad (13.6)$$

where the indices s and p as usual designate the coefficients of reflection for the s and p components of the light wave, respectively. It is significant that we have been concerned above with a boundary which is statistically smooth in the scale of the averaging brought about by the detecting apparatus, independently of the character of the microstructure of the surface of an aggregate of scattering particles (let us say, a powder) known beforehand not to be physically smooth. This specular reflection is completely analogous to that which takes place at grazing incidence for x-rays on a polished surface of glass (not crystal) and which is used for the production of mirror systems for x-ray optics. But it has nothing in common with the reflection of light from the outer boundaries of a rough layer of particles that form a scattering medium. The latter has essentially a diffusive character, and is entirely taken into account by single scattering, which also increases at grazing angles of incidence as a consequence of the elongation of the scattering function for large particles. In this case the surface layer of particles is not

distinguished from any other, except perhaps by the intensity of the single scattering, which is also completely accounted for by the transfer equation (4.1). We add that, with the exception of grazing angles of incidence and very concentrated colloids with sufficiently small particles, in which the effective field differs essentially from the field of the incident wave, the effective specular reflections should be weak and do not have to be taken into consideration.

Thus, the albedo of the boundary separating two scattering media that have the same binding medium (one of the media may also not be scattering) is known to be equal to zero (in each case outside of the region of specular reflection), and the actually observed albedo of the medium is essentially a volume effect, completely taken into account by the transfer equation.

Quite a different picture will be observed in the case in which the binding medium in which the particles are immersed differs from the medium surrounding the scattering volume on the outside (opal glass, emulsions, lacquers, wetted powders, etc.). The existence of a boundary between the binding material of the two-phase scattering medium and the single-phase non-scattering medium bounding it results in the existence of sharply pronounced boundary effects (reflection, refraction), whose character depends materially on the form of the surface — the latter can be either smooth or rough — and is described by the Fresnel formulas.

Account of the effect of such reflecting and refracting boundaries (including the phenomenon of total internal reflection) is one of the most difficult problems of the general theory of propagation of radiation in a scattering medium, and is still far from having a solution acceptable for practical needs. Therefore, we shall not continue with discussions of the general theory and shall only briefly touch on several researches stemming from the considerations of Secs. 10 — 12.

Inasmuch as the differential equations of Secs. 10 and 11 refer to certain "diffuse" radiant fluxes, the authors who have considered the role of the boundary of separation (mirror-like or rough) have concentrated almost exclusively on the problem of its reflectivity and transmission coefficient as applied to diffuse flow. This permits us to return formally to Eqs. (11.1), in place of the corresponding field equations which take angular dependence into account, and thus to generalize directly the results of Secs. 10 and 11 to the case of the presence of a boundary of separation. In this case, as A. A. Gershun[90] has shown, one must distinguish between the external ρ and internal ρ' for the albedo of the boundary ($\rho' > \rho$).

In particular, for the albedo of an infinitely thick layer we obtain[72]

$$\mathcal{R}'_\infty = 1 - \frac{(1-\rho)(1-\mathcal{R}_\infty)}{1-\rho'\mathcal{R}_\infty}, \qquad (13.7)$$

where $\mathcal{R}_\infty$ is the albedo of the same layer without consideration of the boundary effect. It should be noted that the presence of the boundary of separation must (as a consequence of the angular dependence of the Fresnel coefficients) materially change the angular distribution of the radiant fluxes, and that in its turn the character of this distribution must have an important effect on the values of ρ and ρ'.[58,70,72,91] Thus, allowance for the boundary in the manner described introduces new and extremely contradictory assumptions into the treatment of the differential equations. From the point of view of the interpretation of the experimental results, this is connected with the introduction into the theory of two essentially stop-gap parameters ρ and ρ', which makes the interpretation itself completely unreliable. At the same time, the researches described have convincingly demonstrated that the boundary of separation plays a very important role and that it is not possible to ignore it whenever it exists.

Countering this, B. I. Stepanov and his coworkers[77,78] and Bodo,[75] who developed model representations, assume that at the boundary of the scattering medium, even for an identical binding material on both sides of the boundary, external (and only external) reflection takes place, wherein the latter is identified with the scattering ability of the surface layer of particles which, as seen above, has no foundation.

A. S. Toporets[51,91,92] adopted the same position in the interpretation of data on the polarization of light reflected by the scattering medium. In this case, the diffusely reflected flux divides into two components — polarized and unpolarized — and the first of these is fundamentally due to surface reflection. A number of interesting properties, found in the process of these investigations by Toporets will be considered in Part II. Here we shall limit ourselves to certain observations bearing on the interpretation from this viewpoint. Actually, one can unambiguously divide any light flux into polarized and unpolarized components (see, for example, references 2 and 93), and their separate consideration is of some interest. However, there is no basis for connecting one of these with the surface (external), and the other with the volume (internal) reflections. Above all, in the reflection from a rough surface, as a consequence of the difference in the orientations of the individ-

ual reflecting surfaces and the additivity of the components of the Stokes vector-parameter, a partially polarized light beam is formed, i.e., both components are always present. Furthermore, the beams formed as a result of both single and multiple scattering will also be partially polarized. Finally, as we have seen, the very representation of external diffuse reflection in the case of identical binding media (for example, air in the case of dry powders) has no basis of its own. In particular, this pertains to the explanation of the Umov effect[51] (see Sec. 7). The circumstance that the polarized component, owing its origin primarily to single scattering, depends more weakly on β than the unpolarized one, which is due primarily to multiple scattering, is quite natural from the theoretical viewpoint.

On the other hand, in the presence of an interphase boundary, i.e., of a difference of binding materials, the isolation of the surface reflection has a definite physical meaning and polarization studies can undoubtedly contribute to the reliability of this separation. In this connection the investigation of the effect of a boundary that is particularly rough on the polarization of the light reflected from it and transmitted through it takes on great importance. Thus, A. P. Ivanov and A. S. Toporets,[94] considering a diffuse boundary as an aggregate of microsurfaces of different orientations, showed that such a boundary exerts a strong polarizing effect on the diffuse light beam passing through it, an effect that depends materially on the microstructure of the boundary and that increases with departure of the angle of observation from normal.

14. CONCLUSION

We have considered above the principal theoretical foundations that can be established through development of the method of absorption spectroscopy of disperse materials. We have tried here to concentrate on questions of principle, and have not attempted either to encompass all the general literature connected with this circle of questions, or to elaborate on the actual recent experimental procedures. Part II will in chief measure be devoted to the latter. In this part various methodological questions of measuring techniques will be considered along with a review of experimental data. Furthermore, our review touches chiefly only on the possible means of determination of volume coefficients of absorption and scattering of the medium as such, and does not treat the entirely different problems of getting rid of cooperative effects and the transition from the individual characteristics of the scattering particles to the optical constants of the material composing them. However, the material that has been set forth does permit us to make a number of conclusions both as to present-day possibilities, and to the development in other problems of spectral analysis of disperse materials.

Above all, it should be emphasized that the careless attitude to the specific conditions of the propagation of light in scattering media, which is characteristic of many experimental spectral-analysis researches, has no foundation and can lead to serious mistakes even of a qualitative character. On the other hand, the present state of the theory permits us to guarantee trustworthy determination of the specific absorptivity of the medium β and the coefficient of extinction $\mathfrak{k}$ which is sufficient for the separate determination of the volume coefficients of absorption α and scattering σ. Here it is only necessary to construct the measuring methods in strict correspondence with the requirements of the theory. Along with this, it is necessary to note that the majority of theoretical situations still require, if not a direct verification, then the experimental determination of the limits of their applicability. Unfortunately, among the many experimental researches of methodological character, only a few are devoted to this problem.

Further, the existing methods of the determination of β and $\mathfrak{k}$ by no means exhaust all the possibilities that lie in the transfer equation. Rather, one can regard them as the first and thus far rather rough steps in this direction, the more so that even these methods are very poorly adapted for use in practical experiments. Evidently further researches in appropriate experimental situations are necessary, situations for which the approximate solution of the equation of transfer of radiation for arbitrary (unknown) scattering matrix is possible in comparatively simple analytical form, which permits us to obtain from the experimental data the necessary information on the optical properties of the scattering material. In particular, we have given practically no consideration to the different variants of the integrating photometric sphere which are widely used in practice. Here we are obliged to limit ourselves to the warning that data obtained with its help can be completely unreliable in the case of scattering media. No less important is the treatment of methods of experimental determination of the scattering matrix, because without knowing it the exclusion of cooperative effects and the development of the optical

constants of the medium forming the particles become, generally speaking, impractical problems. If we have hardly touched on this question above, it is only because there are no such methods today.

Turning to approximate theories (differential equations, model representations), it must be stated that they are unsatisfactory from the theoretical point of view. However, in a number of cases, the results obtained with their help more or less agree both with the rigorous theory and with experiment, at any rate accurate within the possibility of juggling the parameters. Therefore, clarification of this "insensitivity" of the resulting formulas to violation of theoretical premises, and also the appearance of limits of this "insensitivity," are very important theoretical and experimental problems.

Frequently, even among such experienced spectroscopists as Lecomte,[95] one can meet up with statements in the vein that although the specific properties of the scattering medium affect the behavior of the intensities in the reflection or transmission spectra, the very fact of the existence and the location of the absorption bands are free of this effect, except for rare cases. Actually, under certain precautions, this should be so in the majority of cases. However, the experimenter must be certain that all the necessary precautions have been taken. This in itself is not trivial and requires careful theoretical analysis of the experimental situation, especially since the shape of the band can be subject to considerable distortion.

Finally, many problems connected with account of cooperative effects and the solution of the inverse problem of scattering theory (which as we have seen is quite necessary for the solution for a number of spectroscopic problems) are still not completely clear.

The spectroscopy of dispersive materials follows, both experimentally and theoretically, a more or less isolated path, with its own specific methods of investigation and its practically unbounded range of higher degrees of actual problems and objectives. We should like to draw attention to this as yet only formulated (but already leading to certain success) trend of contemporary optics, the more so that problems of a similar nature are encountered in very widely differing branches of science and industry.

[1] G. V. Rozenberg, Некоторые вопросы распространения электромагнитных волн в мутных средах Some Problems in the Propagation of Electromagnetic Waves in Turbid Media, Dissertation, Moscow, 1954.

[2] G. V. Rozenberg, Usp. Fiz. Nauk, **56**, 77 (1955).

[3] K. S. Shifrin, Рассеяние света в мутной среде (Light Scattering in a Turbid Medium). Moscow, 1951.

[4] Van der Hulst, Light Scattering by Small Particles, London, 1957.

[5] É. V. Shpol'skiĭ and A. A. Il'ina, Izv. Akad. Nauk SSSR, Ser. Fiz. **11**, 401 (1947).

[6] G. V. Rozenberg, Сборник памяти акад. П. П. Лазарева (Collection in Honor of Acad. P. P. Lazarev). Moscow, 1956, p. 132.

[7] N. K. Sethy, Proc. Ind. Cult. Sci. **5**, 121 (1920).

[8] S. M. Sogany, Phil. Mag. **1**, 32 (1926).

[9] Elvegard, Staude, and Weigert, Z. phys. Chem. **2**, 149 (1929).

[10] K. Fragstein, Ann. Physik **17**, 22 (1933).

[11] H. S. Denmark and W. M. Cady, J. Opt. Soc. Amer. **25**, 330 (1935).

[12] C. V. Raman, Proc. Ind. Acad. Sci. **A29**, 381 (1949).

[13] A. P. Prishivalko, Izv. Akad. Nauk SSSR, Ser. Fiz. **21**, 1541 (1957), Columbia Tech. Transl. p. 1528.

[14] B. I. Stepanov and A. P. Prishivalko, Труды Ин-та физ. и мат. АН БССР (Trans. Inst. Phys. and Math. Belorussian S.S.R.) No. 2, 189 (1957).

[15] A. P. Prishivalko, ibid. No. 2, 206 (1957).

[16] Yu. I. Chekalinskaya, Dissertation, Minsk (cited in reference 15).

[17] R. B. Barnes and I. G. Bonner, Phys. Rev. **49**, 732 (1936).

[18] V. A. Malyshev, Труды X совещания по спектроскопии, Львов (Trans. Tenth Conference on Spectroscopy), 1956.

[19] R. L. Henry, J. Opt. Soc. Amer. **38**, No. 9, 775 (1948).

[20] J. R. De Vore and A. H. Pfund, J. Opt. Soc. Amer. **37**, 826 (1947).

[21] E. O. Fedorova, Труды ГОИ (Trans. State Optics Institute) **25**, No. 151 (1957).

[22] L. I. Mandel'shtam, Полное собрание трудов (Complete Works), U.S.S.R. Acad. Sci. 1948-1950.

[23] M. Lax, Revs. Modern Phys. **23**, No. 4 (1941).

[24] Zimm, Doty, and Stein, Theory and Applications of Light Scattering N.Y., 1957 (cited in reference 4).

[25] G. Oster, Chem. Rev. **43**, 319 (1948); Ann. Chem. **25**, 1165 (1953); G. Oster and D. P. Riley, Acta Cristalogr. **5**, 1 (1952).

[26] A. I. Kalyadin, Оптика и спектроскопия (Optics and Spectroscopy) **1**, 907 (1956); Dokl. Akad. Nauk SSSR **109**, 64 (1956), Soviet Phys.–Doklady **1**, 406 (1957); N. A. Voĭshvillo, Оптика и спектроскопия (Optics and Spectroscopy) **2**, No. 3 (1957); **3**, No. 3 (1957); Инж.-физ. (Eng.-Phys. J.) **1**, No. 4 (1958).

[27] R. Fürth and C. L. Williams, Proc. Roy. Soc. Edinburgh A224, 104 (1954).

[28] G. V. Rozenberg, Оптика тонкослойных покрытий (Optics of Thin Films), Moscow, 1958.

[29] G. V. Rozenberg, Труды Московского вечернего машиностроительного ин-та (Trans. of the Moscow Evening Machine Building Institute), No. 2, 290 (1955).

[30] M. V. Vol'kenshteĭn, Молекулярная оптика (Molecular Optics). Moscow, 1951.

[31] Maxwell-Garnett, Phil. Trans. Roy. Soc. A203, 385 (1904); A205, 237 (1906).

[32] P. Debye, J. Appl. Phys. 15, 338 (1944); J. phys. Chem. 51, 18 (1947).

[33] S. Chandrasekhar, Radiative Transfer (Oxford, 1950). Russian translation, Moscow, 1953.

[34] G. V. Rozenberg, Characteristics of the Polarization of Light Scattered by the Atmosphere under Conditions of Twilight Illumination. Dissertation, Moscow, 1946.

[35] V. V. Sobolev, Izv. Akad. Nauk SSSR, Ser. Geogrf. Geofiz. 8, 173 (1944); уч. зап. ЛГУ (Sci. Notes Leningrad State Univ.) No. 116, 3 (1941).

[36] B. I. Stepanov, Izv. Akad. Nauk SSSR, Ser. Fiz. 21, 1485 (1957), Columbia Tech. Transl. p. 1477.

[37] V. A. Timofeeva, Труды Морского гилрофиз. ин-та АН СССР (Trans. Naval Hydrophys. Acad. U.S.S.R. Acad. Sci.) 3 (1953).

[38] V. A. Timofeeva, Izv. Akad. Nauk SSSR, Ser. Geofiz. 2, 265 (1957).

[39] V. A. Timofeeva, Dokl. Akad. Nauk SSSR 113, 556 (1957).

[40] J. Lenoble, Ann. Geophys. 12, No. 1, 16 (1956).

[41] V. A. Ambartsumyan, Izv. Akad. Nauk SSSR, Ser. Geograf. i Geofiz. No. 3, 97 (1942).

[42] V. V. Sobolev, Перенос лучистой энергии в атмосферах звезд и планет (Transfer of Radiative Energy in the Atmospheres of Stars and Planets). Moscow, 1956.

[43] M. V. Maslennikov, Dokl. Akad. Nauk SSSR 118, No. 2 and No. 5 (1957), 120, No. 1 (1958); Soviet Phys.–Doklady 3, 40, 48 (1958) and 521 (1959).

[44] S. G. Slyusarev, Paper delivered at the Conference on Actinometry and Atmospheric Optics, Leningrad, 1959.

[45] G. V. Rozenberg, Оптика и спектроскопия (Optics and Spectroscopy) 5, 440 (1958); Dokl. Akad. Nauk SSSR 122, 211 (1958).

[46] G. V. Rozenberg, Оптика и спектроскопия (Optics and Spectroscopy) (1959) (in press).

[47] E. S. Kuznetsov, Izv. Akad. Nauk SSSR, Ser. Geogrf. i. Geogiz. No. 5, 247 (1943).

[48] G. V. Rozenberg, Dokl. Akad. Nauk SSSR 98, 201 (1954).

[49] V. A. Ambartsumyan, Dokl. Akad. Nauk Arm. SSR 8, 101 (1948).

[50] N. Umov, Physik. Z. 6, 674 (1905).

[51] A. S. Toporets, Izv. Akad. Nauk SSSR, Ser. Fiz. 14, 594 (1950).

[52] Yu. I. Chekalinskaya, Труды Ин-та физ. и мат. АН БССР (Trans. Inst. Phys. and Math. Belorussian S.S.R.) No. 1, 176 (1956).

[53] M. M. Gurevich and L. Chokhrov, Труды ГОИ (Trans. State Optics Inst.) 11, 17 (1936).

[54] G. V. Rozenberg, Usp. Fiz. Nauk 58, 487 (1956).

[55] E. S. Kuznetsov, Dokl. Akad. Nauk SSSR 37, 237 (1942).

[56] G. A. Gamburtsev, Жур. русского физ.-хим. об-ва (J. Russ. Phys–Chem. Soc.), Phys. Part., 56, 225 (1924).

[57] R. Mecke, Ann. Physik 65, 257 (1921).

[58] J. W. Ryde, Proc. Roy. Soc. A131, 451 (1931).

[59] V. G. Kastrov, Ж. Геофизики (Geophysics J.) 3, 123 (1933).

[60] A. N. Gordov, ibid. 6, 295, 371 (1936).

[61] P. Kubelka, J. Opt. Soc. Amer. 38, No. 5, 448 (1948).

[62] A. Schuster, Astrophys. J. 21, No. 1, 1 (1905).

[63] P. Kubelka and F. Munk, Z. techn. Physik 20, No. 11a, 593 (1931).

[64] K. Schwarzschild, Sitz. Ber. König. Preuss. Akad. Wiss., p 1183, (1914).

[65] N. Boldyrev and A. Aleksandrov, Труды ГОИ (Trans. State Optics Inst.) 11, 56 (1936).

[66] S. Q. Duntley, J. Opt. Soc. Amer. 33, No. 5 252 (1943).

[67] L. Silberstein, Phil. Mag. 4, 1291 (1927).

[68] K. Ya. Kondrat'ev, Paper delivered at Conference on Actinometry and Atmospheric Optics, Leningrad, 1959.

[69] V. A. Ambartsumyan, Астрономический журнал (Astron. J.) 19, 1 (1942); Dokl. Akad. Nauk SSSR 38, 257 (1943).

[70] Ake S:son Stenius, Svensk pappers. Tidning. 54, 663, 701 (1951); 56, No. 16, 607 (1953).

[71] M. M. Gurevich, Труды ГОИ (Trans. State Optics Inst.) 6, 1 (1931).

[72] A. A. Gershun, ibid. 11, 43 (1936).

[73] Channon, Renwick, and Storr, Proc. Roy. Soc. London A94, 222 (1918).

[74] D. R. Duncan, Proc. Phys. Soc. London 52, part III, No. 291, 390 (1940).

[75] Z. Bodo, Acta Phys. Hung. 1, No. 2, 135 (1951).

[76] P. Johnson, J. Opt. Soc. Amer. 42, No. 12, 978 (1952).

[77] O. P. Girin and B. I. Stepanov, JETP 27, 467 (1954).

[78] Stepanov, Chekalinskaya, and Girin, Труды Ин-та физ. и мат. АН БССР (Trans. Phys. and Math.

Inst. Acad. Sci. Belorussian S.S.R.) No. 1, 152 (1956).
[79] Yu. I. Chekalinskaya, ibid., No. 1, 176 (1956).
[80] V. V. Antonov-Romanovskiĭ, JETP **26**, 459 (1954).
[81] G. Stokes, Mathem. and Phys. Papers **4**, 145 (1904).
[82] A. Vasicek, Optika Tenkych Vrstev (Optics of Thin Layers). Praha, 1956.
[83] A. P. Ivanov, Оптика и спектроскопия (Optics and Spectroscopy) **2**, 524 (1957).
[84] A. P. Ivanov, Инж.-физ. Ж. (Eng. Phys. J.) **1**, 30 (1958).
[85] C. W. Oseen, Ann. Physik **48** (1915); Phys. Zeits. **16**, 404 (1915).
[86] P. P. Ewald, Ann. Physik **49**, **1**, 117 (1916).
[87] M. Born, Optik (Russian translation, ONTI, 1937).
[88] H. Bartels and Noak, Z. Physik **64**, No. 7-8, 465 (1930).
[89] Ginzburg, Pul'ver, and Fabrikant, Труды ГОИ (Trans. State Optics Inst.) **11**, 24 (1936).
[90] A. A. Gershun, ibid. No. 38 (1928); **6**, No. 59 (1931).
[91] A. S. Toporets, JETP **20**, 390 (1950).
[92] A. S. Toporets, Оптика и спектроскопия (Optics and Spectroscopy) **1**, 90 (1958).
[93] L. D. Landau and E. M. Lifshitz, Квантовая механика (Quantum Mechanics), Moscow, 1948 [Engl. Transl. Pergamon Press, 1958].
[94] A. P. Ivanov and A. S. Toporets, J. Tech. Phys. (U.S.S.R.) **26**, 623 (1956), Soviet Phys.-Tech. Phys. **1**, 598 (1957).
[95] J. Lecomte, Le Rayonnement Infrarouge, Gauthier-Villars, Paris, 1948 (Russ. Transl. Moscow, 1958).
[96] A. A. Il'ina and G. V. Rozenberg, Dokl. Akad. Nauk SSSR **98**, 365 (1954); Сб. памяти акад. П. П. Лазарева (Collection in Memory of Acad. P. P. Lazarev) Moscow, p. 143 (1956).
[97] A. S. Toporets, Оптика и спектроскопия (Optics and Spectroscopy) **4**, 494 (1958).
[98] G. Kortüm and G. Schreyer, Angew. Chem. **67**, No. 22, 694 (1955).

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