RADIATIVE TRANSFER IN DISCONTINUOUS MEDIA

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Summary

The theory of radiative transfer is applied to a scattering and absorbing medium consisting of randomly distributed spherical regions of uniform extinction and scattering coefficients $\varkappa$ and σ, separated by free space.

A general discussion of the diffusion of radiation through an infinite medium is followed by an approximate treatment of the semi-infinite case. It is shown that the reflectance may be very much lower than that of a uniform, continuous semi-infinite medium having the same value of $\sigma/\varkappa$; the reflectance is obtained as a function of $\sigma/\varkappa$ and of the size and mean separation of the spherical regions.

I. INTRODUCTION

The theory of radiative transfer has usually been restricted to media of uniform extinction and scattering coefficients $\varkappa$ and σ. Cases often arise, however, in widely different contexts, where the properties of a diffusing medium are non-uniform; examples of such media are imperfectly dispersed paints and pigmented plastics, clouds, atmospheres of planets and even of the Sun, and diffuse nebulae.

General considerations suggest that the optical properties of non-uniform media may differ markedly from those of uniform media, and that the reflectance of a semi-infinite medium, for example, may depend strongly on its structure even if $\tilde{\omega}_0=1-\lambda=\sigma/\varkappa$ is uniform throughout.

This paper investigates the diffusion of radiation through a model medium in which scattering and absorption occur only within spherical regions of uniform $\varkappa$ and σ, radius r_0, distributed at random and separated by free space. The appropriate integral equation of radiative transfer is obtained in Section II by expressing the intensity of radiation incident on one of the spheres in terms of the radiation emerging from the other spheres. The various quantities involved are discussed in Section III. The method of solution of the equation of transfer, restricted for simplicity to an infinite medium with all sources at infinity, and subject to certain simplifying approximations, is outlined in Section IV. In Section V it is shown that these results can be used for deriving reflectances of semi-infinite media. Finally, numerical results are discussed in Section VI.

II. THE EQUATION OF RADIATIVE TRANSFER

The procedure adopted is to describe the intensity of radiation leaving one of the diffusing spheres in terms of the unknown incident radiation intensity distribution. The mean intensity of radiation incident on a second sphere may

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then be expressed in terms of the radiation leaving the first sphere and of its probability of reaching the second sphere, integrated over all possible positions of the first sphere. This yields the appropriate integral equation of radiative transfer.

More specifically, consider a medium in which the net flow of radiation is in the direction of the negative z-axis. We make the assumption that the intensity of diffuse radiation $I(z,\theta)$ incident on a diffusing sphere depends only on the z-coordinate of the point of incidence F (Fig. 1) and on the angle θ between the ray and the negative z-axis, but not on the position of the sphere centre. Consider possible ray paths commencing in a length range dl and terminating

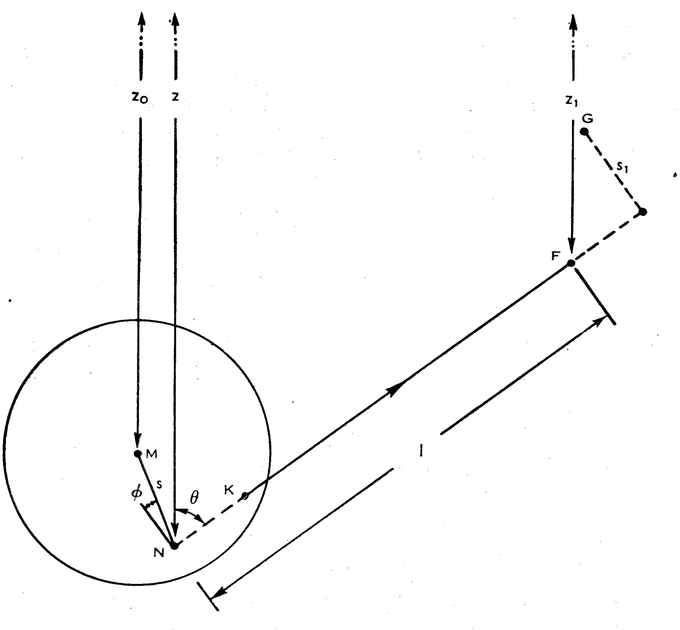

Fig. 1.—Passage of a ray between two diffusing aggregates.

at F in a range Δl, the length l being the distance NF between the centre of the sphere, M, from which the ray departs and the point of termination of the path, when projected on to the ray path. With N sphere centres per unit volume, the probability of a sphere centre lying in the volume element $s\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l$, at perpendicular distance s from the ray path and orientation φ in a plane through the sphere centre perpendicular to the ray, is $Ns\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l$. Let the intensity of a ray leaving the sphere after scattering be I_σ and the mean attenuation in traversing the path be p. Finally, let $NA\Delta l$ be the probability of a second sphere lying in a position to receive the ray in the interval Δl. Then in a source-free region the mean intensity $I(z,\theta)$ of the radiation incident on a diffusing sphere is proportional to

$$\int_0^L\int_0^{2\pi}\int_0^{r_0} I_\sigma pAs\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l,$$

the limit L being set by the position of any boundary, and being ∞ for an infinite medium. The factor of proportionality depends only on the geometry of the medium and on $\varkappa$, and is most easily found by supposing the spheres to be non-absorbing. If, when these spheres are uniformly and isotropically irradiated at unit intensity, the intensity of scattered radiation leaving the sphere at the required point and direction is U_σ, the factor of proportionality is readily seen to be

$$\left[\int_0^L\int_0^{2\pi}\int_0^{r_0} U_\sigma pAs\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l\right]^{-1}.$$

Thus the equation of radiative transfer is

$$I(z,\theta)=\frac{\int_0^L\int_0^{2\pi}\int_0^{r_0} I_\sigma pAs\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l}{\int_0^L\int_0^{2\pi}\int_0^{r_0} U_\sigma pAs\mathrm{d}s\mathrm{d}\varphi\mathrm{d}l}. \quad \dots\dots\dots\dots \quad (2.1)$$

There are two important special cases to which the present discussion is confined.

(i) If negligible radiation is transmitted directly through a sphere without scattering, $U_\sigma=1$.

(ii) If the spheres are widely spaced, so that A is independent of s, φ, and l, the denominator simplifies to $(1-\tau_0)A\pi r_0^2\int_0^L p\mathrm{d}l$, where τ_0 is the fraction of uniformly diffuse flux incident on a sphere which is transmitted directly without scattering.

III. The Quantities Entering into the Equation of Transfer

(a) The Intensity I_σ

The diffuse flux F_i incident per unit area on a diffusing sphere is on the average symmetrical about the z-axis, so that it may be expanded in a series of Legendre polynomials

$$F_i=\tfrac{1}{4}\sum_0^\infty \alpha_n P_n(\mu), \quad \dots\dots\dots\dots \quad (3.1)$$

where $\cos^{-1}\mu$ is the angle between the radius vector and the negative z-axis. Then the flux leaving unit area of the sphere surface may also be expressed in the form

$$F_l=\tfrac{1}{4}\sum_0^\infty \alpha_n g_n P_n(\mu), \quad \dots\dots\dots\dots \quad (3.2)$$

the g_n being functions of $\tilde{\omega}_0$ and of the optical thickness $2\varkappa r_0$.

Giovanelli and Jefferies,* using the Eddington approximation, have shown that the g_n take simple forms provided $\tilde{\omega}_0\gtrsim 0\cdot 9$ (i.e. provided a uniform continuous semi-infinite medium of this material had a reflectance exceeding about $0\cdot 5$) or provided $2\varkappa r_0 \ll 1$; and have given values of these functions.

* Giovanelli, R. G., and Jefferies, J. T. (1956).—*Proc. Phys. Soc. Lond.* **B 69**: 1077–84.

The flux F_l includes both scattered and directly transmitted radiation, though with sufficiently large spheres the latter is negligible. For very small spheres ($2\varkappa r_0 \ll 1$) the directly transmitted component F_d is simply the value of F_l found from (**3.2**) on putting $\sigma=0$ but retaining $\varkappa$ unchanged, so that $\tilde{\omega}_0=0$; for larger spheres it is easiest to evaluate F_d from the relation

$$F_d=\int_0^1\int_0^{2\pi}(1/\pi)F_i\exp\left(-\varkappa y\right)\cos\psi\, d(\cos\psi)d\xi, \quad \ldots . \quad (\mathbf{3.3})$$

where y is the length of the ray path in the sphere, ψ is the angle between the transmitted ray and the outward normal to the sphere, and ξ is an azimuthal angle measured in the tangent plane. F_d may then be expanded in the form

$$F_d=\tfrac{1}{4}\sum_0^\infty \alpha_n\tau_n P_n(\mu), \quad \ldots \quad (\mathbf{3.4})$$

where the τ_n can be found in the usual way via (**3.3**) and (**3.1**). Here τ_0 is the fraction of uniformly diffuse incident flux which is transmitted directly through the sphere without scattering.

For the intensity of scattered radiation leaving a given point on the sphere surface we then take the mean value

$$\begin{aligned} I_\sigma &= (F_l-F_d)/\pi \\ &= (1/4\pi)\sum_0^\infty \alpha_n(g_n-\tau_n)P_n(\mu). \quad \ldots \quad (\mathbf{3.5}) \end{aligned}$$

(b) The Flux Incident on a Sphere

In order to render the equation of radiative transfer tractable the intensity distribution in the neighbourhood of a sphere, required for α_n in (**3.5**), is expanded in a Taylor series in terms of the intensity distribution and its derivatives at a nearby point.

Let the intensity of radiation $I(z,\theta)$ incident at the point z on a diffusing sphere be expanded in a series of Legendre polynomials

$$I(z,\theta)=\sum_0^\infty \varepsilon_n(z)P_n(\cos\theta), \quad \ldots \quad (\mathbf{3.6})$$

the net flow of radiation being in the direction of the negative z-axis and θ being the angle between the ray and the negative z-axis. By Taylor's theorem, the intensity of radiation incident on a sphere at any other point $z+\Delta z$ is then obtainable from the relations

$$\varepsilon_n(z+\Delta z)=\sum_{m=0}^{\infty}\frac{(\Delta z)^m}{m\,!}\varepsilon_n^{(m)}(z), \quad \ldots \quad (\mathbf{3.7})$$

where $\varepsilon_n^{(m)}(z)$ denotes the mth differential coefficient of $\varepsilon_n(z)$.

The flux per unit area incident on a sphere, centre at z_0, at a point whose radius vector makes an angle $\cos^{-1}\mu$ with the negative z-axis (see Fig. 2), is

$$F_i(z-r_0\mu)=\int I(z_0-r_0\mu,\theta)\mu' d\Omega, \quad \ldots \quad (\mathbf{3.8})$$

where $\cos^{-1}\mu'$ is the angle between the incident ray and the normal, $d\Omega$ is the element of solid angle, and the integral is taken over a hemisphere external to the sphere. If the angle between the plane containing the radius vector and

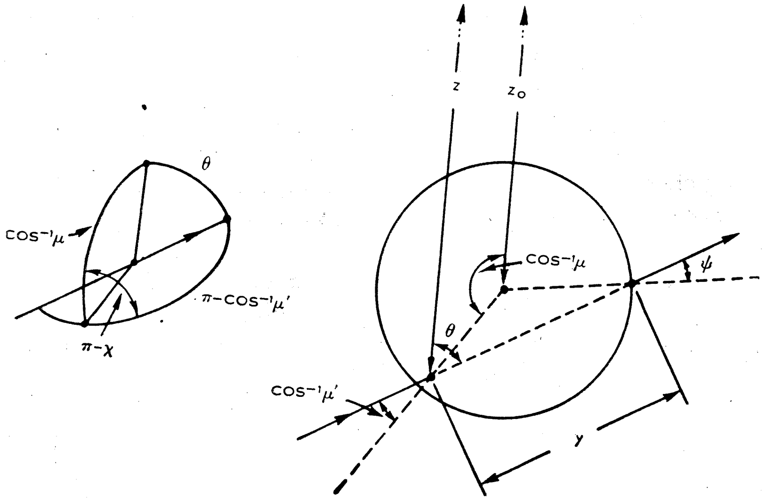

Fig. 2.—Ray incident on a spherical diffusing aggregate (see text). At left, auxiliary spherical diagram for incident ray.

the incident ray, and the plane containing the radius vector and the z-axis, be denoted by χ, (**3.8**) may be written as

$$F_i(z_0-r_0\mu)=\int_0^{2\pi}\int_0^1\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(z_0-r_0\mu-z)^m}{m\,!}\varepsilon_n^{(m)}(z)P_n\,(\cos\theta)\mu'd\mu'd\chi,$$

which, it can be shown, integrates to

$$F_i(z_0-r_0\mu)=\sum_0^{\infty}\frac{(z_0-r_0\mu-z)^m}{m\,!}\Big[\pi\varepsilon_0^{(m)}(z)-\frac{2}{3}\pi\mu\varepsilon_1^{(m)}(z)-\frac{\pi}{8}(1-3\mu^2)\varepsilon_2^{(m)}(z)$$
$$-\frac{\pi}{8}\left(\frac{35}{24}\mu^4-\frac{5}{4}\mu^2+\frac{1}{8}\right)\varepsilon_4^{(m)}(z)+\ldots\Big]. \quad \ldots\ldots\ldots\ldots\ (\mathbf{3.9})$$

Neglecting the anisotropy of the incident radiation at any point, we may now use (**3.9**) to expand $F_i(z_0-r_0\mu)$ in a series of Legendre polynomials, as required for application in (**3.1**) and (**3.5**):

$$F_i(z_0-r_0\mu)=\tfrac{1}{4}\sum_0^{\infty}\alpha_nP_n(\mu),$$

where

$$\alpha_n=2(2n+1)\int_{-1}^{1}F_i(z_0-r_0\mu)P_n(\mu)d\mu. \quad \ldots\ (\mathbf{3.10})$$

(c) *Attenuation*

A ray will traverse the distance between two diffusing spheres without attenuation provided there are no intervening obstacles. We restrict consideration here to spheres of sufficient optical thickness for directly transmitted radiation to be negligible, so that the $\tau_n=0$; the complete range of sphere sizes is discussed in Section V for the special case of well-spaced spheres.

The probability of a ray traversing a given path without obstruction is then the probability of all sphere centres avoiding a certain volume V within a distance r_0 of the ray. Let there be N spheres per unit volume, the unit of volume being chosen so that N is large. We suppose that each sphere occupies volume v, whose actual magnitude depends on the packing and will be considered later.

We now regard the spheres as introduced into unit volume one by one. The probability of the first sphere centre avoiding a given volume V is $1-V$; the probability of the second avoiding V is $(1-V-v)/(1-v)$, and so on. The probability p of all sphere centres avoiding V is thus

$$p=(1-V)\left(\frac{1-V-v}{1-v}\right)\left(\frac{1-V-2v}{1-2v}\right)\cdots\left(\frac{1-V-\{N-1\}v}{1-\{N-1\}v}\right),$$

which, in the relevant case where $V\ll 1$, can be simplified to

$$p\doteq\exp\left(-hV\right), \quad \ldots\ldots\ldots\ldots \quad (\mathbf{3.11})$$

where

$$h=-v^{-1}\log\left(1-Nv\right).$$

It may be noted that $1-Nv$ is the unfilled space per unit volume. If $Nv\ll 1$, then $h\approx N$.

(d) V *and* A

The area A appearing in (**2.1**) and the volume V may be found from a discussion of the geometry of close spheres.

To consider V, let the ray KF leave the surface of a diffusing sphere, centre M, at point K and reach a second sphere, centre G, at point F (Fig. 1). Because of the finite sizes of the spheres, neither G nor the centre of any other sphere can lie within a distance $2r_0$ of M. If KF is short enough, this places a restriction on the relative positions of M and G. Again, the volume V which can contain the centre of any intervening sphere is not simply that of a cylinder of length KF and radius r_0, coaxial with the ray, but is rather the volume of such a cylinder when the regions closer than $2r_0$ to M or G are excluded. To a very good approximation it may be shown that

$$V=\pi r_0^2[1+(r_0^2-s_1^2)^{\frac{1}{2}}]-10\cdot 78r_0^3,$$

when the right-hand side is positive ($l>l_0$, say) and $V=0$ otherwise, s_1 being the distance from G to KF produced. Thus

$$\left.\begin{aligned} p&=1, & (l<l_0)\\ &=B\exp\left(-xl\right), & (l>l_0)\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (\mathbf{3.12})$$

where $x = \pi r_0^2 h$. The quantity B depends slightly on s_1, though little error is introduced by using its mean value

$$B = 2\{\exp(10 \cdot 78 h r_0^3)\}(x r_0^2)^{-1}[1-(1+x r_0)\exp(-x r_0)].$$

To consider A, where $NA\Delta l$ is the probability of a second sphere lying in a position to receive a ray in the length interval Δl, we note that G must lie on the hemisphere of radius r_0, centre F, base HP perpendicular to KF (see Fig. 3). For a given position of M within distance $2r_0$ of the edge of this base, G can lie only on that part of the hemisphere not intersected by the sphere of radius $2r_0$, centre M. Then A is the projection on to the hemisphere base plane

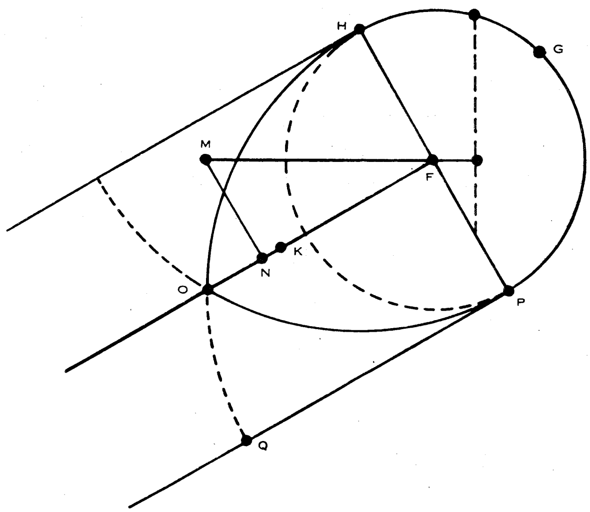

Fig. 3.—Zones in which centres of neighbouring diffusing aggregates may lie.

of that part of the hemisphere accessible to G. When $Nv \ll 1$, so that the spheres are widely spaced, clearly $A = \pi r_0^2$. Otherwise A takes different forms depending on the positions of M and F. As A is small or zero when $l \lesssim r_0$, it is a very good approximation, and renders the problem tractable, to assume that

$$\left.\begin{aligned} A &= 0, \quad (l < l_m) \\ &= \pi r_0^2, \quad (l > l_m) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.13)}$$

where

$$\int_{l_m}^{\infty}\int_0^{r_0} \pi r_0^2 s \, ds \, dl = \int_0^{\infty}\int_0^{r_0} A s \, ds \, dl.$$

It is found numerically that $l_m = 1 \cdot 000 r_0$.

The various simplifications and approximations introduced in this section have been found necessary for obtaining an analytical solution. Their effects are quite small and largely self-compensating.

IV. The Solution of the Equation of Radiative Transfer for an Infinite Medium

In solving the equation of radiative transfer (**2.1**), it is desirable to limit the numbers of terms in the Legendre series for $I(z,\theta)$ and in the Taylor series for $\varepsilon_n(z+\Delta z)$ to as few as possible compatible with the required degree of accuracy, as the work involved increases enormously with the numbers of terms retained. It may be noted that when the diffusing spheres are all far apart the variation of $I(z)$ over a distance equal to the sphere diameter is negligible ; it is necessary to take account of the differential coefficients of $\varepsilon_n(z)$ only when dealing with close spheres. Again, the success of the Eddington approximation, corresponding to the neglect of the term $\varepsilon_2(z)$ in the Legendre series for $I(z,\theta)$ when dealing with uniform media, and the absence of the term in $\varepsilon_3(z)$ in the expansion for $F_i(z_0-r_0\mu)$ in (**3.9**), and hence for α_n, suggest that it would suffice for many purposes to retain only the first two terms in the Legendre series for $I(z,\theta)$. This approximation has been adopted here, though for the case of well-spaced spheres comparison is made later with results obtained when including also the term in $\varepsilon_2(z)$. Furthermore, differential coefficients of $\varepsilon_n(z)$ higher than the first are excluded ; thus the subsequent results apply adequately for well-spaced spheres and give the general trend for closely spaced spheres.

We now note that when the spheres are of sufficient optical thickness for directly transmitted radiation to be negligible (as adopted in Section III (*c*)), $U_\sigma=1$ and $\tau_n=0$, so that from (**3.5**)

$$I_\sigma=(1/4\pi)\sum_0^\infty \alpha_n g_n P_n(\mu).$$

Again, the change in the approximate function for p at $l=l_0$, (**3.12**), necessitates the introduction of the following artifice in evaluating the numerator of (**2.1**) :

$$\int_0^\infty I_\sigma pA\,dl=\int_0^{l_0} I_\sigma A\,dl+\int_0^\infty I_\sigma B\exp(-xl)A\,dl-\int_0^{l_0} I_\sigma B\exp(-xl)A\,dl.$$

For the first and third terms on the right-hand side of this equation, $\varepsilon_n(z_0)$ may be expanded in terms of the components $\varepsilon_n(z_1)$ and their derivatives at the point $F(z=z_1)$ using (**3.7**), the corresponding α_n being obtained from (**3.10**) and (**3.9**). For the second term, $\varepsilon_n(z_0)$ is expanded about the point $N(z=z)$.

The numerator and denominator of (**2.1**) may now be integrated completely, except for a term of the form $\int_0^\infty \exp(-xl).Y\,dl$, where Y is a function of the $\varepsilon_n^{(m)}(z)$. Differentiation of the equation with respect to z, followed by integration with respect to $d(\cos\theta)$ over the range -1 to $+1$, in the first case directly and in the second after multiplication throughout by $\cos\theta$, converts the equation of radiative transfer into a pair of second order differential equations for the $\varepsilon_n(z)$. The solution is most readily completed by noting that in an infinite medium with all sources at infinity the variation in intensity in any given direction must be exponential, and that the relative angular distribution of radiation must be independent of z. Thus we may write

$$\varepsilon_0(z)=\varepsilon \exp(kz), \quad \varepsilon_1(z)=j\varepsilon_0(z), \qquad (4.1)$$

substitution of which into the equations of transfer yields the values of the constants k and j.

V. Reflectances of Semi-infinite Media

While the solution for and even the complete expression of the equation of radiative transfer are generally very complicated in the case of a semi-infinite discontinuous medium, an approximate treatment is very easy.

(a) *Diffusing Spheres of Any Separation*

An infinite medium with a plane source at infinity can be regarded as composed of a semi-infinite medium K containing a source at infinity, together with a contiguous source-free semi-infinite medium M. The distribution of radiation in the source-free medium remains unchanged if the other medium, K, is removed but the surface of M is irradiated in the same way as when the two media were in contact. Thus to a first approximation the reflectance of a semi-infinite medium to diffuse incident radiation having the appropriate distribution

$$I(\theta)=\sum_0^\infty \varepsilon_n P_n(\cos\theta), \quad (0\leqslant\theta\leqslant\tfrac{1}{2}\pi),$$

where the ε_n are those discussed in the previous sections, is

$$R_D=\frac{\int_0^{-1} I(\theta)\cos\theta\, d(\cos\theta)}{\int_0^{1} I(\theta)\cos\theta\, d(\cos\theta)}$$

$$=\frac{\int_0^{-1}\sum_0^\infty \varepsilon_n P_n(\cos\theta)\cos\theta\, d(\cos\theta)}{\int_0^{1}\sum_0^\infty \varepsilon_n P_n(\cos\theta)\cos\theta\, d(\cos\theta)}. \qquad (5.1)$$

This relation holds exactly for a uniform continuous medium and for a medium consisting of well-spaced diffusing spheres. With diffusing spheres close together the boundary conditions are not rigorously satisfied. Nevertheless (5.1) describes adequately the trend of diffuse reflectance as the separations between spheres are reduced. With the approximations adopted in Section IV the reflectance is

$$R_D=(1-\tfrac{2}{3}j)/(1+\tfrac{2}{3}j), \qquad (5.2)$$

when the incident radiation is described by

$$I(\mu)=\varepsilon_0(1+\mu j), \quad (0\leqslant\mu\leqslant 1).$$

(*b*) *Well-spaced Diffusing Spheres*

When the diffusing spheres are well separated we can readily obtain results of greater generality and accuracy, including those for the case of small spheres for which F_d is not necessarily zero. The appropriate attenuation law follows by noting that, of the flux incident on a sphere, the fraction transmitted directly is τ_0. Thus the cross section of a sphere for the attenuation of radiation is $\pi r_0^2(1-\tau_0)$, and with N spheres per unit volume, the attenuation in path l is

$$p=\exp(-x_1 l),$$

where

$$x_1=\pi N r_0^2(1-\tau_0).$$

The equation of radiative transfer is much simpler than for closely spaced spheres, so that terms up to and including $\varepsilon_2(z)$ in the Legendre series for $I(z,\theta)$ can be retained. The reflectances for a semi-infinite medium so derived yield a valuable check on the validity of results obtained neglecting $\varepsilon_2(z)$.

VI. Numerical Results

Table 1 presents results of computations of reflectances of semi-infinite media comprised of large ($\tau_0=0$), well-spaced aggregates obtained including $\varepsilon_2(z)$ (column 3) and excluding $\varepsilon_2(z)$ (column 2). These are tabulated against the reflectances $\tilde{\omega}_0'$ of a semi-infinite continuous medium comprised of the same

Table 1

Reflectance of a semi-infinite medium comprised of large well-spaced aggregates

$\tilde{\omega}_0'$ Reflectance of Semi-infinite Continuous Medium	R_D Reflectance of Medium in Form of Large Well-spaced Aggregates	
	1st Approx.	2nd Approx.
0·999	0·942	0·941
0·990	0·829	0·825
0·950	0·659	0·646
0·900	0·552	0·532
0·700	0·334	0·304
0·500	0·208	0·178

material (column 1); in this case $g_n=G_n=\tilde{\omega}_0'$. The results on the two approximations are very similar, and suggest that it is sufficient to use the simpler approximation of Section IV.

The variation with aggregate diameter of the reflectance of a semi-infinite medium comprised of well-spaced aggregates is given in Table 2 for two values of $\tilde{\omega}_0$. The first approximation has been used. In all cases tabulated, except for $\varkappa r_0=0$, (**3.4**) has been used for computing the directly transmitted flux.

TABLE 2

REFLECTANCE, R_D, AND SPECIFIC OPACITY COEFFICIENT, H, OF A SEMI-INFINITE MEDIUM COMPRISED OF WELL-SPACED AGGREGATES, AS FUNCTIONS OF AGGREGATE DIAMETER

$\varkappa r_0$	1st Approximation			
	$\tilde{\omega}_0=0\cdot99$		$\tilde{\omega}_0=0\cdot999$	
	R_D	$H\varkappa^{-1}$	R_D	$H\varkappa^{-1}$
∞	0·378	0	0·590	0
50	0·402	0·0130	0·655	0·0066
20	0·444	0·0296	0·736	0·0120
10	0·511	0·0494	0·798	0·0174
5	0·599	0·0737	0·849	0·0242
2	0·696	0·1093	0·891	0·0352
1	0·729	0·1320	0·905	0·0418
0	0·793	0·1732	0·930	0·0548

On the other hand, if $\varkappa r_0 \ll 1$ the transmitted flux is best found, as explained in Section III (a), by putting $\sigma=0$. In such a case, it can be shown that

$$\frac{\mathrm{d}R_D}{\mathrm{d}(\varkappa r_0)}=-\frac{8\tilde{\omega}_0\lambda}{9[1+\frac{2}{3}(3\lambda)^{\frac{1}{2}}]^2},$$

whose values are:

$\tilde{\omega}_0$	0·99	0·999
$\left[\dfrac{\mathrm{d}R_D}{\mathrm{d}(\varkappa r_0)}\right]_{(\varkappa r_0\ll 1)}$	$-0\cdot0071$	$-0\cdot00083$

The general trend of results indicates that the reflectances for $\varkappa r_0=1$ as computed from (**3.4**) are rather low.

TABLE 3

REFLECTANCE OF SEMI-INFINITE MEDIUM COMPRISED OF LARGE AGGREGATES, $\varkappa r_0 \gg 1$, AS A FUNCTION OF SPACING

Nv*	R_D		
	$\tilde{\omega}_0'=0\cdot9$†	0·99	0·999
0	0·552	0·829	0·942
0·05	0·527	0·824	0·941
0·1	0·524	0·822	0·940
0·2	0·519	0·820	0·939
0·4	0·503	0·812	0·936
0·6	0·477	0·799	0·932
0·8	0·434	0·775	0·923

* Nv is the fraction of the total volume occupied by the aggregates; for $Nv=0$, v is taken as $(4/3)\pi r_0^3$. For $Nv>0$, v is taken as $2\times(4/3)\pi r_0^3$.

† $\tilde{\omega}_0'$ is the reflectance of a semi-infinite *continuous* medium of the same material.

Before computing reflectances for more closely packed aggregates it is necessary to consider the relation between sphere diameter and the volume v which a sphere excludes from occupation by other spheres. This depends on the nature of the packing. If we write $v=(4/3)\pi r_0^3.c$, then c is unity for well-spaced spheres, and 1·92, 1·47, and 1·35 for close simple, body-centred, and face-centred cubic packing respectively. With close random packing the value of c is rather greater. For present purposes we adopt 2 for all spacings, and the reflectances given in Table 3 have been computed from (**5.2**) on this basis, except for the case $Nv=0$, for which c is taken as unity. The obvious though relatively small discontinuity at this case is due to this cause, and serves as a measure of significance of the assumption.

VII. Discussion

The present analysis shows that the reflectance of a scattering medium depends markedly on the extent to which the particles are aggregated together. While for a continuous medium the reflectance depends only on $\tilde{\omega}_0$, variations in attenuation coefficient through the medium, even though subject to the condition that $\tilde{\omega}_0$ is constant, must result in the lowering of the reflectance. It follows that in measurements of the optical properties of pigments considerable care is needed to ensure complete dispersion of the material.

It also follows that the reflectance of an incompletely dispersed mixture of diffusing media is not necessarily intermediate to and may be very much lower than those of the individual components.

The large reduction in reflectance with large aggregates arises from the necessity for at least part of the incident light to undergo many separate reflection processes before escaping from the medium. In this, it is similar to the well-known photometric phenomenon in which the reflectance of a cavity can be very much lower than that of its walls.

The lowering of the reflectance as the separation between large aggregates is reduced (Table 3) is interesting because, at first sight, an opposite trend might have been expected. While the first approximation, used here, is of reduced accuracy with close packing, it is clear that there is relatively small change in reflectance over the full range of aggregate spacing. However, even with close packing, only some half of the volume is occupied by diffusing matter. There are thus large cavities through which incident radiation may penetrate, directly or after reflection from the outer halves of the aggregates, very largely to be absorbed. It is therefore not surprising to find the reflectances of compact aggregates so low.

These results may be compared with the reflectance of a semi-infinite diffusing medium containing N randomly spaced spherical cavities covering a fraction f, say, of its projected area. If the cavities be large enough for the walls to be regarded as uniform diffusers of reflectance R, it can be shown that the average reflectance of the area intersected by cavities is

$$R_c=3R^{-3}\{-2R+3R^2-\tfrac{2}{3}R^3-2(1-R^2)\log(1-R)\},$$

and the reflectance of the medium as a whole is

$$R_D=fR_c+(1-f)R.$$

It may be noted that R_c is always less than R: as $R \to 1$, $R_c \to 1$, and as $R \to 0$, $R_c \to \frac{1}{2}R$. With $R=0 \cdot 900$, $R_c=0 \cdot 782$. By comparison with the results in Table 3 it is apparent that the shape of surface cavities has a profound effect on the reflectance of any medium when their dimensions are of the order of the penetration depth or greater.

The efficiency of a pigment in rendering a medium opaque depends on the degree of dispersion and may be assessed by the value of k per unit volume of pigment, i.e. by the quantity $k/\{(4/3)\pi r_0^3 N\}$. This term, which is quite different from the conventional " hiding power ", may be termed the specific opacity coefficient, and denoted by H. It can be readily shown that H is given, for well-spaced aggregates, by

$$H\varkappa^{-1}=\tfrac{3}{4}(1-\tau_0)(\varkappa r_0)^{-1}\left\{3(1-G_0)\left(1+\frac{4}{9}G_1\right)\right\}^{\frac{1}{2}},$$

where

$$G_n=(g_n-\tau_n)(1-\tau_0)^{-1}.$$

Values of $H\varkappa^{-1}$ are listed in Table 2, from which it is clear that the specific opacity coefficient increases markedly as the dispersion is improved.