should be increased but, owing to the decrease in the magnitude of the density gradients that stabilize the boundary, more careful control of the temperature would be required. Since it appears essential to have homogeneous layers of solution of appreciable thickness above and below the boundary, the period of observation can only be extended by increasing the height of the cell. Although the fringes are compressed as diffusion proceeds the resolving power of the available photographic emulsions[17] is such that this is not a limiting factor.

It is a pleasure to acknowledge my indebtedness to D. A. MacInnes of these laboratories for his care in the review of this manuscript and to Gerson Kegeles of the University of Wisconsin for clarifying correspondence throughout the course of the investigation.

(17) "Photographic Plates for Use in Spectroscopy and Astronomy," Eastman Kodak Co., 5th edition, 1946, Rochester, N. Y.

Summary

In an accompanying paper Kegeles and Gosting have developed the theory of the spacing of the interference fringes that are formed in the focal plane of a lens when an illuminated horizontal slit serves as the light source and a diffusing boundary is placed in the path of the light. In the present paper this theory is confirmed experimentally and a method is suggested for the use of the fringes in the evaluation of diffusion coefficients. Moreover, results for the diffusion, at 0.5°, of aqueous potassium chloride solutions in the Lamm cell are presented and compared with the Onsager–Fuoss theory. The difficulties that were encountered in the use of this cell for the study of proteins, and in the use of the Tiselius electrophoresis cell as a diffusion cell for both salts and proteins, are also reported.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Theory of an Interference Method for the Study of Diffusion

BY GERSON KEGELES* AND LOUIS J. GOSTING

Introduction

In 1880 Gouy[1] discovered a new interference phenomenon produced from a single wave front which had been distorted on passage through a column of liquid containing a diffusion boundary. Gouy gave a qualitative explanation of his observation, but he published no photographs, and presented no mathematical theory. In a recent review dealing with the subject of diffusion, Longsworth[2] gave an account of this phenomenon and published a photograph that he had taken of the interference fringes. This review stimulated the development of the quantitative theory to be presented in this paper, relating the space and intensity in the interference fringe system to the diffusion coefficient. In the report accompanying this one, L. G. Longsworth[3] presents an experimental verification of this theory, as well as his experimental development of the interference phenomenon into a precision method for the study of diffusion.

A brief qualitative description of the original experiment[1] is repeated here, with the aid of Fig. 1, in order to introduce the mathematical treatment. To make his observations, Gouy collimated the light from an illuminated horizontal slit and, after passing it through a diffusing salt boundary, brought it to focus with a telescope. In the illuminated rectangle at the focal plane of the telescope objective, several decades of fringes could be counted, and the fringe system showed peculiarities foreign to those produced by multiple slits. The originally plane wave front on leaving the diffusion cell takes the form, in projection onto the plane of the paper (Fig. 1), of the refractive index function in the column. For ideal diffusion, this distorted wave front is symmetrical about the inflection point corresponding to the level of the maximum refractive index gradient. Because of this symmetry, two normals from any given level Y in the focal plane may be drawn to the wave front, at points denoted X and X'. This means, according to geometrical optics, that rays passing through two symmetrical levels in the diffusion column are brought to a focus together a distance Y below the undeviated slit image. Gouy pointed out that the disturbance at Y could be calculated as the superposition of the disturbances originating in the wave front at X and X', with a phase difference determined by the difference in path lengths from Y to the wave front at X and X', respectively. The theory of the phenomenon derived on this basis is not in complete accord with experiment,[3] however, and according to wave optics it is necessary to take account of the disturbances arising at all other points in the wave front which must also contribute something to the intensity at Y. In the calculations to be presented, the treatment of the phenomenon will be undertaken from these two different starting assumptions, and the results will be compared. As the assumption of geometrical focussing forms the basis of the refractometric optical methods which are applied to studies of the molecular kinetic properties of dissolved solutes, this comparison

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(1) Gouy, *Compt. rend.*, **90**, 307 (1880).

(2) Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).

(3) Longsworth, THIS JOURNAL, **69**, 2510 (1947).

will also constitute a critique of such optical methods.

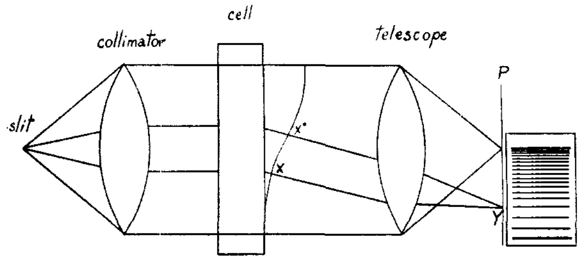

Fig. 1.—The Gouy interference phenomenon.

Elementary Theory

In order to obtain a physical picture upon which to base a more complete treatment, a first order calculation of the magnitude of the path differences for a convergent light optical system may be made with the aid of Fig. 2. Here it may

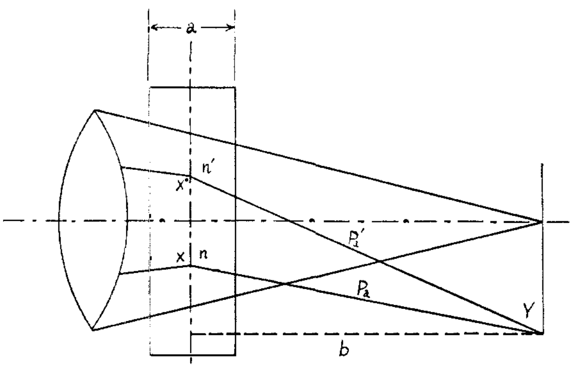

Fig. 2.—Approximate diagram for convergent light.

be seen that the difference in path for two rays entering the cell simultaneously and coming together at a point below the undeviated slit image may be broken into two parts. The first part of this path difference arises because the rays traverse media of different refractive index n and n' in the solution. This solution path difference, for rays which are horizontal at the beginning of their paths through a cell of thickness a, has the magnitude

$$P_s - P_s' = a(n - n')$$

The second part of the path difference arises because the rays on leaving the cell travel different distances to meet at a level below the slit image. As a first approximation, the light paths may be treated as if all the bending takes place in the middle ($a/2$ plane) of the cell,[4] which is separated from the slit image plane by the optical distance b. The air path difference from the middle of the cell to the level Y, Fig. 2, along these two symmetrical rays has the magnitude

$$P_a - P_a' = -2xY/b$$

Adding these two portions, we obtain a total path difference of the order

(4) Wiener, *Ann. Physik*, **49**, 105 (1893).

$$P - P' = a(n - n') - 2xY/b$$

Several not entirely consistent approximations have been made in order to obtain this relation for the path difference. In the first place, the light was assumed to be horizontal on entering the cell, but the inconsistent assumption was then made that on leaving the cell it converges to a focus. In the second place, it might appear that in summing the path differences, the second half of the cell has been counted twice. In the following development, a more rigorous treatment will be shown to lead to the same result.

Geometrical Development

In the present treatment, care will be taken to obtain the total path difference of two co-focussing rays by adding the path difference caused by traverse of different layers of solution to the difference in path lengths of the rays from the plane where they leave the solution to the slit image plane. Account will be taken of the convergence of light, as well as the curvature of the light paths in the solution. As a starting point for the calculation of solution paths, Snell's law is chosen.

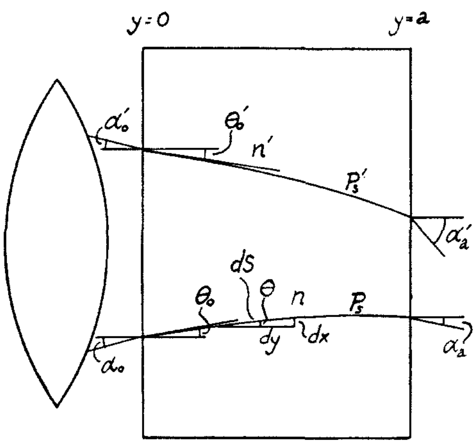

Fig. 3.—Details of the solution paths.

From Fig. 3 it is seen that the element of path length dS in solution is given by

$$dS = \sqrt{1 + (dx/dy)^2}\, dy$$

If θ is the inclination of the lower ray with the horizontal

$$dx/dy = \tan\theta, \text{ and } dS = \sec\theta\, dy$$

But since planes of constant refractive index n are horizontal, Snell's law takes the form

$$n \cos\theta = \text{const.}$$

Differentiation of this equation with respect to y and substitution of $\tan\theta$ for dx/dy, gives

$$d\theta/dy = (1/n)dn/dx$$

If it is now assumed that the curvature of the path is sufficiently small so that both n and dn/dx

are constant over the path,[5,6] we obtain by integration

$$\theta = \theta_0 + (y/n)dn/dx$$

where θ_0 is the value of θ for $y = 0$. The element of optical path length is

$$n\,dS = n \sec\theta\,dy$$

and expansion in series for small values of θ, and integration of this expression from $y = 0$, the entrance plane of the ray into solution to $y = a$, the exit plane of the ray from solution results in the optical path length

$$P_s = \int_{y=0}^{a} n\,dS = an + an\theta_0^2/2 + (a^2/2)\theta_0 dn/dx + (a^3/6n)(dn/dx)^2$$

A similar expression obtains for the optical path length P_s' for the upper co-focussing ray, where dn/dx is the same in both cases, as the gradient alone is assumed responsible for the light bending. The expression for the path difference within the solution then becomes

$$P_s - P_s' = a(n - n') + (a/2)(n\theta_0^2 - n'\theta_0'^2) + (a^2/2)(dn/dx)(\theta_0 - \theta_0') + (a^3/6)(dn/dx)^2(1/n - 1/n')$$

Here θ_0 is taken as a negative angle and θ_0' as a positive angle. If the center of symmetry of the refractive index gradient function lies on the optical axis, the inclination in air α_0 and α_0' of the two rays before entering the cell is given by the symmetry relations

$$-\alpha_0 = -n\theta_0 = \alpha_0' = n'\theta_0'$$

and the solution path difference becomes

$$P_s - P_s' = a(n - n')\{(1 - \alpha_0'^2/2nn' - (a^2/6)(dn/dx)^2(1/nn')\} + (a^2/2)(dn/dx)(\theta_0 - \theta_0') \quad (1)$$

If $a \sim 2.5$ cm., $n - n' \sim 0.002$, $n \sim 1.33$, $\alpha_0' \sim 0.02$, and $dn/dx \sim 0.003$, which would give the second order terms in equation (1) rather high values compared to those normally encountered, the second term in the braces is of the order 10^{-4}, the third term in the braces is of the order $5(10)^{-6}$, $a(n - n')$ is $5(10)^{-3}$, and the final term is of the order $3(10)^{-4}$. Hence, within about one part in 10,000 the solution path difference becomes

$$P_s - P_s' = a(n - n') + (a^2/2)(dn/dx)(\theta_0 - \theta_0') \quad (2)$$

Here the second term takes into account the convergence of the light. Under the present assumptions, terms involving differences in curvature between the two paths have been found to be negligibly small.

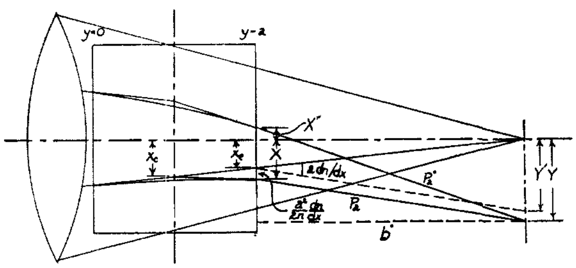

Fig. 4.—Details of the air paths.

(5) Lamm, *Nova Acta Reg. Soc. Sci. Upsala*, **Series IV, 10, No. 6** (1937).

(6) Svensson, *Kolloid-Z.*, **90**, 141 (1940).

The rays have been followed from the entrance plane ($y = 0$) to the exit plane ($y = a$) of the solution. It is necessary now to add their path difference which arises as they traverse the distance from the exit plane of the cell to the slit image plane. This air path difference $P_a - P_a'$ is the difference in hypotenuse of the two right triangles (Fig. 4) whose common base b' extends from the $y = a$ plane at the end of the solution paths to the plane of the undeviated slit image. The expression is

$$P_a - P_a' = \sqrt{b'^2 + (Y - |X|)^2} - \sqrt{b'^2 + (Y + |X'|)^2}$$

For Y and X small compared to b' this simplifies to

$$P_a - P_a' = -(Y/b')(|X| + |X'|) + (1/2b')(X^2 - X'^2) \quad (3)$$

The difference $|X| - |x_e|$ between magnitudes of the actual coördinate of the lower ray at the $y = a$ plane and the value it would have if not for the curvature of the light path in the solution is given by integrating $dx = \theta\,dy$, or

$$|X| - |x_e| = \int_0^a \theta\,dy - a\theta_0 = \int_0^a \{\theta_0 + (y/n)(dn/dx)\}\,dy - a\theta_0 = (a^2/2n)\,dn/dx$$

The corresponding expression for the upper ray in the figure is $(a^2/2n')dn/dx$, but for all practical purposes these terms are identical and we can write

$$|X'| - |x_e'| = -(a^2/2n)dn/dx$$

In terms of $|x_e|$ and $|x_e'|$ equation (3) then becomes

$$P_a - P_a' = -\{(|x_e| + |x_e'|)/b'\}\{Y - (a^2/2n)dn/dx\} + (1/2b')(x_e^2 - x_e'^2) \quad (4)$$

If the center of symmetry of the boundary lies on the optical axis, the last term disappears. It is noted from Fig. 4 that

$$Y' = Y - (a^2/2n)dn/dx$$

Also

$$\theta_a - \theta_0 = \int_0^a (1/n)(dn/dx)dy \text{ or } \alpha_a - \alpha_0 = a\,dn/dx$$

and $Y' = a(dn/dx)b'$ for small angles. Hence

$$Y = a(dn/dx)(b' + a/2n)$$

The new optical distance b is now defined by the relation $b = b' + a/2n$, and in terms of b

$$Y = ab\,dn/dx \quad (5)$$

as given originally by Wiener.[4] It is noted that by this definition b becomes, for convergent light, the optical distance from the plane of the undeviated slit image to the geometrical center of the diffusion cell.[7] Equation (4) can now be re-written

$$P_a - P_a' = -(|x_e| + |x_e'|)Y/b$$

(7) Compare Svensson, *Arkiv. Kemi, Mineral., Geol.*, **22A**, No. 10, **84** (1946).

The heights $|x_e|$ and $|x'_e|$ at the end of the cell ($y = a$) can be expressed in terms of the heights $|x_c| = |x'_c| = x$ which the rays would have at the center of the cell ($y = a/2$), Fig. 4, if all the bending took place in this plane

$$|x_e| = x + (a/2)\theta_0$$
$$|x'_e| = x - (a/2)\theta'_0$$

Here again θ_0 is taken as a negative angle and θ'_0 as a positive angle, while x is taken as always positive. In terms of x, the air path difference becomes, finally

$$\begin{aligned} P_a - P'_a &= -2xY/b - (a/2b)Y(\theta_0 - \theta'_0) \\ &= -2ax\mathrm{d}n/\mathrm{d}x - (a^2/2)(\mathrm{d}n/\mathrm{d}x)(\theta_0 - \theta'_0) \end{aligned} \quad (6)$$

Here the second term is due to the convergence of the light.

The total path difference is obtained by addition of equations (2) and (6)

$$P - P' = a(n - n') - 2xY/b \quad (7)$$

with the restrictions that b is measured for convergent light to the center of the diffusion cell, and x is specifically defined as the height which the ray would have at the center of the cell if all the light bending occurred in this plane. Under these conditions, the first order convergence error vanishes for convergent light, while the errors due to curvature of the light path are very small.

While equation (7) is not completely rigorous for skew boundaries, it is general for any symmetrical refractive index gradient curve, and need not be restricted to apply to ideal diffusion. A general symmetrical curve may be treated if the refractive increment function is represented by

$$n - n_0 = \{(n_s - n_0)/2\}\{1 + \mathrm{F}(x)\}$$

Here $\mathrm{F}(x) = -\mathrm{F}(-x)$, and $-1 \leq \mathrm{F}(x) \leq 1$ for $-\infty \leq x \leq \infty$. In this case equation (7) becomes

$$P - P' = a(n_s - n_0)\{\mathrm{F}(x) - x\mathrm{F}'(x)\}$$

while the corresponding displacement in the slit image plane is

$$Y = \{ab(n_s - n_0)/2\}\mathrm{F}'(x)$$

Of particular practical importance is the case of ideal diffusion.

The type of diffusion experiment to be treated now is that in which an infinitely long column of solvent of refractive index n_0 is superimposed upon an infinitely long column of solution of refractive index n_s containing a single solute. If the diffusion is ideal and the refractive index increment function is proportional to the solute concentration, this function is given by the solution[8] of Fick's second law[9] of diffusion as

$$n - n_0 = \{(n_s - n_0)/2\}\left\{1 + (2/\sqrt{\pi})\int_0^z e^{-\beta^2}\,\mathrm{d}\beta\right\} \quad (8)$$

where the "reduced height" z is defined by

$$z = x/2\sqrt{Dt} \quad (9)$$

Here D is the diffusion coefficient, t is the time, and x and z are measured positive downward.

(8) Stefan, *Sitzber. Akad. Wiss. Wien, Abt. II*, **79**, 161 (1879).

(9) Fick, *Pogg. Ann.*, **94**, 59 (1855).

The differential form of this equation, given by Wiener,[4] is

$$\mathrm{d}n/\mathrm{d}x = \{(n_s - n_0)/2\sqrt{\pi Dt}\}e^{-z^2} \quad (10)$$

Combination of equation (8) for symmetrical levels around the boundary center with the expression (7) for the path difference gives

$$P - P' = a(n_s - n_0)(2/\sqrt{\pi})\int_0^z e^{-\beta^2}\,\mathrm{d}\beta - 2xY/b \quad (11)$$

or by equations (5), (9) and (10)

$$P - P' = a(n_s - n_0)\mathrm{f}(z)$$

where the function f(z) is defined by

$$\mathrm{f}(z) = \left\{(2/\sqrt{\pi})\int_0^z e^{-\beta^2}\,\mathrm{d}\beta - (2/\sqrt{\pi})ze^{-z^2}\right\} \quad (12)$$

The Interference Conditions.—If the intensity contributions from only those two rays which should focus together at Y by the geometrical treatment are considered, then according to wave optics, constructive interference will obtain for

$$a(n_s - n_0)\mathrm{f}(z_j) = j\lambda \quad (13)$$

and destructive interference will obtain for

$$a(n_s - n_0)\mathrm{f}(z_j) = (j + 1/2)\lambda \quad (14)$$

where λ is the wave length of the light used, j is an integer equal to 0, 1, 2, . . ., and z_j is the "reduced height" in the cell corresponding to the fringe numbered j. Moreover, according to equations (5) and (10), the displacement below the undeviated slit image of the fringe numbered j is given by

$$Y_j = \{ab(n_s - n_0)/2\sqrt{\pi Dt}\}e^{-z_j} \quad (15)$$

For the case of parallel light equations (13) and (14) are applicable with approximately the same validity, while equation (15) applies provided that b is measured from the photographic plate to the principal plane of the nearer schlieren lens.[6]

From the definition of the path difference function (equation 12), it is noted that f(z) = 0 for the center of the diffusion boundary at $z = 0$, and, from equation (15), the lowest maximum, or minimum, must thus be defined by $j = 0$. As z increases indefinitely, on the other hand, f(z) approaches unity, and the largest integer for constructive interference fringes, which is here denoted by m, is given by

$$a(n_s - n_0) \geq m\lambda \quad (16)$$

For a given experiment the integral number, $m + 1$, of mathematically possible maxima in the pattern should thus be determined solely by the optical and physical constants of the experiment in relation (16), and the diffusion column itself should constitute an interference refractometer.

We have now expressed as an explicit function of the single variable z both the interference conditions for the fringe numbered j (equations (13) and (14)), and the displacement of this fringe below the undeviated slit image (equation (15)). Knowledge of the fringe number and the factor $a(n_s - n_0)/\lambda$ permits the evaluation of the path difference function $f(z_j)$ and hence the quantity $e^{-z_j^2}$. Combination of $e^{-z_j^2}$ with the fringe displacement Y_j, the time, and the known constants of equation (15) then should give a value of the diffusion coefficient, D, independently from each fringe.

The path difference function $f(z)$ as defined by equation (12) has been computed for a large number of z values, and is tabulated against the quantity $e^{-z_j^2}$ in Table I. The practical utilization of this table for the evaluation of the diffusion experiments is outlined in the companion paper.[3]

TABLE I[a]

THE PATH DIFFERENCE FUNCTION f(z) (EQUATION (12))

$f(z)$	e^{-z^2}	$f(z)$	e^{-z^2}	$f(z)$	e^{-z^2}
0.00000	1.00000	0.25853	0.53574	0.77683	0.11187
.00054	0.99193	.28147	.51048	.79825	.09922
.00303	.97473	.30498	.48554	.81335	.09049
.00587	.96079	.32895	.46098	.82769	.08238
.01005	.94403	.35329	.43687	.84121	.07486
.01576	.92459	.37790	.41329	.85396	.06971
.02116	.90837	.40270	.39028	.86595	.06149
.02759	.89083	.42759	.36787	.87718	.05558
.03513	.87206	.45248	.34614	.88770	.05014
.04377	.85214	.47729	.32510	.89752	.04515
.05360	.83118	.50192	.30479	.90664	.04060
.06460	.80928	.52630	.28524	.91512	.03643
.07678	.78655	.55034	.26646	.92299	.03263
.09016	.76307	.57399	.24848	.93027	.02917
.10471	.73896	.59717	.23129	.93697	.02604
.12042	.71433	.61983	.21489	.94314	.02320
.13723	.68929	.64189	.19931	.94880	.02063
.15513	.66392	.66334	.18451	.95398	.01832
.17404	.63833	.68411	.17052	.98247	.00633
.19391	.61262	.70417	.15730	.99414	.00193
.21466	.58690	.72977	.14086	.99956	.00012
.23623	.56125	.75401	.12573	1.00000	.00000

[a] Compiled with the aid of "Tables of Probability Functions," Vol. I, Federal Works Agency, Works Progress Administration, City of New York (Sponsored by Natl. Bureau of Standards), 1941.

Wave Optical Theory

It is shown in the companion paper[3] that the theory presented above is not in complete accord with experiment. In addition to the light coming from the two points X and X' predicted by geometrical optics, all other points such as X_1 and X_1' in the wave front (Fig. 5) also contribute something to the observed intensity at Y. The wave optical relationship which sums the amplitude contributions over the whole length of the wave front in the plane of the paper is the integral equation obtained from Kirchoff's general theory of diffraction[10]

$$\phi_Y = K\left\{\int_{-H}^{H} \cos(2\pi/\lambda)\ (P - P_0)\,dl - i\int_{-H}^{H} \sin(2\pi/\lambda)(P - P_0)\ dl\right\} \quad (17)$$

Here ϕ_Y is the amplitude at the level Y corresponding to the observed intensity, K is a constant, $-H$ and H are the distances from the center to the edges of the wave front, dl is the element of distance along the wave front, i is $\sqrt{-1}$, and $P - P_0$ is the difference between the path from Y to any level x in the wave front, and the path from Y to the center of symmetry O of the wave front.

With a symmetrical wave front such as is being considered here, there is an x' value above O equal to $-x$ for every x value below O such that $-\{P - P_0\}_{x'} = \{P - P_0\}_x = 1/2(P - P')$ for any chosen value of Y. The path difference $P - P'$ in general form is obtained from equation (11), where Y is now taken as an independently variable parameter. Since $P - P'$ is an odd function of x, the amplitude function becomes

$$\phi_Y \simeq K\int_{-H}^{H} \cos\ (\pi/\lambda)(P - P')\ dx = 4\sqrt{Dt}\ K\int_{x=0}^{x=H} \cos v\ dz \quad (18)$$

as dl is practically identical with dx and the integral of the sine function vanishes. Here v is defined as $(\pi/\lambda)(P - P')$. If v is plotted against z, the maximum in the curve, denoted by coördinates (v_m, z_m), occurs for the condition

$$Y_m = \{ab(n_s - n_0)/2\sqrt{\pi Dt}\}e^{-z_m^2} \quad (19)$$

This relation has the same form as the equation (15) predicted in part by geometrical optics. The maximum value which Y_m can have, denoted by C_t, is then

$$C_t = ab(n_s - n_0)/2\sqrt{\pi Dt} \quad (20)$$

which is the value predicted by geometrical optics for the displacement at the plate of the most downward deflected light. From equations (9) and (11), v may now be written in terms of C_t

$$v = (\pi/\lambda)a(n_s - n_0)\left\{(2/\sqrt{\pi})\int_0^z e^{-\beta^2}\,d\beta - (2/\sqrt{\pi})(Y/C_t)z\right\} \quad (21)$$

Figure 6 shows plots of v/π *versus* z for various arbitrarily chosen constant values of Y/C_t and the assumed data: $a = 2.500$ cm., $n_s - n_0 = 0.001860$, $\lambda = 5.461\ (10)^{-5}$ cm. In order to evaluate the cosine integral of this complicated function, approximate curve fitting methods will be chosen to obtain the integral in forms which have been tabulated. Those curves in Fig. 6 which represent

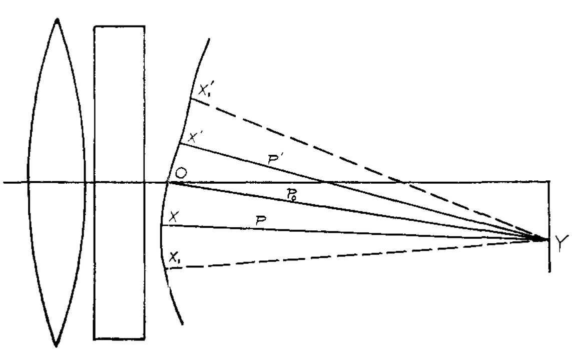

Fig. 5.—Wave front contributing to the amplitude.

(10) Slater and Frank, "Introduction to Theoretical Physics," McGraw-Hill Book Co., New York, 1933, p. 311; Joos, "Theoretical Physics," G. E. Stechert and Co., New York, 1934, p. 363.

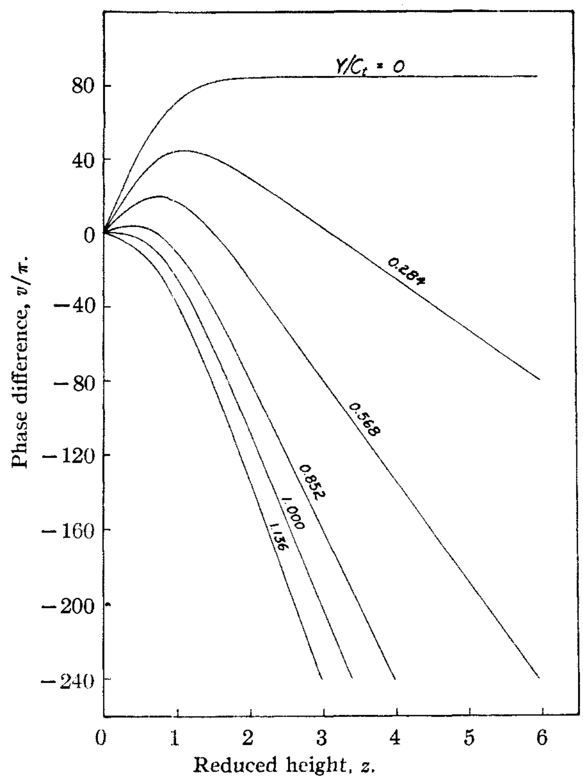

Fig. 6.—Phase difference v/π for arbitrarily chosen values of Y/C_t.

the central portion of the fringe system may be approximated by parabolas in the neighborhood of their maxima, and it is important to note that this region of the curves offers the greatest contribution to the cosine integrals. These parabolas will be made to fit the actual curves at (0, 0) and (v_m, z_m) so that

$$v - v_m = -k(z - z_m)^2$$

and

$$k = v_m/z_m^2$$

This results in a transformation of equation (18) to

$$\phi_Y = 4K\sqrt{Dt}\Big[\cos v_m \int_{x=0}^{H} \cos\{v_m(z - z_m)^2/z_m^2\}\,dz + \sin v_m \int_{x=0}^{H} \sin\{v_m(z - z_m)^2/z_m^2\}\,dz$$

In order to put this in the form of Fresnel integrals,[11] a change of variable is made by defining

$$v_m(z - z_m)^2/z_m^2 = \pi u^2/2$$

and

$$\phi_Y = 4K\sqrt{Dt}(z_m/\sqrt{2v_m/\pi})\left\{\cos v_m \int_{x=0}^{x=H} \cos(\pi u^2/2)\,du + \sin v_m \int_{x=0}^{x=H} \sin(\pi u^2/2)\,du\right\}$$

To evaluate the integrals conveniently, it is now desirable to integrate from $x = 0$ to $x = \infty$, or $u = -\sqrt{2v_m/\pi}$ to $u = \infty$, which will neglect any edge effects of the ends of the cell. In this case, since both integrands are even functions

$$\phi_Y = 4K\sqrt{Dt}(z_m/\sqrt{2v_m/\pi})[\{1/2 + C(\sqrt{2v_m/\pi})\}\cos v_m + \{1/2 + S(\sqrt{2v_m/\pi})\}\sin v_m] \quad (22)$$

where $C(\sqrt{2v_m/\pi})$ and $S(\sqrt{2v_m/\pi})$ are the Fresnel integrals[11]

$$\int_0^{\sqrt{2v_m/\pi}} \cos(\pi u^2/2)\,du \quad \text{and} \quad \int_0^{\sqrt{2v_m/\pi}} \sin(\pi u^2/2)\,du$$

respectively. The intensity I is proportional to ϕ_Y^2, and Fig. 7 gives a diagram of the intensities calculated with equation (22) from the data used for Fig. 6. For even fairly small values of v_m, it may be shown that the minima and maxima of intensity may be accurately obtained by writing equation (22) in the approximate form

$$\phi_Y = 4K\sqrt{Dt}(z_m/\sqrt{2v_m/\pi})(\cos v_m + \sin v_m)$$

The intensity minima are given by $\cos v_m + \sin v_m = 0$ or $v_m = (j + 3/4)\pi$. Since v is defined

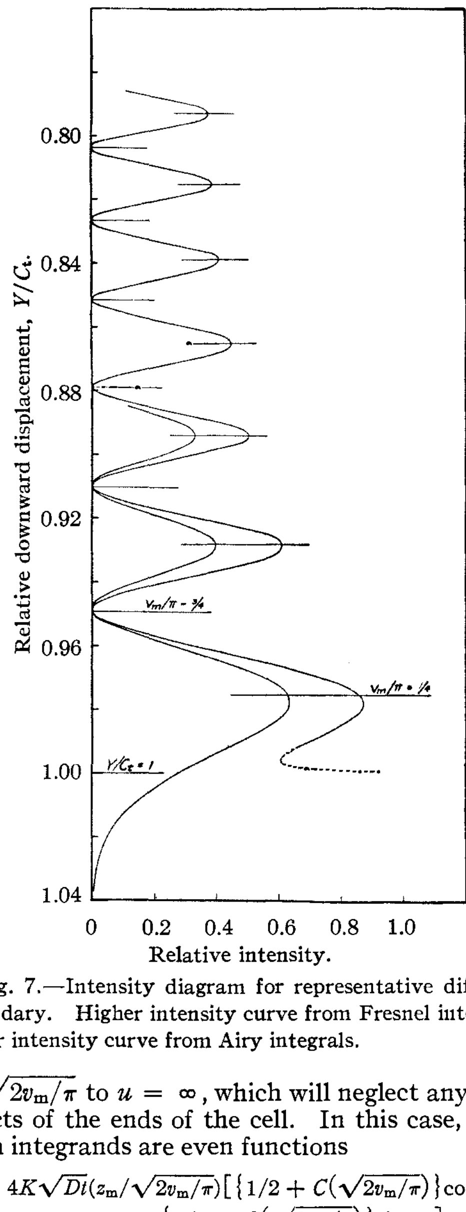

Fig. 7.—Intensity diagram for representative diffusion boundary. Higher intensity curve from Fresnel integrals, lower intensity curve from Airy integrals.

(11) Fresnel, "Oeuvres," Vol. I. Paris. 1866. p. 247 ff.; Jahnke and Emde, "Tables of Functions," Dover Publications, New York, N. Y., 1945.

by equation (21) in terms of Y, and Y is given by equation (19) for $v \doteq v_m$, the condition for minima becomes

$$v_m/\pi = j + 3/4 = \{a(n_s - n_0)/\lambda\}\, f(z_j) \quad (23)$$

where f(z) is the path difference function given by equation (12), and the particular value of z_m corresponding to the fringe numbered j is now denoted by z_j.

For maxima the condition is a little more complicated, but since the coefficient $z_m/\sqrt{2v_m/\pi}$ becomes nearly constant after the first maximum, it is approximately true that maxima obtain for $\cos v_m - \sin v_m = 0$, or

$$v_m = (j + 1/4)\pi$$

which gives

$$\{a(n_s - n_0)/\lambda\}\, f(z_j) = j + 1/4 \quad (24)$$

for maxima. In the case of both maxima and minima the displacement of the fringe at the plate is given by the usual equation (19) as indicated above

$$Y_j = \{ab(n_s - n_0)/2\sqrt{\pi D t}\}\, e^{-z_j^2} \quad (25)$$

Here z_j represents the new wave optical "reduced height" in the cell corresponding to a given maximum or minimum of intensity at the plate, and it is seen by comparison with equations (13) and (14) that the present formulation has shifted z_j a little from its value predicted by the previous classical formulation.[12]

Although the physical significance of z_j has now become obscure, in that light reaches the fringe from all values of z, and not simply from z_j, this is of no practical consequence inasmuch as the physical significance of z_j is not needed in order to solve the equations for the diffusion coefficient.

In Fig. 7, the positions of the maxima and minima obtained from these simple equations (23), (24), and (25) are indicated by horizontal lines, and comparison with the positions given by the complete expression (22) indicates that the simple formulations hold with a very high degree of precision except for the lowest maximum and minimum. It should be noted that these formulations must break down for fringes close to the normal slit image, for two reasons. First, the parabolic curve fit for v *versus* z becomes increasingly poor as the normal slit image is approached, and second, the edge effects of the ends of the cell have been omitted by integrating to infinity.

It is also noted that the parabolic fit becomes poor for Y/C_t values approaching unity, and cannot be expected to hold for Y/C_t values greater than unity. For this region of small z, v may be expanded in series

$$v \simeq 2\{\sqrt{\pi}\, a(n_s - n_0)/\lambda\}\{z(1 - Y/C_t) - z^3/3\} \quad (26)$$

This expansion shows that the v *versus* z curve can be transformed to give the ϕ_Y integral, equation (18), in the form of Airy integrals[13] which have been tabulated

$$\int_0^\infty \cos (\pi/2)(pu - u^3)\mathrm{d}u$$

For Y/C_t values equal to or greater than unity, where the greatest contribution to the cosine integral comes from z values near zero, it suffices to substitute directly for v its expansion in terms of z given by equation (26), giving for the amplitude

$$\phi_Y = (4K\sqrt{Dt}/A)\int_0^\infty \cos (\pi/2)(pu - u^3)\mathrm{d}u \quad (27)$$

where p is defined by $p = 3A^2(1 - Y/C_t)$ and

$$A = \{4a(n_s - n_0)/3\sqrt{\pi}\lambda\}^{1/3}$$

For Y/C_t values smaller than unity, the v *versus* z curves have maxima, which in general occur at sufficiently large z values to make equation (26) inapplicable. But since the greatest contributions to the cosine integral, equation (18), occur at these maxima, it is necessary to choose a cubic expression to fit the v function at its maximum, rather than at small z. If v is taken as $v = g(hz - z^3)$, the maximum is given by

$$\mathrm{d}v/\mathrm{d}z = 0 = g(h - 3z_m^2)$$

so that $h = 3z_m^2$ and $g = v_m/2z_m^3$. Hence we have

$$v = (3/2)v_m(z/z_m) - (v_m/2)(z/z_m)^3$$

Making a change of variable by the definitions

$$(v_m/2)(z/z_m)^3 = \pi u^3/2 \text{ and } 3(v_m/\pi)^{2/3} = p$$

and integrating from $x = 0$ to $x = \infty$, we obtain

$$\phi_Y = 4K\sqrt{Dt}\, z_m/(p/3)^{1/2}\int_0^\infty \cos (\pi/2)(pu - u^3)\mathrm{d}u \quad (28)$$

The intensities obtained from the Airy integrals for both regions are shown in Fig. 7. It is noted that for both the quadratic and the cubic types of curve fitting, the positions of maxima and minima agree very closely, and this lends confidence to the curve fitting procedures used in performing the integration.[14]

The general procedure for the evaluation of diffusion coefficients should now employ equations (23), (24) and (25) in conjunction with Table I, for fringes starting with $j = 1$ and continuing to as high a value of j as leads to consistent spacing according to these equations. It is recalled that for the lowest maximum and minimum, denoted by $j = 0$, more complicated expressions (equations

(12) Comparison of wave optical and geometrical optical formulations for similar cases have also been found to lead to a discrepancy of one quarter of a wave. Compare Mascart, "Traité d'Optique," Vol. I, Gauthiers-Villars Fils, Paris, 1889, p. 398; Gouy, *Ann. Chim. Phys.*, **24**, 145 (1891); Gans, *Ann. Physik*, **47**, 709 (1915); Jentzsch, "Handbook der Physik," Vol. XVIII, Julius Springer, Berlin, 1927, p. 266. Subsequent to the publication of his 1880 note on the diffusion interference phenomenon, Gouy carried out several investigations into the propagation of light, and in the present reference treated very fully the quarter wave anomaly. It is conjectured that his failure to give a mathematical treatment for the diffusion optical phenomenon may have been caused by the inavailability of Stefan's theory for the diffusion process (ref. 8), which appeared only in 1879.

(13) Fletcher, Miller, and Rosenhead, "An Index of Mathematical Tables," Scientific Computing Service, Ltd., London, 1946; Hogner, *Arkiv. Mat. Astron. Fysik*, **17**, No. 12, 37 (1923).

(14) Compare Mascart, ref. (12), p. 406.

(22), (27) and (28)) are required for highest precision.

Discussion

Comparison of the position of the most deflected light, $Y = C_t$, based on the classical geometrical equation (5) with the intensity diagrams calculated on the wave optical basis is made in Fig. 7. This comparison indicates that equation (5) is not exactly true. The error is greatest for the most downward deflected light, and this has the effect, in the schlieren optical systems[6,15,16,17] of compressing the height of the peak. This is seen by reference to Fig. 7, since the region of maximum intensity in the lowest fringe would represent the location of the peak in a schlieren diagram, as obtained with a contrast plate. Moreover, the gradual falling off of intensity for this fringe indicates that the location of the peak will be uncertain, and will be particularly sensitive to the time of exposure. This error should lead to high values for the diffusion coefficient when calculated by the height and area method[3,18] and the inflection point method.[5] However, the method of moments[5] also gives erroneous results because the classical theory breaks down for the edges of the gradient curve. In the case of the scale method,[5] where a small aperture at the lens masks off all but a narrow portion of the wave front arising from each scale line, it appears that the use of Wiener's equation[4] may have somewhat greater validity.

For a polydisperse system which yields symmetrical diffusion curves, it can be shown readily that the application of equation (23) results in the weight average of the path difference function $f(z)$. The diffusion coefficient obtained for the system by further application of equation (25) is a very complicated average value, however. A generalized treatment may make it possible to obtain better defined averages for such a system. The extension of the theory to the case where the diffusion coefficient is concentration dependent has not been developed.

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Summary

A quantitative theory for the spacing and intensity in the interference fringe system formed by focussing light from a horizontal slit through a diffusing boundary has been presented. Observation of the fringe displacement, in combination with the theoretical path difference function, the optical constants of the system and time, permits the evaluation of the diffusion constant for ideal diffusion independently from each fringe.

In the development of this theory by the methods of wave optics, small systematic errors in the schlieren optical methods are indicated, which set a limit to the precision attainable with such methods.

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(15) Philpot, *Nature*, **141**, 283 (1938).
(16) Longsworth, THIS JOURNAL, **61**, 529 (1939).
(17) Andersson, *Nature*, **143**, 720 (1939).
(18) Longsworth, *Ann. N. Y. Acad. Sci.*, **41**, 267 (1941).

[CONTRIBUTION FROM THE INSTITUTE FOR NUCLEAR STUDIES AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Chemistry of Energetic Atoms Produced by Nuclear Reactions[1]

BY W. F. LIBBY

I. Nature of Recoil Excitations

Nuclear reactions in general involve energies of at least 100,000 electron volts (2.3×10^9 cal./mole). This energy usually is divided between two particles—the emitted light particle and the residual recoil heavy nucleus—according to the law of conservation of momentum. Table I summarizes the results for the more common types of nuclear reactions. (In this Table, M is the mass of the recoil nucleus in ordinary units, m the mass of the light particle emitted, μ the mass of the bombarding particle if one is involved, and E_α is the energy of the α particle with a similar notation for other particles. In the case of beta radioactivity, E_0 is the upper energy limit of the continuous spectrum.) The derivations of these expressions are given in Appendix I.

In general these energies are so large with respect to chemical bond energies (1 to 5 electron volts) that there is little doubt that bond rupture will occur in nearly all cases. Suess[1a] has called attention, however, to possibilities of inefficiencies in the dissociation processes in the case that the

(1) Paper given at Nuclear Symposium, Atlantic City Meeting, American Chemical Society, April 1946.

(1a) H. Suess, *Z. physik. Chem.*, **B45**, 312 (1940).