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An Interferometric Method for Recording the Refractive Index Derivative in Concentration Gradients. II. Arrangement for and Theory of the Purely Optical Differentiation of the Refractive Index Function

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The author [1] described recently an interferometric method for recording the refractive index derivative in cells with concentration gradients. This method made use of the Rayleigh interferometer as modified by Philpot and Cook [2] in combination with a twin diffusion cell. In the two compartments of the latter, two identical diffusion boundaries were formed and slightly shifted with respect to each other. Two interfering rays, passing the twin cell at the same level, thus had slightly different paths with respect to the two identical refractive index gradients. It was mentioned in the same article that this interferometric differentiation could also be carried out in one single cell by shifting the two interfering rays from each other in the vertical direction by purely optical means. In the present article, this method of optical differentiation will be described together with the theory of the method.

OPTICAL ARRANGEMENT

The optical system of the differential refractometer is shown in Fig. 1. A is a vertical slit illuminated by monochromatic light. It stands in the focal plane of the lens B. The light is collected again by the lens D to an image of the slit in the plane F. The cell is situated at C between the two lenses. The lens E is a cylindrical lens with a horizontal axis. It throws, in elevation, an image of the cell C on the photographic plate F. In plan, it acts like a plate and does not disturb the image formation of the slit A in the same plane F. The components now mentioned form together the optical system of the Ray-

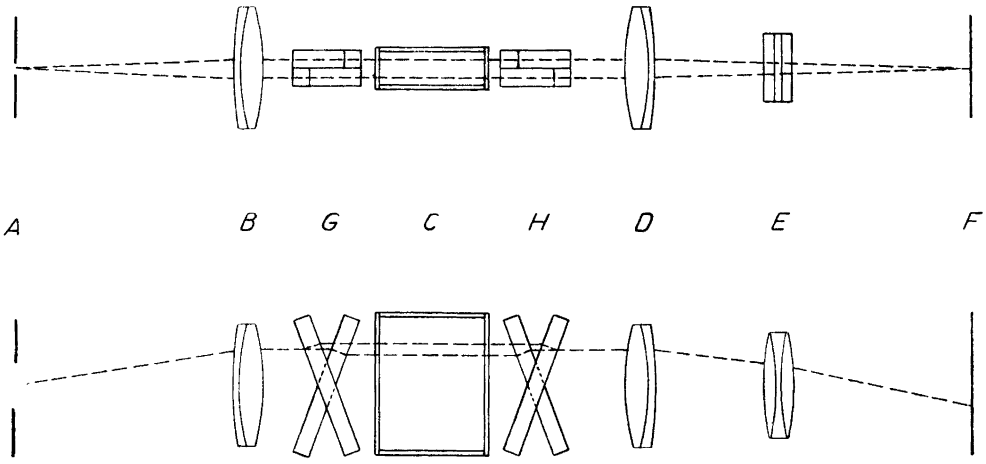

Fig. 1. The optical system. Upper figure: plan. Lower figure: elevation.

leigh-Philpot-Cook interferometer. It is characterized by the simultaneous image formation of the cell and the illumination slit. The vertical coordinate on the plate is related to the cell coordinate, the horizontal coordinate to the slit.

The components to be added for obtaining the refractive index derivative instead of the function itself are the four plano-parallel glass plates at G and H. They all make the same angle with the vertical line, but they tilt in opposite directions. Every light pencil that passes a plate with positive inclination before entering the cell will pass a plate with the same negative inclination after leaving the cell, and *vice versa*. The inclined plates, giving rise to vertical shifts of the light pencils, will cause two coherent and interfering rays to pass the cell at two different levels. The difference between these levels can be chosen arbitrarily by varying the inclination of the plates.

Notation. The following symbols will be used in the theory to be presented.

a = the thickness of the cell in the direction of the optical axis.
b = the angle of refraction in the inclined plates.
d = the thickness of the inclined plates.
D = diffusion coefficient.
e = the base of the natural logarithms.
f = the phase shift of a light pencil produced by the introduction in its path of an inclined plate; it is a function of the angle of incidence.

F = the parallel shift of a light pencil produced by the introduction in its path of an inclined plate; it is a function of the angle of incidence.
i = the angle of incidence at an inclined plate.
m = the refractive index of the inclined plates relative to their surroundings.
n = the variable refractive index of the solution in the cell.
s = optical path length = the product of distance and refractive index.
t = time.
v = the angle of inclination of the plates; it is defined as positive if the plate has been turned clock-wise from its vertical position.
x = the vertical coordinate in the cell; the direction of the positive x-axis is upwards.
X = the vertical coordinate on the plate.
z = the coordinate along the optical axis; the direction of the positive z-axis is towards the light source.
δ = the angle enclosed between a light pencil and the optical axis; it is defined as positive if x and z increase simultaneously along the direction of the pencil.
ε = that fraction of a fringe displacement which can still be measured.
φ = the difference in F between the inclined and vertical positions of the plates.
λ = the wave-length of the light.
ϱ = the relative error.

With this notation, a light pencil is shifted in the positive direction of the x-axis on passage of a plate with positive inclination if the pencil is traced in the direction of the positive z-axis.

THE PARALLEL SHIFT OF A LIGHT PENCIL PASSING THROUGH A PLATE

From Fig. 2 it is easily realized that the shift of the ray perpendicularly to itself is:

$$F(i) = \frac{d \sin (i - b)}{\cos b} \tag{1}$$

the relation between i and b being given by Snell's law:

$$\sin i = m \sin b \tag{2}$$

Elimination of b, however, gives a very complicated expression. Consequently we prefer to use the symbol $F(i)$ as long as possible. For small and moderate

angles, one can use the first and third order approximations obtained by developing $F(i)$ into powers of i. If b is first developed into powers of i, one gets:

$$b = \frac{i}{m} - \frac{i^3(m^2-1)}{m^3} + \ldots\ldots \tag{3}$$

Development of the sine and cosine functions in equation (1) into powers of the respective angles, and introduction of b according to (3) gives the following expression for the parallel shift of the ray:

$$F(i) = \frac{di\ (m-1)}{m}\left[1 + \frac{i^2\,(3+3m-m^2)}{6\,m^2}\right] \tag{4}$$

which is the third-order approximation. The angle of incidence is in our case:

$$i = v - \delta. \tag{5}$$

Thus light pencils having an inclination towards the optical axis are shifted parallel to themselves even for the vertical position of the glass plates. This shift, however, is taken into account by focusing the cylindrical lens on the middle of the cell in the presence of the plates in their vertical positions. The parallel shift which we have to take into account in this theory is only the difference:

$$\varphi\ (v,\ \delta) = F(v-\delta) - F(-\delta) \tag{6}$$

We will now regard the angle δ as a small angle, whereas v may assume fairly high values. It is then permissible to use the first-order approximation in δ and write:

$$\varphi(v,\ \delta) = F(v) - \delta\ F'(v) - F(0) + \delta\ F'(0) \tag{7}$$

The term $F(0)$, however, is the parallel shift of a ray falling perpendicularly on the plate and is thus $= 0$. Hence we have:

$$\varphi(v,\ \delta) = F(v) - \delta\ [F'(v) - F'(0)] \tag{8}$$

Similarly, we get for the plate with opposite inclination:

$$\varphi(-v,\ \delta) = F(-v) - \delta\ [F'(-v) - F'(0)] \tag{9}$$

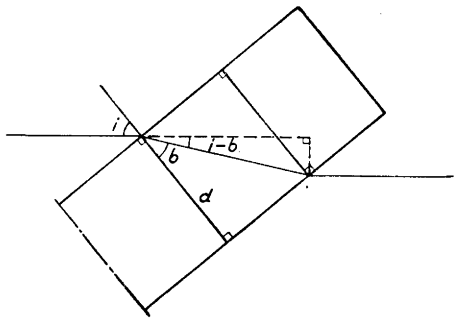

Fig. 2. Optical refraction in a plano-parallel glass plate.

The function F is an odd function of the variable, thus we have:

$$F(-v) = -F(v) \tag{10}$$

On the other hand, the function F' is an even function, and the relation:

$$F'(-v) = F'(\mathrm{v}) \tag{11}$$

holds. Consequently, equation (9) can be written:

$$\varphi(-v,\ \delta) = -F(v) - \delta\ [F'(v) - F'(0)] \tag{12}$$

The relations (10) and (11) are easily realized by inspecting the series development (4). $F(i)$ contains only odd powers of i, consequently $F'(i)$ contains only even powers.

THE PHASE SHIFT OF A LIGHT PENCIL PASSING THROUGH A PLATE

Inspection once more of Fig. 2 reveals that the optical path through the plate is:

$$\frac{md}{\cos b} \tag{13}$$

whereas the projection of this path along the direction of the ray is:

$$\frac{d\cos(i-b)}{\cos b} \tag{14}$$

The phase shift on introduction of the plate is thus:

$$f(i) = \frac{d[m - \cos(i-b)]}{\cos b} \tag{15}$$

This expression can also be developed into powers of i in the same way as was mentioned for the parallel shift. The fourth-order approximation is:

$$f(i) = d(m-1)\left[1 + \frac{i^2}{2m} + \frac{i^4(3 + 3m - m^2)}{24m^3}\right] \tag{16}$$

The angle of incidence i is again given by equation (5), hence $f(i)$ has a considerable value even for the upright position of the glass plates. This is of no importance, however, since we are only interested in the difference in phase between the two interfering rays.

The function $f(i)$ may be written as a first order approximation in δ:

$$f(i) = f(v-\delta) = f(v) - \delta\ f'(v) \tag{17}$$

Similarly, we have for the plate with negative inclination:

$$f(-v-\delta) = f(-v) - \delta\ f'(-v) \tag{18}$$

Equation (16) shows that the following relations hold for the function $f(i)$:

$$f(-v) = f(v) \tag{19}$$

$$f'(-v) = -f'(v) \tag{20}$$

Hence equation (18) can be written:

$$f(-v-\delta) = f(v) + \delta\ f'(v) \tag{21}$$

THE RELATION BETWEEN THE PARALLEL SHIFT AND THE PHASE SHIFT

The similarity between the expressions (4) and (16) indicates that there is some simple relation between these two functions. In fact, differentiation of equation (15) with respect to i gives:

$$f'(i) = \frac{d \sin(i-b)}{\cos b} \tag{22}$$

which yields, with the aid of (1):

$$F(i) = f'(i) \tag{23}$$

THE CONDITIONS FOR INTERFERENCE

The necessary and sufficient condition for interference is that two coherent rays shall be directed to the same spot on the photographic plate.

Coherent are all light pencils coming from the same point of the light source slit. In the optical arrangement depicted in Fig. 1, with this slit in the focal plane of the lens B, such rays are all parallel between the lens B and the cell. Consequently, every two rays having the same angle of incidence δ towards the cell on the light source side are coherent.

The condition that two interfering rays must be directed to the same spot on the photographic plate can of course be subdivided into two conditions, one concerning the horizontal, the other concerning the vertical coordinate on the plate.

Since the light source is a vertical slit which can be imagined as infinitely thin, and since this slit is brought to focus on the plate (in plan), there is but one coordinate in the horizontal direction on the plate as far as geometrical optics is concerned. Light falling outside the vertical line with this coordinate originates from diffraction and interference phenomena.

In order to interfere, two coherent rays must also fall upon the same vertical coordinate on the plate. Since, in elevation, an image of the cell is formed on the plate, this condition can be reformulated in terms of coordinates in the cell. We will assume that the cylindrical lens E is focused on the cell in the presence of the glass plates in their vertical positions. The condition can then be put in the form that the two interfering rays, if traced backwards from the plate through the cylindrical lens and through the vertical plates, shall pass the middle of the cell on the same x-coordinate.

The two interfering rays, having the same inclination to the left of the cell and suffering, in general, unequal deflections in the cell, will in general have different inclinations to the right of the cell. By definition, we will thus state that the angle of inclination of both rays is δ to the left of the cell and δ_1 and δ_2, respectively, to the right of the cell. Further, we will arbitrarily state that the first pencil (angle δ_1) will strike a plate with positive inclination to the right and a plate with negative inclination to the left of the cell, and *vice versa* for the second pencil (angle δ_2).

The condition for interference mentioned above makes it preferable to compute the total phase shift between the rays backwards from the plate to the light source slit. With this mode of approach, we know from the beginning which x-coordinate we are studying. This is the reason why we have defined the direction of the positive z-axis towards the light source.

The paths of two interfering pencils between the cell and the cylindrical lens are given in Fig. 3. Starting from the same X-coordinate on the plate, and tracing the rays backwards, they are in phase in points lying on the same circle with X on the plate as the centre. To the left of the cylindrical lens E, the two rays are in phase in points lying on the same circle with the point O as the centre, where O has the coordinate x corresponding to X and is situated in that plane F which is in focus in the absence of the glass plates. In the presence of a plate in the vertical position (plate P, for better visibility drawn away from the two inclined plates), the point O in the plane F is displaced to O′ in the plane F′, which is the plane of the middle of the cell. It retains the coordinate x. The first pencil (angle δ_1) is broken in the inclined plate P_1 at B_1 and C_1, emerges from it with a certain parallel shift and a certain phase shift, and strikes the plane of the cell in the point E_1. Similarly, the second pencil (angle δ_2) is broken in the inclined plate P_2 at B_2 and C_2, emerges from it with a certain parallel shift and a certain phase shift, and strikes the plane of the cell in the point E_2.

THE PHASE SHIFT BETWEEN THE TWO INTERFERING RAYS TO THE RIGHT OF THE CELL

We will now calculate the difference in phase between the two rays in the points E_1 and E_2, Fig. 3, using the equations derived earlier and the fact that the imagined rays through the vertical plate ($A_1B_1M_1N_1O'$ and $A_2B_2M_2N_2O'$) are exactly in phase in the point O′ (it will be postulated that the cylindrical lens is perfect).

The phase shift of the ray C_1D_1 relative to the ray B_1O is given by equation (17) with δ_1 instead of δ:

$$f(v-\delta_1) = f(v) - \delta_1 \, f'(v) \tag{24}$$

The phase shift of the imagined ray N_1O' relative to the ray M_1O is, according to the same equation:

$$f(0-\delta_1) = f(0) - \delta_1 \, f'(0) = f(0) \tag{25}$$

since $f'(0) = 0$. Consequently, the difference in phase between the ray C_1D_1 and the ray N_1O' is the difference between (24) and (25):

$$f(v) - f(0) - \delta_1 \, f'(v) \tag{26}$$

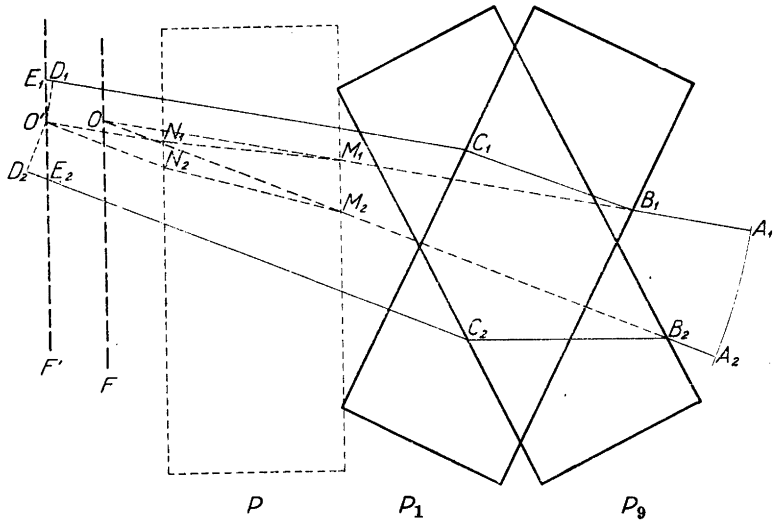

Fig. 3. The optical paths of two interfering rays to the right of the cell.

This phase difference prevails in points on the pencils lying in the same plane perpendicular to them, *e. g.* in the points D_1 and O'.

In the same way, the difference in phase between the points D_2 and O' is derived. The result is the expression (26) with $-v$ instead of $+ v$ and with δ_2 instead of δ_1:

$$f(v) - f(0) + \delta_2 f'(v) \tag{27}$$

By subtracting (27) from (26), we get the phase difference between the points D_1 and D_2:

$$-(\delta_1 + \delta_2) f'(v) \tag{28}$$

Although this is the difference in phase caused by the inclined plates, it is not the phase difference prevailing when the two pencils strike the cell wall. We must also take into account the difference in phase between the points D_1 and E_1 and between D_2 and E_2.

The distance D_1O' is given by equation (6) with δ_1 instead of δ:

$$D_1O' = F(v) - \delta_1 [F'(v) - F'(0)] \tag{29}$$

The distance D_1E_1 is obtained by multiplying this distance by δ_1:

$$D_1E_1 = \delta_1 F(v) - \delta_1^2 [F'(v) - F'(0)] \tag{30}$$

which, however, will be abbreviated to the first term since we are only considering the first power of δ_1:

$$D_1E_1 = \delta_1 \; F(v) \tag{31}$$

In the same way, we find that

$$D_2E_2 = \delta_2 \; F(-v) = -\delta_2 \; F(v) \tag{32}$$

and consequently the difference between the two distances is:

$$(\delta_1 + \delta_2) \; F(v) \tag{33}$$

Remembering the equation (23), we thus find that the phase difference (28) caused by the inclined plates is exactly compensated by the phase difference (33) due to the distances D_1E_1 and D_2E_2. Our conclusion is that the two interfering rays do not undergo any phase shift between the cell and the plate.

THE PHASE SHIFT IN THE CELL

The distance E_1O', Fig. 3, is nearly equal to the distance D_1O' given by equation (29), the difference between them being a correction term containing δ_1^2. The coordinate of the first pencil in the cell is thus $x + \Delta x_1$, where Δx_1 is given by the equation:

$$\Delta x_1 = F(v) - \delta_1 \; [F'(v) - F'(0)] \tag{34}$$

For the second pencil, we get the same expression with $-v$ instead of v and with δ_2 instead of δ_1:

$$\Delta x_2 = -F(v) - \delta_2 \; [F'(v) - F'(0)] \tag{35}$$

The difference between (34) and (35) is:

$$\Delta x = \Delta x_1 - \Delta x_2 = 2 \; F(v) - (\delta_1 - \delta_2) \; [F'(v) - F'(0)] \tag{36}$$

The second term in the above expression is small compared with the first for two reasons. First, $F(v)$ contains the first power of v, whereas $F'(v) - F'(0)$ only contains the second power (equation (4)). Second, δ_1 and δ_2 are nearly equal since the two rays must pass the cell att slightly different levels. As

long as we are not considering the error terms and the limitation of the method, therefore, we can write instead of (36):

$$\Delta x = 2\ F(v) \tag{37}$$

The phase shift between the two rays in the cell thus becomes, to the first approximation:

$$\Delta s_c = a\ n(x + \Delta x_1) - a\ n(x + \Delta x_2) = a\ \Delta x\ n'(x) = 2\ a\ F(v)\ \mathrm{n}'(x) \tag{38}$$

THE PHASE SHIFT TO THE LEFT OF THE CELL

The calculation of the phase difference in the left-hand glass plates and at the left-hand cell wall is very similar to that to the right of the cell, the only difference being that the two interfering pencils are exactly parallel with each other. This difference does of course not invalidate the result arrived at to the right of the cell: even to the left of the cell, the total phase shift between the rays is zero. The phase difference introduced by the inclined plates is found by replacing δ_1 and δ_2 by δ and by replacing v by $-v$ in equation (28):

$$2\ \delta\ f'(v) \tag{39}$$

and exactly the same amount of opposite sign is found at the cell wall.

THE TOTAL PHASE DIFFERENCE

The total phase difference in the whole optical system is thus found to be:

$$2\ a\ F(v)\ n'(x) \tag{40}$$

Since a and $F(v)$ can be measured ($F(v)$ can also be computed from equation (1) if the refractive index is known), $n'(x)$ can be derived if the fringe displacement is measured. We have made the calculation of the fringe displacement for an arbitrary coordinate x in the cell and X on the plate, thus it is valid along the whole x-axis (X-axis), *i. e.*, the interference fringes will take the form of the refractive index derivative in the cell.

The angle δ does not appear in our final expression. This means that the fringe displacement on the plate is independent of the vertical position of the light source if this is a point source. All point sources on the same vertical line will give the same interference pattern, consequently a vertical slit source can be used.

Since all light pencils of the same angle of inclination to the left of the cell are coherent, not only those going side by side on the same level, the left-hand pair of plates is not necessary to get the derivative interference pattern. However, if these plates are omitted, we have to subtract the phase difference introduced by them, expression (39), from the final expression (40). The additive term (39) is independent of x and does not introduce any errors in the interferogram, but since it depends upon δ, a point source will be necessary. The author has verified this conclusion experimentally. If the left-hand pair of plates is removed, and if a point source is applied, the interferogram remains unchanged. On gradually extending the light source in the vertical direction, the pattern becomes more and more blurred and soon disappears. If the point source is moved up and down, the interference fringes are seen to move laterally without changing shape. It is of course preferred to use both pairs of plates because a point source gives only a small fraction of the light intensity given by a slit source. No derivative interference fringes can be obtained if the right-hand pair of plates is omitted. Even in this respect the theory is in agreement with experimental evidence.

THE ERROR TERMS AND THE LIMITATION OF THE METHOD

Several approximations have been used in the above deduction. First, we used the first-order approximations in δ in the equations (7) and (17); the errors introduced thereby are exceedingly small and will not be considered. Second, in equation (34) the quantity Δx_1 was put equal to the distance D_1O' (Fig. 3) although the latter is the parallel shift perpendicular to the rays and the former should be the vertical shift. The correction factor which should have been applied is $1/\cos \delta_1$. It is insignificant and will not be considered. Third, the angles δ_1 and δ_2 were said to be approximately equal, which gave rise to the simplified equation (37). The errors introduced thereby may be important and will be investigated further, especially since they are characteristic of this method of observation. Fourth, the optical path length through the cell was put equal to $a\ n(x)$ although the ray describes a certain curve within the cell along which $n(x)$ varies. This error is inherent in all interferometric methods for the study of refractive index gradients and has been considered by Kegeles and Gosting [3]. It will therefore not be considered here. Fifth, also in equation (38), the series development was stopped with the first power of the increment. Since the second- and third-degree terms of this series are important and constitute the limiting factors in the differential interferometric method, they will be computed in this section.

Let us first consider the third-order approximation in Δx of the length of the optical path through the cell, assuming $a\ n(x+\Delta x_{1,2})$ to be sufficiently good approximations for these path lengths. We then have for the first ray in the cell:

$$s_{c1} = a\ n(x) + a\ \Delta x_1\ n'(x) + a\ \frac{\Delta x_1^2}{2}\ n''(x) + a\ \frac{\Delta x_1^3}{6}\ n'''(x) \tag{41}$$

We obtain the powers of Δx_1 from equation (34), still remembering that we only take into account terms of the first power in δ_1:

$$\Delta x_1^2 = F^2(v) - 2\ F(v)\ \delta_1[F'(v) - F'(0)] \tag{42}$$

$$\Delta x_1^3 = F^3(v) - 3\ F^2(v)\ \delta_1[F'(v) - F'(0)] \tag{43}$$

Introduction of these values into (41) gives:

$$s_{c1} = a\ n(x) + a\ F(v)\ n'(x) + \frac{a}{2}\ F^2(v)\ n''(x) + \frac{a}{6}\ F^3(v)\ n'''(x) - \tag{44}$$
$$- \delta_1[F'(v) - F'(0)][a\ n'(x) + a\ F(v)\ n''(x) + \frac{a}{2}\ F^2(v)\ n'''(x)]$$

For the calculation of δ_1, we have:

$$\delta = \delta_1 + a\ n'(x + \Delta x_1) = \delta_1 + a\ n'(x) + a\ \Delta x_1\ n''(x) + \ldots\ldots \tag{45}$$

and with the aid of (34) (where the second term can now be neglected):

$$\delta_1 = \delta - a\ n'(x) - a\ F(v)\ n''(x) \tag{46}$$

Introduction of this value into (44) gives:

$$s_{c1} = an(x) + aF(v)n'(x) + \frac{a}{2}F^2(v)n''(x) + \frac{a}{6}F^3(v)n'''(x) - [\delta - an'(x) \tag{47}$$
$$- aF(v)n''(x)][F'(v) - F'(0)][an'(x) + aF(v)n''(x) + \frac{a}{2}F^2(v)n'''(x)]$$

The optical path of the other ray, s_{c2}, becomes of course the same expression with $-v$ instead of v, *i. e.*, with $-F(v)$ instead of $F(v)$. Consequently, when we take the difference between s_{c1} and s_{c2}, all terms containing even powers of

$F(v)$ disappear, and those containing odd powers remain with the factor 2. If this is carried out, and if insignificant terms are omitted, there remains:

$$\Delta s = 2\ a\ F(v)\ n'(x) + \frac{a}{3} F^3(v)\ n'''(x) - \tag{48}$$

$$- 2\ a\ F(v)\ n''(x)[F'(v) - F'(0)][\delta - 2\ a\ n'(x)]$$

This is our final expression for the total phase difference between the two interfering rays. We will now investigate the order of magnitude of the two error terms and the conditions under which they can be neglected.

THE RESOLVING POWER

It will now be assumed that the refractive index function under observation is that given by an ideal diffusion. Thus we have:

$$n'(x) = \frac{\Delta n}{2\sqrt{\pi D t}} \exp.\left(-\frac{x^2}{4Dt}\right) \tag{49}$$

where Δn is the total refractive index change across the boundary, D the diffusion constant, and t the time. We also have the relations:

$$n''(x) = -\frac{x\ n'(x)}{2Dt} \text{ and } n'''(x) = \frac{x^2 - 2Dt}{(2Dt)^2} n'(x) \tag{50}$$

A fringe displacement can be measured to within a certain fraction of a fringe. If we call this fraction ε, it should thus be required that

$$\frac{a}{3} F^3(v)\ n'''(x) < \varepsilon\lambda \tag{51}$$

This condition is satisfied everywhere if it is satisfied in the top of the Gaussian curve. Introduction of $n'''(x)$ from (50) and putting $x = 0$ gives:

$$F^3(v) < \frac{12\,\varepsilon\,\lambda\,\sqrt{\pi}\,(Dt)^{3/2}}{a\Delta n} \tag{52}$$

Introduction of this value in the main term in (48) divided by λ gives the maximum fringe displacement in the top of the curve compatible with the precision ε:

$$\Delta s_{\max.} = \left(\frac{12\,\varepsilon}{\pi}\right)^{1/3} \left(\frac{a\Delta n}{\lambda}\right)^{2/3} \tag{53}$$

Neither the time, nor the diffusion constant appears in this expression, hence the maximum fringe displacement that can be used without introducing systematical errors is the same throughout a diffusion experiment. Antweiler [4] and Longsworth [5] claim that it is possible to localize a fringe to within 0.02 of the distance between fringes, and the author has the same experience. Putting $\varepsilon = 0.02$, $a = 2.5$ cm, $\Delta n = 0.00200$, and $\lambda = 5460$ Å, we find a fringe displacement in the top of the curve of 8.6 fringes, *i. e.* a relative precision of 2.3 parts in 1000. A general expression for the relative error can be obtained if the second term in (48) is divided by the main term and if the value (52) is introduced. One thus obtains:

$$\varrho = \left(\frac{\pi}{12}\right)^{1/3} \left(\frac{\varepsilon\lambda}{a\Delta n}\right)^{2/3} \tag{54}$$

This expression, again, refers to the top of the curve. In other parts thereof, it varies as

$$\frac{n'''(x)}{n'(x)} = \frac{x^2 - 2Dt}{(2Dt)^2} \tag{55}$$

If the correction (54) is constantly applied, the value of $F(v)$ need not be chosen in close agreement with equation (52), but can be considerably greater. For instance, if $F(v)$ is doubled, the total number of fringes is also doubled, and the relative error is four times greater. Still the result will be quite adequate if the correction (54) is applied. In this way accidental errors can be minimized when measuring small concentrations.

THE SECOND ERROR TERM

This term, containing the second derivative of the refractive index as a factor, is without influence in the top of the curve. It consists of two parts, one containing the first derivative, and one containing the angle δ. The former gives rise to a systematic error without causing blurring, as does the first error term treated above, the latter causes blurring without introducing systematical

errors, provided that the light source slit has a symmetrical position with respect to the optical axis.

The systematical error is:

$$4\ F(v)\ [F'(v) - F'(0)]\ a^2\ n'(x)\ n''(x) \tag{56}$$

and gives rise to the relative error:

$$\varrho_2 = 2\ a\ n''(x)\ [F'(v) - F'(0)] \tag{57}$$

It is at its maximum in the inflexion points, where we have:

$$n''(x_i) = \frac{\Delta n}{2Dt\sqrt{2\pi e}} \tag{58}$$

The value of $F'(v)$—$F'(0)$ is:

$$F'(v) - F'(0) = \frac{d\,v^2(m-1)\,(3+3\,m-m^2)}{2\,m^3} \tag{59}$$

We take the value of v from the first order approximation of $F(v)$:

$$F(v) = \frac{d\,v\,(m-1)}{m} \tag{60}$$

and, moreover, we choose the maximum permissible $F(v)$ value derived from the first error term, equation (52). Hence we get:

$$\varrho_2 = \frac{(3+3m-m^2)\sqrt[3]{9a\,\Delta n\,(\varepsilon\lambda)^2}}{dm\,(m-1)\sqrt{e}\,\sqrt[6]{2\pi}} \tag{61}$$

If we require that this relative error be smaller than 10^{-3}, we can formulate this condition in terms of a minimum thickness of the inclined plates:

$$d > \frac{1000\,(3+3\,m-m^2)\sqrt[3]{9\,a\,\Delta n\,(\varepsilon\lambda)^2}}{m\,(m-1)\sqrt{e}\,\sqrt[6]{2\pi}} \tag{62}$$

With the following numerical figures, which are rather unfavourable with

regard to this error, *viz.* $m = 1.5$, $a = 5$ cm, $\Delta n = 0.002$, $\varepsilon = 0.1$, and $\lambda = 5460$ Å, this becomes:

$$d > 0.43 \text{ cm} \tag{63}$$

For technical reasons already, d should be chosen at least 1 cm. It can thus be concluded that the second error term will never be able to cause any detectable systematical errors if the first error term is negligible. The conditions for a correct refractive index analysis derived in the former section are therefore sufficient conditions.

The part containing δ in the second term, which part only causes blurring and no systematical errors, is of the same order of magnitude as the part treated above since δ and $a\, n'(x)$, when they have their maximum values, are of about the same size. Hence the blurring is quite unimportant under the conditions which have to prevail for a correct analysis.

DISCUSSION

The differential interferometer described in this paper seems to be capable of giving an accuracy of about 2 parts in 1000 in the refractive index derivative under standard experimental conditions and thus compares favourably with other methods for measuring this derivative. By a simple manipulation of the optical components, the interferometer can be converted into an integral interferometer which is capable of giving the total refractive index change with a very high precision, much greater than that obtainable by integration of the Gaussian curve. Although this method cannot be expected to supersede the very precise Gouy method for measuring diffusion constants (Kegeles and Gosting [3]; Longsworth [6]; Coulson, Cox, Ogston, and Philpot [7]), it is advantageous that it makes possible a direct viewing of the Gaussian curve. This method, moreover, is useful for boundary systems, such as those appearing in electrophoresis and adsorption analysis, whereas the Gouy method is not.

The direct measurement of the maximum derivative with the aid of the scale method and the diagonal slit method is open to systematic errors which can only be corrected for by an involved wave-optical theory (Adler and Blanchard [8]; Kegeles and Gosting [3]). The differential interference method does not seem to be open to such errors.

Like the integral interferometer of Philpot and Cook [2], the differential interferometer can also be built into the optical system of the diagonal slit method (*cf.* Svensson [9]).

An entirely different method of producing interference between two vertically displaced light pencils through the cell has been reported by Vallet [10].

SUMMARY

An optical arrangement for making direct records of the refractive index derivative in stratified solutions by interferometric means has been presented. A theory for the method has been given, which shows that the phase differences between the two interfering rays occurring outside the cell neutralize each other and that the phase difference within the cell can be made very nearly proportional to the refractive index derivative in each point. The theoretical resolving power, as derived from higher terms in the analytical expression for the phase difference, compares favourably with that of other known methods for recording the refractive index derivative. The conditions for getting unblurred interferograms have been considered.

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