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On the Use of Rayleigh-Philpot-Cook Interference Fringes for the Measurement of Diffusion Coefficients

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It is known that certain types of interferometers in conjunction with an optical device for making an image of a certain object are capable of giving interferometric patterns which are to be regarded as topographic maps of the object, each interference fringe indicating a change of the optical thickness of one wave-length. This fact was made use of by Labhart and Staub [1] for electrophoresis measurements. They used a Jamin interferometer. Later, Lotmar [2] has presented a number of possible optical arrangements more or less based on the Michelson interferometer.

In the Rayleigh interferometer, it is necessary to produce an image of the light source slit. Hence the possibility of producing a topographic map of an object does not exist in this case because the introduction of a lens focused on the object would destroy the interference phenomenon altogether. However, using an astigmatic optical system, it is sufficient to produce an image of the slit in the plane perpendicular to it; in its own plane, it need not be in focus. Consequently, in the image of the slit, the dimension along the same is free for the production of an optical image of the object. Hence it is possible, using the Rayleigh interferometer, to obtain one-dimensional interferograms of an object whose optical thickness does not vary in the direction perpendicular to the slit. Since in diffusion cells, electrophoresis cells, etc., the optical thickness is constant along a horizontal line, it is evident that a Rayleigh interferometer in combination with an astigmatic optical system is capable of yielding exact information of the refractive index course along the vertical coordinate.

This fact was first understood and tested experimentally by Philpot and Cook [3] and, independently, by the present author [4*]. It has later been found

* Added in proof: Rögener describes in a recent article (*Kolloid-Z.* **118** (1950) 10) an optical system which was designed in the years 1943/44 and which, to judge from the interferograms published, works according to the same principles as the Philpot-Cook system. However, the

that the optical system widely used for more than 10 years in electrophoretic measurements, the diagonal slit method, serves the purpose as well (Svensson [5]). The integral fringe method, so called because it gives directly the refractive index function and not the derivative, has already been tested by Longsworth [6] in connection with an investigation of two new types of diffusion cells, and its importance in electrophoresis has also been stressed by him (Longsworth [7]). The present author has not until now had the opportunity of making methodical experiments with the new method. In this paper, the use of the integral fringe method for the determination of diffusion coefficients by the height-area method will be described. In addition, the method of computation used by Longsworth will be considered.

EXPERIMENTAL

The optical system of the diagonal slit method (see Svensson [5], Fig. 1) was used in this investigation with the modification that the light source slit was vertical and the diagonal slit removed. On adjusting this system, it was found that the angular orientation of the cylindrical lens was very critical, much more than in the diagonal slit method. By screening off the slit to essentially a point source, however, the fringes could always be easily found. Then the point source was gradually extended to a slit, the cylindrical lens being turned a little after each increase in length in order to retain the fringes. After the slit had been opened to its total length again, a final adjustment of the cylindrical lens gave fringes as bright and well-defined as in the optical system originally suggested by Philpot and Cook.

The diffusion cell was the flowing-junction cell which was described in an earlier publication (Svensson [4]). It is very similar to the stainless steel cell recently described by Longsworth [6], the main difference being that the suction slit of the latter can be closed. Unfortunately, no thermostat was available during these experiments, but they were carried out in an underground room without windows and with a remarkably constant temperature. Distilled water was constantly stored in this room, and the preparation to be studied was dissolved in this water an hour or two before the experiment was started.

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very essential feature of producing an optical image of the cell in elevation is not mentioned in the text, nor is it evident from the optical arrangement. Possibly Rögener's second slit-focusing lens serves this purpose also. Rögener's earlier arrangement (*Kolloid-Z.* **105** (1943) 110) works with horizontal slits and is more related to the Gouy interference method than to the Philpot-Cook method.

An attempt to use the Rayleigh interferometer for diffusion studies has also been made by Kroepelin (*Sitzungsber. physikal.-med. Soz. Erlangen* **58/59** (1926/27) 237), yet without any cell-focusing device.

Care was taken not to warm up the water or the diffusion cell by touching or by radiation from the body. A thermometer placed close to the cell showed, in general, a variation in temperature of less than $\pm$ 0.1° C during an experiment.

Cane sugar (Merck) of analytical purity was chosen as the test substance. Very accurate measurements of the diffusion of this preparation have recently been performed by Gosting and Morris [8].

As also recommended by Longsworth [6], the first fringe photograph was taken before starting, with both solutions still flowing through the exit slit. This photograph was subsequently used for measuring the fractional part of the total fringe displacement between top and bottom solutions. The time for closing the stop-cock in connection with the exit slit was noted as the experimental zero time of the diffusion. Five to eight exposures were taken during the diffusion process, the last one 14 000 to 16 000 seconds after the start.

The cross section of the diffusion channel was round 3 $\times$ 50 mm^2. The reference channel was filled with distilled water.

COMPUTATION OF THE DIFFUSION COEFFICIENT BY THE HEIGHT-AREA METHOD

This method makes use of the equation:

$$D = \frac{(n_1 - n_2)^2}{4\ \pi\ t\ n'^2_{\text{max.}}(x)} \tag{1}$$

where n_1 and n_2 are the refractive indices of the two solutions, t the time, and $n'_{\text{max.}}(x)$ is the maximum derivative of the refractive index function with respect to the position in the cell. Since a fringe is, in this case, as good a unit of refractive index as any other, and since n is present in the same power in numerator and denominator, the readings need not be recalculated to real refractive index units. Consequently the calculation can be carried out without knowledge of the thickness of the cell.

The integer part of the total fringe displacement was counted from any one of the later exposures, while the fractional part was measured from the first exposure in a comparator with a cross-motion arrangement for the table. The plate was aligned in the comparator so that the hair-cross in the microscope, on moving the table cross-wise, followed the middle of a fringe along the whole half-cell on one side of the boundary. The distance between the hair-cross and that fringe on the other side of the boundary which was last passed by it on bringing this side into view, was then measured by moving the

table in the direction of the micrometer screw (perpendicular to the fringes). Similarly, the distance between two consecutive fringes was measured. This measurement should be carried out across the original position of the hair-cross since the distance between fringes varies somewhat across the interferogram, especially if the number of fringes is small. This is explained by the fact that the outer fringes are situated on the sloping light intensity curve in the central diffraction band. The ratio between the two distances thus measured is the fractional part of the total fringe displacement. It could be measured with a reproducibility of 0.02 fringes.

The experimental determination of the maximum derivative is more difficult. Taking the differences between consecutive readings and inverting them gives rise to large accidental errors and too large a spreading in the resulting derivative curve. On the other hand, taking the differences between, say, every tenth fringe and dividing 10 by them, is likely to give little spreading but serious systematic deviations from the true derivative. Plotting the integral curve and using a mechanical differentiator gives an accuracy far behind that inherent in the interferogram.

In order to find the best way of computing the maximum derivative, we will study the systematic deviation from the true derivative resulting from taking too large differences in the numerical differentiation. In every numerical differentiation, the quantity $\Delta n/\Delta x$ is measured. By writing this quantity in the form:

$$\frac{\Delta n}{\Delta x} = \frac{n(x + \Delta x/2) - n(x - \Delta x/2)}{\Delta x} \tag{2}$$

and by development into powers of Δx, we get the following third-order approximation:

$$\frac{\Delta n}{\Delta x} = n'(x) + \frac{(\Delta x)^2}{24} n'''(x) \tag{3}$$

If we require that the third-order term be less than a certain fraction ϱ of the main term, we get the condition:

$$(\Delta x)^2 < \frac{24\, \varrho\, n'(x)}{n'''(x)} \tag{4}$$

At the top of the Gaussian curve this reduces to:

$$(\Delta x)^2 < 48\, \varrho\, Dt \tag{5}$$

Table 1. Determination of the maximum derivative.

Comparator reading mm	Δx for $\Delta n = 5$ mm
23.287	
23.729	
24.132	
24.546	
24.930	
25.312	3.799
25.673	3.709
26.051	3.643
26.380	3.576
26.748	3.513
27.086	3.469
27.438	3.462
27.775	3.439
28.122	3.435
28.443	3.433
28.781	3.420
29.135	3.435
29.490	3.449
29.815	3.497
30.181	3.522
30.506	3.585
30.873	3.643
31.224	3.707
31.619	3.793
31.965	
32.366	
32.778	
33.197	
33.608	

This is the condition in terms of the abscissa increment that has to be satisfied in a numerical differentiation with the precision ϱ. For the interferograms in question, however, it is more convenient to have a condition in terms of the ordinate increment since the ordinates are integers. Consequently, we introduce the value of Δx according to (5) into the numerator of (2) and get:

$$\Delta n = \Delta x \; n'(x) = (n_1 - n_2) \sqrt{\frac{12 \, \varrho}{\pi}} \tag{6}$$

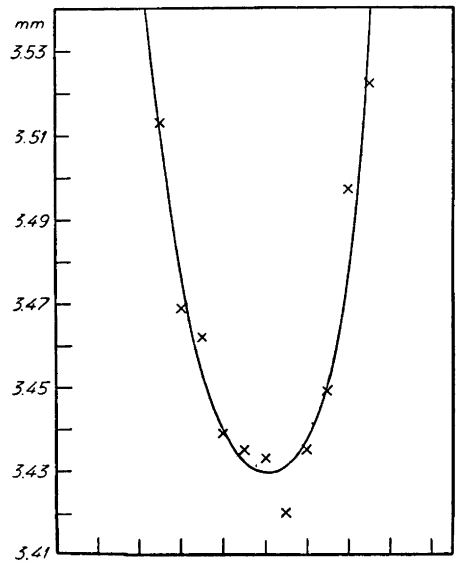

Fig. 1. The distance between every fifth fringe as a function of the fringe number.

For a precision of 1 part in 1 000, therefore, we get a permissible ordinate difference of 0.062 (n_1—n_2), *i. e.*, with 50 fringes between the two solutions, one can measure the distance between every third fringe without introducing a greater relative error than 0.1 per cent. However, the author prefers to use still greater ordinate differences and to apply the correction ϱ according to the equation:

$$\varrho = \frac{\pi}{12}\left(\frac{\Delta n}{n_1 - n_2}\right)^2 \tag{7}$$

If the correction is allowed to rise to one per cent, it is possible to compute the maximum derivative using ordinate differences of 20 per cent of the total refractive index change. The relative accidental errors are then extremely small. It should be noted that the correction (7) is independent of the time.

The procedure that has been followed in the determination of the maximum derivative is consequently the following. After the plate had been aligned on the comparator table, every fringe or half-fringe was measured throughout a region round the centre of the boundary comprising about 40 per cent of the total number of fringes. The readings were written down in a table, and the differences between every mth fringes were taken, the integer m being chosen in each case to give a correction ϱ of about one per cent. The differences were plotted against the fringe number in a diagram, and a smooth curve was drawn through the scattered points. The minimum of this curve was read. Division of the integer m by this minimum gave the approximate derivative

Table 2. The calculation of diffusion coefficients by the height-area method.

Time sec.	Maximum derivative fringes per cm	Inverted and squared maximum derivative	Time calculated sec.	Time discrepancy sec.
187	93.47	0.0001145	166	+ 21
480	60.15	0.0002764	469	+ 11
1080	40.44	0.0006115	1097	− 17
2220	28.68	0.0012157	2228	− 8
3180	24.02	0.0017332	3197	− 17
5640	18.18	0.0030256	5617	+ 23
8580	14.73	0.0046089	8582	− 2
Equation of the line: $n'^2(x)\ (t + 48) = 1.8725 \cdot 10^6$				

according to (2), and finally the correction (7) was computed and applied to give the true derivative.

Table 1 and Fig. 1 give a typical example of such a calculation. The uncertainty in the minimum value of Δx is round 0.003 mm, which is consistent with the sharpness of the fringes and their separation. The relative accidental error, therefore, becomes of the order of 0.001.

The data in Table 1 are taken from an experiment with an 0.2 per cent sugar solution diffusing against water. With the cell used, round 50 mm thick, this gave 26.43 fringes. In all exposures, the ordinate increments used in the differentiation were 5 fringes, and the correction applied was $\varrho = 0.0094$. In Table 2, the first column gives the experimental times from the start of the diffusion, whereas the second column gives the corrected maximum derivatives. In the third column, we have the squared and inverted values of the maximum derivatives, which, according to equation (1), should be proportional to the time. After having controlled in a plot that no point deviated seriously from a linear relationship between the data in the columns 1 and 3, the equation of the straight line that best satisfied the data was computed with the aid of the method of least squares. The constant term in this equation is the zero-time correction, which serves as a quantitative measure of the quality of the starting boundary and of the reliability of the experiment as a whole. The second parameter of the equation of the straight line is the slope, which was inserted into equation (1) to give the diffusion coefficient. The two last columns in Table 2 contain the times calculated from the equation of the straight line and the discrepancy between them and the experimental times. The latter is in no case greater than the time of exposure, 30 seconds.

Table 3. Results.

Sugar concentration per cent	Total fringe displacement	Mean temperature °C	Zero-time correction seconds	Diffusion constant $cm^2/sec. \cdot 10^6$	Remarks
0.2	26.43	20.6	46	5.231	Two calculations of
			48	5.221	the same material
0.5	66.33	21.1	21	5.250	
0.5	66.33	21.5	52	5.198	
0.5	67.80	21.65	8	5.201	
0.5	67.16	20.6	63	5.234	
0.75	98.46	20.5	59	5.246	
0.25	33.81	20.3	55	5.301	Large temperature variation
0.5	67.1	20.1	63	5.38	The same, and bad starting boundary

In all, eight experiments were carried out. In order to compare the diffusion constants obtained with the values given by Gosting and Morris [8], corrections were applied to zero concentration using Gordon's relation and to 25.0° C using Stokes-Einstein's relation (see Gosting's and Morris' paper). These data are given in Table 3. The first column gives the concentration of sugar, the second the total number of fringes, the third the temperature, the fourth the zero-time correction, and the fifth the diffusion constant corrected to zero concentration and to 25.0 °C.

DIRECT COMPUTATION OF THE DIFFUSION COEFFICIENT FROM THE POSITION OF THE INTEGRAL FRINGES

The numerical differentiation of the refractive index function in the cell in order to use equation (1) may seem to be a somewhat round-about way since the integral of the error function is well known and available in mathematical tables. By direct comparison between the coordinates of the fringes and a table of the integral function it is possible to derive a value of the diffusion constant for each fringe or half-fringe. This method, which was originally suggested by Gosting and described by Longsworth [6], is, like the former method, based on the assumption that the diffusion is ideal, but it is capable of showing up deviations from the ideal behaviour very clearly since calculations can be carried out from every part of the curve.

The procedure adopted by the author was the following. The interferogram in question was aligned in the comparator so that the fractional part of the

Table 4. Normal analysis of the boundary.
$(n_1-n_2 = 66.33)$

Fringe number (ν)	Comparator reading mm	$\frac{n_1-n_2-2\nu}{n_1-n_2}$	z	Plate coordinate calculated	Discrepancy μ
0.5	16.460	0.98492	1.7186	16.462	− 2
1	17.955	0.96985	1.5331	17.942	+ 7
2	19.579	0.93969	1.3283	19.577	+ 2
3	20.615	0.90954	1.1971	20.624	− 9
4	21.404	0.87939	1.0976	21.418	− 14
6	22.613	0.81908	0.9461	22.627	− 14
8	23.564	0.75878	0.8287	23.565	− 1
10	24.350	0.69848	0.7306	24.348	+ 2
12	25.028	0.63817	0.6448	25.032	− 4
15	25.938	0.54771	0.5315	25.937	+ 1
18	26.751	0.45726	0.4304	26.744	+ 7
21	27.489	0.36680	0.3375	27.485	+ 4
24	28.190	0.27634	0.2500	28.183	+ 7
27	28.853	0.18589	0.1663	28.851	+ 2
30	29.513	0.09543	0.0848	29.502	+ 11
35	30.577	− 0.05533	− 0.0491	30.571	+ 6
40	31.658	− 0.20609	− 0.1847	31.653	+ 5
43	32.325	− 0.29655	− 0.2692	32.327	− 2
46	33.036	− 0.38700	− 0.3577	33.034	+ 2
47	33.281	− 0.41716	− 0.3884	33.279	+ 2
50	34.054	− 0.50761	− 0.4855	34.054	0
53	34.904	− 0.59807	− 0.5927	34.909	− 5
55	35.540	− 0.65837	− 0.6724	35.546	− 6
57	36.255	− 0.71868	− 0.7618	36.259	− 4
59	37.076	− 0.77898	− 0.8654	37.086	− 10
61	38.080	− 0.83929	− 0.9919	38.096	− 16
63	39.447	− 0.89959	− 1.1617	39.451	− 4
65	41.782	− 0.95990	− 1.4515	41.764	+ 18
66 *	44.885	− 0.99005	− 1.8227	44.726	+ 159

* Excluded from the treatment by least squares.

fringe number became the same as that measured in the exposure of the flowing boundary. Then the position of a great number of fringes (the measurement and computation of every intensity maximum and minimum is generally too time-consuming) was measured throughout the entire interferogram. In Table 4, the first column gives the number of the fringe (number 0 being that fringe with which the hair-cross of the microscope coincided outside the bound-

ary), and the second column contains the comparator readings. The third column is headed $(n_1—n_2—2\nu)/(n_1—n_2)$ and is the fraction of the total area of the error curve enclosed between the comparator reading and the symmetrically situated coordinate on the other side of its centre. In a Table of the integral function, the values of the independent variable corresponding to these figures were found by interpolation, column 4. The figures in the columns 2 and 4 should now show a linear relationship, which was controlled in a plot. The readings of the first and last fringes, running almost parallel to the micrometer screw, are naturally very inaccurate and must often be discarded. The rest of the points were treated by the method of least squares to get the equation of the straight line. The plate coordinates corresponding to this line are presented in column 5, and the discrepancies between them and the observed values, column 2, are given in column 6. With few exceptions, they are smaller than 1/50 of the distance between consecutive fringes. This means that, in this particular case, the concentration distribution in the boundary was that required by the law of ideal diffusion.

From the slope of the line, the diffusion constant can be calculated with the aid of the equation:

$$D = \frac{x^2}{4\,t\,z^2} \tag{8}$$

and these values check reasonably well with those obtained by the height-area method. However, to get good results the zero-time correction has to be applied, which necessitates the complete evaluation of all exposures according to the above procedure or to use the zero-time correction derived from the height-area method. Since the former alternative would be too time-consuming, the author has restricted the use of that method to one exposure in each experiment in order to control the shape of the boundary. Even if the method of least squares is omitted, the interpolation of a great number of data in the table of the integral function remains and is very laborious. Although the method is more direct than the height-area method, the differentiation being omitted, it requires much more work.

DISCUSSION

If the two last experiments in Table 3 are excluded, the individual diffusion constants deviate from the mean value, $5.226 \cdot 10^{-6}$, by less than 0.5 per cent. The value given by Gosting and Morris for 24.95 °C is 5.224, which yields 5.231 at 25.0 °C. The latter figure is 0.1 per cent higher than the mean value from Table 3. Taking into consideration that these experiments were

carried out without thermostating and that great temperature corrections have been applied, the conclusion seems justified that the new method of observation is capable of a precision that can be compared with that of the Gouy method. Moreover, the results seem to indicate that accurate temperature regulation is not as essential in diffusion measurements as is generally believed.

From the normal analysis of the boundary carried out as suggested by Gosting and Longsworth directly from the integral fringes and as demonstrated in Table 4, two interesting conclusions can be drawn. First, the exact linear relationship between the comparator readings and the quantity z shows that Longsworth [6] was right when he blamed the cylindrical lens for the non-linear relationship found by him. In his optical system, which was identical with that originally described by Philpot and Cook, an uncorrected cylindrical lens was used at a comparatively high relative aperture (axis horizontal, point source). In the present investigation, the cylindrical element had its axis parallel to the light source slit, hence it was active at a very low relative aperture. In addition, it was spherically and chromatically corrected.

The possibility of using the diagonal slit method simultaneously with the integral fringe method, as discussed in reference 5, also speaks in favour of that optical system. However, if no use is made of the diagonal slit method, there is no point in using the longer optical system required by the two-fold image formation of the light source slit. In such cases, other ways of restricting the relative aperture of the cylindrical lens should be tried. One possibility is to use an astigmatic lens system composed of a spherical objective and a negative cylindrical lens with a vertical axis. The spherical objective, then, is focused on the cell and the compound objective on the light source slit. The conditions for interference are then again fulfilled.

The second conclusion that can be drawn from the normal analysis is that the diffusion cell is working satisfactorily. It is certainly free of leakage since there are no sliding parts. The optical precision is good; clamping of windows in general gives rise to less distortion than does cementing. The small volume of solution which is left in the exit slit and which could be feared to cause trouble by back-diffusion has been found to be unimportant. These conclusions are in agreement with Longsworth's tests of similar diffusion cells of the flowing junction type.

The method of direct computation of the diffusion constant by comparison with the tables of the integral of the error function renders good service as a method of normal analysis. As a method of calculating the diffusion constant, it involves an excessive amount of work if use is made of every fringe in every exposure. In Table 4, only 29 readings were taken out of 133 possible read-

ings. The number of readings can of course be reduced still more, with a corresponding reduction of the numerical calculations, if the diffusion is ideal.

The calculation with the aid of the height-area method is fairly rapid. It involves the measurement, under standard conditions, of some 20 fringes, taking and plotting of some 10 differences, and some numerical work with the minimum difference, everything in each exposure. The determination of the total fringe displacement is simple. The work is not in any way overwhelming, yet it would be very advantageous with a more convenient way of determining the maximum derivative. The differential interference refractometer described recently (Svensson [9]) will probably be valuable in this respect. It requires only four plano-parallell glass plates in addition to the optical equipment of the integral interferometer. From the differential interferogram, the maximum derivative (as well as the derivative in any point) can be directly measured. The use of this method, in combination with the integral fringe method, will be described in a forthcoming communication.

A comparison between this type of interferometer and those giving the optical path differences as functions of both dimensions in the cell mentioned in the beginning of this article reveals the following. In the case of optical distortions along horizontal lines in the cell, the Rayligh-Philpot-Cook interferogram is blurred, and it will be necessary to use only a narrow vertical strip of the cell for the optical analysis. With a Michelson or Jamin interferometer, direct information of the lateral distortions in the cell is gained, and no blurring of the fringes occurs. On the other hand, the Rayleigh-Philpot-Cook interferometer has two great advantages, that of permitting direct photographing of the refractive index function, and the possibility of measuring small fractions of a wave-length. The arrangement described by Labhart and Staub [1] has the former advantage, but not the latter, while that described by Antweiler [10] possesses the latter advantage, but not the former. Fractions of wave-lengths, however, can be measured in Labhart's and Staub's arrangement by visual observation during the experiment if Antweiler's device for that purpose is introduced. Correspondingly, Antweiler's arrangement permits photography if a monochromatic light source is applied. In no case, however, can fractions of wave-lengths be measured on the photographic plates.

SUMMARY

The use of the interference refractometer devised by Philpot and Cook in diffusion measurements has been submitted to experimental tests. Although a differentiation is necessary, it has been shown that the conventional height-area method of computing diffusion coefficients can be used successfully. A

detailed description of a method for the accurate determination of the maximum derivative of the refractive index in the cell has been presented.

The direct comparison between the fringe distribution with tables of the integral of the error function, as suggested by Gosting and Longsworth, has also been tested, and the results discussed.

The influence of too poor a correction of the cylindrical element of the optical system has been discussed in relation to the relative aperture of this lens. Optical systems have been proposed in which the cylindrical element is working at a very low relative aperture. In such systems, it should be possible to get satisfactory results even with simple cylindrical lenses.

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