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Intensity Measurements Applied to Gouy Diffusiometry

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A method is described which has been used to verify the intensity distribution in the lower fringes in a Gouy diffusion fringe pattern predicted by the general theory for the Gouy method. The position of the zeroth turning point predicted by the theory has also been shown to be correct. Two techniques for the direct recording of Gouy diffusion data for use in the actual determination of diffusion coefficients are presented briefly.

Introduction

The rediscovery of the Gouy phenomenon[1] and the development of quantitative methods for the analysis of the information obtained from Gouy fringe patterns[2-4] have provided a precise and rapid means for measuring diffusion coefficients in solutions. By use of well described procedures[5,6] determinations can be made from measurements of the positions of known minima in the fringe system at known times after the start of the diffusion experiment. There is an abundance of experimental evidence which indicates that the intensity distribution functions provided by the various theories to predict intensity in a Gouy pattern as a function of position do satisfactorily predict positions of minima in the patterns corresponding to the zeros in the distribution functions. One purpose of this work was to determine the validity of the prediction of the actual intensity distribution and the utility of a knowledge of the positions of maxima in the fringe pattern corresponding to turning points in the distribution functions. In addition, the same equipment was to be used to permit objective, direct recording methods of locating fringe minima and maxima at known times allowing for the determination of diffusion coefficients.

Experimental

For this work a conventional single lens diffusiometer was used for which general descriptions are available.[5] Tall form Tiselius cells of two channel sizes were used as diffusion cells. Distances along the optical path in these cells, "*a*" distances, were 2.5 cm. and 5 cm. The mercury green line was selected from a mercury A H-4 lamp by a 77A filter. The bath temperature during all experiments reported was controlled at 25 ± 0.01°. The distance from the center of the Tiselius cell to the focal plane corrected for the indices of refraction of the various elements in this path was about 209 cm. (This "*b*" distance varied slightly with choice of cell and photomultiplier slit position.)

Direct recording of intensities was accomplished by placing a slit in the focal plane of the diffusiometer which could be moved vertically by a suitably controlled synchronous motor. Light entering the slit impinged on a photomultiplier tube whose output was recorded on a modified Leeds and Northrup Speedomax recorder.

In order to achieve this purpose the following equipment was assembled. A Gaertner traveling microscope table (for simplicity later called a comparator) was mounted vertically in a rugged support on a massive base which had been slotted to fit the optical bench of the Gouy diffusiometer. The design of the support allowed for direct coupling of the comparator to one of several synchronous motors (Bodine type KYC-22RC). The desired scanning rate determined the particular choice of motor speed. The travel of the comparator was limited by appropriately positioned micro-switches. Switching arrangements were provided so that the motor drive could either be reversed automatically at the extremes of the scanning travel or at will at any time.

A threaded sleeve replaced the microscope which usually was screwed into the comparator table. To this sleeve was fastened a 5″ × 2.5″ × 2″ aluminum box which served as the housing for a 1 P-21 photomultiplier-tube and as a support for input d.c. high voltage and output signal connectors. A conventional voltage divider for the tube was mounted inside the housing. On the front face of the box was fastened an adjustable, calibrated, bilateral slit about 1″ in length.

As a power supply for the photomultiplier tube 90 volt batteries were used in series. A coarse switch selected any multiple of 90 volts up to 1350. An additional fine control allowed for a continuous adjustment within the 90 volt steps.

The photomultiplier tube output, without intermediate amplification, was recorded directly on a Type G Speedomax recording microammeter. Although the normal range for the recorder is 0–1 microampere, a modification of the input circuit to the recorder amplifier permitted the selection of an additional range of 0–0.1 microampere. A variety of strip-chart speeds up to 1080″ per minute was available by manipulation of the chart-drive gear ratios. At one minute intervals an auxiliary pen operated by a solenoid, which in turn was actuated by a clock motor, printed an independent time scale on the chart paper. The relevant motors in the equipment were calibrated with conventional laboratory timing devices.

It would be of doubtful value to describe the equipment in more detail than has been done, since the apparatus was assembled largely from parts already available in this Laboratory. Doubtless, each individual component could be somewhat better designed for the particular purpose which it serves in this experiment.

Intensity Distribution.—In order that the photoelectric measurements should unambiguously refer to well characterized boundaries, behaving in a normal fashion, the ordinary Gouy experiment was usually performed in all details leading to a determination of the diffusion coefficient. This procedure is quite well described elsewhere.[5] Photoelectric measurements were interspersed in these normal measurements. For convenience additional check runs were made with the photographic details omitted.

As was mentioned earlier two types of photoelectric measurements were employed: 1, measurements yielding the relative intensities in the lower Gouy fringes; 2, measurements giving positions of known maxima or minima at known times by: (a) determination of times at which known maxima and minima appeared at definite positions in the focal plane or (b) simultaneous determination of fringe position and time. For the determination of the relative intensities the lower fringes were repeatedly scanned at the rate of 250 μ per second throughout the course of the diffusion experiment. Figure 1 is a typical scanning record. Relative intensities were computed from the amplitudes of the 0th, 1st and 2nd fringes corrected for background.

In determining diffusion coefficients using direct recording of Gouy fringe data there are quite a few variations which might be employed. Two of the more obvious of these are described here.

In the first method the slit was positioned at known distances from the undeviated slit image (at known values of Y) in the focal plane. During the course of the experiment

(1) L. G. Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).
(2) G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947).
(3) C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).
(4) L. J. Gosting and L. Onsager, THIS JOURNAL, **74**, 6066 (1952).
(5) L. J. Gosting and M. S. Morris, *ibid.*, **71**, 1998 (1949).
(6) A. G. Ogston, *Proc. Roy. Soc.* (*London*), **A196**, 272 (1949).

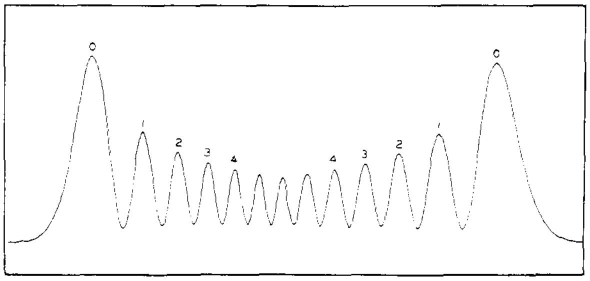

Fig. 1.—Record of consecutive upward and downward scanning of lower Gouy fringes.

the lower fringes in Gouy pattern collapsed across the slit. Since the output of the photomultiplier was recorded on a chart upon which time was being simultaneously indicated, the record provided times at which known maxima and minima had precisely determined Y values.

A 50 μ per second scanning of the fringe system by the photomultiplier unit was used in the second method. Just before the scanning slit reached the undeviated slit image position, a reference interference pattern which defined this position was produced by changing the masking details at the cell.[5] On the chart, distances between various maxima and minima and the central fringe in the reference pattern represented precisely known intervals of time. Since both the photomultiplier unit and the chart were driven by calibrated synchronous motors these differences in time were directly related to distances of the various fringe positions from the undeviated slit image position.

For both these methods the "δ" values representing the deflection of light rays by the cell and its contents in the absence of a boundary were measured in a way analogous to the photographic technique.[5] A Rayleigh interference pattern, produced by a double-slotted mask placed immediately before the diffusion cell, was scanned by the photomultiplier unit. As the center of the Rayleigh bundle was approached the masking was quickly changed so that a similar pattern was formed through the reference path immediately adjacent to the cell. By extrapolation of either pattern the displacement of the second could be accurately estimated. Precisely the same technique was used to estimate the fractional part of a fringe in the Gouy fringe system. The total number of fringes in the Gouy pattern could be estimated by scanning downwards from the undeviated slit image position immediately after the start of the diffusion process.

Definitions and Equations.—Later computations assume the validity of the fringe displacement equation

$$Y_j = \{ab(n_2 - n_1)/(2\sqrt{\pi Dt})\}e^{-z_j^2} \qquad (1)$$

proven in the original theory for the Gouy method.[2] "a" and "b" are equipment constants mentioned earlier. n_1 and n_2 are refractive indices, referred to air, of the original liquids normally below and above the initial boundary, respectively. The hypothetical time from the formation of an infinitely sharp boundary is indicated by t and z is related to the actual distance in the cell from the position of the maximum index gradient, x, by $z = x/2\sqrt{Dt}$.

The total number of fringes in the system, j_m, is related to the cell dimension, a, through the equation

$$j_m = a(n_2 - n_1)/\lambda \qquad (2)$$

where λ is the wave length in air of the light used. The equations

$$C_t = ab(dn/dx)_{max} = j_m\,\lambda b/(2\sqrt{\pi Dt}) \qquad (3)$$

define the greatest deflection of light in the focal plane which is predicted by geometric optics. Corrections to the interference conditions

$$(j + 3/4) \cong j_m f(z_j) \qquad (4)$$

for intensity zeros and

$$(j + 1/4) \cong j_m f(z_j) \qquad (5)$$

for intensity maxima where

$$f(z_j) = (2/\sqrt{\pi})\int_0^{z_j} e^{-\beta^2}\,d\beta - 2/\sqrt{\pi}(z_j e^{-z_j^2}) \qquad (6)$$

were obtained from Table I of reference 5. Obtaining from error function tables values of $e^{-z_j^2}$ corresponding to given values of $f(z_j)$ and rewriting equation 1 in the form

$$Y_j = C_t e^{-z_j^2} \qquad (7)$$

allows for the computation at any time, t', the apparent diffusion coefficient

$$D' = (j_m^2\lambda^2 b^2)/(4\pi C_t^2 t') \qquad (8)$$

A plot of D' *vs.* $1/t'$ and extrapolation to infinite time gives the true diffusion coefficient and an estimate of a time correction, Δt, which allows for slight initial boundary mixing.[7]

In the section which deals with the distribution of intensity in the Gouy fringe pattern, a comparison is made with the prediction of equation 22 in reference 4.

$$I(Y) = (16\pi^2K^2Dt)/\epsilon \left\{A_i(\alpha)\left[1 - \frac{2\alpha}{5\epsilon} + \frac{1}{\epsilon^2}\left(\frac{2\alpha^2}{7} + \frac{\alpha^5}{200}\right) - \frac{1}{\epsilon^3}\left(\frac{47}{675} + \frac{2347\alpha^2}{9450} + \frac{81\alpha^6}{14000}\right) + \ldots\right] + A_i^1(\alpha)\left[-\frac{\alpha^2}{10\epsilon} + \frac{1}{\epsilon^2}\left(\frac{17}{105} + \frac{8\alpha^3}{105}\right) - \frac{1}{\epsilon^3}\left(\frac{1223}{4725}\alpha + \frac{1163\alpha^4}{18900} + \frac{\alpha^7}{6000}\right) + \ldots\right]\right\}^2 \qquad (9)$$

where

$$\epsilon = (2\sqrt{\pi}j_m)^{2/3} \qquad (10)$$

and

$$\alpha = \epsilon[(Y/C_t) - 1] \qquad (11)$$

$A_i(\alpha)$ and $A_i^1(\alpha)$ are the Airy integral and its first derivative.

Results and Discussion

In Table I are collected results of the determination of relative intensities in the lower Gouy fringes. The significant comparison is between the experimentally determined ratios I_0/I_1, I_0/I_2 and I_1/I_2 for the lowest three maxima and the values for these ratios predicted by equation 9. Figure 2 is a plot of the relative intensity distribution in the lowest fringes which was obtained with the Airy Integral approximation by the Gosting–Onsager treatment for a 100 fringe pattern.[4]

Excellent refractive increment data are available for solutions of KCl[8] and sucrose[5] which permit the direct preparation of solutions to yield 100 fringes $\pm$ 0.03 thereby minimizing computational work. For moderate increments in concentration the diffusion process in aqueous sucrose solutions is nearly ideal.[5] The diffusion boundaries for KCl solutions are slightly skewed. For both systems the agreement with theory is established under favorable conditions within about 1%.

(7) L. G. Longsworth, This Journal, **69**, 2510 (1947).
(8) L. J. Gosting, *ibid.*, **72**, 4418 (1950).

TABLE I

OBSERVED RELATIVE INTENSITY DISTRIBUTION

t'	I_0/I_1	I_0/I_2	I_1/I_2
A. Sucrose, $\bar{c}$ = 1.1444 g./100 ml., Δc = 0.7652, j_m = 100.01			
1140	1.57	1.89	1.20
1410	1.54	1.86	1.21
1530	1.57	1.93	1.23
2280	1.62	1.95	1.20
2460	1.61	1.95	1.21
B. Sucrose, $\bar{c}$ = 1.1444 g./100 ml., Δc = 0.7652, j_m = 100.01			
1500	1.60	1.91	1.19
1560	1.60	1.90	1.19
2840	1.56	1.89	1.21
3360	1.60	1.94	1.22
C. Sucrose, $\bar{c}$ = 1.1444 g./100 ml., Δc = 0.7652, j_m = 100.18			
1260	1.58	1.94	1.23
3780–4000	1.61	1.95	1.20
	1.64	1.95	1.19
	1.64	1.93	1.18
D. KCl, $\bar{c}$ = 0.3322 moles/l., Δc = 0.22273, j_m = 99.97			
390 [a]	1.58	1.82	1.15
430 [a]	1.63	1.91	1.18
630–660	1.56	1.91	1.21
925–940	1.57	1.93	1.24
975–995	1.57	1.94	1.24
1055–1085	1.60	1.93	1.22
1110–1140	1.58	1.92	1.22
1165–1185	1.57	1.93	1.23
1215–1245	1.59	1.95	1.23
1275–1300 [a]	1.62	1.95	1.21
1700–1720 [a]	1.64	2.04	1.24
1900–2010 [a]	1.66	2.06	1.24
2155–2175 [a]	1.67	2.04	1.23
Av. of ratios	1.59	1.93	1.21
Theor. av.	1.58	1.93	1.22

[a] Omitted from averages for reasons discussed in the text.

Early in the diffusion process the measured values differ from theory for at least two reasons. First, at early times the speed of collapse of the fringe system and the rapid increase of intensity with time (the intensity for a given position in the fringe system $I_{(y)}$ is directly proportional to the time, t) causes obvious difficulties. This is evident in the 390 and 430 second data for KCl in Table I. As would be expected the measured ratios, I_0/I_1 and I_0/I_2 are low when the fringes are scanned upwards (390 seconds) and high when scanned downwards. Corrections could in principle be made if this first experimental difficulty were the only one encountered. Superposed on this effect is a second. Apparently the center of the index gradient curve (relating to the lowest fringe) remains non-Gaussian for some time after boundary sharpening is discontinued. Quite a bit of data collected on KCl solutions showed that the intensity in the lowest fringe is too high at very early times. Ratios as high as $I_0/I_1 = 2$ were measured and were strongly time dependent. There is no straight-forward way of correcting for this error.

After the pattern collapses considerably the measured intensity distribution agains differs from theory. This is understandable from a consideration of the ratios of the widths of the scanning slit and fringes. The finite width of the scanning slit ($\sim$10 μ) tends to suppress somewhat the true maxima, which effect is more pronounced the narrower the fringe. For comparable fringe widths the effects tend to cancel whereas the $I_{(0)}/I_{(1)}$ and $I_{(0)}/I_{(2)}$ ratios are high. Typical of this type data are the 2155 and 2175 second data for KCl in Table I.

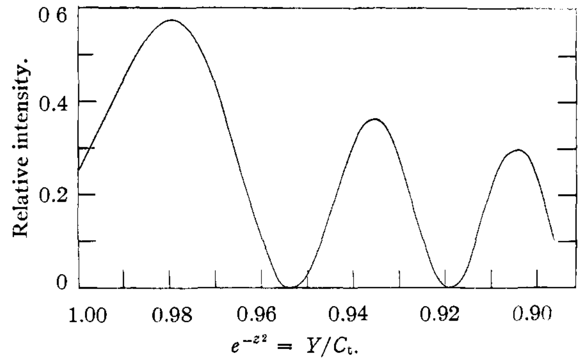

Fig. 2.—Relative intensity against e^{-z^2} for a 100 fringe pattern.

The data which have been chosen to compare with theory are those collected at intermediate times when no corrections were required. The values reported are, except when indicated, averages of the results from upward and downward scanning in the same time interval. The results are not measurably changed by slight alterations in masking, diffusion cell channel length or the position of scanning slit with respect to the true focal plane. The values reported represent measurements made during experiments which, photographically, were "good" runs. That is, correct values for D were obtained, negligible drifts in C_t were observed, and the time corrections estimated during sharpening agreed with those obtained experimentally.

In Table II are included data indicating the time dependence of the intensity in a Gouy fringe system. As seen in Fig. 3 the intensity of a given position in the Gouy pattern is directly proportional to elapsed time as predicted by equation 9.

Direct Recording Diffusion Experiments.—In the usual photographic technique the lower fringe minima (quite often excluding the lowest) are used in the computation of diffusion coefficients. Direct recording of intensity permits the utilization of both maxima and minima. The two techniques involving direct recording which were investigated will be considered separately.

1. Direct Recording with Fixed *Y*.—This method is very precise. Typical data for KCl solutions follow: $\bar{c} = 0.3322_0$ moles/liter, $\Delta c = 0.22099$, $j_m = 98.44$, $D = 1.8405 \times 10^{-5}$ with an average deviation of D' from the least square plot of D' *vs.* $1/t'$ of 0.04%. The Airy integral approximation is valid within the precision stated above for even the lowest maximum and minimum at times later than 1200 seconds. At earlier times the lowest maximum gives low values for D'.

TABLE II

TIME DEPENDENCE OF RELATIVE INTENSITY IN THE GOUY FRINGE SYSTEM

Measured I_0/I_1 = 1.58, theory I_0/I_1 = 1.58

t[a]	I_0[b]	I_1[c]	I_0/t	I_1/t
1842	49.6		269	
1877		32.5		173
1901		32.4		171
1926	51.5		267	
2243	61.1		272	
2275		39.2		172
2300		39.5		172
2322	62.4		269	
2486	67.4		271	
2560	69.4		271	
2712	73.8		272	
2738		47.5		174
2760		47.5		172
2782	75.4		271	
2963	81.1		274	
3009		52.5		174
3207	87.7		274	
3231		56.1		174
3252		56.3		173
3272	89.1		272	
3533	95.3		270	
3556		61.1		172
3577		61.3		171
Av.			271	172.5
Av. dev.			±0.6	±0.6

[a] t = time in seconds for the diffusion experiment corrected for the initial blurring (Δt = 27 sec.) of a sucrose-water boundary for which j_m = 100.27. [b] I_0 = relative intensity of zeroth maximum. [c] I_1 = relative intensity of first maximum.

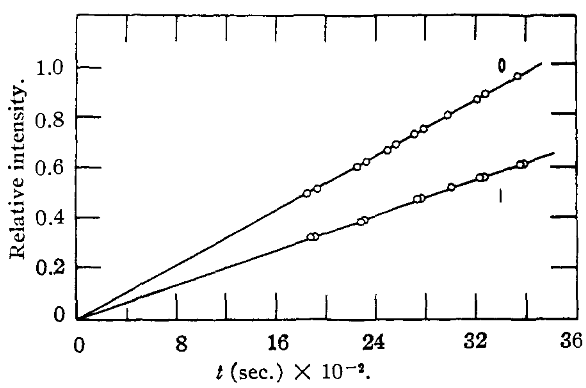

Fig. 3.—Relative intensity against time for the zeroth and first maxima.

Other experimental work in this Laboratory on other systems indicates a greater than normal drift in C_t for photographic data at quite early times. These facts are not inconsistent with the previous observation that the boundary early in the run is non-Gaussian in the region corresponding to the lowest fringe (24% of the gradient curve for a 100 fringe run). It has been pointed out[2] that the ordinary schlieren height–area determinations of diffusion coefficients should be high since the position of maximum contrast in the gradient peak is not as high in the gradient pattern as the correct location of C_t. It is interesting that for height–area determinations performed at early times there might be a small compensating error due to the non-Gaussian nature of the central part of the gradient curve which has been pointed out by these intensity and direct recording measurements.

This first recording method is limited in applicability since it can only reasonably be used for experiments involving normal boundaries. No information is available for fringes of high j values.

2. Direct Recording with Varying Y.—As previously mentioned, in this method the comparator was moved vertically with a calibrated synchronous motor at a speed of 50 μ per second. Since the strip-chart speed also was calibrated, the difference in time between the recording of a particular maximum or minimum and that of the undeviated slit image position was readily converted to a corresponding value of Y at a well defined value of t'. The computation is once again essentially the same as used in the conventional photographic technique and involves the use of equations 4, 5, 7 and 8 as well as the usual D' *vs.* $1/t'$ plot.

Typical results obtained by this method are

For sucrose solution: $\bar{c}$ = 0.7635 g./100 ml., Δc = 1.5270 j_m = 100.27

$D = 5.18_0 \times 10^{-6}$
$D = 5.16_5 \times 10^{-6}$
$D = 5.16_4 \times 10^{-6}$
$D_{(\text{photographic})} = 5.17_0 \times 10^{-6}$
$D_{(\text{estimated from data in reference 5})} = 5.16_7 \times 10^{-6}$

For KCl solution: $\bar{c}$ = 0.3322 moles/l., Δc = 0.2212, j_m = 99.31

$D = 1.83_6 \times 10^{-5}$
$D_{(\text{photographic})} = 1.840 \times 10^{-5}$
$D_{(\text{Gosting})} = 1.841 \times 10^{-5}$

The advantages in a method of this sort are manifest. It is rapid, objective, non-fatiguing and produces quite a bit of data for most of the gradient curve. Since it too provides an estimate of C_t from the zeroth maximum it would permit a much shorter extrapolation of $\sqrt{C_t}t$ against $Z^{2/3}$ to get the height–area diffusion coefficient of interest in three component studies.

While not so obvious, the disadvantages are nonetheless real. The average deviation of D' from the best least squared line of D' against $1/t'$ is about ± 0.1%. Some values of D' had to be entirely eliminated in the averaging being unaccountably high in error. No satisfactory data were obtained after 5000 seconds, even for the slow moving sucrose system, which made the extrapolation of the plot of D' against $1/t'$ less firm than usual. The extrapolation probably defined D no better than ± 0.2% as compared with about ± 0.1% for other methods. It is not felt that minor improvements in the experimental set-up such as working at a longer "b" distance or substitution of a more substantial screw than is now used would sufficiently improve the precision to make it competitive from this viewpoint with other methods.

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