

INTERFEROMETRIC MEASUREMENT OF A DIFFUSION COEFFICIENT

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Abstract: In this paper we present two methods to measure the diffusion coefficient in transparent media using electronic speckle pattern interferometry (ESPI). Although these methods are not new, it appears that they have not been compared, and that the proposed scheme of data treatment by least-squares adjustment for one of these methods has not been applied before. The methods were tested on a cell containing a 1.75 M NaCl solution diffusing into distilled water. Results using either method were very similar and they compare well with the value of the diffusion coefficient reported in the literature for the two substances.

Keywords: diffusion coefficients, interferometry, least-squares adjustment.

1. INTRODUCTION

The coefficient of diffusion of some substance in a fluid can be predicted theoretically or found from available experimental correlations [1-3]. However, values obtained with either procedure are only approximate. If greater precision is needed, experimental methods should be applied. Optical interferometry is one among the wide variety of techniques available. The procedure applies to transparent fluids, and is based on the fact that the concentration distribution in a diffusion process alters the optical path length of light that traverses the medium. By making this light interfere with a reference beam, the information encoded in the interference pattern can be used to reconstruct the concentration distribution, from which the diffusion coefficient may be inferred. Although classical interferometry can be employed, the techniques preferred currently are holographic interferometry and electronic speckle pattern interferometry (ESPI) [4].

A number of investigators have used interferometry to calculate diffusion coefficients for various mixtures from data obtained in diffusion experiments. To minimize practical difficulties, and to simplify the mathematical analysis, the experiments have consisted on cells in which one-dimensional vertical concentration distributions have been established.

Two different interferometric methods have been extensively reported in the literature. In the first [5-11], horizontal parallel fringes are obtained at various times after

diffusion has started; the diffusion coefficient is calculated by fitting the fringe data to the analytic solution of the one-dimensional diffusion equation. In the second method [12-22], one arm of the interferometer is tilted slightly between exposures; this produces curved fringes, the separation between the extrema of which allows calculating the diffusion coefficient directly.

In this paper we report on the use of both methods to obtain the diffusion coefficient of common salt in distilled water. The interferometer was of the Mach-Zehnder type and fringes were produced through the ESPI technique. Results are in good agreement with those published elsewhere [23].

2. THEORY

Consider a one-dimensional test section in which there is an index of refraction (IR) $n(y,t)$, where y is a Cartesian coordinate and t is the time. A coherent light beam of wavelength λ travels at time t_1 along a length d in the x direction and is made to interfere with a reference beam. The process is repeated at a later time t_2 . The two images are stored and then subtracted from each other. The theory of ESPI shows that bright fringes will appear on the resulting image at those values of the coordinate y that satisfy:

$$n(y,t_2) - n(y,t_1) = \frac{\lambda}{d} N_y \quad (1)$$

where N_y is an integer called the fringe order.

In general, the IR is a function of several parameters; one of them is the concentration of a species within the diffusion cell. For relatively small total differences in concentration, and if temperature is kept constant, one may assume that the IR in the cell is a linear function of the concentration, thus allowing to write

$$\Delta n = k \Delta C \quad (2)$$

where k is a constant of proportionality.

A monotonic one-dimensional IR distribution can be established by setting up a transparent diffusion cell where a

boundary separates two regions of a solvent with uniform but different initial concentrations of a certain species. Let the boundary be at $y = 0$ on the horizontal $x - z$ plane, and let it be carefully removed at time $t = 0$. If the initial concentrations at negative and positive values of y are C_0 and 0, respectively, the concentration at a later time t is:

$$C(y, t) = \frac{C_0}{2} \operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}}\right) \quad (3)$$

where D is the diffusion coefficient and erfc is the complementary error function. Equation (3) is well known; it corresponds to the solution of Fick's second law in one dimension for constant D .

By substituting equations (1) and (2) into equation (3), one gets

$$\operatorname{erfc}\left(\frac{y}{2\sqrt{Dt_2}}\right) - \operatorname{erfc}\left(\frac{y}{2\sqrt{Dt_1}}\right) = \delta N_y \quad (4)$$

where $\delta = \lambda/(kd)$ is the difference in concentration difference, at arbitrary times t_1 and t_2 after the start of diffusion, between consecutive fringes in the interferogram. The shape of the left-hand side of equation (4) is seen in figure 1.

It will be shown below that to obtain the coefficient D it is not required to know the laser wavelength, nor to measure the length of the cell, the proportionality constant k , or the initial concentration C_0 . However, the sensitivity of the interferometer is proportional to d , k and λ^{-1} , in that more fringes will appear for a given concentration C_0 if any one of these quantities is increased.

It should also be stressed that equation (4) assumes that the IR is linearly related to the concentration and that the diffusion coefficient is constant. Since in general both D and n depend on temperature, to obtain good results it is essential that temperature be kept as constant as possible during the diffusion process. Also, the initial concentration C_0 must not be too large, otherwise the linearity between n and C may be lost.

2.1. Method 1

In the first method one uses the fringe orders, so they must be numbered correctly, and their positions with respect to the initial boundary must be identified accurately. Either dark or bright fringes can be used, but the former are easiest to visualize. Fringe number 1 should correspond to the first dark fringe farthest from the initial boundary between the two concentrations, at either end. The rest of the fringes must then be numbered sequentially, as depicted for the first two dark fringes in figure 1. Then, from (4) one gets:

$$\frac{\operatorname{erfc}\left(\frac{y_i}{2\sqrt{Dt_2}}\right) - \operatorname{erfc}\left(\frac{y_i}{2\sqrt{Dt_1}}\right)}{\operatorname{erfc}\left(\frac{y_j}{2\sqrt{Dt_2}}\right) - \operatorname{erfc}\left(\frac{y_j}{2\sqrt{Dt_1}}\right)} = \frac{N_i}{N_j} \quad (5)$$

where y_i and y_j are the coordinates of the fringes with orders N_i and N_j , respectively.

In practice, it is more convenient to determine D by considering all possible combinations of fringes pairs. We can do this by minimizing the sum of squared residuals:

$$\chi^2 = \sum_i \sum_j \left[f_{i,j}(D) - \frac{N_i}{N_j} \right]^2 \quad (6)$$

where $f_{i,j}(D)$ is the left-hand side of equation (5), and where subscripts i and j include all fringe pairs that one can or wishes to take into account, but considering each pair only once.

Despite the simplicity in its derivation, it appears that equation (6) has not been used by other investigators. However, other types of least-squares fitting procedures are described in [5-11].

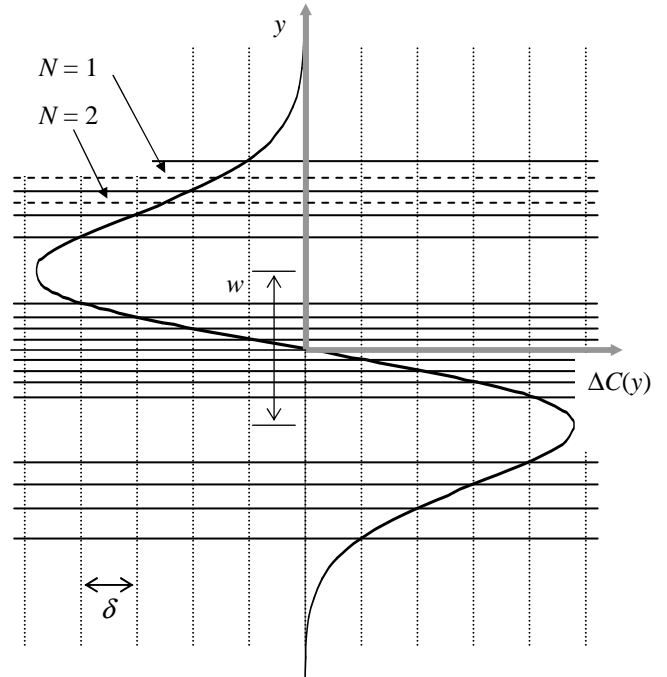


Fig. 1. Profile of concentration difference at two given times after starting the diffusion process. The initial boundary is at the grey horizontal axis ($y = 0$). The black horizontal lines correspond to the bright fringes observed in method 1. Dark fringes are in between. In order not to crowd the figure, only the first two dark fringes at the top are shown with dashed lines. Fringes in method 2 reproduce the curved concentration profile.

2.2. Method 2

In the second method one uses the separation w between the maxima of the profile given by equation (4), see figure

1. As was first derived in [12], the diffusion coefficient is then given explicitly by:

$$D = \frac{w^2}{8} \frac{t_1^{-1} - t_2^{-1}}{\ln(t_2/t_1)} \quad (7)$$

To apply equation (7) one needs to measure only the times t_1 and t_2 , and the separation w . The problem is that this separation cannot be measured from an interferogram such as depicted in figure 1, because from the fringe positions it is not possible to know where the maxima occur.

This problem was solved in [13], where it was realized that, by adding a system of carrier vertical fringes before the second exposure, the resulting system of curved fringes will follow precisely the shape described by equation (4), thus allowing distance w to be measured directly from the interferogram.

Being simpler than method 1, method 2 has been used more often [14-22].

3. EXPERIMENTAL PROCEDURE

Experiments were carried out on a cell made of two sheets of glass, 2 mm thick, 50 mm high and 30 mm wide. A distance $d=7$ mm separated the inside of the glass surfaces. A 1.75 M solution of NaCl and distilled water was prepared and kept inside the air-conditioned room where the experiments were carried out.

The experimental setup was as shown in figure 2. It consisted of a Mach-Zehnder interferometer illuminated by a 35 mW He-Ne laser. The beam was first passed through a neutral density filter to avoid saturating the CCD camera. It was then divided by a beam splitter. Both arms of the interferometer were spatially cleaned, collimated and recombined by a second beamsplitter after the object beam passed through the diffusion cell. To minimize the influence of refraction, an object lens was used to relay the image of the cell onto an opal screen, to which the camera was focused.

The cell was first half-filled with distilled water. After allowing for residual motions to dissipate, the salt solution was slowly injected from below using a powered syringe; this took about 30 s. Time was measured from the time injection was stopped. Images were then captured and stored each 5 min. During this time, the temperature in the laboratory was monitored with a mercury thermometer; to within 0.1 °C, it was stable at 23.5 °C.

The two methods were used on the same experiment. To achieve this, after the first 45 min the object mirror (M3 in figure 2) was tilted some 50 μ rad about the vertical axis by using a piezoelectric actuator. This introduced the carrier fringes that method 2 requires.

After completion of the experiment, the stored images were subtracted using an image processing software. In method 1, subtracted images corresponded to those acquired either before or after tilting the mirror. In method 2, it was

necessary to subtract images taken after the tilt from those acquired before the tilt.

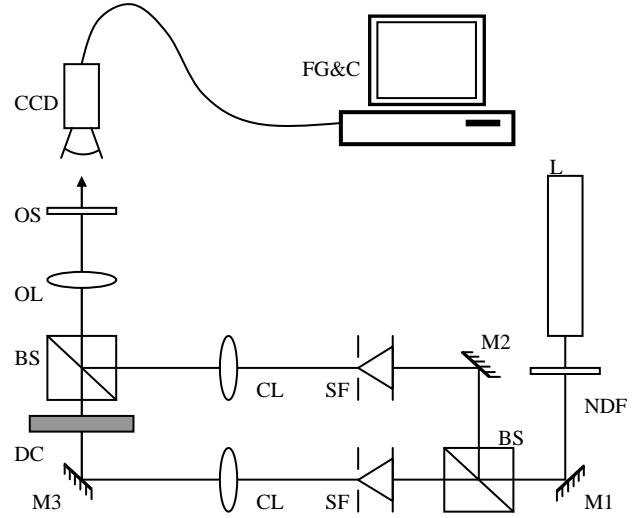


Fig. 2. ESPI interferometer. BS: beam splitters; CL: collimating lenses; DC: diffusion cell; FG&C: frame grabber and computer; L: laser; M: mirrors; NDF: neutral density filter; OL: object lens; OS: opal screen; SF: spatial filters.

Figure 3 illustrates typical interferograms corresponding to both methods. The image on the left, with horizontal fringes, corresponds to method 1; it was obtained by subtracting images obtained after tilting the mirror, at 75 min and 60 min. The image on the right, with curved fringes, corresponds to method 2; it was obtained by subtracting images at 45 min (right after the tilt) and 40 min (just before the tilt).

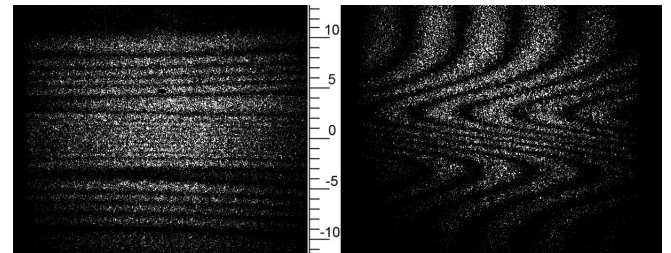


Fig. 3. Interferograms for methods 1 (left) and 2 (right). The vertical scale is in millimeters; the boundary is at the zero of the scale.

Processing the interferograms according to equation (6) gave a diffusion coefficient of $1.4293 \times 10^{-9} \text{ m}^2/\text{s}$. The second method, equation (7), gave $1.4297 \times 10^{-9} \text{ m}^2/\text{s}$. These results apply for a temperature of 23.5 °C and are in excellent agreement with those published elsewhere [23,24].

4. CONCLUSIONS

In this paper we have presented two interferometric methods to measure the diffusion coefficient of a transparent solution. Both methods are relatively easy to implement. Although they are not new, it appears that they have not

been compared, and that the proposed scheme of data treatment by least-squares adjustment for one of these methods has not been applied before.

The methods were tested on to the same experiment to measure the diffusion coefficient of common salt diffusing into distilled water. Results using either method were very similar and they compare well with the value of the diffusion coefficient reported in the literature.

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