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Rapid yet accurate measurement of mass diffusion coefficients by phase shifting interferometer

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Abstract. The technique of using a phase-shifting interferometer is applied to the study of diffusion in transparent liquid mixtures. A quick method is proposed for determining the diffusion coefficient from the measurements of the location of fringes on a grey level picture. The measurement time is very short (within 100 s) and a very small transient diffusion field can be observed and recorded accurately with a rate of 30 frames per second.
The measurement can be completed using less than 0.12 cc of solutions. The influence of gravity on the measurement of the diffusion coefficient is eliminated in the present method. Results on NaCl–water diffusion systems are presented and compared with the reference data.

1. Introduction

Diffusion in transparent solution can conveniently be studied by means of optical interferometer. Both conventional interferometer and holographic interferometer have been employed. Compared with the conventional interferometer, holography requires simpler elements and less effort as pointed out by Bochner and Pipman [1]. In a holographic interferometer one is able to record the fringe which is a line of equal phase difference between waves coming through the cell at two moments of time. This kind of double-exposed holography has been applied to the study of diffusion [2, 3]. However, the aforementioned works involved long measurement times (5000 to 20 000 s) and the diffusion fields were observed over a large area. Hence, the effects of the environment and the gravitational field are unavoidable. Moreover, large errors may be introduced due to the difficulty in determining the location of two peaks in the differential concentration profile [2].

A phase shifting interferometer (PSI) was developed in the 1970s by Bruning *et al* [4]. The most important improvement of this technique as compared with the conventional interferometer is the great increase of phase resolution. This interferometer searches an object by scanning the interference fringes, which enables a detailed pattern to be obtained all over the observed area. Because of the enhanced information, one can detect a local profile between the two neighbouring fringes on an atomic level. This technique has been used to investigate surface phenomena in crystal growth processes [5, 6]. Because of the high spatial and time resolutions in the PSI technique, it can be employed to study the real time diffusion field in a small diffusion area.

We used the spatial phase-stepping interferometer to investigate the diffusion field in a small area. A simple mathematical formulation was derived which allows the immediate deduction of the diffusion constant. The measurement time is much shorter compared with the conventional methods and the result is accurate. The influence of gravity is also discussed.

2. Experimental procedures

A schematic diagram of the experimental system is shown in figure 1, in which the optical system is a Mach–Zehnder interferometer. However, higher accuracy is attained by using the phase-shifting technique [5] as compared with the conventional interferometer. The refractive index of the dilute liquid solution varies linearly with the concentration of solute. As a result, the interferometer, which records the change in the refractive index, can be used to determine changes in the concentration profile.

A laser diode beam is separated into reference and measurement beams by a polarizing beam splitter. The planes of electric field of these two beams are perpendicular to each other. After passing a compensator and a test cell, the beams are mixed by another beam splitter. The beams do not interfere since the polarized planes are perpendicular with respect to each other. A quarter-wave plate is placed in front of the charge coupled device (CCD) camera, so that the two linearly polarized beams become right- or left-circularly polarized before entering into the phase dividing 3-CCD camera. The camera has three polarizers and a specially made 3-CCD dichroic prism, in which three CCD sensors are fixed, as shown in figure 1. The dichroic prism is modified from a commercial product (Olympus Co Ltd). Mutual alignment of

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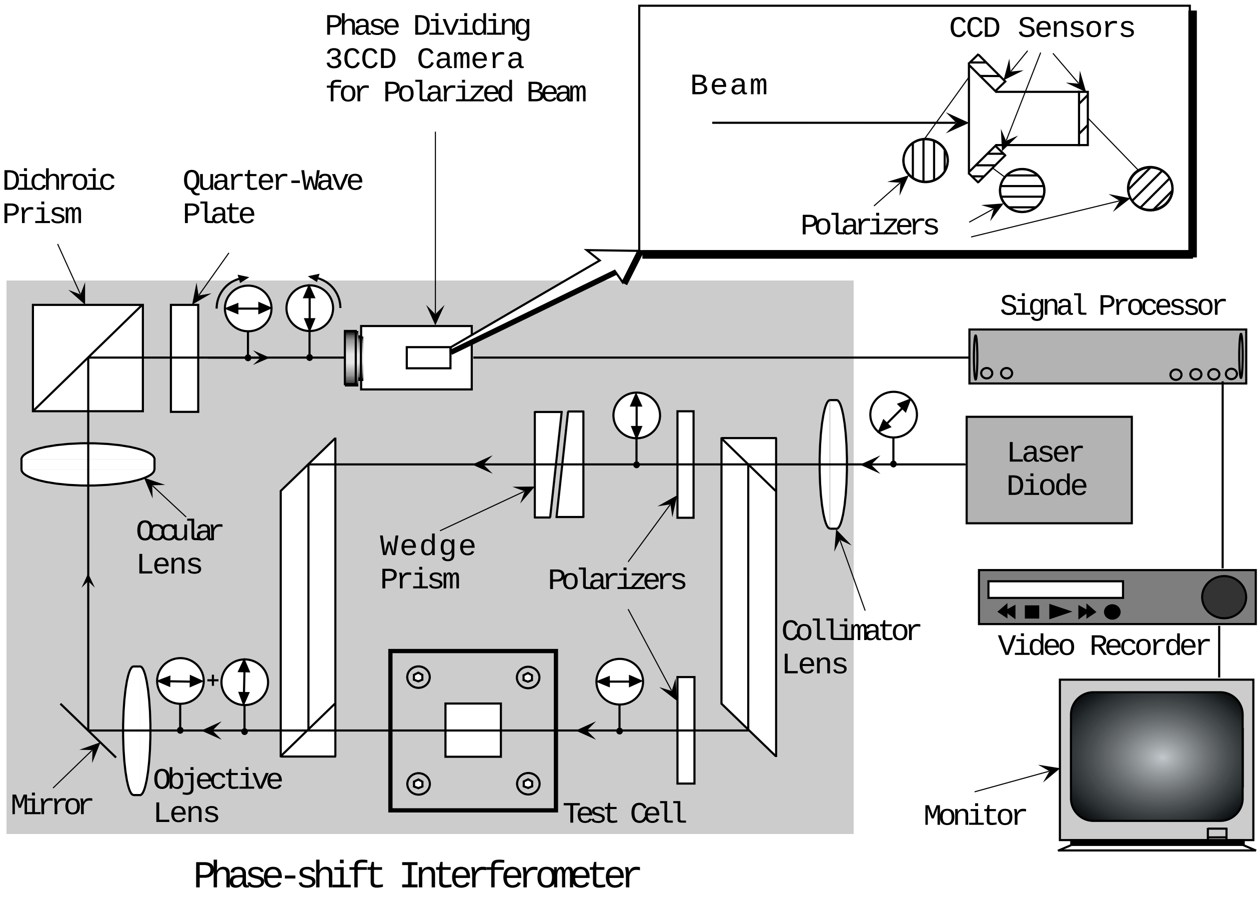


Figure 1. Schematic sketch of the experimental system.

the three CCD sensors is the same as the commercial one. The three polarizers are set with their directions $-\pi/4$, 0 and $\pi/4$ to the beam direction, resulting in three interferograms whose phases shifting $\lambda/4$ with respect to each other. Uncertainty of the phase shift data was investigated by Nakadate and Isshiki [7], and it was estimated that the error of the phase data is less than $\lambda/100$ if the signal-to-noise ratio is less than 1%. This accuracy is extremely better than the conventional Mach–Zehnder interferometer.

The specially designed shearing test cell is composed of a quartz glass case and two liquid baths made of polytetrafluoroethylene (TEFLON), as shown in figure 2. The inner surface of the quartz glass was coated to provide water resistance. The denser solution is put into the lower bath first. Next the lighter solution is injected into the upper bath through a hole. The two baths are initially separated so that a sharp step change of concentration field is achieved as an initial condition. The upper bath is gently slid to match with the lower bath. Compared with other methods [1–3], the present test cell is less disturbed at the initial diffusion stage. The size of each bath is 1 mm wide, 10 mm thick and 6 mm high. Only 0.12 cc solution is enough for the two baths in the present experiment. The aspect ratio of thickness to width is 10:1, so that the diffusion field can be treated as a one-dimensional process.

A small area of diffusion field (2 mm in height) is observed and recorded by the 3-CCD camera. The interferograms of the transient diffusion field are processed by a rapid signal processor [5] and transformed into phase shifting data. The phase values are displayed as grey scale pictures from 0 to 255 which correspond to $-\pi/2$ to $\pi/2$. The pictures are recorded on videotape with the rate of 30 frames per second.

3. Analysis

The equation of phase distributions $\Phi(x, y)$ on the observed x–y plane (central line located at the interface of the two baths) is expressed as [8]

$$\Phi(x, y) = \tan^{-1}[(I_1 - I_2)/(I_2 - I_3)]. \tag{1}$$

I_j $(j = 1, 2, 3)$ are interferograms which are formed after passing the three polarizers. This equation is also a function of the refractive index difference Δn as follows:

$$\Phi(x, y) = \frac{2\pi}{\lambda}\Delta n l \tag{2}$$

in which l is the path length of the diffusion field. Since the phase value is expressed by a grey level changes of 256 patterns, the minimum difference of the refractive index detected is

$$\Delta n_{min} = \Delta\Phi_{min}\frac{\lambda}{2\pi l} = \frac{1}{256}\frac{\lambda}{l}. \tag{3}$$

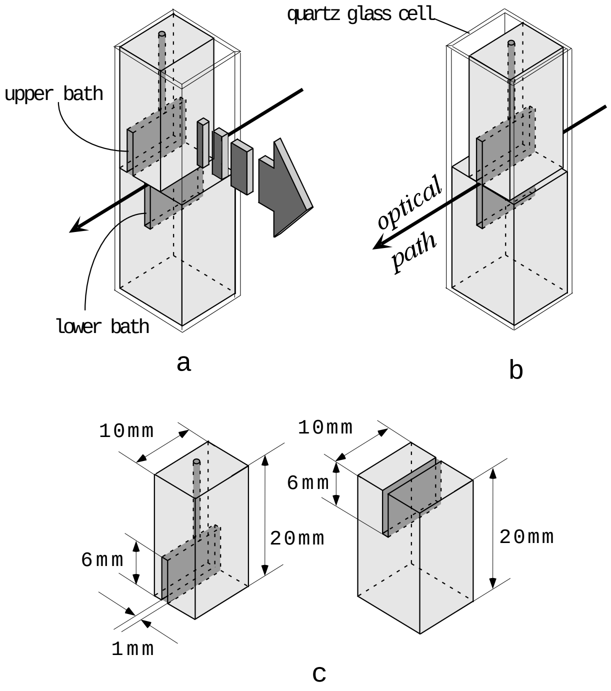


Figure 2. Design of the test cell: (a) the positions of the two baths before experiment; (b) the positions of the two matched baths in the experimental process; (c) the size of the baths.

The grey level fringe repeats every π phase difference. This means that the grey level picture changes from black to white in each neighbouring fringe. The location of the fringes and the distance between any two neighbouring fringes can be used to determine the diffusion coefficient in a method described in the following.

In the presence of a gravitational field, the diffusion of a liquid solution of concentration $C(x,t)$ obeys [9]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 x} - \mu g\frac{\partial C}{\partial x} \tag{4}$$

in which D is the diffusion coefficient, assumed to be independent of concentration, since the experiment was carried out for a small difference in concentration, μ is a parameter that represents the drift of the molecules due to gravitational field. It is well known that the lighter molecules will drift upwards and the heavier ones will drift downwards in the presence of gravitational force. The influence of gravity is the so-called barodiffusion effect in liquid solution [10]. The parameter μ is also assumed to be independent of concentration in dilute liquid solutions. In the present method we will find that the term due to gravity in (4) does not affect the measurements of the diffusion coefficient.

The solution of (4) is an error function of the form

$$C(x,t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2}\mathrm{erf}(\mathrm{z}) \tag{5}$$

where

$$\mathrm{erf}(\mathrm{z}) = \frac{2}{\sqrt{\pi}}\int_0^{\xi} \exp(-\mathrm{z}^2)\,\mathrm{dz} \tag{6}$$

and

$$\xi = \frac{x - \mu g t}{2\sqrt{Dt}}. \tag{7}$$

In the above, C_1 and C_2 are the initial concentrations of the two solutions. The influence of gravity is reflected in (7), in which the central diffusion location x_0 ($C(x_0,t) = (C_1 + C_2)/2$) will drift upwards (drift velocity $= \mu g$) as time advances.

For a fixed time instant, the change of concentration is $\mathrm{d}C = (\partial C/\partial x)\,\mathrm{d}x$. Hence, the change of concentration between two neighbouring fringes located at X_i and X_{i+1} is

$$\Delta C = \frac{\mathrm{e}^{-\xi^2_{i+1/2}}}{2\sqrt{Dt}}(X_{i+1} - X_i). \tag{8}$$

Here we introduce a new coordinate X and $X = x - \mu g t$. The change of concentration is linearly proportional to the change of refractive index. Since the change of refractive index is constant between any two neighbouring fringes, we find

$$\frac{\mathrm{e}^{-\xi^2_{i+1/2}}}{2\sqrt{Dt}}(X_{i+1} - X_i) = \frac{\mathrm{e}^{-\xi^2_{j+1/2}}}{2\sqrt{Dt}}(X_{j+1} - X_j). \tag{9}$$

Finally the diffusion coefficient can be calculated by

$$D = \frac{X^2_{i+1/2} - X^2_{j+1/2}}{4t}\left(\ln\frac{X_{i+1} - X_i}{X_{j+1} - X_j}\right)^{-1} \tag{10}$$

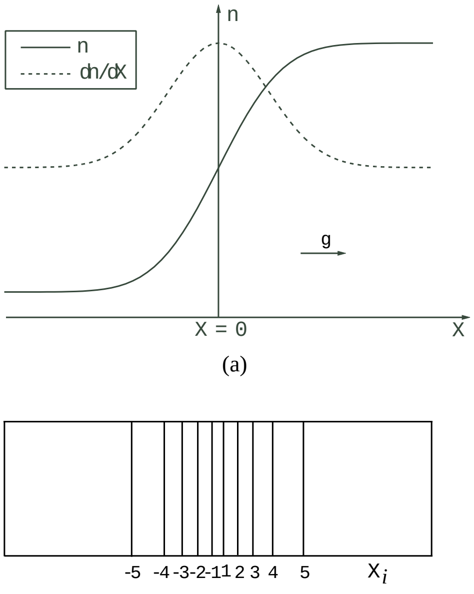
in which, $X_{i+1/2} = (X_i + X_{i+1})/2$ and $i \neq j$. This equation depends only on the locations of the fringes and the location difference between any two neighbouring fringes. Since $\mu g t$ is constant for a fixed time instant, the effect of gravity is eliminated in (10) due to the use of the new coordinate X.

4. Experimental results

Since the refractive index of the solution is linearly proportional to the concentration, the profile of the refractive index has the same shape as the profile of concentration. Figure 3(*a*) shows the profiles of the refractive index and the gradient of the refractive index at time instant t. Consequently, the profile of the fringes is shown in figure 3(*b*). In our experiments, the fringes are changed from black to white with 256 grey level patterns. The fringes schematically shown in figure 3(*b*) are only the black lines.

From figure 3(*a*), it can be seen that the gradient of the refractive index is a maximum at the location $X = 0$. This means that the distance between two neighbouring fringes is a minimum around the location of $X = 0$ as shown in figure 3(*b*). The location of $X = 0$ is decided by the narrowest patterns between two neighbouring fringes with minimum distance. After determining the location of $X = 0$, the locations of other fringes can be measured. Figure 4 shows the fringe profile at time instant $t = 60$ s in a real experimental run with NaCl solution (0.25 wt%) at room temperature (298 K). A set of real-time fringe profiles like figure 4 is recorded on a videotape starting from $t = 0$. From each fringe profile at any time instant a value of the diffusion coefficient D is deduced from (10).

The results are shown in table 1 measured from the grey level pictures at several specific time instants. The error in table 1 is the standard statistical error of the mean value obtained from different neighbouring fringes. The totally



(a)

(b)

Figure 3. (a) Profiles of the refractive index and the gradient of the refractive index at time instant t; (b) profile of black fringes.

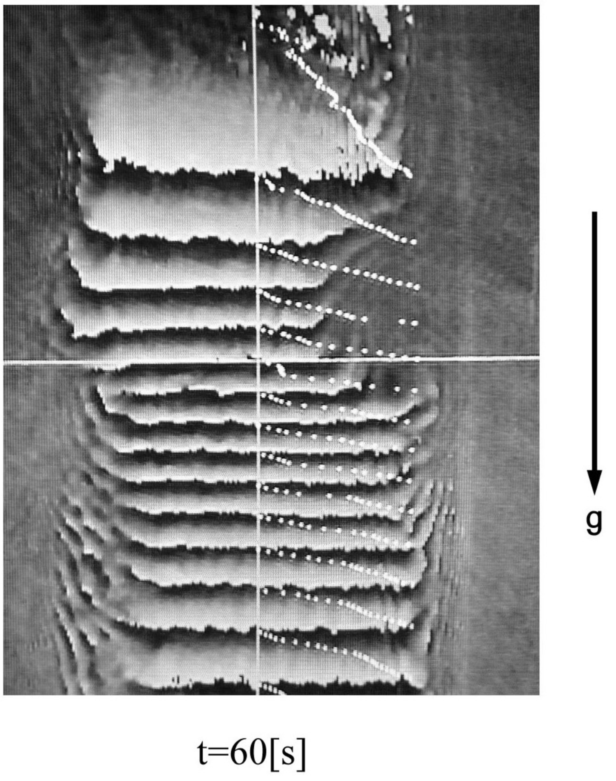


Figure 4. The measured fringe profile in the experiment run at time instant $t = 60$ s.

averaged value of D in table 1 is 1.554×10^{-9} m^2 s^{-1}. Compared with the reference datum of $D = 1.507 \times 10^{-9}$ m^2 s^{-1} [11], a good agreement was found. When the experiment time is not less than 60 s, the accuracy of the measurement of the diffusion coefficient is within 2% at each time instant.

Table 1. Summary of data in one experimental run at several time instants. note: n is the number of the measured diffusion coefficients.

t (s)	n	D (10^{-9} m^2 s^{-1})
30	15	1.789 ± 0.357
45	15	1.559 ± 0.104
60	15	1.499 ± 0.051
75	15	1.484 ± 0.056
90	15	1.487 ± 0.040
100	15	1.508 ± 0.037

5. Discussion

The essential feature of the present method is that the measurement is finished in a very short time and in a small diffusion area. The accuracy is high and the measurement can be achieved by using small amount of solution. A number of measurements of the diffusion coefficient can be made on each interferogram. The total number of measurements is equal to $(m-1)(m-2)/2$, where m is the number of fringes recorded on the grey level picture. This character ensures an accurate mean value of D. Another important feature of the present method is that the influence of gravity on the calculation of D is eliminated due to the measurement of X.

The effect of gravity on the diffusion field is displayed by the drift of the location of $X = 0$. It is found that the location of $X = 0$ drifts upwards by the observation of the real-time fringe profiles. However, the drift velocity is very small since the test cell is so small that only 0.12 cc solutions are enough for the experiment. The drift distance after 1000 s is less than 0.01 mm. Compared with the measurement area (2 mm) and the measurement time (within 100 s), such a small drift is negligible.

From figure 4 it is found that the location of $X = 0$ is lower than the location of the interface between the two baths. Because of the surface tension of the heavy solution in the lower bath, it is difficult to fully fill the lower bath with liquid solution. When the upper bath is corrected to the lower bath, the interface goes down due to the weight of the upper liquid. The difference of location between $X = 0$ and the interface is usually in the range of $0.02 \sim 0.04$ mm in our experimental runs. This induces a slight disturbance in the diffusion field at the initial time stages. However, we found that the disturbance disappeared after about 2 s. The initial disturbance in our test cell is smaller compared with the frozen cell method [1] and the lifting injection method [3]. Because of the initial disturbance in the diffusion field, the results measured before $t = 50$ s are somewhat questionable. From table 1 it can be seen that the result at $t = 30$ s deviates from the reference datum by about 20%. If we do not take account the diffusion coefficient measured at $t = 30$ s in table 1, the mean value of D is $(1.507 \pm 0.027) \times 10^{-9}$ m^2 s^{-1}, which is almost equal to the reference datum of $D = 1.507 \times 10^{-9}$ m^2 s^{-1}. The accuracy of the method is estimated to be within 2%.

The validity of the assumption of the one-dimensional diffusion process is demonstrated by the straightness of the fringes of the cell as shown in figure 4. The measurement of locations is done along the centre of the fringes. The deflection at the edge of the fringes does not affect the measurement. The disturbance at the right-hand edge of the fringes above the interface shown in figure 4 is caused by a small bubble which is difficult to remove from the present test cell. However, it does not influence the diffusion field.

The accuracy of an individual measurement in the present method could be improved by more accurate measurement of the fringe locations. In the present measurements, the location data were obtained by a ruler measurement. If the data were analysed by a computer signal processor the results would be more accurate. A possible source of error in the present experiment arises from the temperature control in the experimental process. The experimental system was placed in a specially designed working space, where the room temperature was controlled by an air-conditioner. However, the diffusion can be considered as a constant temperature process since the experiment is completed in a very short time period. This is also one of the advantages of the present method over other methods which need long periods of time for measurement.

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