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# FAST MEASUREMENTS OF GAS-LIQUID DIFFUSION COEFFICIENT IN THE GAUSSIAN WAKE OF A SPHERICAL BUBBLE

N. DIETRICH\*, J. FRANCOIS, M. JIMENEZ, A. COCKX, P. GUIRAUD, G. HEBRARD

Université de Toulouse; INSA; LISBP, 135 Avenue de Rangueil, F-31077 Toulouse, France

INRA, UMR792, Ingénierie des Systèmes Biologiques et des Procédés, F-31400 Toulouse, France

CNRS, UMR5504, F-31400 Toulouse, France

Fédération de Recherche FERMAT, CNRS, Toulouse, 31400 Toulouse, France

\* Corresponding Author: Nicolas Dietrich

E-mail: [Nicolas.Dietrich@insa-toulouse.fr](mailto:Nicolas.Dietrich@insa-toulouse.fr) Phone number : 335-61-55-97-81 Fax : 335-61-55-97-60

**Abstract:** A fast method is proposed for determining the oxygen gas-liquid diffusion coefficient from measurements of the fluorescence quenching behind a bubble. The approach consists of capturing pictures of concentration field at micro-scale in the laminar bubble wake. The Gaussian concentration profiles measured in the wake are demonstrated to be systematically equivalent to an instantaneous plane diffusion case. It permits to evaluate accurately the gas-liquid diffusivity in a very short time around one second.

**Keywords:** diffusion, gas-liquid, bubble, wake, oxygen

## Introduction

Transport properties, such as conductivity, viscosity, and mass diffusion coefficients, are important in the design of chemical processes. In particular, the molecular diffusion coefficient,  $D$ , is one of the most important physical properties to characterize the nature of molecules in solution phase from both the scientific and technological viewpoints. According to Fick's law (1855), it is defined as the constant ratio of proportionality between molecular flux and concentration gradient of the species. In physical and, above all, chemical processes, the mass transfer rate is governed by convection, turbulence of flow and molecular diffusion. Therefore, much research has been carried out on the measurement of diffusion coefficients since the first experiments on the subject (Graham 1829). The diffusion coefficient plays an important role in many processes (such as petrochemical processes, biological reactors, and waste water treatment) because it is required for the solution of the governing equations of mass transfer

phenomena. Extensive research has been conducted on the diffusion coefficient over more than a hundred years, and it is well recognized that  $D$  reflects not only the molecular size or solution viscosity but also the shape of the molecule and the intermolecular interaction. Several measurement methods have been developed, such as the steady state method (Tham et al. 1967), absorption measurement (Sovová & Procházka 1976), bubble size calculation (de Blok & Fortuin 1981), interferometry (Guo et al. 1999), optical probes (Bowyer et al. 2004), chemical reactions (Jamnongwong et al. 2010), etc.

But classical determination methods present some limitations because of measurement by probes, intrusive and indirect technique, to which should be added hydrodynamic perturbation, natural convection, long response time, impact of the liquid media, etc. (Blackadder & Keniry 1973; Blackadder & Keniry 1974). Thus available experimental data on mass diffusion coefficients are actually not sufficient because of the complications of the system and difficulties of the experimental measurements. Therefore, the objective of this study is to develop a new method for obtaining the oxygen diffusion coefficients through short-time and non-intrusive measurement in order to establish a new data base. The system uses an optical technique for accurate measurement of small transient diffusion areas. The target materials in this study are transparent solutions of several concentrations and species.

In order to contain and control the hydrodynamics, the measurement is performed in the wake of a spherical bubble. The flow in the wake of the bubble is totally controlled and occurs in the same direction  $z$  as the bubble rising velocity  $U_B$  (Oseen 1910). The velocity profile  $V_w$  in the wake has a Gaussian profile given by:

$$V_w = \frac{Q_0 U_B}{4\pi\nu z} e^{\left(\frac{-U_B r^2}{4\nu z}\right)} \quad (1)$$

Where  $Q_0$  is the wake flowrate and  $\nu$  the cinematic viscosity. This solution is valid far from the bubble and expresses a two-dimensional configuration ( $r, z$ ). Close to the single bubble, the potential contribution has also a significant contribution and a near-wake solution was described by Hallez & Legendre (2011).

Unlike for free gas-liquid interface plane, where natural convection occurs, this forced convection situation is perfectly controlled. Planar Laser Induced Fluorescence with Inhibition (PLIFI, Jimenez et al. 2013) present a non-intrusive alternative method. This technique is based on the addition of a fluorescent molecule absorbing light (wavelength  $\lambda_a$ ) that re-emit an amount of the received energy (wavelength  $\lambda_f$ ). The principle of the PLIFI technique is to illuminate a fluid containing the fluorescent dye with a laser sheet and acquire images of the

studied solution in the enlighten area with cameras. These molecules are called quenchers because they can inhibited the fluorescence (Francois et al. 2011; Dani et al. 2007). It is observed that the fluorescence intensity decreases with the increase of the quencher concentration following the Stern-Volmer equation (1919):

$$\frac{I_Q}{I_0} = \frac{1}{1 + K_{SV}[Q]} \quad (2)$$

$K_{SV}$  is the Stern-Volmer constant ( $L \cdot mg^{-1}$ ),  $I_Q$  the fluorescence intensity and  $I_0$  this intensity in the absence of quencher. Several works have presented the possibility of visualizing the oxygen concentration field (Herlina & Jirka 2004) or in the wake of a single bubble (Francois et al. 2011a & 2011b, Jimenez et al. 2012, 2013a & 2013b). Qualitative measurements have been obtained for the oxygen transferred in the wake of a rising bubble (Someya et al. 2005; Dani et al. 2007; Bork et al. 2005; S. Roy & S. R. Duke 2000 & 2004; François et al. 2011a & 2011b; Kerbeche et al. 2013; Dietrich et al. 2013b; Jimenez et al. 2013a, 2013b & 2014) and also for the carbon dioxide concentration map around a single bubble (Stöhr et al. 2009; Someya et al. 2005).

The main limits of the PLIFI technique results from the light reflection and refraction on the bubbles surfaces. A light ring is observed around the bubble, with a shadow on the side of the bubble creating a strong contrast between the both sides of the picture. Considering these results obtained in previous works, the PLIFI technique appears quite promising despite its obvious optical limitations. Some authors (François et al. 2011a & 2001b, Jimenez et al. 2013b) proposed an alternative configuration to avoid these problems in order to follow the oxygen concentration field in the wake of bubbles. In this configuration, the laser sheet was perpendicular to the bubble trajectory and horizontal sections in the bubble wake were obtained. From these experiments, a mass transfer coefficient was calculated and we propose to develop in this paper a new approach to calculate fluid properties of the liquid from this alternative configuration.

## **Materials and Methods**

The experimental set-up Fig. 1(a) consists in a glass column ( $0.1 \times 0.1 \times 0.3 \text{ m}^3$ ) transparent with a side fitted with the system of injection (1) to generate bubbles of specific sizes (Dietrich

et al. 2013a & 2013c). It was composed of a thin glass capillary (diameter order of 100  $\mu\text{m}$ ) linked to a syringe pump (Harvard PHD 2000). The tank was filled with a fluid enclosing the fluorescent dye (ruthenium-complex  $\text{C}_{72}\text{H}_{48}\text{N}_8\text{O}_6\text{Ru}$  from Nanomeps, France) at a concentration of 30  $\text{mg.L}^{-1}$ . A laser sheet was generated (2) by a Nd:Yag laser (3) ( $\lambda_a = 532 \text{ nm}$ , 10 Hz, 200 mJ) in the horizontal xy plane. As shown on figure 1.b, the laser sheet is perpendicular to the bubble trajectory. A 12 bits Charge-Coupled Device camera (4) (Imager Intense, LaVision, Germany, 10 Hz, 1040 x 1376 pixels<sup>2</sup>) was placed below the column along the vertical z axis, i.e. perpendicularly to the laser plane, to acquire picture of the fluorescence emitted by the fluid. A 105 mm objective with three teleconverters were fitted to the camera to reach a spatial resolution of 2.3  $\mu\text{m}.\text{pixel}^{-1}$ . In order to visualize only the fluorescence, a 570-nm high-pass filter (5) was used.

A Programmable Trigger Unit (LaVision, Germany) synchronize the camera and the laser device. A second camera (PCO 1200, Germany, 10 bits, 770 Hz 1024 x 1280 pxl<sup>2</sup>) was placed on the lateral side (6) of the column (y axis) to record at a high frequency the bubble movement and then make possible the measurement of bubble size and bubble velocity. A 60 mm objective was fitted to this camera (55  $\mu\text{m}.\text{pixel}^{-1}$ ).

## Results

For each experimentation, the solution was previously deoxygenated with nitrogen. Then a single bubble (two sizes:  $d_B \approx 1.5 \text{ mm}$  and  $d_B \approx 0.7 \text{ mm}$ ) of oxygen was formed in the immobile fluid. The experimental conditions are presented in Table 1.

Experiment n°	glycerol % w/w	$\mu$	$d_B$	$U_B$	$Re$	$Flux$
		$10^{-3}$ Pa.s	mm	$\text{m.s}^{-1}$		$10^{-3} \text{ g.m}^{-2}.\text{s}^{-1}$
1	43	58	1.88	0.047	1.8	0.208
2	18	7.0	1.29	0.117	26	1.43
3	18	7.0	0.72	0.032	3.4	1.05
4	8	2.6	1.30	0.203	107	4.96

5	8	2.6	0.78	0.071	22	1.78
6	0	1.0	0.72	0.110	74	7.43

**Table 1.** Hydrodynamic conditions for the six sets of experiments at 20°C.

The image processing, using Matlab software, of the high speed camera images permit the calculation of the bubble diameter,  $d_B$ , and velocity,  $U_B$ . Then the distance  $z$  between a fluorescent recording and the position of the bubble could also be determined.

The different oxygen concentration field cross-sections in the bubble wake were then recorded with the CCD camera at a frequency of 10 Hz. As an example, a raw image is displayed on Fig. 1.c. For a recording, the information was originally acquired in gray values and then converted into mass concentration with the suitable calibration curve (Eq. 2). Figure 2 displays six superimposed elevated cross-sections recording with approximately  $100 d_B$  distance between them. It acts that the oxygen concentration fields appears symmetric with a 3D Gaussian profile forming a concentric, rounded gradient of oxygen with the maximum concentrations at the centre of the spot. On this figure, a diffusion phenomenon is discernible, with a substantial flattening and widening with the time and distance far from the bubble ( $t = 0$  is chosen for the first picture).

## Discussion

The validity of the assumption of a two-dimensional diffusion process is demonstrated by the straightness of the symmetry of the oxygen spots. From these concentration fields, one can estimate the flux value calculated at successive distances  $z$  from the bubble:

$$Flux = \frac{2.U_B}{d_B^2} \int_0^{\infty} [O_2] r.dr \quad (3)$$

After the near wake of the bubble (corresponding approximately to  $z = 10\sqrt{Re}$ ), the oxygen flux (Eq. 3) becomes constant and corresponds to the total amount of mass transferred by the single bubble (Francois et al. 2011). The convection in the wake becomes essentially axial (Eq. 1) whereas the oxygen transport is essentially radial and dominated by diffusion (Fig 3.a). In terms of time, it corresponds to about [1 s - 1.3 s] after the bubble passage. The oxygen concentration profile  $[O_2]$  is measured from the bubble wake cross section images. A sample of averaged ortho-radial oxygen concentration profiles acquired at different times is plotted in Fig. 3(a). As

these experimental profiles are very similar, they can be superimposed in Fig. 3(b). The dimensionless concentrations are presented versus the dimensionless radial position  $r/\sigma$  where  $\sigma$  is the standard deviation of the Gaussian equation. The graph obtained demonstrates the perfect self-similarity of the measurements which implies that the results are auto-validated and really accurate

At  $t \approx 0$ , the oxygen spot always has a radius of around 100  $\mu\text{m}$ . Due to the small size of the concentration field behind the bubble (around 10% of the bubble size), it can be estimated with Oseen equation (1) that the velocity in this field can be assumed to be constant, axial and equal to the Gaussian maximum velocity. Then, after several bubble diameters, the oxygen radial transport due to convection can be neglected as regards radial diffusion. The oxygen field in the wake is then observed to evolve as a Gaussian curve. This observation is in total agreement with the analytical solution of the Fickian diffusion equation (Crank 1975). In particular, the transient solution for an instantaneous plane source  $M_0$  in an infinite medium is:

$$[O_2] = \frac{M_0}{4\pi Dt} e^{-\frac{r^2}{4Dt}} \quad (4)$$

where  $M_0$  is the linear amount of substance diffusing from a Dirac point. This solution can be used far from the bubble with,  $M_0 = \text{Flux}/U_B$  and  $4Dt = 2\sigma^2$  to express the two-dimensional concentration Gaussian profile:

$$[O_2] = \frac{\text{Flux}}{2U_B \pi \sigma^2} e^{-\frac{r^2}{2\sigma^2}}$$

The standard deviation of the Gaussian profile can then be expressed as:

$$\sigma = \sqrt{2Dt} \quad (5)$$

This term could be measured experimentally for each oxygen spot (Figure 3). The standard deviation  $\sigma$  depends on square root of the time  $\sqrt{t}$  and the slope of this function (Eq. 5) makes it possible to quickly calculate the diffusion coefficient corresponding to the medium under

study (slope =  $\sqrt{2D}$ ). In this method, the determination of the concentration can be adimensionalized by the maximum of the concentration field in  $r=0$ ,  $[O_2]/[O_2]_{\max}$  (fig 3.b) and thus the liquid solubility as any calibration curve are not necessary:

$$\frac{[O_2]}{[O_2]_{\max}} = e^{-\frac{r^2}{2\sigma^2}}$$

In our experiments, the initial ( $t=0$ ) standard deviation  $\sigma_0$  for the first spot image varied from 67 to 85  $\mu\text{m}$ . In Figure (4), the ordinate axis has been translated by  $\Delta\sigma = \sigma - \sigma_0 = \Delta\sigma = \sqrt{2Dt}$  to allow the comparison between experiments. A very clear linear trend can be observed for all the systems, with a regression linearity coefficient of less than 1%, confirming the applicability of the diffusion model of equation (4). It is observed that the slope of the curve increases as the viscosity decreases. The diffusion coefficient was quantified in six hydrodynamic conditions representing four different media. The oxygen diffusion coefficients obtained in liquid media are reported in Table 2. Firstly, the oxygen diffusion coefficient measured in clean water (at 20°C,  $D_{\text{water}} = 2.09 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ ) is in agreement with the mean value of  $2.14 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  found in the literature (Bennett & Momentum 1967; Perry & Green 1997; Scheibel 1954).

The decrease in viscosity with decreasing concentrations of glycerol is mainly responsible for increasing diffusion coefficients (Table 1). This is explained as the usual dependence of  $D$  on the inverse of the viscosity, as predicted by the Stokes-Einstein-Sutherland equation (Einstein 1905) and the correlation of Wilke and Chang (1954). For all water-glycerol mixtures, the latter correlation gives values very close to our experimental results (deviation < 2.24%).

Experiment n°	Glycerol % w/w	$D_{\text{measured}}$ $\text{m}^2/\text{s}$	$D_{\text{Literature}}$ (Wilke & Chang 1955) $\text{m}^2/\text{s}$
1	43	$3.97 \times 10^{-11}$	$4.03 \times 10^{-11}$
2	18	$3.22 \times 10^{-10}$	$3.21 \times 10^{-10}$
3	18	$3.26 \times 10^{-10}$	$3.21 \times 10^{-10}$
4	8	$9.03 \times 10^{-10}$	$9.19 \times 10^{-10}$
5	8	$9.15 \times 10^{-10}$	$9.19 \times 10^{-10}$
6	0	$2.09 \times 10^{-09}$	$2.14 \times 10^{-09}$

**Table 2.** *Hydrodynamic conditions for the six sets of experiments at 20°C.*

The reproducibility of the experiments was also tested by reiterating the same measurement five times in the identical operating conditions. The deviation of the measured diffusion coefficient was of the order of 3%. For two concentrations of glycerol (8% and 18% w/w), the experiments were done for two different sizes of bubbles (0.7 and 1.3 mm). The diffusion coefficient varied by less than 1% between the two bubble sizes. Even though the initial sizes of the oxygen spots  $r_{i,0}$  were quite different, their time evolution depended only on diffusive transport. In particular, Eq. 4 is the solution for a point source  $r_{i,0} = 0$ . This equation is then remarkably applicable whatever the bubble size (0.7 - 1.88 mm) as long as the experimental configuration can be assumed to be axisymmetric and without any radial convection. All these results clearly validate the magnitude of the experimental quantitative measurements.

The essential feature of the present method is that the measurement is accomplished in a very short time within a few seconds. The time necessary for the diffusion spot to reach the bubble size is estimated from equation 5 as  $t = d_B^2 / 16D$ . The accuracy is high (less than 2%) and the measurement need to be achieved at microscale (diffusion area  $\ll d_B^2$ ). Another important feature of the present method is that the influence of saturation concentration on the calculation of  $D$  is eliminated due to the measurement of the Gaussian curve standard deviation versus time. As the molecular diffusion ( $\text{m}^2/\text{s}$ ) depends only on the spread of the spot, any calibration for concentration is necessary. 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. Moreover, the diffusion can be considered as a constant temperature process since the experiment is completed within a very short time period around one second. This is also one of the advantages of the present method over other methods that need long measurement times.

## **Conclusion**

The approach developed here uses PLIFI as an interesting optical configuration for the quantification of the diffusion of an oxygen spot created by a single bubble rising in viscous fluids. The determination of the diffusion coefficient only requires knowledge of the oxygen spots in a cross-section in the bubble wake as a function of time. The diffusion coefficient from classical established theories and the experimental valued obtained in this study are in a good agreement demonstrating the relevance of this method. The application of the technique to

different transparent fluid could extend the current data and so become a useful tool for diffusion analysis and visualization.

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