VISUALIZATION OF A PURE DIFFUSIVE PHENOMENON AT A PLANAR GAS/LIQUID INTERFACE BY PLANAR LASER INDUCED FLUORESCENCE

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ABSTRACT

A new and promising technique for determining mass diffusion coefficients of gases in liquids is proposed in this paper. The technique is based on the use of PLIF (Planar Laser-Induced Fluorescence) applied to the study of a flat gas/liquid interface in a Hele-Shaw cell ($5 \times 5 \times 0.2$ cm^3). Using this technique, a direct visualization of the diffusive process through this interface is possible as well as the measurement of diffusion coefficient based on a simplified mathematical resolution. The relevance of the technique consists of the fact that no properties of the liquid or the gas (such as the saturation concentration for instance) is required, which would be particularly useful in complex media. The formulated hypotheses have been carefully checked by another optical technique, namely the Particle Image Velocimetry (PIV). Experiments presented in the paper have been carried out with an air/liquid system for studying the diffusion of oxygen in three different aqueous solutions (viscosities ranging from 1 to10 mPa.s). The determined diffusivities are in good agreement with the literature which seems to confirm the reliability of the proposed technique.

INTRODUCTION

When studying mass transfer in gas/liquid system, diffusion is a phenomenon as crucial as awkward to characterize accurately. The experimental determination of molecular diffusion coefficients in gas/liquid system is a delicate purpose. The difficulties for studying a diffusive phenomenon are many-sided since this phenomenon is dramatically sensitive to any disruption (natural convection, vibration, etc.) and is very slow. The experimental set up for such measurements has thus to limit all the external perturbations while ensuring a sufficient accuracy to quantify the diffusive process. Besides the experimental set-up, the mathematical analysis to be developed for determining a molecular diffusion is not straightforward either. This analysis is commonly based on the classical equation of diffusion, the Fick's law[1], adapted for the corresponding experimental set-up. However, in several studies, strong hypothesis have to be satisfied to obtain a molecular diffusion coefficient while their appositeness could not be always proved[2]. Another limiting step is the prior knowledge of some characteristics of the studied gas-liquid system (gas saturation concentration for instance) for applying the mathematical analysis which is not that easy, especially in complex media[3]. Due to these difficulties, the diffusion coefficients measurement strongly differs from technique to technique despite their small announced uncertainties. For instance, a deviation of about 40% has been observed when comparing different oxygen diffusion coefficients in water at 20°C presented in literature. As a consequence, there is no unique technique that seems to win unanimous support and the determination of diffusion coefficient is thus commonly restricted to the use of empirical correlations, Wilke and Chang[4] for instance, only applicable under a restricted domain.

The main purpose of this paper is to set up a new and promising technique avoiding the previously mentioned limiting steps and thus to reach an accurate and reliable experimental determination of molecular diffusion coefficients in gas-liquid systems. This technique is based on PLIF (Planar Laser-Induced Fluorescence) to perform a direct visualization of the diffusive process.

PLIF is based on the use of a fluorescent dye, inserted in the liquid phase, that can reemit light (fluorescence phenomenon) when being excited by an appropriate light excitation, usually generated by a laser. Depending on the

dye, the fluorescence phenomenon can be sensitive to some specific parameters such as temperature or pH changes or sensitive to the presence of a gas in the liquid phase (O_2, CO_2, etc.) which is of prime interest in our study. PLIF is widely used for the visualization of gas/liquid mass transfer since it is a non intrusive technique allowing a high spatial and temporal resolution. However, studies dealing with this subject mainly focused on the determination of liquid side mass transfer coefficients or mass boundary layers ([5]Francois *et al.* 2011, [6]Walker et Peirson 2008, [7]Dani *et al.* 2007, [8]Herlina et Jirka 2004, [9]Takehara et Etoh 2002, [10]Wolff et Hanratty 1994) but scarcely on pure diffusive processes. In this paper, PLIF has been used to first visualize and then to quantify the diffusion of oxygen through a flat air/liquid interface. Based on PLIF experiments, a simplified mathematical analysis is proposed to determine the diffusion coefficient of oxygen in the studied liquid. This analysis does not require any characterization of the gas/liquid system to be applicable in large range of fluids and to avoid uncertainties due to this characterization. Particle Image Velocimetry (PIV) experiments coupled with simulations have also been performed to visualize the hydrodynamic behavior in the both gas and liquid phases during the diffusive process. The proposed technique has been applied in three different aqueous phases and the resulting diffusion coefficients have been compared to literature to ensure the relevance of the visualization techniques used in this study.

MATERIALS AND METHODS

As mentioned before, this study focuses on the visualization of the oxygen diffusion through a flat air/liquid interface. The experimental set-up proposed for this visualization is depicted in Figure 1.
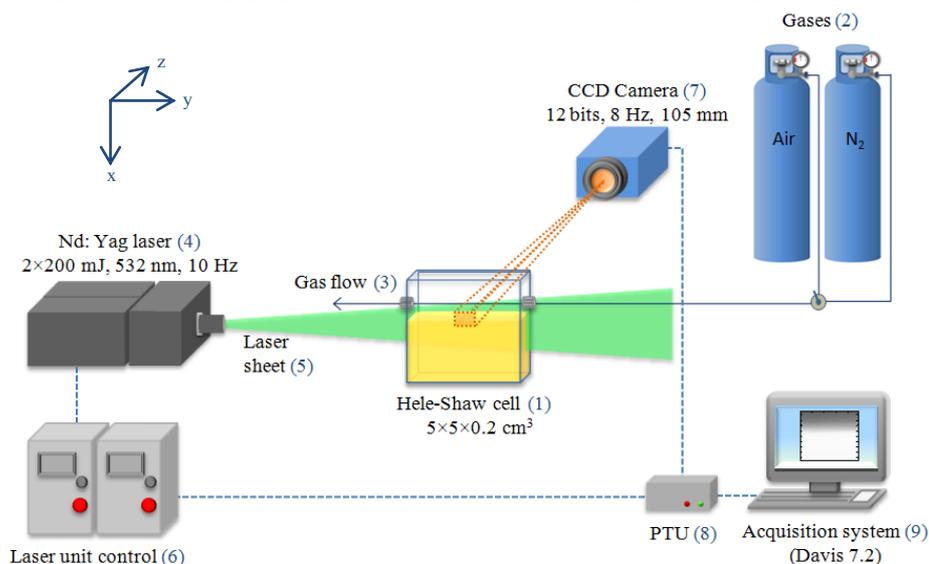

Figure 1. Experimental set-up for PLIF measurements in a Hele-Shaw cell.

A Hele-Shaw cell ($5\times5\times0.2$ cm^3), characterized by a small gap separating the two plates of the cell, has been used to consider a two-dimensional approach (contribution along the *z*-axis neglected). The cell was made of transparent PMMA (Polymethyl methacrylate) and has two openings at about 1 cm to the top of the cell (*xz* plane) to let air flow in the cell. The cell has been filled with about 3 mL of the liquid to be studied (water for instance). To observe the fluorescence phenomenon and the mass transfer of oxygen, a ruthenium complex ($C_{72}H_{48}N_8O_6Ru$, Nanomeps, France) has been selected and incorporated in the liquid (25 mg/L)[5,7]. When this dye is excited by a laser light (532 nm), it will go to an excited state and will emit light. When oxygen is transferring in the liquid phase and due to the collision between molecules, oxygen will be able to absorb the excess energy of the dye. The dye can thus return to its fundamental state by a non radiative process[11]. As a consequence, when there is no oxygen in the liquid, the fluorescence level will be maximum and as soon as oxygen will appear in the liquid phase the fluorescence phenomenon will be inhibited. The oxygen mass transfer can thus be tracked in the liquid phase and quantified based on the Stern-Volmer correlation.

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

with I_Q and I_0 the fluorescence levels (characterized by grey levels) in presence and absence of quencher (O_2) respectively, K_{SV} the Stern-Volmer constant (L/mg), and $[Q]$ the concentration of the quencher (mg/L).

The fluorescence level of the solution is thus directly proportional to the inverse of the gas concentration in the liquid phase. Values of K_{SV} and I_0 have been determined using a calibration curve that corresponds to the fluorescence level measurement for different known and uniform oxygen concentrations in the liquid phase (ranging from about 0 mg/L to the saturation concentration of the gas, 9 mg/L). It has to be note that the coefficient of determination of the Stern Volmer correlation was about 99% for each experiment. The ruthenium complex has been chosen for its high sensitivity to the presence in oxygen allowing a range of about 2000 grey levels between a solution fully deoxygenated and a saturated solution. The main inconvenient of this dye is that it is not directly soluble in aqueous solution, 20%w/w of ethanol has to be added to the liquid phase. Three different liquid phases have been tested to determine the impact of viscosity on the diffusion (Table 1).

	Composition (%w/w)			ρ (kg/m3)	μ (Pa.s)
	Water	Ethanol	Glycerol		
Case 1	80	20	0	970	0.0010
Case 2	60	20	20	1029	0.0017
Case 3	50	20	30	1042	0.0024

Table 1. Composition and characteristics of the three studied liquids.

The excitation of the fluorescent dye has been performed by a Nd: Yag laser (Quantel, λ = 532 nm, 10 Hz, 2 × 200 mJ) that generates a laser sheet along the *xy* plane. The fluorescence level has been recorded by a CCD camera (Imager Intense, LaVision, 12 bits, 8 Hz) focalizing at the gas/liquid interface, along the *xy* plane. To obtain a recorded picture of about 9×12 mm², a 105 mm objective has been added to the camera (Micro-Nikkor 105 mm f/8, Nikon) with a 570 nm high pass filter to block the laser light and to only record the fluorescence level of the dye. The laser and the camera were synchronized by a PTU (Programmable Trigger Unit, LaVision) and the recorded images are displayed by a specific software (Davis 7.2, LaVision).

The experimental set up for PIV experiments was similar to the PLIF one except for the laser (Dantec Dynamics, Nd: Yag laser, λ = 532 nm, 15 Hz, 2 × 30 mJ) and for the dye. In PIV experiments, reflective particles (silver-coated hollow glass spheres with a 20 μm diameter, Dantec Dynamics) have been incorporated to the liquid phase. These particles, that follow the liquid motion, reflect the light generated by the laser. Using a specific program (Flow Manager) their displacement can be deduced and thus the velocity field in the liquid phase can be calculated. The size of the interrogation areas was 32×32 pixels². The delay between two successive images was 32 ms and an overlap of 50% was set.

To visualize the diffusion of oxygen through a flat air/liquid interface in a Hele-Shaw cell, the following method is proposed.

The first step consisted of checking the cleanliness of the Hele-Shaw cell. Then the cell has been filled with the liquid phase (liquid to be studied, ruthenium complex and ethanol) and deoxygenated by nitrogen. A nitrogen flow ran above the interface and a first set of images has been recorded to ensure that oxygen from the ambient air was not transferring in the liquid. After few minutes, the gas was carefully switched to air and a 0.01L/s air flow has been established above the interface (corresponding to the time t = 0 of experiments). Then a laser sheet has been generated each minute during about 30 minutes. The duration of experiments was quite short to avoid any evaporation issue in the cell. For each recording time, 5 images have been recorded at 8 Hz. All the experiments have been performed in a

temperature regulated room at 20°C. An example of diffusion visualization is shown in Figure 2 corresponding to experiments performed with the liquid phase "Case 1" (Table 1).
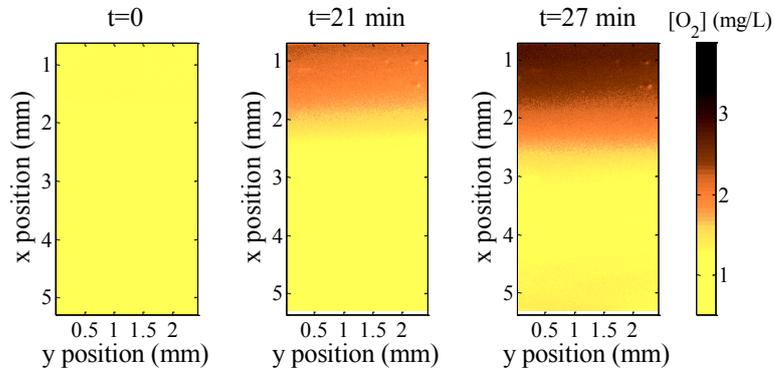

Figure 2. Evolution of the oxygen diffusion in a water-ethanol(20%w/w) liquid phase at 20°C.

Due to the reflection occurring at the gas-liquid interface, the determination of the oxygen concentration at the near vicinity of the interface cannot be determined. In the resulting images, the maximum oxygen concentration that can be reached is thus about 4 mg/L in spite of the expected 9 mg/L, corresponding to the saturation concentration of oxygen. It is also noteworthy to specify that an image processing is performed on all the recorded images. This image processing consisted of first averaging pixel by pixel the five images recorded at each time to obtain an averaged image. Then the Beer-Lambert dispersion of the laser light (Figure 3) has been estimated to correct the grey level of each image assuming a uniform dye concentration in the liquid phase. This dispersion corresponded to a difference of about 200 grey levels (about 0.3 mg/L) between the left and the right sides of the image. Finally, a Gaussian filter averaging a window of 5×5 pixels² has been applied to denoise the raw images.
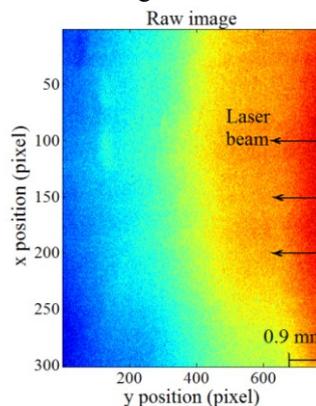

Figure 3. Raw image with the Beer-Lambert dispersion of the laser light along the y-axis.

HYDRODYNAMICS BEHAVIOR

To perform experiments as those presented in Figure 2, the control of the hydrodynamic behavior of both phases is of prime interest. The critical step concerns the switch of gas (from nitrogen to air) that could easily disrupt the interface if not realized carefully. The diffusive process could also be interrupted if the air flow is neither well controlled nor well selected. PIV experiments have thus been performed to visualize the hydrodynamic behavior in the liquid phase depending on the gas flow rate running above it. It has been showed that for gas flow rate smaller than 0.01 L/s, the interface was not disrupted by the air (Figure 4.a). In the area of measurement (9×12 mm²), there was just a horizontal displacement of the liquid at the interface, the slowness of this displacement being due to the small flow rate and the configuration of the Hele-Shaw (close plates that slow down the liquid). However, for higher flow rates, the disruption is clearly visible on the recorded images (Figure 4.b). To achieve a complete information of the hydrodynamic behavior in the cell, simulation with the COMSOL Multiphysics 3.5a software have been performed based on the 2D Space dimension with a laminar flow module and a stationary study type.
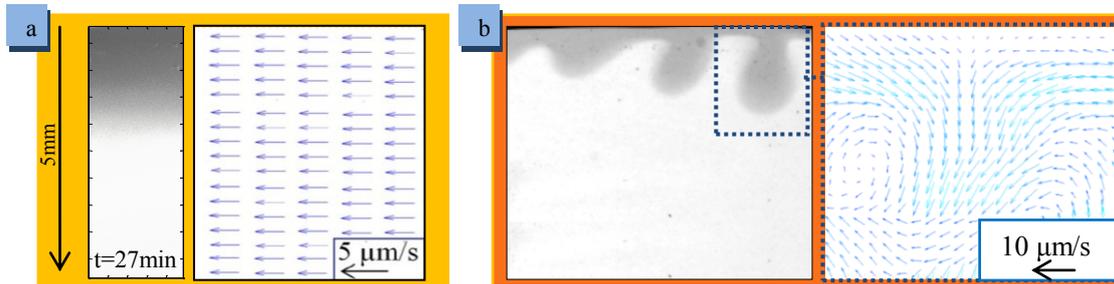
Figure 4. Mass transfer and velocity field visualization for a diffusive process without disruption (a) and with instabilities occurring at the interface (b).

COMSOL simulations and PIV experiments in the Hele-Shaw cell are superimposed in Figure 5 for an air flow supposed to be equal to 0.01 L/s.
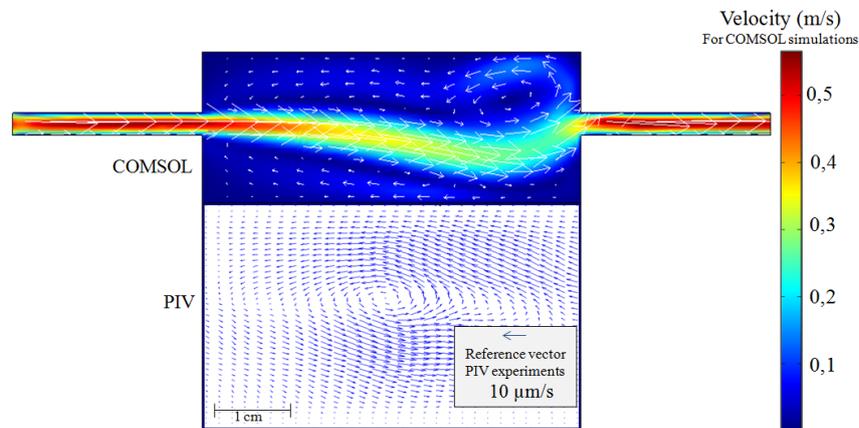

Figure 5. Hydrodynamics behavior in the Hele-Shaw cell for a 0.01 L/s air flow and liquid phase "Case 1" extracted from [12] (Jimenez et al. 2012)

Based on these two visualization techniques, PLIF and PIV, thorough information of both mass transfer and hydrodynamic behavior have been performed. The coupling of these techniques is a powerful tool to achieve reliable experiments and to directly visualize the studied phenomenon. Based on these results, a specific mathematical analysis is proposed to determine the oxygen diffusion coefficient in a simple way.

MATHEMATICAL ANALYSIS

By considering a 2D approach (contribution along the *z* axis neglected), with a concentration gradient along the *x*-axis and assuming that there is no convection along the gradient-axis, Fick's law can be written as follow.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

with *C* the oxygen concentration in the liquid phase (mg/L), *x* the distance to the gas-liquid interface (m), *t* the time since the beginning of the diffusive process (s) et *D* the diffusion coefficient (m²/s).
Note that the hypothesis of no convection along the *x*-axis has been already checked by PIV experiments (Figure 4.a).

The analytical solution of (2) in a semi-infinite media is [13]

$$\frac{C - C_0}{C_S - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (3)$$

with C_0 et C_s the oxygen concentration in the bulk region and at saturation respectively and $erf(.)$ the error function. Based on (3), it can be observed that by knowing $C(x,t)$ and C_0 et C_s, the diffusion coefficient D can be easily determined using a least-square method. The obtaining of $C(x,t)$ is quite simple since there is just to average oxygen concentrations on recorded images (Figure 2) for each line. However, as mentioned before, the prior knowledge of C_s is not straightforward [3]. Moreover, due to reflection at the interface, this parameter cannot be directly determined from experiments. To avoid these issues, a probabilistic approach is proposed [12].

Based on the analytical solution (3), the expression of $\partial^2 C / \partial x^2$ is

$$\frac{\partial^2 C}{\partial x^2} = \frac{x}{\sqrt{\pi Dt}.2Dt}.\exp(\frac{-x^2}{4Dt}).(C_s - C_0) \qquad (4)$$

This expression (4) is directly proportional to a density probability function of a gamma distribution defined as in (5) by considering the change variables $X = x^2$, $\theta = 4Dt$ and $k = 3/2$.

$$f(X, k, \theta) = \frac{X^{k-1} \exp(\frac{-X}{\theta})}{\Gamma(k).\theta^k} \qquad (5)$$

The main advantage to consider this density probability function is that its maximum can be easily determined just by knowing the parameter of the function. In other words, the maximum of f can be calculated just with X, K and θ using the following formula

$$X_{max} = (k-1).\theta, k \geq 1 \qquad (6)$$

According to the change of variables $X = x^2$, $\theta = 4Dt$ and $k = 3/2$, it means that the point maximizing $\partial^2 C / \partial x^2$ is located at (7).

$$X_{max} = x^2_{max} = (\frac{3}{2} - 1).4Dt = 2Dt \qquad (7)$$

Based on (7), just by localizing the maximum of $\partial^2 C / \partial x^2$, the diffusion coefficient can be determined in a very simple way without any characterization of the gas-liquid system. To avoid uncertainties based on the determination of the time t=0 of experiments, (7) is applied between two different times of measurement.

$$x^2_{max\ 1} - x^2_{max\ 2} = 2D(t_1 - t_2) \qquad (8)$$

APPLICATIONS AND RESULTS

To apply the proposed mathematical analysis, the maximum of $\partial^2 C / \partial x^2$ has to be located. This location has been performed by fitting the experimental points $C(x)$ for each time of measurement with a 6-order polynomial whose second derivative can easily be determined. The maximum of $\partial^2 C / \partial x^2$ can thus be located in a simple way as shown in Figure 6. As shown in this figure, the displacement between two successive maximum points x_{max} has to decrease time after time since the gradient at the interface becomes smaller too.
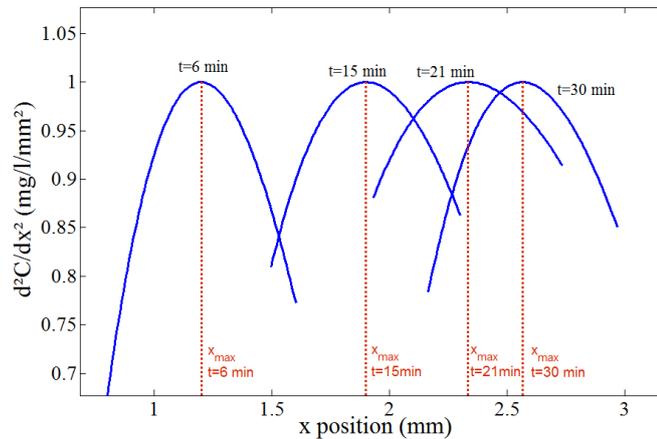
Figure 6. Determination of the maximum of $\partial^2 C / \partial x^2$ for different times of measurement. [12]

By plotting x^2_{max} as a function of time, t, a straight line is obtained whose slope is directly proportional to the diffusion coefficient D (slope $=2D$). Experimental values of D are presented in Table 2.

	D_{exp} (m²/s)	$\Delta D_{exp}/D_{exp}$	D Wilke and Chang [4] (m²/s)
Case 1	1.9×10^{-9}	3%	1.994×10^{-9}
Case 2	1.2×10^{-9}	3%	1.3×10^{-9}
Case 3	9.5×10^{-10}	5%	9.5×10^{-10}

Table 2. Values of experimental oxygen diffusion coefficients compared to literature.

A good agreement has been performed using this technique compared to the literature and uncertainties on the results are small (<5%) when considering this kind of measurement which seems to confirm the relevance of the proposed technique. The impact of viscosity on diffusion is confirmed by these results. The higher the viscosity, the slower the diffusion. Some tests have been performed in other liquid media, more complex, to check the feasibility of the technique and it has been observed that the measurement is not possible in certain media (for instance in presence of surfactants). Further efforts have to be supported to understand the impact of some component on the fluorescence phenomenon.

CONCLUSIONS

The set up proposed in this paper is based on the use of a powerful optical technique, PLIF. This technique presents several advantages such as a direct visualization of a pure diffusive process and a high accuracy to quantify the oxygen concentration field in the liquid phase near the interface. PLIF has been coupled with PIV experiments to control the hydrodynamic behavior which is strongly linked to mass transfer. Optimal parameters have thus been obtained to avoid disruption of the oxygen diffusion. Based on the experimental results, a simplified mathematical analysis has been developed to determine the diffusion coefficient without any characterization of the studied gas-liquid system. This analysis has been tested on three different liquid media. Results are very promising and seem to confirm the reliability of the technique. A limiting step of the proposed approach is the necessity to incorporate ethanol in the solution to solubilize the fluorescent dye. Even if it does not distort the principle presented in the paper, the presence in ethanol obviously alters the results. Efforts are supported to find another dye compatible with the laser equipment and as sensitive to oxygen as the ruthenium complex. PLIF is also limited to the study of gases able to be tracked by a fluorescent dye. However, the mathematical analysis can be applied to other laser techniques, such as holographic interferometry that does not need any dye in the liquid phase to track the transfer of a gas in a liquid phase even if the

constraint of having a transparent liquid phase remains. Experiments with other gases, such as CO_2, are also in progress. This new approach represents thus a promising step in the improvement of the gas-liquid mass transfer comprehension.

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