THE EXCHANGE OF OXYGEN AT THE SURFACE OF OPEN WATERS UNDER WIND FORCING

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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Abstract

A series of detailed laboratory investigations were conducted to examine low solubility gas transfer across wind-forced wavy air-water interfaces. The study focuses on the increase in gas flux associated with the microphysical interfacial wind momentum exchange and the complex wave coupled hydrodynamics. Key elements of the laboratory investigations included the measurement of hydrodynamic behaviour within the aqueous viscous sub-layer using a particle image velocimetry (PIV) system and the development of a Laser Induced Fluorescent (LIF) system capable of measuring reliable dissolved oxygen concentration profiles to within 28µm of the air-water interface. Major achievements and findings included:

1. The first phase resolved gas flux measurements along wind forced microscale waves, indicating the highest mean gas fluxes are located in the wave troughs. This finding demonstrated the relative importance of wave orbital straining in gas flux enhancement; a wave coupled hydrodynamic process whose significance has previously been neglected.

2. The relative contributions to gas flux from wind shear, wave orbital straining, increased surface area of the waves, parasitic capillary ripples and microscale breaking are quantified with respect to friction velocity, wave steepness and an efficiency of microscale wave breaking. The parasitic capillary ripples are shown to have a negligible role in gas enhancement. A hybrid model is developed to estimate the gas flux based on both wind and wave characteristics.

3. Gas enhancement due to microscale wave breaking and the significance of the highly localised subduction at the toe of the spilling region on the leeward face of the wave crests was investigated using data from the LIF experiments. The highly localised subduction was shown to substantially reduce the thickness of the diffusion sub-layer, resulting in an increase in gas flux when waves transitioned from the incipient breaking to the microscale breaking wave form.

4. Consideration of previously unidentified optical distortions in LIF imagery due to non-linear effects is presented that is critical for robust LIF data processing and experimental design. A formal mathematical description of optical distortions has been developed and presented.
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SUMMARY
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DECLARATION

ORIGINALLY STATEMENT

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James William Walker
24 August 2009
ACKNOWLEDGEMENTS

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Investigations of the air-water interface at a microphysical scale were demanding and led to the development of new insights into gas exchange processes. These challenges were met by my supervisor’s research diligence and continuous curiosity. Bill was always available to critique my latest experimental results or my most recent gas flux theory. Our fruitful discussions helped to extend my understanding of the microphysical processes at the air-water interface, refine my research skills and to continually review concepts developed in this study. Bill’s efforts are greatly appreciated.

This research project encompassed countless hours of laboratory experiments. Many of these hours were spent refining experimental techniques at both macro and microphysical scales. These tasks were supported by a group of skilled craftsmen and technicians whose experience and enthusiasm contributed to the successful outcomes of this investigation. I express my gratitude to Messrs. John Hart, John Baird and Hector Martinez for their assistance and willing advice.

I thank the librarians Margaret Titterton and Caroline Hedges for retrieving reference material and Monika Steiler for the preparation of schematic and technical drawings.

I also wish to express my gratitude to family, friends and colleagues who have supported and encouraged me over the course of this study.
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LIST OF SYMBOLS

\( a \)  
wave amplitude

\( A \)  
equivalent slab cross-sectional area

\( c \)  
wave speed

\( C \)  
concentration of the dissolved gas (mg/L)

\( C_B \)  
concentration of the dissolved gas in the bulk of the liquid body

\( C_h \)  
concentration of the dissolved gas at a reference depth \( h \)

\( C_I \)  
concentration of the dissolved gas in the aqueous phase at the interface

\( C_{PBA} \)  
molar concentration of the PBA

\( \hat{C}_{95\%} \)  
the 95 percentile dimensionless dissolved gas concentration

\( \hat{C}_{100\mu m} \)  
dimensionless dissolved gas concentration at 100\( \mu m \) water depth

\( \hat{C} \)  
dimensionless dissolved gas concentration

\( d \)  
water depth in the tank

\( D \)  
molecular diffusion coefficient (m\(^2\)/s)

\( e \)  
subduction event efficiency coefficient

\( f \)  
wave frequency

\( f_L \)  
characteristic frequency of eddies adjacent to the surface

\( F \)  
gas flux

\( g \)  
acceleration due to gravity

\( I \)  
fluorescent intensity

\( I_I \)  
fluorescent intensity at the water interface

\( I_{LB} \)  
laser intensity at a distance \( I \) through the fluid

\( I_{LB0} \)  
laser intensity before it enters the fluid

\( I_{0q} \)  
fluorescent intensity in the absence of a quencher

\( \hat{I} \)  
recorded intensity

\( \hat{I}_B \)  
fluorescent intensity in the bulk of the water

\( k \)  
wave number

\( k_{\text{day}} \)  
gas transfer velocity (m/day)

\( k_v \)  
transfer velocity (m/s)

\( k_{\text{bulk}} \)  
transfer velocity obtained from the bulk dissolved oxygen measurements

\( k_{\text{bulk,20}} \)  
transfer velocity obtained from the bulk dissolved oxygen measurements corrected to 20\( ^\circ \)C

\( k_{\text{LIF}} \)  
transfer velocity obtained from the LIF dissolved oxygen profiles

\( K_c \)  
turbulent diffusion coefficient

\( K_u \)  
turbulent viscosity coefficient

\( l \)  
travel distance of the laser sheet through the fluid

\( M \)  
molecular weight of water
$p$ wave breaking probability
$\overline{Q}$ average heat flux
$r$ average rate of renewal
$\langle s^2 \rangle$ mean square wave slope
$Sc$ Schmidt number
$t$ time (s)
$T$ temperature ($^\circ$C)
$T_e$ time of exposure to the gas
$T_K$ absolute temperature ($^\circ$K)
$T_w$ laser waist beam in the vicinity of the water surface
$u, v, w$ velocity components in the $x, y, z$ planes respectively (m/s)
$u_s$ surface velocity
$u_{sw}$ wave-coherent tangential surface velocity
$u'_w$ friction velocity in the air (m/s)
$u'_w$ friction velocity in the water (m/s)
$U$ mean wind speed (m/s)
$U_{10}$ mean wind speed measured 10m above the surface
$V$ molar volume of oxygen
$w_s$ surface velocity
$W$ effective enhancement
$x, y, z$ Cartesian coordinates (m)
$z_{sub}$ surface optical blurring depth
$z_0$ air roughness length
$z_{95\%}$ depth at which the dissolved oxygen concentration is 95% of the bulk

$\alpha$ quenching rate constant
$\gamma$ thermal diffusion coefficient
$\delta_d$ thickness of the diffusion sub-layer
$\delta_v$ thickness of the aqueous viscous sub-layer
$\varepsilon$ turbulent viscosity
$\theta$ camera mounting angle
$\Gamma$ wave divergence
$\kappa$ von-Kármán constant
$\lambda$ wave length
$\mu$ dynamic viscosity of water (kg m$^{-1}$ s$^{-1}$)
$\rho$ density of water
$\rho_w$ density of water
$\rho_a$ density of air
$\sigma$ standard deviation
\( \tau \)                   total wind stress  
\( \tau_{\text{form}} \)     form drag  
\( \tau_{\text{tan g}} \)     tangential surface stress (Pa)  
\( \tau_{\text{tan g, wc}} \) wave-coherent tangential surface stress (Pa)  
\( \tau_q \)                 fluorescent lifetime  
\( \tau_{0q} \)              fluorescent lifetime in the absence of a quencher  
\( \phi \)                   velocity potential  
\( \nu \)                   kinematic viscosity of water  
\( \nu_{\text{air}} \)        kinematic viscosity of air  
\( \psi \)                   stream function  
\( \psi_{\text{ap}} \)        solvent “association parameter”  
\( \psi_{\text{mc}} \)        molecular constant
1. INTRODUCTION

1.1 Scope and significance of this investigation

The exchange of heat, mass and momentum across air-water interfaces are micro-physical processes that have an influence on a global scale. Exchanges at the surface of ocean waters have a causal effect on climate, weather systems, global warming, pollutant fate and the environmental integrity of ecosystems. On a local scale, the processes are of importance in numerous industrial applications in which absorption, evaporation, heat and condensation play a role. The exchange of gases (particularly O₂) in the treatment of wastewater is a crucial industrial process that ultimately has both an environmental and health benefit. The estimated flux uptake of CO₂ by the world’s oceans are based on simplistic parameterisations and are a key limitation in the accuracy of present global warming and sea level rise predictive models.

Existing bulk parameterisations of air-water exchange of low solubility gases are based primarily on the intensity of wind forcing, a surface renewal statistic or changes in surface colour associated with bubble entrainment (Jähne and Haußecker 1998, Asher et al. 2002). Present low solubility exchange relationships show only limited agreement with available field and laboratory data, with the scatter in gas exchange rate in field and laboratory data greater than one order of magnitude. A microphysical understanding of interfacial behaviour is required to resolve the source(s) of this observed scatter in exchange rate.

Gases such as oxygen, carbon dioxide and hydrogen sulphide are known as sparingly soluble gases, having a low solubility in water. The resistance to transfer across the air-water interface for low solubility gases is in the aqueous phase (Lewis and Whitman 1924). In such cases the transport of heat, mass and momentum is controlled by a combination of molecular and turbulent processes within the upper 1mm of the water column. For gases such as oxygen, these processes occur within the diffusion sub-layer which typically occupies the upper 200 to 300μm of the water column.
Turbulent processes generated by agitation of a water body, results in enhanced gas exchange across the air-water interface (Downing and Truesdale 1955). In oceanic waters these turbulent processes are primarily generated by wind forcing (momentum exchange) and waves. In rivers and estuaries the turbulent processes may also emanate from bed shear. As the wind speed or bed shear increases, so do the turbulent intensity and the rate of gas exchange across the air-water interface (Downing and Truesdale 1955).

The investigations reported herein focus on increased oxygen flux associated with wind related momentum exchange across the air-water interface and the complex wave-coupled hydrodynamics. Of primary interest is that portion of the wave spectrum termed microscale, having lengths between 50 and 300mm and covering a large proportion of the sea-surface (Figure 1.1). At wind speeds exceeding approximately 5ms\(^{-1}\) the microscale waves commence to break and are characterised by a confined spilling region immediately leeward of the wave crest (Peirson 1998). Microscale breaking waves respond swiftly to fluctuations in both wind speed and direction. They are also associated with high vorticity and therefore dissipate quickly in the absence of wind forcing (Longuet-Higgins 1995).

Oxygen exchange also occurs through other processes such as air entrainment via more visible larger waves observed breaking on shorelines or evident as “white caps” on open waters. Similarly, significant exchange of oxygen is observed in rivers and streams by means of cascades and the surface renewal motions observed in rapids and fast flowing reaches. Nonetheless in both cases, the aerial extent is usually small in comparison to that of microscale waves. Other oxygen exchanging processes include rainfall, biological activity (photosynthesis and respiration) and chemical reactions.

This thesis describes a detailed laboratory investigation of key aspects of gas exchange across air-water interfaces under wind forcing. Many previous laboratory-based wind-wave studies have only considered wind as the surface forcing medium. However, the rapid growth and decay of microscale waves can result in significant wave energy variations and wave characteristics along the length of the flume. Jähne et al (1987) used circular wind/wave tunnels in order to remove fetch dependency, but other hydrodynamic
processes associated with preferential centrifugal wave motion and radial stresses are then introduced promoting stem wave breaking at the outer wall. During these gas flux experiments, it was important that wave energy remained relatively constant along the length of the test flume. Hence, waves were generated using a combination of wind and paddle forcing. Whilst laboratory experiments cannot exactly duplicate field conditions they provide a controlled environment under which specific aspects of processes can be investigated to enlighten our knowledge of key mechanisms.

A number of important developments in the measurement and understanding of gas exchange at air-water interfaces was achieved during the course of these investigations, including:

- Measurement of dissolved oxygen concentration gradients to within 28μm of the air-water interface for strongly forced wind-wave surfaces.

- The first phase resolved gas flux measurements for wave populated air-water interfaces. Gas flux measurements were achieved at the crest, trough and mid points of the rising and falling limbs of waves.

- The relative importance of capillary waves, orbital straining, microscale breaking and localised zones of convergence and divergence on enhancement of gas flux has been quantified.

- The first direct measurements of the wave surface velocity structure and surface convergence/divergence along the entire wavelength of mechanically generated waves using Particle Image Velocimetry (PIV).

A major component of the investigation was the development of a Laser Induced Fluorescent (LIF) technique to undertake non-intrusive measurements of the dissolved oxygen concentration profile within the aqueous diffusion sub-layer that typically occupies the upper 200 to 300μm of the water column. LIF is an optical technique that has
principally developed through its broad application in the study of biological cells and related medical fields and has more recently been applied to investigating the structure of the aqueous diffusion sub-layer.

The development of the specialised LIF technique during the course of this study revealed a number of optical distortions related to the experiment set-up that had not previously been identified. These optical distortions limit the accuracy of the LIF data and may have a significant bearing on the interpretation of measurements of the aqueous diffusion sub-layer using LIF techniques. An understanding of these optical distortions has enabled measurements to within 28μm of the air-water interface, at least a 5 fold improvement on previous studies. Given that the diffusion sub-layer is typically of the order of 200μm or less, measurements made during the course of this study could arguably be considered the first detailed measurements within this layer.

This thesis is structured into six sections:

1. A review of the current understanding of gas exchange across the air-water interface (Chapter 1).

2. A general description of the experimental facilities common to all experiments conducted as part of this study (Chapter 2).

3. Presentation and assessment of PIV data collected to assist in understanding the hydrodynamic structure within the viscous sub-layer and near surface region along mechanically generated waves (Chapter 3).

4. Development of the LIF technique and presentation of gas flux data as measured by both LIF and bulk oxygen methods (Chapter 4).
5. Assessment of the dominant turbulent processes within the upper portion of the water column (<1 mm from the surface) and their relative contributions to enhanced gas flux across the air-water interface (Chapter 5).

6. Major conclusions drawn from these investigations including recommendations for future work (Chapter 6).

Appendix A contains copies of publications accepted over the duration of this study.

1.2 Gas exchange across the air-water interface

Present understanding of gas exchange across the air-water interface is limited by the absence or scarcity of microphysical measurements of concentration profiles within the diffusion sub-layer (Jähne et al. 1987). The measurement of concentration profiles within the diffusion sub-layer has only recently been attempted and the methodologies are discussed in detail in Chapter 4. The absence of detailed concentration profile data has led to the development of:

- **Bulk parameterisations** of gas exchange across the air-water interface based on wind forcing (Jähne et al. 1987), surface renewal statistics, change in surface colour associated with bubble entrainment (Asher et al. 2002) and more recently using the thermal infra-red surface signature (Garbe et al. 2002 and Zappa et al. 2004).

- **Theoretical models** of gas exchange across the air-water interface based on the microphysical processes associated with wave hydrodynamics and momentum and boundary layer models. Where possible, verification of the theoretical models is based on the bulk field and laboratory data. Thus, in the absence of data within the diffusion sub-layer, bulk data measurements are used to validate microphysical processes (e.g. Lewis and Whitman 1924, Higbie 1935, Danckwerts 1951, Witting 1971, Deacon 1977 and Peirson and Banner 2003).
• Use of **Proxy tracers** such as heat to infer gas exchange behaviour across the air-water interface. Thermal imagery techniques have been developed to investigate heat flux across the air-water interface (Jähne et al. 1989, Garbe et al. 2002, Haußecker et al. 2002, Siddiqui et al. 2002 and Zappa et al. 2004).

### 1.2.1 Bulk parameterisations

In gas exchange experiments wind speed is the most common variable used for parameterisation. Researchers have reported linear, quadratic and cubic wind speed dependencies for gas exchange. From gas exchange field data, Liss and Merlivat (1986) developed empirical relationships to estimate the global oceanic CO₂ uptake as:

\[
\begin{align*}
  k_{\text{dip}} &= 0.17U_{10} \quad (U_{10} < 3.6 \text{m/s}) \\
  k_{\text{dip}} &= 2.85U_{10} - 9.65 \quad (3.6 \text{m/s} < U_{10} < 13 \text{m/s}) \\
  k_{\text{dip}} &= 5.9U_{10} - 49.3 \quad (U_{10} > 13 \text{m/s})
\end{align*}
\]  

[1.1a] [1.1b] [1.1c]

Using long term averaged winds Wanninkhof (1992) found:

\[
k_{\text{dip}} = 0.39U_{10}^2
\]  

[1.2]

and Wanninkhof and McGillis (1999) found:

\[
k_{\text{dip}} = 1.09U_{10} - 0.333U_{10}^2 + 0.078U_{10}^3
\]  

[1.3]

where: \( k_{\text{dip}} \) is the gas transfer velocity in m/day, and;

\( U_{10} \) is the mean wind speed in m/s at a reference height of 10m.

The parameterisations (Equations 1.1 to 1.3) yield global CO₂ uptakes that, between them, vary by a factor of 3. Donelan and Wanninkhof (2002) note that the differences are based on the uncertainty in field measurements and acknowledge that other factors (beside wind
speed) affect gas exchange. The uncertainty in existing bulk parameterisations is further highlighted in Figure 1.2 where field and laboratory data show scatter in gas exchange rate greater than one order of magnitude.

The relatively large scatter in the data has led to the development of further empirical relationships based on other parameters that may influence gas exchange; with the most notable being the surface wave characteristics. Jähne et al. (1987) and Zappa et al. (2004) show there is a strong relationship between the mean square wave slope $\langle s^2 \rangle$ and the transfer velocity. Asher and Wanninkhof (1998) and Asher et al. (2002) developed empirical relationships for transfer velocity based on whitecap coverage and bubble entrainment.

The infrared heat signature has also been used to map the thermal structure of the surface from which zones of surface convergence and divergence may be inferred (Haußecker et al. 1995, Jessup et al. 1997, Garbe et al. 2002, Haußecker et al. 2002, Siddiqui et al. 2002 and Zappa et al. 2004). Zappa et al. (2004) related the areal extent of microscale breaking using the infrared technique to a measured gas flux. A more detailed discussion of the infrared techniques is left until Section 1.2.3, where the application of heat as a proxy tracer is reviewed.

### 1.2.2 Theoretical models

The unsteady transport of a scalar such as mass is described by the three dimensional advection-diffusion equation (Fick’s second law):

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} + D \frac{\partial^2 C}{\partial z^2} = DV^2 C$$  \[1.4\]

where $C$ is the concentration of the dissolved gas (mg/L);

$D$ is the molecular diffusion coefficient (m$^2$/s);

$x, y, z$ are the Cartesian coordinates (m);

$u, v, w$ are the velocity components in the $x, y, z$ planes respectively (m/s), and;
Formal solutions to the three dimensional advection-diffusion equation only exist for relatively simple cases. We start with the simplest form of the equation.

### 1.2.2.1 Molecular diffusion

For a still body of water \( u = v = w = 0 \) with initial uniform concentration, the advection-diffusion equation (Equation 1.4) reduces to:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \tag{1.5}
\]

and the mass flux \( F \) is given by the one dimensional form of Fick’s steady state first law:

\[
F = -D \frac{\partial C}{\partial z} \tag{1.6}
\]

The molecular diffusion coefficient of oxygen in air is approximately \( 10^4 \) times greater than that for oxygen in water. As described mathematically by Lewis and Whitman (1924) and experimentally verified by Scriven and Pigford (1958) the major resistance to transport is the aqueous phase for low solubility gases. Therefore it is assumed that phase equilibrium exists at the interface at all times and that the exchanging gas obeys Henry’s Law (Becker 1924).

Setting initial and boundary conditions for Equation 1.5 such that;

\[ C(z) = C_B \text{ at } t = 0 \text{ for all } z \]
\[ C(z) = C_I \text{ at } z = 0 \text{ for all } t \]
\[ C(z) = C_B \text{ as } z \to \infty \text{ for all } t \]

and solving, yields;
\[
\frac{C_I - C(z)}{C_I - C_B} = \text{erf}\left(\frac{z}{2\sqrt{D}t}\right)
\]  \[1.7\]

where the subscript \(I\) denotes a value at the interface immediately on the aqueous side and the subscript \(B\) denotes a location in the assumed well mixed bulk water.

A graph of Equation 1.7 for \(C_I=10\,\text{mg/L}\) and \(C_B=1\,\text{mg/L}\) is presented in Figure 1.3. At \(t=0\) seconds the dissolved oxygen concentration in the water is \(1\,\text{mg/L}\). At \(t=10^7\) seconds (or 115 days) the dissolved oxygen concentration at a depth of 0.5m is 1.1mg/L. In isolation molecular diffusion is a relatively slow process. Even after 3 years the dissolved oxygen concentration at a depth of 0.5m is only 5.8mg/L.

Despite the fundamental importance of dissolved oxygen in both the aquatic environment and industrial applications, relatively few data have been published on the molecular diffusion coefficient of oxygen in water. The CRC Handbook (2005) reports three experimentally derived values for the molecular diffusion coefficient for oxygen in water. The International Critical Tables (2003) reports a single experimentally derived value for the molecular diffusion coefficient for oxygen in water. These values are reproduced in Table 1.1 and in a graphical format in Figure 1.4.

<table>
<thead>
<tr>
<th>Table 1.1</th>
<th>Experimentally derived molecular diffusion coefficients for oxygen in water ((D \times 10^{-9},\text{m}^2,\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>15°C</td>
</tr>
<tr>
<td>CRC Handbook</td>
<td>1.67</td>
</tr>
<tr>
<td>Critical Tables</td>
<td>-</td>
</tr>
</tbody>
</table>

Wilke and Chang (1955) suggest an empirical relationship (Equation 1.8) for molecular diffusion in water, based on the Stokes-Einstein equation and experimental data (i.e. directly proportional to temperature and inversely proportional to the liquid viscosity). They estimated the average error to be of the order of 10%.
where: $\psi_\text{ap}$ is the solvent “association parameter” (2.6 for water);

$M$ is the molecular weight of water $\text{(18.0g.mol}^{-1})$;

$T_K$ is the absolute temperature ($^\circ\text{K}$);

$\mu$ is the dynamic viscosity (kg m$^{-1}$ s$^{-1}$), and;

$V$ is the molar volume of oxygen $\text{(25.6cm}^3/\text{g.mol)}$

A plot of the relationship developed by Wilke and Chang (1955) is also reproduced in Figure 1.4. In comparison to data from the CRC handbook (2005), the Wilke and Chang (1955) equation overestimates the diffusion coefficient for temperatures below 25°C. At a temperature of 20°C the error is of the order of 5% and at 15°C the error is closer to 10%.

Scheibel (1954) and Othmer and Thakar (1953) have also developed empirical relations for the determination of molecular diffusion in water. Similar error bounds are reported in their work.

Diffusion coefficients used throughout this study are based on those tabulated in the CRC Handbook (2005) and reproduced in Table 1.1. For temperatures other than 15°C, 20°C and 25°C the diffusion coefficients have been interpolated or extrapolated using the second order polynomial fit plotted in Figure 1.4 and defined in Equation 1.9.

$$D = (0.0014T^2 + 0.019T + 1.07) \times 10^{-9}$$

where: $T$ is the temperature ($^\circ\text{C}$).

1.2.2.2 Stagnant film model

The boundary conditions applied in the formulation of Equation 1.7 imply a semi-infinite depth and a concentration profile that continues to develop with depth through the water
column over time. With the onset of sub-surface transport processes and turbulence, the development of the concentration profile with depth through the water column is no longer due only to pure molecular diffusion. Hence, in the bulk of the fluid where turbulent diffusion dominates molecular processes, the concentration profile is uniform (Figure 1.5).

Lewis and Whitman (1924) postulated that the transfer of gases across the air-water interface is controlled by the rate of diffusion through “surface or stagnant films” of gas and liquid at the interface (sub-layers). This is commonly referred to as the two-film theory. With the major resistance to gas transfer being in the aqueous phase for low solubility gases they deduced that that the mass flux could be described by:

\[
F = k_v (C_i - C_a)
\]  

[1.10]

where: \(k_v\) is the transfer or piston velocity (m/s).

Lewis and Whitman (1924) noted that the transfer velocity \(k_v\) is influenced by a number of variables including temperature and the thickness of the liquid film layer (the diffusion sub-layer). They also observed that stirring of the liquid body resulted in an increase in mass flux across the air-water interface. They suggested that the turbulence generated by the stirring caused a decrease in the thickness of the diffusion sub-layer, resulting in a decrease in liquid phase resistance.

Taking the concentration gradient as constant and simple rearrangement of Equations [1.6] and [1.10] yields:

\[
\delta_d = \frac{D}{k_v}
\]  

[1.11]

where: \(\delta_d\) is defined as the thickness of the diffusion sub-layer (Figure 1.5).
A fundamental assumption in the development of the two film theory and the consequent relationship between the transfer velocity $k_v$ and the thickness of the diffusion sub-layer $\delta_d$ (Equation 1.11) is that the concentration profile within the diffusion sub-layer is linear. Two-film theory assumes a quasi steady-state system in which the concentration of the bulk liquid changes over a relatively long period of time and the thickness of the diffusion sub-layer is relatively stable.

Although the two film theory for fluid flow is physically idealistic, it is often used as a convenient model for data interpretation of measured gas fluxes.

1.2.2.3 Boundary layers and the small-eddy model

The mixing length theory proposed by Prandtl assumes that eddy size diminishes as the distance from the surface reduces, giving rise to the “small-eddy model” identity. In this model, turbulent eddies cannot penetrate to the surface and subsequently molecular diffusion increasingly becomes the dominant process as the interface is approached.

A schematic showing the viscous and mass diffusion sub-layers for both the air-phase and aqueous-phase of a wind sheared flat air-water interface is presented in Figure 1.5. With Schmidt ($\delta c = \nu/D$) numbers close to unity in the air-phase, the thickness of the viscous and diffusion sub-layers are of similar magnitude. In the aqueous-phase, Schmidt numbers are between 500 and 600 and the oxygen mass diffusion sub-layer lies well within the viscous sub-layer. The aqueous diffusion sub-layer is an order of magnitude smaller than the aqueous viscous boundary (Jähne et al. 1987). Consequently thinning of the diffusion sub-layer is subject to near-surface viscous hydrodynamic behaviour. The viscous sub-layer does not imply laminar flow, but is a layer in which viscosity dominates behaviour. Experimentally it has been shown that adjacent to a solid wall, the thickness of the aqueous viscous sub-layer $\delta_v$ (Monin and Yaglom 1971 §5.3 p272 and Douglas et al. 1979 §9.3 p287) can be approximated by:

$$\delta_v = \frac{5\nu}{u^*}$$

[1.12]
where: \( \nu \) is the kinematic viscosity and \( u''_w \) is the friction velocity in the water.

In the absence of streamwise pressure gradients, the total stress is given by:

\[
\tau = \rho_w (u''_w)^2 = \rho_a (u''_a)^2
\]  
[1.13]

Within the viscous sub-layer assuming Newtonian behaviour:

\[
\tau = \rho_v \frac{du}{dz} = \mu \frac{du}{dz} = \text{constant}
\]  
[1.14]

At distances between:

\[
\frac{30 \nu}{u''_w} \leq z \leq \frac{500 \nu}{u''_w}
\]  
[1.15]

in the logarithmic layer (Monin and Yaglom 1971 §5.3 p276), turbulence dominates and

\[
\tau = \varepsilon \frac{du}{dz}
\]  
[1.16]

where: the turbulent viscosity \( \varepsilon \) is given by:

\[
\varepsilon = \kappa u''_w z
\]  
[1.17]

and \( \kappa \) is the von-Kármán constant.

Numerous researchers (Hinze 1959) have suggested a turbulent viscosity coefficient \( K_u \) that varies with distance from the surface such that:
\[ \tau = \rho(n + K_u) \frac{du}{dz} \]  
\[ \text{and } K_u = \varepsilon/\rho \text{ within the logarithmic layer.} \]

A similar analogy is applied to the diffusion sub-layer where a turbulent diffusion coefficient \( K_e \) is introduced that varies with distance from the surface (Deacon 1977 and Coantic 1986) such that:

\[ F = -(D + K_e) \frac{dC}{dz} \]  

This had led to the small-eddy model also being commonly referred to as the K-model.

Two theoretical approaches have been adopted. One in which the interface is considered a solid wall, and the second in which the boundary is considered as a free surface.

**Solid Wall**

Applying Reynolds decomposition and a zero horizontal pressure gradient within the boundary layer, the classical turbulent boundary layer equations are:

\[ \frac{\partial \tilde{u}}{\partial x} + \frac{\partial \tilde{w}}{\partial z} = 0 \]  
\[ \frac{-\partial \tilde{u}}{\partial x} + \frac{w \partial \tilde{u}}{\partial z} = \nu \frac{\partial^2 \tilde{u}}{\partial z^2} - \frac{\partial}{\partial z} \left( u'w' \right) \]  
\[ \frac{-\partial \tilde{C}}{\partial x} + \frac{w \partial \tilde{C}}{\partial z} = D \frac{\partial^2 \tilde{C}}{\partial z^2} - \frac{\partial}{\partial z} \left( C'w' \right) \]  

and
\[ C = \bar{C} + c' \quad u = \bar{u} + u' \quad w = \bar{w} + w' \]  

[1.23]

where the over bar and primed letters denote the mean and fluctuating components of the constituents respectively.

For a solid wall Reichardt (in Hinze 1959), Monin and Yaglom (1971) and more recently Coantic (1986) derived a relationship for \( K_u \) with distance from the surface using a Taylor series expansion. Assuming a no-slip condition at the wall (denoted by the subscript 0), such that:

\[ u_0 = v_0 = w_0 = u'_0 = v'_0 = w'_0 = 0 \]  

[1.24]

\[ \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} + \frac{\partial w'}{\partial z} = 0 \]  

[1.25]

\[ \frac{\partial w'_0}{\partial z} = 0 \]  

[1.26]

They found that \( K_u \) increased with the distance cubed from the wall.

For low wind speed (flat water) Deacon (1977) applied Reichardt’s velocity profile (Hinze 1959) to estimate the turbulent diffusion coefficient \( K_c \) in Equation 1.19 and the enhanced mass flux due to wind-induced turbulence within the viscous sub-layer. Deacon (1977) found that the gas transfer velocity varied with a Schmidt number exponent of \(-2/3\) and:

\[ k_v = \frac{1}{12.2} Sc^{-\frac{2}{3}} u' \]  

[1.27]

Deacon (1977) used laboratory data from Hoover and Berkshire (1969) and Liss (1973) to verify his model. At wind speeds greater than 3.5\( \text{ms}^{-1} \) (\( u_* \approx 0.16 \text{m/s} \)) and the onset of
waves, Deacon’s model substantially under predicts observed flux rates (Equation 1.27 is plotted in Figure 1.2). Deacon (1977) conjectures that the sudden increase in the mass flux at wind speeds greater than 3.5m s\(^{-1}\) is likely to be due to the formation of capillary ripples on the water surface and the possible thinning of the viscous sub-layer on the crests and windward slopes of waves due to wind induced turbulence. Later, Deacon (1981) attributes the difference to the onset of microscale breaking waves (Banner and Phillips 1974) and dismisses the ripples as a major contributor to enhanced gas flux.

**Free Surface**

For the free surface condition, surface parallel velocity fluctuations are possible and \(u'_x\) and \(u'_0\) are no longer subject to the requirement that they be zero. Consequently the continuity equation now gives:

\[
\frac{\partial \omega'_0}{\partial z} = -\left(\frac{\partial u'_x}{\partial x} + \frac{\partial v'_0}{\partial y}\right) \neq 0
\]  

[1.28]

The implications are that at the surface, zones of convergence or divergence may exist. Coantic (1986) assumed that for a wave field the near surface motion is essentially two-dimensional and hence:

\[
\frac{\partial \omega'}{\partial z} = -2 \frac{\partial u'}{\partial x}
\]  

[1.29]

For these boundary conditions it was found that the turbulent viscosity coefficient \(K_v\) and the turbulent diffusion coefficient \(K_e\) increased proportionally to the distance squared from the surface. Ledwell (1984) and Coantic (1986) found that for free surface interfaces:

\[
k_v \propto Sc^{-1/2}
\]  

[1.30]

and Jähne et al. (1987) shows:
Consequently, Jähne et al. (1987) concluded that the effective thickness of the diffusion sub-layer is in part controlled by zones of surface convergence and divergence. Equation 1.31 is plotted in Figure 1.2. Jähne et al. (1987) shows a transition of the Schmidt number exponent form \(-2/3\) to \(-1/2\) with the onset of waves. Csanady (1990) directly attributed the formation of convergent and divergent zones to microscale breaking. McKenna and McGillis (2004) show good collapse of their flux data in relation to a characterisation of surface divergence when wave activity is small.

An important aspect of air-water gas transfer work is the prediction of transfer rates of more exotic or constituents which are difficult to quantify using exchange rates obtained for more easily measured tracers. Most direct measurements have been accomplished for CO\(_2\) and O\(_2\). Jähne et al. (1987) show that extrapolation from constituent \(a\) to a second constituent \(b\) can be accomplished via:

\[
k_{v,a}/k_{v,b} = \left(\frac{D_a}{D_b}\right)^n = \left(\frac{Sc_a}{Sc_b}\right)^{-n}
\]

[1.32]

However, for wind forced surfaces, a systematic decrease in the exponent \(n\) from 2/3 to 1/2 can be observed with increasing wind speed or increasing mean squared slope of the water surface (Jähne and Haußckecker, 1998, Figure 3). For constituents (e.g. low solubility gases) and tracers (e.g. heat) with very different diffusivities, the value of \(n\) is crucial to reliable predictions but for constituents with similar diffusivities, it is less so. For example, at 20°C, for carbon dioxide \((D_{CO_2}=1.67\times10^9\text{m}^2\text{s}^{-1})\) and oxygen: \(k_{v,a}/k_{v,b} = 0.92\), \(n=0.5\) and \(k_{v,a}/k_{v,b} = 0.90\), \(n=0.67\). In this contribution, all transfer rates are presented in terms of the behaviour of oxygen: multiplying the presented value by 0.91 will yield the equivalent CO\(_2\) value accurate to ±2%.
1.2.2.4 Surface renewal

An alternative to the two film phase resistance model was first suggested by Higbie (1935) and Danckwerts (1951) who proposed a surface renewal theory for the observed increase in mass flux across the air-water interface in the presence of turbulence. Turbulent eddies in the bulk of the water rise to the air-water interface and expose “fresh surfaces” to the gaseous phase. More vigorous turbulence, results in a greater frequency of eddies and a higher mass flux across the air-water interface.

If the surface is renewed periodically then:

\[ k_v = \frac{D}{\pi T_e} = \sqrt{Dr} \]  \hspace{1cm} [1.33]

where: \( T_e \) is the time of exposure to the gas, and;
\( r \) is the average rate of renewal.

More recently Komori et al. (1993) investigated a surface renewal parameterisation for strongly sheared wavy interfaces that related the frequency of turbulent eddy structures to observed flux rates. They found:

\[ k_v = 0.34 \sqrt{Df_L} \]  \hspace{1cm} [1.34]

where: \( f_L \) is the characteristic frequency of eddies adjacent to the surface.

1.2.2.5 Gravity wave orbital straining

Witting (1971) investigated the effects of plane progressive irrotational waves on thermal boundary layers and reported that gravity wave orbital straining can enhance the average heat flux \( \bar{Q} \) by factors of no more than 1.38 where the maximum wave steepness \( ak \) is 0.446. The effective enhancement \( W \) is defined relative to a “rectangular equivalent slab” where:
The “rectangular equivalent slab” is essentially a reference thermal diffusion sub-layer thickness for a flat interface and has a horizontal length \( \lambda \), a cross-sectional area \( A \) and a vertical thickness of \( A/\lambda \). To incorporate the effect of waves, Witting (1971) assumes the wavy surface sub-layer thickness has an identical cross-sectional area \( A \) bounded by the surface stream function \( \psi = 0 \) and a stream function at depth \( \psi \) and the velocity potentials \( \phi \) and \( \phi + \Delta \phi \). The stream function \( \psi \) is considered the depth of the thermal boundary layer at which the water temperature is constant.

Witting (1971) was then able to define the effective enhancement \( W \) as:

\[
W = \frac{\Delta \phi \psi}{\lambda^2 \psi} \int_0^{\phi+\Delta \phi} \left| \frac{dZ}{d\psi} \right|^2 d\phi d\psi
\]  

Whilst Witting (1971) does not explicitly report maximum changes in temperature gradients, it may be surmised that local changes due to wave orbital straining may be considerably higher.

Deacon (1981) and Csanady (1990) conclude from their investigations that zones of convergence and divergence due to orbital staining are too weak to significantly influence gas transfer.

1.2.2.6 Capillary waves

MacIntyre (1971) and Szeri (1997) investigated the potential of capillary waves to reduce the thickness of the diffusion sub-layer. They show that the localised periodic surface divergence produced by capillary ripples is capable of decreasing the thickness of the diffusion sub-layer and increasing gas transfer. Using the Crapper ripple formulation
(Crapper 1957) and assuming a surface covered with parasitic capillaries, MacIntyre (1971) shows that transfer velocities localised in the vicinity of the parasitic capillaries may be enhanced up to 3.5 times relative to the average over the entire wave surface.

Longuet-Higgins (1992) establishes that steep capillary waves are associated with high vorticity that may contribute to the turbulence at the crest of short gravity waves.

1.2.2.7 Microscale breaking - subduction

Peirson and Banner (2003) predict aqueous diffusion sub-layer destruction at the onset of microscale breaking based on their PIV observations of near surface velocity structure. They observed intense magnitudes of vorticity (>1000s⁻¹) generated at the toe of the spilling regions of microscale breaking waves (Figure 1.6) and proposed that the toe of the spilling region is a point of highly localised subduction, forcing mixing of the thin diffusion sub-layer to a relatively deep depth.

The intense localised subduction results in a very thin diffusion sub-layer at the crest of waves that thickens with increasing residence time at the surface. As the surface fluid travels rearward relative to the wave speed, the diffusion sub-layer gradually thickens as it travels along the wave windward limb, through the wave trough and finally along the wave leeward limb before being subducted at the toe of the spilling region (Figure 1.6). This model is therefore coupled to the wave frequency and the existence of the spilling region.

Using an order of magnitude analysis, the transfer velocity for microscale breaking waves may be approximated by:

\[ k_v = (1.0 \rightarrow 1.15)\sqrt{pDa} \]  

where: \( f \) is the wave frequency, and;
\( p \) is the breaking probability.
Peirson and Banner (2003) noted a spatial and temporal intermittency of the microscale breaking waves. Wave grouping, was also observed to influence breaking statistics. Predictions based on Equation 1.37 are supported by recent bulk measurements of oxygen transfer rate (Peirson et al. 2007).

Csanady (1990) developed a surface vortex model to simulate the effects of microscale breaking in thinning the diffusion sub-layer. He found localised surface divergence on the windward face of the waves reduced the thickness of the diffusion sub-layer and thereby made a significant contribution to gas flux enhancement.

1.2.3 Heat exchange across the air-water interface

The difficulties associated with measuring the concentration of a mass constituent in close proximity to a moving air water interface at microphysical scales has led to the development of other novel approaches using proxy tracers. The most notable of these is the use of thermal imagery. Heat is a scalar like mass and the three dimensional advection-diffusion equation (Equation 1.4) may be rewritten in terms of temperature as:

\[
\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} + w \frac{\partial T}{\partial z} = \gamma \frac{\partial^2 T}{\partial x^2} + \gamma \frac{\partial^2 T}{\partial y^2} + \gamma \frac{\partial^2 T}{\partial z^2} = \gamma \nabla^2 T
\]  

[1.38]

where: \( \gamma \) is the thermal diffusion coefficient.

The application of infrared techniques to measure the surface skin temperature and infer bulk parameterisations for gas flux was introduced in Section 1.2.1. The surface skin temperature is usually several tenths of a degree cooler than the bulk water temperature (Jessup et al. 1997). For turbulent events, disruption of the surface skin may occur and warmer bulk water transported to the surface. The infrared heat signature can then be used to map the thermal structure of the surface and regions of surface convergence and divergence identified (Haußcker et al. 1995, Jessup et al. 1997, Garbe et al. 2002, Haußcker et al. 2002, Siddiqui et al. 2002 and Zappa et al. 2004).
The infrared technique has also been used to measure the frequency and areal coverage of microscale wave breaking (Jessup et al. 1997). Garbe et al. (2002) used the infrared technique to measure the frequency of renewal events and to estimate heat flux. Zappa et al. (2004) related the areal extent of microscale breaking using the infrared technique to a measured gas flux. They found that microscale breaking waves disrupted the thermal boundary layer and concluded that microscale breaking is a key parameter in controlling air-water gas transfer. From infrared imagery Siddiqui et al. (2002) and Zappa et al. (2004) found that the disruptions were most evident at the crest and its wake (windward limb).

The thermal signature has also been used to directly estimate gas fluxes. The controlled flux method (CFT) has been used by Jähne et al. (1989), Garbe et al. (2002), Haußecker et al. (2002), Siddiqui et al. (2002) and Zappa et al. (2004) as a method to directly measure the heat flux. This technique generally entails creating a localised heat patch on the water surface using a CO₂ laser and recording the decay of the heat signature with time. Whilst rapid decay of the heat signature has been observed at the crest of microscale breaking waves, no data appears to presently be available relating heat flux to wave phase location. The heat flux measurements are then used to directly predict gas flux behaviour for the same wind-wave conditions.

Thermal imagery experiments have provided a new insight into mechanisms associated with heat flux across the air-water interface. Unfortunately the present methods can only be used at the surface and provide no detail of the thermal structure with depth. Consequently the temperature profile over the thermal sub-layer remains uncertain. Secondly, the Schmidt number for heat in the aqueous phase is approximately 7. Therefore, the thermal sub-layer is of smaller but approximately similar thickness to the viscous sub-layer. Caution should be employed when heat data is used to infer gas flux behaviour where the Schmidt number is 509 at 20°C for oxygen in water.
1.3 Concluding remarks

Numerous models have been presented that highlight the complexities of gas transfer across the air-water interface. Generally, these models describe gas exchange either generically or for a specific hydrodynamic feature (i.e. capillary waves, surface renewal etc.).

In reality, gas exchange is a combination of global (wave length scale) and highly localised hydrodynamic features. A key question is: What is the contribution of each of the hydrodynamic features to the overall gas flux budget?

Current models and theories are limited by the availability of data that describes in detail the mass diffusion sub-layer. A key component of this study was to undertake measurements of the hydrodynamic structure and the dissolved oxygen concentration profile in the upper 200μm of a wavy air-water interface.

The following Chapters present the findings of this study.
Figure 1.1  Surface waters populated with microscale breaking waves offshore of the southern island of New Zealand in July 2007
Figure 1.2  Dependence of gas transfer velocity with friction velocity as measured by various researchers and compiled by Komori et al. (1993) with all data normalised to a Schmidt number of 600. Solid line shows the Deacon (1977) model (Equation 1.27) with a Schmidt number dependency to the exponent -2/3. Dashed line shows the Jähne et al. (1987) model (Equation 1.31) with a Schmidt number dependency to the exponent -1/2.
Figure 1.3 Theoretical dissolved oxygen concentration profile from the one dimensional form of Fick’s second law ($D=2.01\times10^{-9}\text{m}^2/\text{s}$). At $t=0$ the bulk dissolved oxygen concentration is assumed to be $1\text{mg/L}$. The curves show the relatively slow molecular diffusion process in the absence of surface disruptions and sub-surface turbulence. After 3yrs the dissolved oxygen concentration at a depth of $0.5\text{m}$ has only increased from $1\text{mg/L}$ to $5.8\text{mg/L}$.
Figure 1.4  Published experimental data for the molecular diffusion coefficient of oxygen in water (black and green symbols). Also included is experimental data for the molecular diffusion coefficient of carbon dioxide (purple symbols). The theoretical relationship derived by Wilke and Chang (1955) for the molecular diffusion coefficient of oxygen in water as a function of temperature is also plotted.
Figure 1.5  Viscous sub-layers and oxygen diffusion sub-layers at the air-water interface for a temperature of 20°C. The viscous and diffusion sub-layers are of similar thickness on the air-side. The diffusion sub-layer is an order of magnitude smaller than the viscous sub-layer in the aqueous phase.
Figure 1.6  Upper panel describes features associated with microscale breaking waves. Lower panel describes aeration model of Peirson and Banner (2003). Figures reproduced from Peirson and Banner (2003).
2. GENERAL EXPERIMENTAL FACILITIES

A general description of the facilities common to all experiments undertaken in this study is presented in this chapter. More specific details of equipment and instruments used for the PIV and LIF experiments are presented in Chapters 3 and 4 respectively. For ease of reference across all sections of this thesis, tables containing key experimental data are presented in this chapter and have been printed on blue paper. The standard set of wind and wave experiments established for this study are tabulated, together with key results for the PIV and LIF experiments.

The wind-wave tank used in this investigation had been established prior to the commencement of this study for the purpose of other laboratory experiments. Major modifications were made to the wind-wave tank to make it suitable for PIV, gas flux and LIF studies and to address the occupational health and safety issues associated with the use of high power lasers.

During the early stages of the study it became apparent that the diurnal and seasonal variations in Sydney temperatures experienced in the main laboratory at the University of New South Wales, Water Research Laboratory (WRL) were too great to conduct controlled LIF experiments. Laboratory daytime temperatures during summer could soar to +40°C and fall to 15°C overnight. During winter temperatures may drop to around 5°C. To minimise temperature variations between and during experiments a thermally controlled room was constructed around the wind wave-tank. The room has an overall length of 10.8m, width of 3.6m and height of 3.6m and is thermally insulated with fibreglass batts and reflective sheeting (Figure 2.1). The room is maintained at a constant temperature of 21.5±0.5°C.

The temperature controlled room has no windows and is sealed to avoid the ingress of dust and to maintain a uniform humidity. The darkened room is ideal for undertaking laser experiments. The enclosed room eliminates many of the laser-related occupational health and safety issues and also provides an adequately dark environment to capture LIF images.
The construction of the temperature controlled room has resulted in a world class facility that enables technically complex experiments to be undertaken under controlled conditions. This is a significant advancement in the technical facilities and capabilities at WRL.

2.1 Wind-wave tank

The wind-wave tank used for all experiments conducted in this study is shown in Figures 2.2 and 2.3. The tank has an overall length of 8.955m, width of 0.245m and height of 0.610m. An electro-mechanical flap type paddle (Figure 2.4) was used to generate monochromatic waves. Wind was generated by a fan fitted to the end of the tank. Guide vanes ensured a relative uniform air flow across the width of the tank and provided a smooth transition from the fan to the water surface.

The configuration and position of the wave paddle and fan was established for a water depth of approximately 0.250m. Consequently all tests reported herein were undertaken for water depths between 0.230m and 0.255m. The roof of the wind-wave tank is adjustable and was positioned to provide a zero pressure gradient along the length of the test section.

The fetch length of the tank could be adjusted by repositioning of the sealed surface skimming weir. The effective length of the tank was adjusted to ensure that wave energy near the paddle was consistent over the entire fetch length. A dissipative beach was installed at the downwind end of the fetch length to minimise wave reflections.

2.2 Water surface contaminants

The presence of adventitious surfactant films on the water surface can lead to systematically low gas transfer rates across the air-water interface. McKenna and McGillis (2004) and Saylor and Handler (1999) experimentally show that a purposely introduced oleyl alcohol monolayer can reduce gas transfer by a factor of approximately 2. Zappa et al. (2004) and McKenna and McGillis (2004) also verify that microscale wave breaking and turbulence are dampened in the presence of surfactants. Therefore, it was important to
ensure that in this study considerable care was exercised so that all experiments were
conducted with a slick free, clean water surface.

To minimise biological growth and eliminate surface contaminants a recirculating pump
with a diatomaceous earth filter and a UV steriliser was fitted to the tank. Water surface
skimming was accomplished by recirculating water from the test chamber across an
overflow weir fitted to the outlet chamber (Figure 2.2). A light wind was applied to ensure
that surface material was driven across the overflow weir. Skimming was undertaken over
a period of at least one hour prior to all experiments. Our microscopic observations of the
free surface clearly showed any surface contamination present and none was observed
during these experiments.

2.3 Wave measurement
An extensive review of instruments used to measure detailed features associated with
microscale breaking wind forced waves was undertaken by Peirson (1998). The review
included a description of optical methods currently used in laboratories worldwide. These
optical methods are generally based on reflection and/or distortion of the light beam/sheet
on a changing water surface slope. An obvious advantage of these optical methods is there
non-intrusive nature, however the techniques have limitations in the range of slopes that
can be measured and the resolution/accuracy of the systems.

Peirson (1998) concluded that capacitance wave probes were the most suitable for the
measurement of the detailed features associated with microscale breaking wind forced
waves. Capacitance wave probes similar to those used by Peirson (1998) and based on the
design of Clymo and Gregory (1975) were used for this study.

Three wave probes were positioned in the wind-wave tank at locations: near the wave
paddle, in the vicinity of the measurement section and near the dissipative beach. Data
acquisition of the analogue wave probe outputs was via a digital converter board (Eagle
Technology, model USB26 μDAQ) to a laptop computer. When detailed wave traces were
required, channels were logged at the rate of 1000Hz.
2.4 Wind measurement

Air velocity profiles above the water surface were measured using a pitot tube. The pitot tube was mounted on a vernier scale rule on the top of the wind-wave tank and referenced to the still water level. The pitot tube was connected to a MKS Baratron pressure transducer (model 223BD) with a range of 0.2Torr and recorded to a data acquisition computer. Air velocity measurements commenced as close as practical to the water surface (immediately above the crest of the waves) and extended to near the roof of the wind-wave tank.

The wind friction velocity $u^*$ and the air roughness length $z_0^*$ were derived from the measured logarithmic portions of the air velocity profiles using the technique described by Kawamura et al. (1981).

2.5 Bulk oxygen measurement

Bulk dissolved oxygen levels in the wind-wave tank were measured using an Orion model 835A dissolved oxygen meter with data logged to a computer at 5s intervals. The dissolved oxygen probe was calibrated in accordance with the manufacturers’ specifications and was shown to respond linearly over the full required measurement range. A number of systematic errors were initially identified in the experimental use of the dissolved oxygen probe. At first the probe was fixed to a stainless steel rod that profiled up and down over the full depth of the water column by use of an external motor and drive. The objective was to check that the water in the wind-wave tank was well mixed with depth (except close to the surface). Whilst initial tests concluded that the water was well mixed with depth, the profiling motion of the probe was insufficient to provide adequate flow across the probe membrane. This resulted in unreliable dissolved oxygen measurements that were systematically low.

In order to ensure that a sufficient water flow across the dissolved oxygen probe membrane was achieved, the probe was fitted with a glass flow-cell attached to a peristaltic pump (Figure 2.5). With the flow-cell mounted external to the flume, discrepancies in water temperature measurements were observed. These discrepancies resulted from more than
half of the probe protruding from the flow-cell. Also, small aeration like bubbles formed in
the flow-cell over extended periods of time resulting in erroneous measurements of
dissolved oxygen. Both of these problems were overcome by immersing the flow-cell in
the flume at a reference depth of 150mm below the surface.

Oxygen depletion in the tank was achieved by nitrogen sparging. A perforated 13mm
polypropylene pipe was affixed to the base of the flume and connected to a supply of
nitrogen. Nitrogen was bubbled through the water until the dissolved oxygen concentration
was reduced to approximately 0.7mg/L (Figure 2.6).

The transfer velocity \( k_{\text{bulk}} \) for each experiment was obtained from the bulk dissolved
oxygen measurements by the following relationship (Equation 1.5):

\[
\frac{dC}{dt} = \frac{k_{\text{bulk}}}{d} (C_I - C(t))
\]  

[2.1]

and following integration (Wolff and Hanratty 1994) gives:

\[
\ln \left( \frac{C_I - C(t)}{C_I - C(0)} \right) = \frac{k_{\text{bulk}}}{d} t
\]  

[2.2]

where: \( C_I \) is the saturation dissolved oxygen concentration on the aqueous side of the
interface;
\( C(t) \) is the bulk dissolved oxygen concentration at time \( t \);
\( C(0) \) is the bulk dissolved oxygen concentration at \( t = 0 \), and;
\( d \) is the water depth in the wind-wave tank.

A typical example of measurements from a bulk dissolved oxygen experiment is shown in
Figure 2.7. A plot of Equation 2.2 in Figure 2.7 demonstrates the dissolved oxygen probe
is linear over the full measurement range.
2.5.1 Water temperature observations

Despite a constant room temperature, during the course of these experiments it was noted that the water temperature in the wind-wave tank systematically decreased depending on the strength of the wind and wave action. The stable, ultimately achieved water temperature in the tank would decrease as the wind speed increased. Prior to the application of wind, the water temperature would be in balance with the room temperature (21 to 22°C). With the onset of wind, a reduction in water temperature (1 to 2°C) was observed. With the introduction of paddle driven waves a further reduction in water temperature (1 to 2°C) was noted. Hence, in the microscale wave breaking experiments reductions in water temperatures of up to 4°C were recorded (Table 2.1).

Systematic cooling of the water has not been reported in previous gas transfer experiments. For example, Broecker et al. 1978 and Hoover and Berkshire 1969 report that wind and wave forcing only commenced following purging by nitrogen sparging. This suggests that in many instances gas flux measurements were undertaken in conditions that were not in thermal equilibrium. In fact many of the gas flux experiments that use heat as a proxy tracer are conducted at elevated water temperatures. The cooling of the surface with the onset of wind, for the elevated water temperature experiments, is likely to result in strong near-surface thermally generated currents that would not exist if the water body was close to a thermal equilibrium.

Temperature variations in the mass diffusion and viscous boundary layers may have a significant bearing on gas exchange. Molecular diffusion $D$, kinematic viscosity $\nu$ and oxygen solubility are all temperature dependant. Therefore, all gas exchange experiments conducted herein were only commenced following an equilibrium temperature in the tank being obtained. Nitrogen sparging did not commence until this had been achieved. To minimise thermal gradients in the wind-wave tank, the side walls of the tank were insulated with polystyrene blocks (Figure 2.3). The insulation minimised the heat flux through the side walls of the wind-wave tank. This reduced possible systematic experimental errors associated with the generation of thermal currents caused by side wall heat exchange.
Several measurements of the thermal skin temperature were made using a Horiba infrared sensor when equilibrium temperatures were achieved. These measurements were within 0.1°C of the bulk temperature measured by the dissolved oxygen probe (i.e. within the uncertainty specifications of the instruments).

2.6 CCD camera and lens
The digital camera selected for all PIV and LIF imagery was a Santa Barbara Instrument Group (SBIG) ST-10XME Charged Couple Device (CCD). For LIF imagery it is advantageous to have a camera with high quantum efficiency in the UV spectra. The SBIG camera meets this criteria as well as being suitable for PIV imagery. The camera consists of 2184 horizontal pixels x 1472 vertical pixels. With the aid of a Nikon ED 80 to 200mm focal length lens effective pixel dimensions in each image were between 4 and 5μm.

A more complete description of the SBIG camera and its adaption for the LIF experiments is contained in Chapter 4.

2.7 Wind-wave conditions
A total of eight wind-wave cases were investigated. The defining parameters for each experiment, namely wind strength, wave forcing and bulk aeration rate are presented in Table 2.1. Whilst LIF was undertaken for all eight cases, PIV was restricted to those experiments in which hydrodynamic features were considered most important. The LIF derived transfer velocity data for each of the eight wind wave experiments is presented in Table 2.2

Photographs of the water surface for each of the eight wind-wave experiments are presented in Figures 2.8 to 2.11. Several water surface descriptors are used throughout the text, these are defined as follows:

1. A flat water condition which remains free of any wave motion but with evidence of high frequency motion due to pressure fluctuations in the weakly forced wind. The maximum wind speed without wave formation was 2.1m/s (Figure 2.8).
2. A *ripple* condition for which the water surface is covered with vigorous high frequency capillary ripples and can no longer be classified as a uniformly smooth surface. These ripples may be up to 2-3mm in height. The distinction between the *flat water* and *ripple* surfaces is clearly evident in Figures 2.8 and 2.10.

3. A *low wave* condition in which the waves have lengths between 135 and 350mm but have low wave steepness and do not show evidence of parasitic capillaries (Figures 2.8 and 2.10).

4. An *incipient breaking* mode in which the waves are as steep as possible without lapsing into a microscale breaking state. These waves are characterised by well-developed parasitic capillaries leeward of the wave crests (Figure 2.11).

5. A *microscale breaking* case in which a confined spilling region is evident immediately leeward of the wave crest with attendant capillaries further downwind. The presence of parasitic capillary waves and microscale spilling leeward of the crest is evident in Figure 2.11.

Each experiment is assigned a number from 1 to 8 (Table 2.1) and also a designation tag that is unique to each experiment. The designation tag provides information on the wave frequency, wind speed and wave steepness. For example, the experiment tag “f34u21ak18” represents a wave frequency of 3.4Hz, a wind speed of 2.1m/s and a wave steepness of 0.18. In some instances throughout the text it is simpler to assign the experiment number of 1 to 8. In other cases, the designation tags are used in the text as a quick reference to the experimental conditions, without the need for the reader to continuously return to Table 2.1.

The fetch dependence of waves was minimised using mechanically generated waves forced by wind. This also enabled control over the wave frequency. In Experiments 1 to 4 the wave frequency was constant (3.4Hz). Whilst the same wind speed (2.1m/s) was used in
Experiments 1 to 3, a higher wind speed (5.7 m/s) was required to maintain the surface in a microscale breaking regime (Experiment 4).

In Experiments 5 to 8 the same wind speed (3.9 to 4.2 m/s) was used and the wave frequency varied. Waves could be forced between the different water surface regimes using the same wind speed by varying the wave frequency.

The variation in wave characteristics is shown in Table 2.1 with the stated errors in $a_k$ indicating the range observed from the upstream to downstream ends of the tank.

### 2.8 Bulk aeration behaviour

The two distinct groups of experiments enabled the relative contribution of enhanced transfer velocity to be quantified for a number of different wind and hydrodynamic features. For example:

- An increase in the average transfer velocity $k_v$ measured in the bulk by the Orion dissolved oxygen probe is evident between the flat water and low wave experiments (1.8 fold). Given that the same wind speed was applied to both cases, the increases observed in the transfer velocity can be attributed to the presence of the 3.4 Hz paddle generated waves.

- Similarly the observed increase in average transfer velocity between the low wave and incipient breaking wave regimes can be ascribed to steepening of the waves together with the formation of parasitic capillaries.

- For Experiments 7 and 8 the relative contribution to the average transfer velocity when the waves transition from incipient breaking to microscale breaking may also be quantified without the complication of a contribution due to increased wind speed.
Whilst wind speed was maintained constant for a number of experiments, increases in roughness and form drag result in an increase in friction velocity. The dependence of the bulk average gas transfer velocity on friction velocity in air for each of the eight experimental cases is plotted in Figure 2.12. Each of the bulk gas transfer velocity experiments were conducted repeatedly (up to 10 occasions). Uncertainty in the measured bulk gas transfer velocity was small and within 4% of the mean.

This data set is the first that endeavours to uncouple wind and hydrodynamic features and provide a quantitative measure of the relative contribution of each to observed increase in gas transfer velocity. A more detailed description of these features is provided in the following chapters.

### 2.9 Temperature considerations

Whilst all experiments were conducted at the same room temperature, variations in water temperature were measured between experiments (Table 2.1). These temperature variations were caused by different wind forcing and water surface regimes and were discussed in Section 2.5.1.

To date, all transfer velocity data has been presented without consideration of these temperature variations. The temperature variations between experiments are small; however molecular diffusion, kinematic viscosity and oxygen solubility in water are all sensitive to relatively small temperature changes. Therefore to draw direct comparisons between experiments it is sometimes pertinent to normalise the transfer velocity data to a common reference temperature (usually 20°).

Daniil and Gulliver (1988) compare several different approaches that yield similar results. The first is the empirical relationship recommended by APHA(1980) and ASCE (1984) where:

\[
k_{v_{\text{bulk},20}} = \frac{k_{v_{\text{bulk}}}}{1.024 F^{-20}}
\]  \[2.3\]
and the second is a Schmidt number dependency where:

\[ k_{\text{bulk}20} = k_{\text{bulk}} \left( \frac{Sc(T)}{Sc(20)} \right)^{\frac{1}{2}} \]  

[2.4]

Using Equation 2.4 bulk transfer velocity data in Table 2.3 (5th column) has been adjusted to 20°C using a Schmidt number for oxygen in water of 509. The adjustment is plotted in Figure 2.13. The adjustments in the bulk transfer velocity data are less than 10%.

Gas transfer velocity data is often normalised to a Schmidt number of 600 (representing carbon dioxide in water at a reference temperature of 20°C). This enables direct comparisons with experiments conducted using other low solubility gases and is the approach adopted by Komori et al. (1993) in compiling the gas transfer data presented in Figure 1.2. Using Equation 2.4 bulk transfer velocity data in Table 2.3 (6th column) has been adjusted to 20°C using a Schmidt number for carbon dioxide in water of 600. The adjusted data is plotted with the gas transfer data compiled by Komori et al. (1993) in Figure 2.14.

Deacon (1977) found that the gas transfer velocity varied with a Schmidt number exponent of \(-2/3\) (Equation 1.27) and therefore Equation 2.4 could also be expressed as:

\[ k_{\text{bulk}20} = k_{\text{bulk}} \left( \frac{Sc(T)}{Sc(20)} \right)^{\frac{2}{3}} \]  

[2.5]

Using Equation 2.5 bulk transfer velocity data in Table 2.3 (7th column) has been adjusted to 20°C using a Schmidt number for carbon dioxide in water of 600.

Adjustments to the measured bulk gas transfer velocity based on Equations 2.4 and 2.5 (Table 2.3) are small in comparison to the data scatter shown in the Komori et al. (1993)
plot reproduced in Figure 2.14. Temperature and gas species adjustments to the bulk gas transfer velocity data assume a Schmidt number dependency or relationship. The exact relationship is still unresolved and to avoid creating a bias in the data analysis throughout this report, where possible, data comparisons are made using the measured gas transfer velocity (4th column).
<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>f34u21ak18</td>
<td>f34u21ak27</td>
<td>f34u57ak32</td>
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<td>f21u39ak10</td>
<td>f24u39ak24</td>
<td>f31u39ak28</td>
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<td>low</td>
<td>incipient microscale</td>
<td>ripple</td>
<td>low</td>
<td>incipient microscale</td>
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<td>19.1</td>
<td>18.4</td>
<td>18.4</td>
<td>18.3</td>
<td>17.3</td>
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<td>2.1</td>
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<td>0.140</td>
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<td>0.023</td>
<td>0.164</td>
<td>1.03</td>
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<td>0.020</td>
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<td>0.326</td>
<td>0.039</td>
<td>0.069</td>
<td>0.122</td>
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<td>-</td>
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<td>-</td>
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<td>0.015</td>
<td>0.062</td>
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<td>0.043</td>
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<td>sample mean $\tau_{ung}U_{rn}/c$ (Pa)</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>binned mean $\tau_{ung}U_{rn}/c$ (Pa)</td>
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<td>Bulk gas exchange</td>
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<tr>
<td>$K_{v bulk}$ (m/s) x10⁶</td>
<td>7.57</td>
<td>13.8</td>
<td>24.0</td>
<td>88.6</td>
<td>16.0</td>
<td>26.2</td>
<td>32.2</td>
<td>63.4</td>
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*ripple frequency
Table 2.2  Transfer velocity as measured in the bulk and by LIF.

<table>
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<tr>
<th>Surface descriptor</th>
<th>Experiment</th>
<th>Bulk $k_{v,\text{bulk}}$ (m/s) x10^6</th>
<th>Accepted LIF images $k_{v,\text{LIF}}$ (m/s) x10^6</th>
<th>$k_{v,\text{LIF}}$ Std dev. x10^6</th>
<th>% $k_v$ difference</th>
<th>$z_{95%}$ (μm)</th>
<th>$\hat{C}_{100%,v}$</th>
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<tr>
<td>Flat water</td>
<td>1 (f00u21ak0)</td>
<td>7.57 71</td>
<td>7.94±0.61</td>
<td>5.13 5</td>
<td>5</td>
<td>550 (580)</td>
<td>0.32</td>
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<td>Low wave</td>
<td>2 (f34u21ak18)</td>
<td>13.8 mean 22.8±1.4</td>
<td>16.4 65</td>
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<tr>
<td></td>
<td>crest</td>
<td>111 23.8±1.3</td>
<td>13.8</td>
<td>330 (280)</td>
<td>0.50</td>
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<td>920 (970)</td>
<td>0.48</td>
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<tr>
<td></td>
<td>trough</td>
<td>135 23.6±1.6</td>
<td>19.1</td>
<td>960 (600)</td>
<td>0.45</td>
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<tr>
<td></td>
<td>windward</td>
<td>125 18.7±1.1</td>
<td>12.5</td>
<td>910 (450)</td>
<td>0.42</td>
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<td>19.5 41</td>
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<td>470 (340)</td>
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<td></td>
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<td>105 58.0±3.0</td>
<td>30.6</td>
<td>580 (240)</td>
<td>0.78</td>
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<tr>
<td></td>
<td>windward</td>
<td>129 20.6±1.0</td>
<td>11.8</td>
<td>960 (510)</td>
<td>0.40</td>
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<td>Microscale</td>
<td>4 (f34u57ak32)</td>
<td>88.6 mean 82.5±11.0</td>
<td>48.8 -7</td>
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<td></td>
<td>crest</td>
<td>7 45.6±10.4</td>
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<td>570 (550)</td>
<td>0.74</td>
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<td></td>
<td>leeward</td>
<td>22 84.7±12.8</td>
<td>60.2</td>
<td>158 (100)</td>
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<td></td>
<td>trough</td>
<td>27 138±15.1</td>
<td>78.5</td>
<td>330 (170)</td>
<td>0.88</td>
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<td></td>
<td>windward</td>
<td>27 61.5±5.6</td>
<td>29.0</td>
<td>480 (300)</td>
<td>0.76</td>
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Table 2.2 (continued)  Transfer velocity as measured in the bulk and by LIF.

<table>
<thead>
<tr>
<th>Surface descriptor</th>
<th>Experiment</th>
<th>Bulk $k_{v_{bulk}}$ (m/s) x10^6</th>
<th>Accepted LIF images</th>
<th>LIF $k_{v_{lif}}$ (m/s) x10^6</th>
<th>$k_{v_{lif}}$ Std dev. x10^6</th>
<th>% $k_{v}$ difference</th>
<th>$z_{95%}$ (μm)</th>
<th>$\hat{C}_{100,\mu m}$</th>
</tr>
</thead>
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<td>Ripple</td>
<td>5 (f63u42ak00)</td>
<td>16.0</td>
<td>163</td>
<td>20.3±1.1</td>
<td>14.2</td>
<td>27</td>
<td>710 (640)</td>
<td>0.48</td>
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<td></td>
<td>Low wave</td>
<td>6 (f21u39ak10)</td>
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<td>mean</td>
<td>18.8±1.2</td>
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<td>Incipient</td>
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<td>mean</td>
<td>24.9±1.3</td>
<td>15.3</td>
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<tr>
<td></td>
<td>Microscale</td>
<td>8 (f31u39ak28)</td>
<td>63.4</td>
<td>mean</td>
<td>53.2±4.4</td>
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<td>-16</td>
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</table>

|                     | crest      | 115                           | 39.4±3.5           | 37.2                        | 480 (300)                | 0.69               |
|                     | leeward    | 91                            | 47.0±4.0           | 37.7                        | 200 (130)                | 0.85               |
|                     | trough     | 148                           | 70.3±4.1           | 49.7                        | 590 (200)                | 0.86               |
|                     | windward   | 97                            | 56.0±5.8           | 57.5                        | 740 (300)                | 0.78               |
Table 2.3 Transfer velocity data corrected to a reference temperature of 20°C (O₂ and CO₂).

<table>
<thead>
<tr>
<th>Surface descriptor</th>
<th>Experiment</th>
<th>Water temperature</th>
<th>Measured Transfer velocity $k_{v_{bulk}}$ (m/s) x10^6</th>
<th>Transfer velocity $k_{v_{bulk20}}$ (m/s) x10^6 $\propto Sc_{56}^{V2}$</th>
<th>Transfer velocity $k_{v_{bulk20}}$ (m/s) x10^6 $\propto Sc_{600}^{V2}$</th>
<th>Transfer velocity $k_{v_{bulk20}}$ (m/s) x10^6 $\propto Sc_{600}^{V3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat water</td>
<td>1 (f09u21ak0)</td>
<td>19.3</td>
<td>7.57</td>
<td>7.66</td>
<td>7.06</td>
<td>6.89</td>
</tr>
<tr>
<td>Low wave</td>
<td>2 (f34u21ak18)</td>
<td>19.1</td>
<td>13.8</td>
<td>14.1</td>
<td>12.9</td>
<td>12.7</td>
</tr>
<tr>
<td>Incipient</td>
<td>3 (f34u21ak27)</td>
<td>19.1</td>
<td>24.0</td>
<td>24.4</td>
<td>22.5</td>
<td>22.0</td>
</tr>
<tr>
<td>Microscale</td>
<td>4 (f34u57ak32)</td>
<td>18.4</td>
<td>88.6</td>
<td>92.2</td>
<td>84.9</td>
<td>83.8</td>
</tr>
<tr>
<td>Ripple</td>
<td>5 (f63u42ak00)</td>
<td>18.4</td>
<td>16.0</td>
<td>16.7</td>
<td>15.3</td>
<td>15.1</td>
</tr>
<tr>
<td>Low wave</td>
<td>6 (f21u39ak10)</td>
<td>18.3</td>
<td>26.2</td>
<td>27.4</td>
<td>25.2</td>
<td>24.9</td>
</tr>
<tr>
<td>Incipient</td>
<td>7 (f24u39ak24)</td>
<td>17.3</td>
<td>32.2</td>
<td>34.7</td>
<td>31.9</td>
<td>31.9</td>
</tr>
<tr>
<td>Microscale</td>
<td>8 (f31u39ak28)</td>
<td>17.0</td>
<td>63.4</td>
<td>68.9</td>
<td>63.5</td>
<td>63.5</td>
</tr>
</tbody>
</table>
Figure 2.1 Thermally insulated room containing wind-wave tank at the University of New South Wales, Water Research Laboratory. The sealed room assisted in controlling surface contamination and the absence of windows provided an ideal environment for LIF imagery.
Figure 2.2   The general arrangement of the wind-wave tank. The surface skimming weir ensured a slick free, clean water surface for all experiments. Fetch dependence of waves was minimized using mechanically generated waves forced by wind.
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3. MEASUREMENT OF NEAR-SURFACE VELOCITY STRUCTURE USING PIV

An essential component of the studies reported herein was the development and application of laboratory experimental techniques to investigate the hydrodynamic behaviour within the aqueous viscous sub-layer at the air-water interface. Flow behaviour within the viscous sub-layer has the potential to disrupt the concentration structure within the mass diffusion sub-layer. Consequently the microphysical wave kinematics within the viscous sub-layer influences gas flux across the air-water interface. This Chapter describes the application of PIV to investigate near surface velocities within the viscous sub-layer.

This Chapter also encompasses a description of notable advancements in the application of PIV near the air-water interface. These include:

- The use of Pliolite VT-AC-L, a white material with a relative density of 1.03 and excellent light scattering properties as the fluid tracer.
- The first direct measurements of wave surface velocity structure along the entire wave length.
- The first direct measurements of tangential stress beneath wind-driven air-water interfaces along the entire wave length.
- Instantaneous and average measurements of surface convergence and divergence at the wave interface.

3.1 Previous application of PIV within the viscous sub-layer of wind-forced wavy surfaces

Whilst there are numerous publications on the application of PIV in fluid flow, only two research groups (Okuda et al. 1977, Peirson and Banner 2003) have dealt with detailed flows within the aqueous viscous sub-layer of wavy air-water interfaces (upper 400μm). In
most cases the size of the particle tracers and/or the detection of the dynamic air-water interface have prevented the accurate measurement of the velocity structure and near-surface shear in the aqueous viscous sub-layer.

Earlier studies using surface floating drogues by researchers including Keulegan (1951), Phillips and Banner (1974) and Wu (1975) have reported that the mean surface transport for wind waves is given by \( \frac{0.55 \pm 0.1}{u^*} \). However, surface floating tracers may be influenced by “particle surfing” down the leeward slope of microscale breaking waves (Phillips and Banner 1974) and direct exposure to wind drag.

The most prominent PIV experimental studies of near surface shear at wavy air-water interfaces have been undertaken by Okuda et al. (1977), Banner and Peirson (1998) and Peirson and Banner (2003). Peirson and Banner (2003) used fluorescent particles with diameters between 20 and 60μm and a relative density of 1.2 as a fluid tracer to estimate the mean surface drift induced by the wind as \( \frac{0.23 \pm 0.02}{u^*} \) in the trough and \( \frac{0.33 \pm 0.07}{u^*} \) at the crest for microscale breaking wind waves. They also observed that in a frame of reference moving with the wave, the transport in the surface layer immediately beneath the air-water interface is rearward along its entire length, except within and immediately upwind of the spilling region. In contrast to previous understandings of wind drift surface layer flow, Peirson and Banner (2003) rarely observed transport of surface fluid forward over the crest and into the spilling region.

Okuda et al. (1977) reported surface tangential stress and surface velocity distributions based on hydrogen bubble measurements (bubble diameter 120 to 160μm) and found that very intense tangential stresses were induced at wave crests by the wind. They also conclude from their studies of short, strongly forced wind waves that the tangential stress in the surface layer immediately beneath the wavy interface contributes the entire interfacial stress. Banner and Peirson (1998) provide an alternative view in which they suggest that as the wave field develops, the waveform drag becomes increasingly prominent. They also
show that the tangential stress component modulates in phase with the wave surface elevation.

Peirson (1997) restricted the majority of his measurements to the windward faces of the waves and revealed regions of locally intense flow divergence. He concluded that these regions of observed divergence were significantly more diffuse than the convergent zones observed at the toes of spilling regions.

Several researchers including Chu and Jirka (1992), Brumley and Jirka (1998) and McKenna and McGillis (2004) have investigated gas transfer across the air-water interface and undertaken PIV measurements of the hydrodynamic structure beneath the free surface of grid stirred tanks. Such PIV measurements are of great value to the scientific community in understanding gas exchange enhancement due to disruption of the aqueous diffusion sub-layer. However, grid stirred tanks do not replicate the tangential stresses and wave hydrodynamics associated with wind forced waves and their influence on the aqueous diffusion sub-layer in open waters. The intensity of surface divergence and convergence measured by McKenna and McGillis (2004) for their grid stirred experiments was very low (20s⁻¹) in comparison to that measured by Peirson and Banner (2003) for microscale breaking waves where highly localised convergences regularly exceeded 100s⁻¹.

3.2 Surface and sub-surface velocity flow visualisation using PIV

The PIV technique adopted for this study follows that developed by Peirson (1997 and 1998). The four fundamental system apparatus in application of PIV are: light sheet generation; fluid particle tracers; synchronous image capture; and data processing techniques. PIV is essentially a *Langrangian* technique whereby individual particles are tracked along flow paths. Particle motion can be measured by single light pulses on a sequence of image frames (cross-correlation) or by multiple light pulses on individual image frames (auto-correlation). A significant advantage of the auto-correlation technique is that rapid image frame rates and high data transfer speeds are not essential. With an expected minimum time scale of approximately 2ms (Peirson 1998) required for imaging near the surface, auto-correlation is used in this study.
3.2.1 Light sheet generation

A 6W water-cooled argon ion laser was used for particle illumination. The argon ion laser emits a continuous beam with low divergence. Peirson (1997) developed an electro-mechanical driven precision wheel that was used to generate the light sheet. The light sheet generator was adapted for use on the wind-wave tank used in this study with its general arrangement shown in Figure 3.1.

Four high quality mirrors (12.5mm x 12.5mm) are mounted on the precision wheel, together with a 4:1 gear system used as the laser shutter (Figures 3.2 and 3.3). The angular frequency of the precision wheel was set such that the time between laser pulses was 2ms. Consequently four laser pulses were produced for each PIV image. At the water surface the light sheet was approximately 80mm wide by 1mm thick.

In each PIV image it was necessary to identify the laser pulse sequence to ascertain the direction of particle movement. A low transmission optical window was mounted to the laser shutter mechanism such that the fourth pulse was always of lower intensity. This was evident in the PIV images as the least bright particle in the sequence of four particle illuminations.

3.2.2 Fluid particle tracers

To examine the flow structure in the viscous sub-layer it is essential that the seeding particles:

- follow the fluid.
- have good light scattering properties.
- are of similar density to the fluid.
- are dimensionally significantly smaller than the flow field scales.
are cost effective.

are available in sufficient quantity to enable seeding at relatively high densities.

Peirson (1998) undertook a comprehensive review of particle tracers and selected Dayglo ZQ-17 particles for his PIV experiments. These particles are used as a fluorescent pigment by plastic manufacturers and have a relative density of 1.2. Initial trials in this study using Dayglo ZQ-17 indicated that the particles remained in suspension for a relatively short period of time and consequently continuous seeding close to the imaging location was required to maintain sufficient particles in suspension. Continuous seeding can be problematic: seeding rates need to be controlled; the seeding mechanism should not disrupt the local flow field, and some particles can float to the surface and subsequently cause difficulties in image processing.

Initial trials of Pliolite VT-AC-L, a white material with a relative density of 1.03 were encouraging. These particles were relatively inexpensive and available in large quantities. The particles came in a wide grading with most having diameters exceeding 1mm. Particle size was reduced by using a ball mill grinder to produce a size range as shown in Figure 3.4. The Pliolite is tightly graded with $d_{20}=12\,\mu m$, $d_{50}=27\,\mu m$ and $d_{80}=50\,\mu m$.

The Pliolite has very good light scattering properties and with a relative density close to unity, particles would remain in suspension for several weeks. Therefore, continuous seeding of the water was not required. Pliolite was used for all the PIV investigations reported herein.

For high density PIV investigations undertaken at scales to examine the aqueous viscous sub-layer a seeding density of approximately 10 particles/mm$^3$ is required. At lower seeding densities too few particles are visible for analysis and at higher seeding densities the water becomes opaque and a reduction in optical transparency inhibits particle identification.
3.2.3 Imaging

The Santa Barbara Instrument Group (SBIG) ST-10XME Charged Couple Device (CCD) camera was used for PIV imagery. As discussed in Chapter 2, this camera was primarily selected for its suitability to LIF imagery. The camera consists of 2184 horizontal pixels x 1472 vertical pixels. With the aid of a Nikon ED 80 to 200mm focal length lens and an extension bellows, the effective pixel dimensions in each image were between 4 and 5μm. The camera and lens arrangement is depicted in Figure 3.5.

The camera was mounted at an oblique angle (8°) as shown in Figure 3.1. This enables the viscous sub-layer immediately adjacent to the water surface to be observed in spite of cross-tank surface slope or the side wall meniscus.

For high resolution images, the SBIG camera requires approximately 15s to capture and download each image. Therefore, images were captured at 15s intervals, the highest capture rate possible. Images were also downloaded to the computer screen and could be readily inspected for acceptance or rejection based on the quality and presence/identification of the water surface.

A wave probe was mounted adjacent to the imaging sector to measure water surface elevation and an optical sensor was installed to detect the timing of the laser pulses. The camera shutter operation, water surface elevation and laser pulse detection was processed through the Eagle data acquisition board to a computer. This synchronous data was then used to determine wave phase location.

3.2.4 Image analysis

For wind sheared wavy interfaces, floating surface particles may be influenced directly by wind drag and hence, may bias inferred aqueous surface velocity measurements. Therefore, the sub-surface velocity field within the viscous sub-layer was used to estimate velocities at the surface by:
where: \( u_i, \ w_i \) and \( z_i \) are the coincident velocity and depth measurements of a pair of near surface particles.

The tangential stress \( \tau_{\text{tan}} \) is estimated by:

\[
\tau_{\text{tan}} = \mu \frac{u_i - u_2}{z_1 - z_2} \]

Once a PIV system is established, measurement of velocities in the flow field is relatively straightforward. However, the accurate positioning of the particles relative to the free surface is considerably more problematic and is the reason why all PIV analysis was undertaken manually rather than by an automated process. Peirson (1998) investigated a number of techniques for detection of the local free surface and surmised that the most accurate method was to make use of the oblique camera angle and the reflected image of particles from the surface (Figure 3.6).

Peirson (1998) noted, in the absence of the surface reflection signature, that the small but finite width of the laser light sheet could also cause a significant error (up to 80\( \mu \)m) in the vertical position of the particles relative to the air-water interface. Consequently, whilst images contained many particles (Figure 3.7), only particles where their surface reflection was present were used for velocity determination. The state of the water surface can have a significant bearing on analysis of PIV images. Peirson (1998) found that at the crests and leeward limbs of microscale breaking waves, reflected particles were not often visible and, hence, data at these locations was limited. This may lead to a potential bias in the data, with measurements only achievable when the surface is relatively smooth.
The absolute error in locating the coordinates of an individual particle was 4μm based on the pixel resolution and optical lens apparatus. For near surface velocities of 0.1m/s, the total velocity error is less than 5%.

3.3 Results
The PIV data presented herein is the most comprehensive data set presently available for wind sheared wavy interfaces and compliments the LIF data to be presented in subsequent chapters. The general wind and wave conditions, together with the PIV data for each experiment has been presented in Table 2.1 (Chapter 2). PIV was undertaken for five of the eight wind-wave experiments namely: the flat water case, the two incipient breaking cases and the two microscale breaking wave cases.

PIV data for the flat water case is presented in Figure 3.8 PIV data for the incipient and microscale breaking wave cases is presented in Figures 3.9 to 3.24 as a function of wave phase. Data for each of the wave cases is composed of four sets of figures. The first figure for each data set consists of a:

- typical wave profile
- $u$ and $w$ surface velocity components.
- total surface velocity.

Within a PIV image the spatial position of each illuminated particle is captured at four discrete locations (four laser pulses/image). The black, red and green data points (Figures 3.9, 3.13, 3.17 and 3.21) represent the mean velocity between the first and second laser pulses, the second and third laser pulses, and the third and fourth laser pulses respectively. Whilst each data point is an individual measurement, a statistical dependency also exists between the three data velocities derived from the four laser pulses (namely the data represented by the black, red and green points). Subsequently, an average of the three
velocities was undertaken to remove the statistical dependency within the data set. This effectively reduced the data sample set to 1/3 of its original size. The second figure for each data set is with the statistical dependency removed (Figures 3.10, 3.14, 3.18 and 3.22). Peirson (1998) found that the wave profile closely followed the theoretical 5th order Stokes Wave Equations. The solid lines in each of the plots represent the theoretical 5th order Stokes estimate (Skjelbreia and Hendrickson 1961).

The measured surface velocity before and after averaging is similar indicating that the absolute error in locating the coordinates of an individual particle is small. The averaged velocity data is used in all subsequent plots and analysis.

The phase location of each velocity measurement is determined relative to the preceding and proceeding wave crests. The wind forced waves are slightly asymmetric, with the leeward faces of the waves generally steeper than the windward faces. The asymmetry is evident in the upper panels of Figures 3.10, 3.14, 3.18 and 3.22. Consequently, the wave trough is not located midway between the wave crests. This can result in a misalignment of the calculated wave phase by up to ±10° for the microscale breaking wave cases.

The third figure (Figures 3.11, 3.15, 3.19 and 3.23) for each data set consists of:

- typical normalised wave profile.
- $u$ surface velocity component in a frame of reference moving with the wave.
- normalised surface velocity measurements.

Peirson (1998) found that for deep water waves the measured wave speed ($c$) was close to the theoretical estimate. The theoretical wave speed $c = g/2\pi f^2$ is used in this study to determine the surface velocity components in a reference frame moving with the wave.
The fourth figure (Figures 3.12, 3.16, 3.20 and 3.24) for each data set consists of five panels showing:

- $u$ surface velocity data and $u$ surface velocity data in 22.5° bins.
- tangential stress as a function of wave phase.
- 22.5° binned tangential stress.
- wave-coherent tangential stress and wave coherent tangential stress in 22.5° bins.
- surface convergence/divergence as a function of wave phase.

The first panel presents the surface velocity data in 22.5° bins. In Table 2.1 the mean surface velocity is estimated by two methods. The first method is a mean of all the data. This approach was used by Banner and Peirson (1998) and is only valid if the data is evenly distributed along the length of the wave. The second method, adopted for this study, was to bin the surface velocity data in 22.5° increments and then take an average of all the bins along the length of the wave. The second method is mathematically correct and adopted for subsequent analysis.

Banner and Peirson (1998) collected the majority of their PIV data on the windward face and crest region of microscale breaking waves as this was the critical region of their investigations. Their PIV data sets were the most comprehensive available on viscous sub-layer behaviour for wind forced waves. However, their estimates of mean surface velocity and total tangential stress were based on extrapolated profiles along the leeward face and troughs of the waves. In this study PIV data has been collected along the full length of the waves.
The second and third panels present the tangential stress data. In Table 2.1 the mean tangential stress is estimated by two methods. The first method is a mean of all the data and the second method is an average of the 22.5° tangential stress bins.

The fourth panel presents the wave-coherent tangential stress:

\[ \tau_{\text{tan,wc}} = \left( \tau_{\text{tan}} u_{sw} \right) / c \]  

[3.4]

where the local wave-coherent tangential surface velocity \( u_{sw} \) was estimated by subtracting the average binned tangential velocity \( u_{s} \) from the measured tangential surface velocity along the wave.

The fifth panel shows the measured surface convergence/divergence \( du/dx \) along the wave. The data points are effectively an instantaneous measurement of the surface convergence/divergence and are derived from two pairs of near-surface particles in the same image. The estimated surface convergence/divergence is sensitive to the distance \( dx \) between the two pairs of particles. If the horizontal distance between the two pairs of particles was less than 1mm the data was rejected for the purpose of estimating the surface convergence/divergence.

Relatively few estimates of the surface convergence/divergence were made at the crests of the waves. The highest velocities were measured at this location and in the majority of processed PIV images only one pair of near-surface particles is visible. A much shorter time between laser sheet pulses is required to effectively measure surface convergence/divergence at the crests of waves. This was beyond the operating capability of the equipment used in this investigation.

The binned surface convergence/divergence data are derived from the binned tangential surface velocity \( u_{s} \) shown in the first panel. \( du \) is generated from the difference between adjacent binned tangential surface velocities \( u_{s} \), and \( dx \) is the computed wave distance.
between the 22.5° bins. Thus, the binned surface convergence/divergence data is effectively an observed mean along the wave. The solid curve is the 5th order Stokes estimate of surface convergence/divergence.

3.4 Discussion

3.4.1 Surface velocities

For the flat water case a mean surface velocity of 0.0795 m/s was estimated from the PIV data (Table 2.1). Given that freely-propagating waves are absent from the surface, the mean surface velocity is the surface drift formed directly from wind-induced skin friction. The mean surface drift $\langle u_s \rangle / u^* = 0.66$ is approximately 20% greater than that estimated by Banner and Peirson (1998) for a much shorter fetch but with stronger wind forcing. A measure of the variability in the mean surface drift is given by $\sigma(u_s) / u^* = 0.12$.

For the incipient and microscale breaking cases, the measured surface velocity is significantly higher than that determined from Stokes 5th order theory (Figures 3.10, 3.14, 3.18 and 3.22). Adopting the Stokes theory as representative of the wave orbital component, the difference can then be attributed to wind surface drift or spilling at the wave crest. The measured mean drift for the incipient and microscale breaking cases is $\langle u_s \rangle / u^* = 0.22 \pm 0.03$ in the wave troughs, increasing to $\langle u_s \rangle / u^* = 0.35 \pm 0.03$ at the wave crests. These results are in good agreement with Peirson and Banner (2003).

The Stokes estimates form a lower bound to the velocity data. As the friction velocity increases the variability in the surface velocities also increases. The variability in surface velocity data is notably larger near the wave crests. Peirson (1998) found that at low wind speeds the variability in the surface velocities was principally due to modulations in the wave field associated with wave groups. For stronger wind forcing (higher friction velocity) Peirson (1998) suggested that the greater variability could possibly be attributed to fluctuations in the skin friction or turbulence in the wake of the spilling region.
In a frame of reference travelling with the wave, transport in the aqueous surface layer is rearward along the entire wavelength, except for the strongly wind forced microscale breaking case, where the measured surface velocity at the crest of the waves is similar in magnitude to the wave speed (Figure 3.15). This finding is consistent with the measurements by Peirson and Banner (2003). For the incipient cases, the measured surface velocity at the crest of the waves is approximately 50% of the wave speed.

Okuda (1982) concludes that the surface drift at the crests of microscale breaking waves is strongly modulated. Measurements presented herein indicate a gradual and steady increase in the mean phase-averaged surface drift between the wave trough and wave crest. There is approximately a 60% increase in the mean drift velocity between the troughs and crests of the waves.

3.4.2 Mean tangential stress
For the same wind speed, only a small decrease in the binned mean tangential stress is observed for developing waves despite significant changes in the visual appearance of the water surface roughness (Table 2.1). Comparable water surface images are presented in the upper panels of Figures 2.8 and 2.9 (Experiments 1 and 3) and Figure 2.11 (Experiments 7 and 8).

As the friction velocity increases the variability in the tangential stress also increases (Figures 3.12, 3.16, 3.20 and 3.24). For the microscale breaking cases there is a considerable population of negative tangential stress measurements. These are most likely indicative of disturbances in the viscous sub-layer caused by near surface turbulent structures. In addition to the attendant well structured parasitic capillary waves on incipient and microscale wave surfaces, less structured (wind induced) capillary waves populate most of the water surface. Longuet Higgins (1992) shows that at the crest of these capillary waves vorticity acts in an anti-clockwise direction, whilst in the troughs of these capillary waves vorticity is clockwise, for progressive surface waves travelling from the observers left to right hand side. The vorticity associated with the wind induced capillaries may be responsible for the measured negative tangential stresses.
The binned tangential stress data indicates a general peak at a wave phase location of between -70° and 0° (i.e. on the windward side of the wave crest). This is in agreement with the findings of Banner and Peirson (1998). Banner and Peirson (1998) undertook relatively few tangential stress measurements on the leeward faces of microscale waves (wave phase 0° to 180°) and assumed a profile based on experimental visual air flow detachment and reattachment points. Their assumed lower bound profile assigned a tangential stress of zero between phase points 70° and 160°. Measurements along the leeward faces of waves in this study suggest that the tangential stresses may be more uniformly distributed between the crest and trough.

In the flat water experiment, form drag should be negligible and the mean tangential stress is equivalent to the total stress (Table 2.1) given by:

\[ \tau = \rho \left( \bar{u}_*^{'} \right)^2 \]  

[1.13]

As the waves develop, the influence of form drag on the total stress becomes more pronounced. For the incipient wave cases the tangential stress accounts for between 26% and 39% of the total stress and for the microscale breaking wave cases only 20% of the total stress is due to the tangential component. The influence of the form drag is in agreement with the findings of Banner (1990) and Banner and Peirson (1998) for well developed waves.

The fraction \( \frac{\tau_{\text{tan},g}}{\tau} \) as a function of non-dimensional parameters such as the wave Reynolds number \( U\lambda/\nu_{\text{air}} \), the roughness Reynolds number \( z_0\lambda/\nu_{\text{air}} \) or the wave age \( c/U \) has been explored by Banner and Peirson (1998) for small data sets. The Banner and Peirson (1998) data sets are included with the experimental data from this investigation and plotted in Figures 3.25 to 3.27. The wave Reynolds number (Figure 3.25) and the wave age (Figure 3.26) non-dimensional parameters do not provide a good correlation of the data, although \( \frac{\tau_{\text{tan},g}}{\tau} \) asymptotes towards 0.2 to 0.3. The roughness Reynolds number (Figure
3.27) provides a systematic collapse of the data with $\tau_{\tan g}/\tau$ trending toward 0.2, which is consistent with the microscale breaking wave cases of this investigation.

Early investigations had assumed that the sea surface becomes fully aerodynamically rough (Donelan 1990). Banner and Peirson (1998) show that $\tau_{\tan g}/\tau$ trends towards a value of 0.3, whilst Buckles et al. (1984) show that for comparably steep solid waves $\tau_{\tan g}/\tau \approx 0.11$. For the microscale breaking wave cases investigated in this study $\tau_{\tan g}/\tau$ trends towards a value of 0.2. These results indicate a transitional rather than fully rough surface.

### 3.4.3 Wave-coherent tangential stress

An objective of the investigations undertaken herein was to minimise the variation of gas transfer velocity with fetch by maintaining a constant wave field along the length of the flume by using mechanically generated waves forced by wind. Subsequently, the uniform wave field provided the opportunity for a reconciliation of bulk and local gas fluxes.

The transfer of wind momentum to the water is via contributions from the form drag and skin friction at the interface. The momentum flux from the wind is partitioned between the surface drift current and wave motion. Peirson (1998) shows that the entire form drag contributes directly to wave development, whereas skin friction contributes to both wave growth and the surface drift current (Figure 3.28). The skin friction contribution to wave growth can be estimated by measuring the tangential stresses coherent with the wave $\langle \tau_{\tan g,we} \rangle$.

For the incipient and microscale breaking cases (Table 2.1) the mean wave coherent tangential stress was between 0% and 9% of the total tangential stress, indicating that skin friction contributed very little to wave growth along the fetch of our test facility. The mean wave coherent tangential stress in all cases was less than 4% of the total wind stress.

Whilst form drag was not measured in this study it can be estimated from:
\[ \tau_{\text{form}} = \tau - \tau_{\text{tan} g} \]  

Consequently, it was found that wave coherent stresses are dominated by wave form drag.

### 3.4.4 Surface convergence/divergence

Using Stokes 5\textsuperscript{th} order wave theory the maximum surface convergence/divergence for the wave cases investigated is between 3.4 and 6.1s\textsuperscript{-1} (lower panel of Figures 3.12, 3.16, 3.20 and 3.24). The binned surface convergence/divergence in the same plots are derived from the binned surface velocity data and is in good agreement with Stokes theory. The observed difference in the mean surface drift between the wave crests and troughs also contributes a mean surface convergence/divergence of approximately 1.0s\textsuperscript{-1}.

Maximum instantaneous measurements of surface convergence/divergence are in the order of 20s\textsuperscript{-1}. As the friction velocity increases, the variability in the measured surface convergence/divergence also increases. Peirson and Banner (2003) showed highly localised convergence of surface fluid within the spilling region of microscale breaking waves (>100s\textsuperscript{-1}) and also concluded that surface convergence due to parasitic capillary waves was relatively small. As discussed in Section 3.3, the PIV experimental arrangement available for this study had limitations that made it infeasible to obtain extensive measurements of surface convergence/divergence near the crests of microscale waves.

### 3.4.5 Gas exchange at the air-water interface

The present measurements of the surface layer kinematics suggest that gas exchange across the air-water interface is a complex process, involving disruption of the aqueous diffusion sub-layer through both tangential stresses and wave motion. Prior to the development of waves, disruption to the aqueous diffusion sub-layer must be due to momentum flux from the wind and the formation of a surface wind drift current through tangential stresses. Whilst measurements of the wind drift current and tangential stress for the flat water case is relatively uniform (Figure 3.8), variability in the data is evident, giving rise to an unsteady hydrodynamic regime and the presence of convergent and divergent zones at the water
surface. This is in contrast to the gas exchange model proposed by Deacon (1977) in which a solid hydrodynamic boundary is assumed at the air-water interface.

As waves begin to develop the wind drift current at the wave crests is approximately 60% higher than in the wave troughs. Consequently, the tangential stresses near the wave crests must be higher than those in the wave troughs. This is in general agreement with the data presented herein. Greater variability in the wind drift current is also observed at the crests of the waves. Disruption or thinning of the mass diffusion sub-layer due to tangential stresses is therefore likely to be more dominant near the wave crests.

Form drag also becomes more pronounced as waves develop. Wave orbital velocities impart a cyclic convergence/divergence at the surface that modulates the thickness of the aqueous diffusion sub-layer. As the wave steepness increases, the convergence/divergence strengthens in magnitude. Mean convergence is experienced on the leeward face and mean divergence on the windward face of waves. Thus, surface convergence/divergence from both wave orbitals and the surface drift current have the potential to thin the mass diffusion sub-layer.

At the onset of microscale breaking waves, Peirson and Banner (2003) showed highly localised convergence of surface fluid within the spilling region (>100s⁻¹), but also concluded that surface convergence due to parasitic capillary waves was relatively small. Therefore, with the commencement of microscale breaking a further hydrodynamic mechanism (subduction at the toe of the spilling region) is triggered that has the potential to disrupt the mass diffusion sub-layer.

The role of these processes in gas exchange is developed further in Chapter 5 complemented by the LIF data.

3.5 Summary

PIV techniques have been successfully used to measure the microphysical hydrodynamics within the viscous sub-layer of a near-uniform field of wind forced mechanically-generated
waves. PIV experiments conducted herein are the first that examine the surface hydrodynamic structure along the entire wavelength. There are several new observations that have been obtained during this aspect of the study that yield unique insights:

- for the flat water case (before the onset of waves and form drag) the measured tangential stress is equal to the total wind stress. This confirms the reliability of the measurement approach.

- the measured mean wind drift current for the incipient and microscale breaking cases is $\langle u_x \rangle / u^*_w = 0.22 \pm 0.03$ in the wave troughs, increasing to $\langle u_x \rangle / u^*_w = 0.35 \pm 0.03$ at the wave crests. These results are in agreement with Peirson and Banner (2003).

In a frame of reference travelling with the wave, transport in the aqueous surface layer is rearward along the entire length of the wave, except for the strongly wind forced microscale breaking case, where the measured surface velocity at the crest of the waves is similar in magnitude to the wave speed.

For the microscale breaking wave cases only 20% of the total stress is due to the tangential component, the remaining 80% is due to form drag. The wave coherent tangential stress accounts for less than 4% of the total wind stress.

The average surface convergence/divergence is similar to that estimated by 5th order Stokes theory, however, significantly larger instantaneous measurements of surface convergence/divergence were observed using PIV.

The contributions of the tangential stress and wave form drag to disruption of the mass diffusion sub-layer have been discussed in relation to the PIV observations. With the aid of the LIF measurements this understanding is developed further in Chapter 5.
Figure 3.1 The general arrangement of the PIV system components. Figure reproduced from Peirson (1998).
Figure 3.2  Scale drawing of the PIV light sheet generator. Figure reproduced from Peirson (1998).
Figure 3.3  Photograph of the light sheet generator installed for this study.
Figure 3.4  Particle size distribution for milled pliolite. Following milling the pliolite was passed through a 63µm sieve. $d_{50} = 27\mu m$. The pliolite size grading was established using a laser particle sizer and is reported as % less than by weight.
Figure 3.5  Photograph showing SBIG ST-10XME camera, extension bellows and Nikon ED 80 to 200mm focal length lens. The camera was mounted at an oblique angle of 8°.
Figure 3.6   Schematic showing the error in estimated particle distance from the surface induced by a cross-tank surface slope (Peirson 1998).
Figure 3.7  PIV image (9.5mm x 6.4mm).  A particle and its reflected image are indicated by the arrows. The surface is determined as the mid point of the location of the particle and its reflected image. The arrows are positioned at the first of the four laser pulses. The fourth laser pulse is of lower intensity and hence the particle appears dimmer. The particles are moving from left to right in the image. For particles at greater depths, the reflected image cannot be detected and therefore these particles are not used in image processing.
Figure 3.8  Experiment 1 (Flat water f00u21ak0) surface velocity and tangential stress data. Data is plotted as a series to demonstrate variability in PIV observations.
Figure 3.9 Experiment 3 (Incipient f34u21ak27) PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.10  Experiment 3 (Incipient f34u21ak27) Averaged PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.11  Experiment 3 (*Incipient f34u21ak27*) PIV surface velocity data. Upper panel: normalised typical wave profile (dashed curve) and normalised $5^{th}$ order Stokes profile (solid curve). Second panel: surface velocity in a frame of reference moving with the wave and $5^{th}$ order Stokes estimate (solid curve). Third panel: normalised surface velocity in a frame of reference moving with the wave and $5^{th}$ order Stokes estimate (solid curve).
Figure 3.12 Experiment 3 (*Incipient f34u21ak27*) Distributions as a function of wave phase. Upper panel: surface velocity and 22° binned surface velocity. Second panel: tangential stress. Third panel: 22° binned tangential stress. Fourth panel: wave coherent tangential stress and 22° binned wave coherent tangential stress. Fifth panel: surface convergence/divergence, 22° binned surface convergence/divergence derived from binned surface velocity data and estimated surface convergence/divergence using 5th order Stokes theory.
Figure 3.13 Experiment 4 (Microscale f34u57ak32) PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.14  Experiment 4 (Microscale f34u57ak32) Averaged PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.15  Experiment 4 (Microscale f34u57ak32) PIV surface velocity data. Upper panel: normalised typical wave profile (dashed curve) and normalised 5th order Stokes profile (solid curve). Second panel: surface velocity in a frame of reference moving with the wave and 5th order Stokes estimate (solid curve). Third panel: normalised surface velocity in a frame of reference moving with the wave and 5th order Stokes estimate (solid curve).
Figure 3.16  Experiment 4 (Microscale f34u57ak32) Distributions as a function of wave phase. Upper panel: surface velocity and 22° binned surface velocity. Second panel: tangential stress. Third panel: 22° binned tangential stress. Fourth panel: wave coherent tangential stress and 22° binned wave coherent tangential stress. Fifth panel: surface convergence/divergence, 22° binned surface convergence/divergence derived from binned surface velocity data and estimated surface convergence/divergence using 5th order Stokes theory.
Figure 3.17  Experiment 7 (Incipient) PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.18  Experiment 7 (Incipient f24u39ak24) Averaged PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.19  Experiment 7 (Incipient f24u39ak24) PIV surface velocity data. Upper panel: normalised typical wave profile (dashed curve) and normalised 5\textsuperscript{th} order Stokes profile (solid curve). Second panel: surface velocity in a frame of reference moving with the wave and 5\textsuperscript{th} order Stokes estimate (solid curve). Third panel: normalised surface velocity in a frame of reference moving with the wave and 5\textsuperscript{th} order Stokes estimate (solid curve).
Figure 3.20  Experiment 7 (Incipient f24u39ak24) Distributions as a function of wave phase. Upper panel: surface velocity and 22° binned surface velocity. Second panel: tangential stress. Third panel: 22° binned tangential stress. Fourth panel: wave coherent tangential stress and 22° binned wave coherent tangential stress. Fifth panel: surface convergence/divergence, 22° binned surface convergence/divergence derived from binned surface velocity data and estimated surface convergence/divergence using 5th order Stokes theory.
Figure 3.21  Experiment 8 (Microscale f31u39ak28) PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.22  
Experiment 8 (Microscale f31u39ak28) Averaged PIV surface velocity data. Upper panel: typical wave profile (dashed curve) and 5th order Stokes profile (solid curve). Second panel: horizontal velocity component and 5th order Stokes estimate (solid curve). Third panel: vertical velocity component. Fourth panel: total surface velocity magnitude.
Figure 3.23  Experiment 8 (Microscale f31u39ak28) PIV surface velocity data. Upper panel: normalised typical wave profile (dashed curve) and normalised 5th order Stokes profile (solid curve). Second panel: surface velocity in a frame of reference moving with the wave and 5th order Stokes estimate (solid curve). Third panel: normalised surface velocity in a frame of reference moving with the wave and 5th order Stokes estimate (solid curve).
Figure 3.24  Experiment 8 (Microscale f31u39ak28) Distributions as a function of wave phase. Upper panel: surface velocity and 22° binned surface velocity. Second panel: tangential stress. Third panel: 22° binned tangential stress. Fourth panel: wave coherent tangential stress and 22° binned wave coherent tangential stress. Fifth panel: surface convergence/divergence, 22° binned surface convergence/divergence derived from binned surface velocity data and estimated surface convergence/divergence using 5th order Stokes theory.
Figure 3.25 Relative contribution of the tangential stress to the total wind stress as a function of the wave Reynolds number. Data from Banner and Peirson (1998) is shown as black circular symbols. Data from this study is shown as red diamond symbols.
Figure 3.26 Relative contribution of the tangential stress to the total wind stress as a function of the wave age, where $c$ is the phase speed of the dominant wave. Data from Banner and Peirson (1998) is shown as black circular symbols. Data from this study is shown as red diamond symbols.
Figure 3.27  Relative contribution of the tangential stress to the total wind stress as a function of the roughness Reynolds number. Data from Banner and Peirson (1998) is shown as black circular symbols. Data from this study is shown as red diamond symbols.
Figure 3.28 A model of air-sea interface processes proposed by Peirson (1998) for the transfer of wind momentum to waves and the drift current.
4. MEASUREMENT OF NEAR-SURFACE CONCENTRATION PROFILES USING LIF

A major component of the studies reported herein was the development and application of laboratory experimental techniques to investigate gas transfer across wind-forced wavy air-water interfaces. The key content of this chapter has been published in Walker and Peirson (2008).

For these investigations gas transfer across the air-water interface was measured by two techniques:

1. The bulk dissolved oxygen method.

2. Laser induced fluorescence (LIF).

The apparatus and method used to measure the bulk dissolved oxygen concentration are discussed in Chapter 2. The development and application of the considerably more complex LIF experiments are presented herein.

This Chapter also encompasses a description of notable advancements in the application of LIF near the air-water interface. These include:

- The first reliable measurements of the dissolved oxygen concentration profile to within 28μm of a moving air-water interface.

- The first phase resolved gas flux measurements at the crest, trough and mid height of both the rising and falling limbs of waves.

- The first deep water tests for which the laser sheet has been directed through the base of the wind-wave tank. By careful selection of the fluorescent tracer concentration, the illuminating optical path length has been sufficiently extended to
enable experiments to be conducted for deep water wave conditions for wind sheared wavy interfaces.

- A formal mathematical description of previously unidentified optical distortions has been developed and the implications of these optical distortions on the potential under-prediction of transfer velocities or over-prediction of the diffusion sub-layer thickness are discussed.

The LIF experiments were designed to measure the dissolved oxygen concentration profile in the upper 2 to 3mm of the water column with particular emphasis on the dissolved oxygen concentration profile in the diffusion sub-layer (the upper 200 to 300μm). The LIF experiments principally consist of dissolving pyrenebutyric acid (PBA) in the flume, pulsing a UV laser sheet through the water column to excite the PBA molecules and capturing the PBA fluorescence with a digital camera system. Collisional quenching of PBA fluorescence occurs in the presence of oxygen. The fluorescent signal is inversely proportional to the dissolved oxygen concentration and therefore each digital image is essentially an instantaneous measure of the dissolved oxygen concentration profile at a discreet location. The dissolved oxygen concentration profile can then be examined to determine the gas flux across the air-water interface at that location.

4.1 The diffusion sub-layer
As discussed in Chapter 3 reliable velocity measurements within the thin viscous sub-layer for wind sheared wavy air-water interfaces are extremely difficult and have been successfully undertaken by few researchers. The difficulties are primarily associated with the:

- microscale thickness of the viscous sub-layer.
- the unsteady location of the air-water interface.
- suitable particle tracers.
time and length scales for accurate measurements.

With Schmidt numbers for oxygen of approximately 500 to 600, the mass diffusion sub-layer is over an order of magnitude smaller than the viscous sub-layer. Consequently reliable measurements of the diffusion sub-layer have proven to be even more challenging.

Recent developments in computer, laser and CCD technology has seen advances in fluorescent imaging techniques for a wide variety of applications. The use of LIF to measure the dissolved oxygen concentration gradient has only recently been applied to examine the near-surface concentration structure.

From the one-dimensional form of Fick’s steady state first law:

$$ F = -D \frac{\partial C}{\partial z} $$  \[1.6\]

gas fluxes across the air-water interface may be estimated from the dissolved oxygen concentration gradient.

As previously discussed in Chapter 1, numerous researchers have suggested a turbulent diffusion coefficient $K_e$ that varies with distance from the surface such that:

$$ F = -(D + K_e) \frac{d\bar{C}}{dz} $$  \[1.19\]

and by applying Reynolds decomposition, $K_e$ is found theoretically to increase proportionally as the distance cubed from a rigid surface and as the distance squared from a free surface.
From Equation 1.19, Deacon (1977) found theoretically that \( k_v \propto Sc^{-1/2} \) for a smooth surface. For free surface interfaces Ledwell (1984) and Coantic (1986) found theoretically that \( k_v \propto Sc^{-1/2} \). Based on bulk transfer velocity experimental data Jähne et al. (1987) also found evidence that for free surface interfaces \( k_v \propto Sc^{-1/2} \). Subsequently they concluded that the effective thickness of the diffusion sub-layer is in part controlled by zones of surface convergence and divergence.

With knowledge of the concentration profile immediately adjacent to the surface, Equations 1.6 and 1.19 can be applied to determine localised instantaneous gas fluxes.

### 4.2 Previous measurements of concentration profiles in the diffusion sub-layer

There have been relatively few microphysical measurements of the diffusion sub-layer to verify the theory. Chu and Jirka (1992) developed a polarographic oxygen microprobe to measure dissolved oxygen concentrations within the diffusion sub-layer. This technique allowed profiling at discrete depth intervals of approximately 100μm adjacent to flat water surfaces. However, its spatial resolution was still only suitable for identifying a diffusion sub-layer thickness rather than determining a dissolved oxygen concentration gradient.

The first non-intrusive experiments to measure dissolved oxygen concentration profiles in the diffusion sub-layer were undertaken by Wolff and Hanratty (1994) utilising collisional oxygen quenching of PBA illuminated by a laser light sheet. This LIF technique was subsequently developed by Woodrow and Duke (2001).

Wolff and Hanratty (1994) recorded instantaneous profiles of fluorescent intensity between the surface and a depth of 3mm. The fluorescent intensity profile was subsequently processed to determine a dissolved oxygen concentration profile over the same water depth for wind forced and flowing water, in a tank 11m long x 0.35m wide. Woodrow and Duke (2001) investigated flat water and paddle generated wavy interfaces in a tank 1.2m long x 0.3m wide with an 11mm water depth and recorded a reduction in the diffusion sub-layer thickness when small waves were present.
Wolff and Hanratty (1994) and Woodrow and Duke (2001) directed the laser sheet through the base of the tank to the water surface. Due to absorption of the laser light through the water column they were restricted to relatively shallow water depths (<11mm). Herlina and Jirka (2004) undertook similar experiments in a water depth of 473mm by directing the laser down through the water surface. However, such application is restricted to relatively weak sub-surface forcing due to refraction effects associated with surface curvatures arising from strong sub-surface turbulence or wave generation.

For the composition of a concentration profile from LIF imagery it is necessary to identify the spatial coordinates of the water surface. Woodrow and Duke (2001) and Herlina and Jirka (2004) used a symmetry algorithm to identify the location of the water surface. Whilst for their applications a symmetry algorithm was adequate, this method becomes less robust for steep waves or sloping surfaces. Both groups of researchers also observed a measured concentration distortion near the surface (optical blurring) resulting from their experimental set-up. The optical blurring limited the proximity of valid concentration measurements close to the air-water interface.

A relevant parallel study of the transfer of a reactive gas (HCl) across a wind sheared air-water interface was undertaken by Münsterer and Jähne (1998) using fluorescein as the fluorescence indicator. The fluorescent intensity is determined by the pH of the water arising from absorption of the HCl gas. Fluorescein illumination was provided by a 1W argon-ion laser directed from above the water surface. They found that the thickness of the HCl diffusion sub-layer changed rapidly with time and that the fluctuations in the sub-layer thickness were of the same order of magnitude as the mean thickness of the sub-layer. Woodrow and Duke (2001) also observed significant fluctuations in their measurements of the thickness of the diffusion sub-layer.

Takehara and Etoh (2002) used a similar method to Münsterer and Jähne (1998) by substitution of CO2 for HCl to visualise CO2 gas transfer at the air-water interface under wind wave conditions in the laboratory. Whilst detached surface layers of CO2 rich water
were observed, measurements were not of sufficient detail to measure the concentration gradient within the diffusion sub-layer.

4.3 Experimental Facilities

A detailed investigation of the PBA technique has been completed and then developed for practical application to strongly-forced laboratory conditions. In this contribution a description of the key apparatus assembled to undertake precise LIF measurements is presented. The general experimental arrangement is described in Chapter 2.

The insulated room containing the wind-wave flume was maintained at a temperature of 21.5±0.5°C. It was noted that the water temperature in the wind-wave tank varied depending on the strength of the wind and wave action. Therefore all gas exchange experiments were only commenced following an equilibrium temperature in the tank being attained. This encompassed operation of the wind-wave tank overnight prior to the commencement of detailed measurements.

Profile measurements of dissolved oxygen concentration were recorded in the upper 2 to 3mm of the water column using an LIF system with the objective of capturing the dissolved oxygen concentration profile in the diffusion sub-layer along the surfaces of wind-forced surfaces.

4.3.1 Light Sheet Generation

LIF illumination was provided by a PTI model GL3300 nitrogen laser. The nitrogen laser emits light in the UV spectrum at a wavelength of 337.1nm and has a pulse width of 600ps. At the point of exiting the laser, the beam has dimensions of 6mm wide x 3mm thick and has a divergence half angle of 0.007 radians in the horizontal plane and 0.003 radians in the vertical plane.

A series of UV fused silica lenses were used to contract and focus the light sheet to approximately 6mm wide x 0.4mm thick at a distance of 985mm from the laser. The lenses consist of a 600mm focal length plano-convex spherical lens to minimise expansion of the
beam exiting the laser followed by a 300mm focal length plano-convex cylindrical lens to produce the 6mm wide sheet at the water surface. A second 300mm focal length plano-convex cylindrical lens was used to form a light sheet of 0.4mm thickness in the vicinity of the water surface. A 45° incidence angle 337nm nitrogen gas unpolarised flat mirror was used to reflect the laser sheet up through the base of the wind-wave tank and into the water column (Figures 4.1 and 4.2).

4.3.2 PBA Fluorescence and Concentration
Pyrenebutyric acid (C\textsubscript{20}H\textsubscript{16}O\textsubscript{2}) has a molecular weight of 288.35. The fluorescence spectrum for PBA is shown in Figure 4.3. The optimum concentration of PBA is a compromise between absorbance and fluorescence.

The intensity of the pulsed UV light sheet diminishes exponentially as it travels through the water column and is described by the Lambert-Beers decay equation:

\[
\frac{I_{LB}}{I_{LB0}} = \exp\left(-\psi_{mc}C_{PBA}l\right) \tag{4.1}
\]

where

- \(I_{LB0}\) is the laser intensity before it enters the fluid;
- \(I_{LB}\) is the laser intensity at a distance \(l\) through the fluid;
- \(C_{PBA}\) is the molar concentration of the PBA; and,
- \(\psi_{mc}\) is a molecular constant.

Therefore, to minimise absorption of the light sheet the distance through the water column should be short and/or the molar concentration of the PBA should be low.

The intensity range of the PBA fluorescent signal is described by the Stern-Vollmer equation
\[
\frac{I_{0q}}{I} = \frac{\tau_{0q}}{\tau_q} = 1 + \alpha C
\]

where \( I \) is the fluorescent intensity;
\( \tau_q \) is the fluorescent lifetime;
\( \alpha \) is the quenching rate constant; and,
\( C \) is the concentration of the quencher (oxygen).

The subscript \( 0q \) denotes the absence of a quencher.

All experiments were conducted in total water depths between 230mm and 255mm. From preliminary calculations and pilot experiments it was evident that decay of the laser sheet was too great for these water depths. To minimise absorbance of the UV laser sheet, it was directed through a hollowed cylindrical section (capped with a UV silica lens, 50mmØ) extending 170mm into the water column from the base of the tank (Figure 4.4). For the wave periods investigated in this study a water depth of 80mm above the optical cylinder maintained the integrity of the deepwater wave classification. Consequently the optical cylinder had a negligible effect on the near surface hydrodynamics.

Transmission of UV light through “Perspex” and tempered glass is low. Therefore, the side wall of the wind-wave tank was also fitted with 50mmØ UV silica lens to facilitate image capture of the fluorescence (Figure 4.4, lower panel). The silica lens was mounted on a sliding mechanism so that its position could be adjusted to align with the water surface.

Having established the dimensional length criteria for the LIF experiments numerous solutions of PBA at different molar concentrations were tested to determine the optimal concentration. Optimising the molar concentration of the PBA reduces the noise/signal ratio to a minimum. Results depicting fluorescent intensity versus PBA molar concentration for fully saturated oxygen solutions are shown in Figure 4.5. The rising limb of the graph indicates that the molar concentration of the PBA is too low resulting in a low
fluorescent signal. The falling limb of the graph indicates that the molar concentration of
the PBA is too high due to high absorbance of the UV laser sheet resulting in a low
fluorescent signal. The peak of the graph indicates the optimal molar concentration of
PBA. A concentration of approximately 7x10^{-6} M PBA was adopted for all experiments.
This value is considerably lower than that used by other researchers but permitted use of
the greater water depths during these experiments.

The PBA is not readily soluble in water. Initially 3.028g of PBA was dissolved in 15L of a
0.05M solution of warm NaOH to form a 7.0x10^{-4} M PBA solution. This solution was then
added to the wind-wave tank to form a 7x10^{-6} M PBA solution. The solution was well
mixed prior to the commencement of experiments.

The quenching rate constant $\alpha$ in Equation 4.2 is proportional to the sum of the diffusion
coefficients for oxygen and PBA in water. Münsterer et al. (1995) determined a value of
683±70L/mol for PBA. Vaughan and Weber (1970) found the quenching rate constant to
be 645±79L/mol for PBA, whilst Lee (2002) appears to adopt a value greater than
1150L/mol. Experiments by Herlina and Jirka (2004) supported the value of the constant
found by Münsterer et al. (1995). There are substantial variations in the value of the
quenching rate constant as determined by a number of researchers. The reasons for this are
not immediately clear, but may include the experimental set-up, calibration methods and
the sensitivity of the CCD camera to the UV spectra.

For experiments conducted herein the quenching rate constant was independently
established and found to be 870L/mol or 0.0272mg/L. Using the Stern-Vollmer
relationship (Equation 4.2) the relative PBA fluorescent intensity is plotted for several
quenching rate constants and is presented in Figure 4.6.

The quenching rate constant was determined experimentally. Care was taken to ensure that
the experimental arrangement was exactly the same for both the derivation of the
quenching rate constant and each LIF gas flux experiment. Data processing for
determination of the quenching rate constant was also identical to each of the LIF gas flux
experiments. Therefore, the quenching rate constant could also be independently verified for each LIF gas flux experiment.

From a series of LIF images the bulk dissolved oxygen concentration as measured by the Orion oxygen probe is compared to the measured fluorescence in the bulk of the water. By rearrangement of the Stern-Vollmer equation (Equation 4.2):

$$\alpha = \frac{I_{0q} - I}{IC}$$

[4.3]

and optimisation of $I_{0q}$, the quenching rate constant $\alpha$ is plotted against the bulk dissolved oxygen concentration as shown in Figure 4.7. The optimal value for $I_{0q}$ will yield a line of best fit to this data with zero slope. The upper and lower panels in Figure 4.7 are for two independent data sets. The dashed horizontal line is the quenching rate constant used by Herlina and Jirka (2004) and the solid horizontal line is that used in this study. Clearly, the value used by Herlina and Jirka (2004) is too low for our experimental arrangement. A similar plot was created for each experiment to validate the accepted quenching rate constant.

The scatter in the data is principally due to small variations (<2%) in the laser illumination. At low dissolved oxygen concentrations, or as $I$ approaches $I_{0q}$, the data scatter is greater. Treatment of variations in laser illumination for each LIF experiment is discussed later in this Chapter.

4.3.3 Imaging

A Santa Barbara Instrument Group (SBIG) ST-10XME Charged Couple Device (CCD) camera was selected for the LIF visualisation. The CCD detector is a KAF3200ME with relatively high sensitivity in the UV spectra and has specifications as follows:
Table 4.1 Camera specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of pixels</td>
<td>2184 x 1472</td>
</tr>
<tr>
<td>Pixel dimensions</td>
<td>6.8μm x 6.8μm</td>
</tr>
<tr>
<td>Array dimensions</td>
<td>14.9mm x 10.0mm</td>
</tr>
<tr>
<td>Read noise</td>
<td>11e-` rms</td>
</tr>
<tr>
<td>Full well capacity</td>
<td>77ke-</td>
</tr>
</tbody>
</table>

PBA fluorescence occurs at wavelengths between 375nm and 425nm (Figure 4.3). The quantum efficiency of the CCD for these wavelengths varies between 50 and 60%. The camera has a minimum frame capture cycle time of 15s that is limited by the data transfer from the camera to computer storage.

Random readout noise and dark current are sources of error in the captured images. Dark current is thermally generated in the CCD and can be reduced by cooling. The camera has an internal solid-state thermoelectric cooler for temperature control. For all LIF experimental imagery the camera was cooled to -10°C. Cooling the camera below -10°C showed no further improvement in the signal to noise ratio. Residual charge is another noise source associated with the CCD readout electronics. Double correlated sampling was undertaken during image generation to minimise the residual noise.

A Nikon ED 80 to 200mm focal length lens with an extension bellows (Figure 4.4) was used to magnify the image to provide an effective in situ pixel dimension of 4.15μm high x 4.15μm wide within the light sheet. Between the Nikon lens and the CCD camera a long pass edge filter was inserted to remove scattered incident laser light. The edge filter provided greater than 99% transmission for light with wavelengths longer than 370nm and provided greater than 99% blockage of light with wavelengths shorter than 340nm (nitrogen laser 337.1nm).

The image capture sequence was: 1.) the electro-mechanical camera shutter opened; 2.) a trigger signal sent to the UV laser to fire a single pulse; 3.) the camera shutter closed, and; 4.) the image downloaded to the host computer. The total duration from opening of the
camera electro-mechanical shutter, firing of the laser pulse to closing of the camera shutter was 0.12s. For surface waves, it was important to determine the position along the wave at which LIF images were taken. Consequently a wave probe was mounted in the wind-wave tank adjacent to the UV laser sheet. A second computer recorded the wave data at 150Hz together with the instant of illumination. To facilitate image capture at specified locations along the length of the wave, the wave data was processed in real-time based on determining a height threshold trigger value on either the rising or falling surface water levels.

Images were captured at the crest, trough and mid height of both the rising and falling limbs of the wave. The camera height was adjusted based on the location of the images (e.g. troughs or crest). Thus, the same LIF gas flux experiment was conducted at least 4 times in order to capture images along the 4 segments of the wave. Images were captured at intervals between 15 and 120s depending on the experiment duration.

Bulk dissolved oxygen levels in the wind-wave tank were monitored using an Orion model 835A dissolved oxygen meter and flow cell arrangement with data logged to a computer at 5s intervals (Chapter 2). Each experiment commenced following the stripping of dissolved oxygen from the water column using nitrogen sparging (Figure 2.6).

### 4.4 LIF optical distortions

To measure dissolved oxygen concentration profiles within the diffusion sub-layer of wind-forced waves requires the camera to be mounted at an oblique angle to the water surface (Figure 4.8). This enables the concentration boundary layer immediately adjacent to the water surface to be observed in spite of cross-tank surface slope or the side wall meniscus. However, an oblique camera angle also induces optical distortions. There are two key forms of optical distortion that influence the capture and processing of LIF images.

#### 4.4.1 Surface optical blurring

Optical distortion occurs immediately adjacent to the surface and is induced by surface reflection (Figure 4.8). For example, along ray 2 the observed intensity is obtained from
the light path CDF which includes reflections in the water surface. This surface induced optical distortion (surface optical blurring) limits the proximity of valid concentration measurements close to the surface and has been observed by Woodrow and Duke (2001) and Herlina and Jirka (2004).

The depth below the surface over which surface optical blurring occurs can be minimised by careful experimental design. This can be achieved by reducing the thickness of the UV laser sheet and/or reducing the camera angle. The depth below the surface over which surface optical blurring is present \( z_{nob} \) is given by:

\[
z_{nob} = \frac{T_w}{2} \tan \theta
\]  

[4.4]

where \( T_w \) is the laser waist beam or thickness of the UV laser sheet in the vicinity of the water surface and \( \theta \) is the camera angle. For PIV observations adjacent to strongly-forced air-water interfaces, Peirson (1997) found an optimal camera angle \( (\theta) \) of about 8º. Many real laser illuminations are non-gaussian in intensity distribution, consequently, extensive trial and error optimisation was required to obtain a UV laser sheet with a waist beam of 0.4mm in the vicinity of the water surface. This enabled surface optical blurring effects to be restricted to the upper 28μm (=7pixels) of the water column (Figure 4.9a).

4.4.2 Optical distortion of non-linear intensity/concentration profiles

The second form of optical distortion occurs in the presence of a non-linear concentration and/or fluorescent intensity profile. As shown in Figure 4.8, at depth, the recorded intensity is an average of the varying intensities along the line of observation. For example along ray 1 the observed intensity arises from fluorescence along path AB which is not normal to the fluorescent light sheet. The recorded intensity may be expressed as:

\[
i = \frac{I_{0q}}{B - A} \int_A^B I(z)dz
\]  

[4.5]
where $\hat{I}$ is the recorded intensity and A and B are depths at the finite bounds of the light sheet as depicted in Figure 4.8.

A fundamental assumption in the development of the two film theory (Lewis and Whitman, 1924) and the consequent relationship between the transfer velocity $k_v$ and the thickness of the diffusion sub-layer $\delta_d$ (Equation 1.11) is that the concentration profile within the diffusion sub-layer is linear. Two-film theory assumes a quasi steady-state system in which the concentration of the bulk liquid changes over a relatively long period of time and the thickness of the diffusion sub-layer is relatively stable.

$$k_v = \frac{D}{\delta_d} \quad [1.11]$$

Studies by Woodrow and Duke (2001) and Herlina and Jirka (2004) assumed a linear concentration profile near the surface and adopted a linear extrapolation from a location of identified surface optical blurring (point of maximum intensity gradient) to the surface to determine diffusion sub-layer thickness and transfer velocity. However, extrapolated dissolved oxygen concentrations should achieve saturation values at the water surface by Henry’s Law.

Münsterer and Jähne (1998) have shown for wind-forced surfaces that the thickness of the diffusion sub-layer changes rapidly with time. Our LIF data also showed significant fluctuations in the thickness of the diffusion sub-layer. Therefore, in the presence of rapid changes in the concentration profile near the air-water interface, the concentration profile in the diffusion sub-layer can not be assumed to be linear.

Beyond the depth of surface optical blurring, the oblique viewing of the intensity profile generated by a finite width laser sheet illuminating a concentration gradient can potentially compromise the measurement technique. This arises from two processes: the relationship
between intensity and concentration is non-linear (Equation 4.2); and, the impact of non-linearity in the concentration gradient itself. We consider a local concentration profile which varies as a polynomial of order \( n \) in the vicinity of a reference depth \( h \) and we use superscripts in brackets to denote differentiation with respect to depth \( z \):

\[
C(z) = C_h + C^{(1)}_h (z - h) + C^{(2)}_h \frac{(z - h)^2}{2!} + \ldots + C^{(n)}_h \frac{(z - h)^n}{n!}
\]  \[4.6\]

where:

\[
C^{(n)}_h = \frac{\partial^n C}{\partial z^n}
\]  \[4.7\]

evaluated at depth \( z = h \).

Approximating the Stern-Vollmer equation (Equation 4.2) as a Taylor series yields:

\[
I(C(z)) = \frac{I_{0q}}{1 + \alpha C_h} \left[ 1 - \alpha \left( \frac{C(z) - C_h}{1 + \alpha C_h} \right)^2 + \frac{\alpha^2 (C(z) - C_h)^2}{(1 + \alpha C_h)^2} + \text{HOT} \right]
\]  \[4.8\]

Neglecting higher order terms and substitution of Equations 4.6 and 4.8 into Equation 4.5 yields a difference between the mean intensity observed at an angle \( \theta \) for a sheet thickness \( T \) and the intensity at the centre-line of the light sheet at depth \( h \) as:

\[
I_{z=h} - \hat{I} = \frac{I_{0q} \alpha}{(1 + \alpha C_h)^2} \sum_{n=1}^{\infty} \frac{(T \tan \theta)^{2n} C^{(2n)}_h}{(2n)!(2n+1)2^{2n}} + \frac{I_{0q} \alpha^2}{(1 + \alpha C_h)^3} \sum_{n=1}^{\infty} \sum_{i=1}^{n} \frac{(T \tan \theta)^{2n} (C^{(n)}_h)^2}{(n!)^2 (2n+1)2^{2n}} + \frac{(T \tan \theta)^{2n+2} C^{(n)}_h C^{(n+2)}_h}{(n+2)!n!(2n+2i+1)2^{2n+2i-1}}
\]  \[4.9\]
The first term on the RHS of Equation 4.9 represents the error contribution by the first order term in Equation 4.8. If the concentration profile is linear then this term is zero and the errors in the measured intensity are relatively small (second order intensity term only). However, as the concentration profile becomes progressively more non-linear, higher order variations in $C_h$ make significant contributions to both first and second order intensity terms. For a uniform concentration with depth all terms on the RHS of Equation 4.9 equal zero and no optical distortions are induced.

Adopting a one-dimensional error function concentration profile (representative of unsteady aeration) such that:

$$C(z) = C_i - (C_i - C_h) \text{erf} \left( \frac{z}{2\sqrt{Dt}} \right)$$  \hspace{1cm} [1.7]

where $t$ is the time from commencement of aeration, the sensitivity of valid LIF measurements with respect to camera angle, laser waist beam and transfer velocity as derived from Equation 4.9 are plotted in Figures 4.9a to 4.9f. For smooth water surfaces (low transfer velocity), image distortion is relatively small and a linear extrapolation between the commencement of surface optical blurring to the air-water interface may under some circumstances be a valid approximation. However, for strongly wind forced surfaces a more oblique camera angle ($\theta=12^\circ$) or wider laser beam waist ($T=0.8mm$) is clearly unsuitable and a linear extrapolation to the surface will systematically predict a surface oxygen concentration well below saturation.

It was not practically feasible to reduce our beam waist below 0.4mm. Non-linearity in concentration within the diffusion sub-layer increases with increasing gas flux. Therefore to minimise optical distortion effects during data processing, a first order error function solution is fitted to the data from the location of surface optical blurring to the air-water
interface. For our experimental arrangement (based on a theoretical sensitivity analysis) this reduces errors in the measured surface flux due to optical distortions to less than 10%.

Note that in Figure 4.9, increasing beam waist also increases the apparent thickness of the diffusion sub-layer. Consequently the optical distortion has two critical effects: the measured gradients of the concentration profile are reduced; and the depth of the diffusion sub-layer is artificially extended.

During this study, a very small angle of view has been used (1.7°). Therefore, variation in ray angle across our images is small. Measurements incorporating a horizontal lens axis but much wider angles of view will be subject to increased optical distortions away from the lens axis.

4.5 Data processing
During each LIF experiment at least 400 images required processing to determine wave phase resolved gas fluxes. Each LIF image consists of 2184 columns and 1472 rows (Figure 4.10a). Image processing was semi-automated by developing a number of user defined Fortran subroutines. Key steps in the data processing are: 1). signal selection; 2.) identification of the air-water interface; 3.) illumination compensation using Lambert-Beers decay relationship and conversion of the fluorescent signal to dissolved oxygen concentration using the Stern-Vollmer equation; 4.) removal of surface optically blurred data, and; 5.) determination of near surface dissolved oxygen concentration gradient and gas flux.

4.5.1 Data signal selection
The generated UV laser sheet is non-gaussian in form and has a width of approximately 6mm. Because the width of the UV laser sheet is only 6mm the fluorescent imprint does not extend across the full width of the captured CCD image. Each image was stripped to a width of 202 adjacent columns consisting of the region of uniform illumination with the highest fluorescent signal to noise ratio (Figure 4.10b). A 3x3 box car smoothing filter was
then applied to the data to further improve the signal to noise ratio, reducing the data file width to 200 columns (Figure 4.11).

Adaptive smoothing filters were used by Woodrow and Duke (2001) and Herlina and Jirka (2004) to reduce noise in their data. A danger with most smoothing filters is their tendency to reduce the magnitude of sharp peaks. This is of particular concern near the air-water interface where distinct changes in dissolved oxygen gradients were evident.

For this investigation several data sets were fully processed without any data filtering. The same data sets were then processed using a simple 3x3 box car filter. It was clear that the box car filtering reduced the noise, but maintained the integrity of the data signal (Figure 4.11). That is, the strong concentration gradient near the surface was maintained.

4.5.2 Location of air-water interface

The general location of the air-water interface is visible to the eye in most captured images by the presence of a near horizontal or sloping dark band across the width of the fluorescing part of the image (Figure 4.12). The dark band (i.e. low fluorescent signal) is an indicator of a region of higher dissolved oxygen and assuming saturation on the aqueous side of the air-water interface, the darkest pixels in the band correspond to the surface.

The interface in each image was determined by finding the minimum intensity in each of the columns of data. A linear equation was fitted to the row number corresponding to the minimum fluorescent intensity. Given that the width of the fluorescent component of the image being processed was only 0.83mm (i.e. 200 columns) a linear fit to the surface is more than adequate in most cases. The linear fit to the surface was deemed poor when $r^2$ was less than 0.9 and the image was not used in further processing and analysis.

For a sloping interface such as that shown in Figure 4.12 the minimum intensity in a nominated column may not be located at the air-water interface. Therefore to avoid such irregularities in the data, a user based range of rows over which to determine the location of
the interface must be specified for each image. This user based range of rows is specified in the Fortran suite of programs.

In some images the air-water interface is not present because the surface is either above or below the image extent or is obscured due to the water surface slope across the tank. In such cases the images could not be used for analysis.

4.5.3 Conversion of fluorescent image to concentration profile

Lambert-Beers decay or absorption of the laser light through the water column is solely a function of the PBA concentration.

\[
\frac{I_{LB}}{I_{LB0}} = \exp(-\psi_{mc} C_{PBA} l) \quad [4.10]
\]

Prior to each experiment at least ten LIF images were captured for fully saturated, well mixed conditions (to avoid concentration gradients). These images were processed and a logarithmic equation then fitted to the data to determine a mean molecular constant \( \psi_{mc} \).

Whilst each data file consists of 1470 rows, row 1400 is used as the reference for \( I_{LB0} \) and rows 1401 to 1470 are discarded. This is done to avoid any possible edge effects in the image. Each column within the vertical image strip was then corrected for Lambert-Beers in accordance with:

\[
\begin{bmatrix}
  b_{11} & b_{12} & \cdots & b_{1j} \\
  b_{21} & b_{22} & \cdots & b_{2j} \\
  \vdots & \vdots & \ddots & \vdots \\
  b_{i1} & b_{i2} & \cdots & b_{ij}
\end{bmatrix}
= \frac{1}{\exp(-\psi_{mc} C_{PBA} l)}
\begin{bmatrix}
  a_{11} & a_{12} & \cdots & a_{1j} \\
  a_{21} & a_{22} & \cdots & a_{2j} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{i1} & a_{i2} & \cdots & a_{ij}
\end{bmatrix} \quad [4.11]
\]

where \( a_{ij} \) is the measured pixel intensity and \( b_{ij} \) is the Lambert-Beers corrected pixel intensity.
A correction to a typical fluorescent profile using the Lambert-Beers relationship is shown in Figure 4.13. The uniform fluorescent intensity below a depth of approximately 800 pixels verifies the adopted Lambert-Beers decay corrections.

Using the Stern-Vollmer equation (Equation 4.2) the fluorescent data was then converted to a dissolved oxygen concentration. The 200 columns of data were then averaged into a single column using the surface position in each column as the air-water interface reference depth.

Small variations (<2%) in light sheet intensity occurs between laser pulses. The bulk dissolved oxygen concentration $C_b$ as determined by LIF was obtained from an average of the lowest 200 rows of concentration data in each image strip. This was compared to the bulk oxygen concentration as determined by the Orion oxygen probe (Figure 4.14). Differences between the two bulk readings are a measure of the variation in laser pulse intensity. Raw fluorescent intensity data was then corrected for this variation and reprocessed to determine a dissolved oxygen concentration profile.

A typical measured concentration profile from an LIF image is shown in Figure 4.15. Below a depth of 2mm the dissolved oxygen concentration profile is uniform, indicating that the bulk of the water has a dissolved oxygen concentration of approximately 2.3mg/L. At the surface the maximum measured dissolved oxygen concentration is well below the saturation value of 9.2mg/L. This is indicative of surface optical blurring.

It has previously been noted that the relationship between fluorescent intensity and dissolved oxygen concentration is not linear. Most researchers [Wolff and Hanratty (1994), Woodrow and Duke (2001) and Herlina and Jirka (2004)] who have investigated the thickness of the diffusion sub-layer using PBA and LIF techniques have presented their data in the form of a normalised dimensionless concentration. Woodrow and Duke (2001) defined their dimensionless concentration $\hat{C}(z)$ as:
where $I_I$ is the fluorescent intensity at the water interface, and;

$\bar{I}_B$ is the fluorescent intensity in the bulk of the water.

Using this relationship, it is possible to directly use the fluorescent signal to define a concentration profile without using the Stern-Vollmer equation and its associated calibration constants (namely $I_{0q}$ and $\alpha$). A critical limitation in this approach is the determination of the fluorescent signal at the interface ($I_I$). Woodrow and Duke (2001) and Herlina and Jirka (2004) have described the presence of “optical blurring” at image pixels close to the surface. Corrections to their data sets were made by applying a linear extrapolation of the fluorescent signal near the surface (Figure 4.9c). This approach is not valid and consequently the concentration profile is incorrectly distorted during processing.

### 4.5.4 Removal of surface optical blurred data

The depth below the surface at which the dissolved oxygen concentration gradient is largest is then located. Data above this location is influenced/contaminated by surface optical blurring and is not included in subsequent analysis.

### 4.5.5 Local flux

The dissolved oxygen concentration on the aqueous side of the air-water interface is assumed to be at saturation [Lewis and Whitman (1924), Scriven and Pigford (1958) and Deacon (1977)]. An error function curve is then fitted between the data and the saturated surface and $dC/dz$ determined (Figure 4.15).

The transfer velocity was then determined from:

$$k_v = \frac{D}{(C_I - C_B)} \frac{\partial C}{\partial z}$$  \[4.13\]
For each data set a number of images were rejected during processing based on conditional criteria. Images were rejected if: 1). the air-water interface could not be clearly identified; 2). the depth below the surface at which optically blurring occurred could not be defined, or; 3) a concentration gradient (diffusion sub-layer) could not be identified. Extreme flux values (both high and low) that passed the conditional criteria were also manually checked for acceptance/rejection by ensuring a concentration gradient existed.

4.6 Results

As discussed in Chapter 2, a total of eight wind-wave experiments were undertaken. The defining parameters for each experiment, namely wind, wave and aeration are presented in Table 2.1.

In Experiments 1 to 4 the wave frequency was constant (3.4Hz). Whilst the same wind speed (2.1m/s) was used in Experiments 1 to 3, a higher wind speed (5.7m/s) was required to maintain the surface in a microscale breaking regime (Experiment 4).

In Experiments 5 to 8 the same wind speed (3.9 to 4.2m/s) was used and the wave frequency varied. Waves could be forced between the different water surface regimes using the same wind speed by varying the wave frequency.

For six of the eight LIF experiments, images were captured and concentration gradients resolved at the crest, trough and mid height of both the rising and falling limbs of the wave. For the flat water and ripple LIF experiments, gravity waves are not present and wave phasing was not considered. A summary of the LIF results for the eight wind-wave experiments is presented in Table 2.2. Gas transfer data for each of the eight cases is presented in Figures 4.16 to 4.23. The majority of the data are presented as a transfer velocity, rather than a fictional diffusion sub-layer thickness.
Data from the experiments is also presented in an exact phase resolved format in Figures 4.24 to 4.29. In Figure 4.24 the four symbols depict the four wave phase resolved locations. For example, at the wave crest (0°) the data extends over a bandwidth of approximately 30° and likewise for other phase locations. All data within the bandwidth is used to determine the statistical mean and standard deviation of the transfer velocity in Table 2.2. In Table 2.2 the mean transfer velocity for each experiment is determined from the arithmetic means of the four discrete phase locations.

The state of the water surface has a significant bearing on both PIV and LIF imagery. For PIV imagery, Peirson (1998) found that at the crests and leeward limbs of microscale breaking waves, reflected particles were not visible and hence accurate positioning of the water surface was often not possible. Consequently, data at these phase locations was limited or often not available. Similar difficulties were experienced during the PIV component of this study. The stronger wind forcing at the crests of the waves and the subduction at the toe of the crest spilling region are apparent contributors to these difficulties.

Similar problems were also experienced in the LIF experiments at the crest of microscale breaking waves. This is particularly noticeable in Experiment 4 (f34u57ak32), which was the most vigorous wave breaking case with a wind speed of 5.7m/s. A secondary difficulty is the relative thickness of the diffusion sub-layer. Due to surface optical blurring we are unable to detect the diffusion sub-layer if it lies substantially within this region. Despite the lower data recovery in Experiment 4, the data follows trends similar to that of the other experiments.

During this study approximately 3000 images were accepted for processing to determine gas transfer at the air-water interface. The data processing and data acceptance criteria are comprehensively more rigorous than any previous studies. Researchers such as Münsterer and Jähne (1998), Woodrow and Duke (2001) and Herлина and Jirka (2004) do not document data acceptance criteria for their experimental investigations of the aqueous diffusion sub-layer.
Flux estimates by the LIF method are within 30% of the bulk measurement method, with the exception of Experiments 2 and 3. For Experiments 2 and 3 the LIF method overestimates the flux by 65% and 41% respectively. In Experiment 2 \textit{(low wave case, f34u21ak18)} the measured flux at each of the four discrete wave phase locations is higher than that measured by the bulk measurement method. In Experiment 3 \textit{(incipient case, f34u21ak27)} only the measured flux in the trough and leeward limb exceed that measured by the bulk method. However, it is also noted that these LIF estimates are based on the arithmetic mean of the flux measured at four discrete wave phase locations exhibiting substantial variation about the mean value. The magnitude of the errors is a significant improvement on estimates by Woodrow and Duke (2001) who reported differences of up to 140% between LIF and bulk measurements.

The bulk aeration transfer velocity is derived from contributions from the entire tank surface area and, in spite of our objective to minimise variations in wave conditions along the tank, some fetch dependence will occur. The localised width and thickness of the laser sheet represent the surface area over which the instantaneous LIF measurements are made. This area is relatively small \((3 \times 10^{-5} \%)\) in comparison to the total surface area over which gas exchange occurs in the wind-wave tank.

The mean of the transfer velocities in the time series presented in Figures 4.16 to 4.23 are representative of the data sets for the entire duration of the experiments. This observation is extremely important in supporting the validity of the data quality and implies that:

- with the exception of dissolved oxygen concentrations in the water, the experiments are in an equilibrium state prior to and over the duration of the test.

- the water surface remains contaminant free over the duration of the experiment.

- the quenching rate constant adopted for this study is valid.
the influence of optical distortions has been sufficiently reduced to not adversely effect the data.

In Experiments 4 and 8 (microscale cases, \( f_{34u57ak32}, f_{31u39ak28} \)) it has been demonstrated that the experimental set-up is capable of measuring very high transfer velocities (Figures 4.26 and 4.29). Diffusion sub-layer thicknesses of less than 10\( \mu \)m and transfer velocities greater than \( 1 \times 10^{-4} \text{m/s} \) have been recorded at all four wave phase locations. The exceedance curves presented in Figures 4.16 to 4.23 provide evidence that the limiting values set in the conditional criteria are not inadvertently removing both high and low extreme flux data from the analysis.

4.7 Discussion

The variation in the transfer velocity (Figure 4.16 to 4.29) between images and between locations along the wave is indicative of rapid changes in the thickness of the diffusion sub-layer. For example, in Experiment 1 (flat water case, \( f_{00u21ak0} \)) the standard deviation of the transfer velocity is 65% of the mean. In Experiment 4 (microscale case, \( f_{34u57ak32} \)) the standard deviation of the transfer velocity along the length of the wave varies from 47% to 71% of the mean.

For the flat water case the fluctuations may possibly be attributed to localised zones of surface convergence and divergence. For the low wave and incipient cases, unsteady wind forcing associated with wave form drag may also contribute to the observed variability in the transfer velocity. For the microscale cases the waves are less uniform and are constantly collapsing and reforming into a breaking state. Consequently, wave steepness is more variable, which may also influence the observed fluctuations in the transfer velocity.

Komori et al. (1993) collated experimental data sets obtained from the bulk measurement method from numerous researchers that are reproduced in Figure 4.30. Transfer velocity data obtained from the bulk measurement method in this study is also included in the Komori et al. (1993) plot in Figure 4.30. Data for the ripple, low wave and incipient cases closely follows the Jähne et al. (1987) formulation (Equation 1.31) where:
It is interesting to note that the transfer velocity data for the two microscale cases is located above the line defined by Equation 1.31. Equation 1.31 would appear to systematically under-predict the transfer velocity when the friction velocity exceeds approximately 0.5 m/s (i.e. when the water surface enters a fully developed microscale breaking state).

In Experiment 1 (flat water case, $f_{00u21ak0}$) the transfer velocity measured by both the bulk and LIF methods is approximately 1.4 times that predicted by Deacon (1977). Included in Figure 4.30 is a plot of the Deacon model which appears as a lower bound to most of the data. The Deacon model is based on boundary layer theory across a solid wall and does not consider surface convergence and divergence. The time based variations observed in the measured transfer velocity for the flat water case may explain the differences observed between Deacon’s model estimate and the mean observed transfer velocity as measured by both the bulk and LIF methods.

The PIV data presented in Chapter 3 and the associated localised surface divergence and convergence and its implications on gas transfer velocities is developed further in Chapter 5.

A consistent trend is observed in the incipient and microscale breaking experiments in which the highest fluxes are measured in the wave troughs and the lowest fluxes at the crests of waves. A thinner diffusion sub-layer in the wave troughs was visually evident in the LIF images prior to any processing. Gas fluxes measured on both the leeward and windward limbs of the waves were bounded by these upper and lower limits. In the low wave experiments there is no statistical difference between fluxes measured at the crest and trough.

\[
k_v = \frac{1}{16} \text{Sc}^{-\frac{1}{4}} u^*\quad [1.31]
\]
Orbital straining of gravity waves is associated with a flow convergence zone on the leeward face of the wave and a flow divergence zone on the windward face of the wave. As the wave steepness increases, the strength of the convergence and divergence also intensifies. The high fluxes observed in the wave troughs for the steeper wave cases are likely to be associated with the wave orbital straining. This concept is developed further in Chapter 5 using both linear and 5th order Stokes wave theorem.

Peirson and Banner (2003) predicted subduction of the aqueous diffusion sub-layer at the onset of microscale breaking from their observations of near surface velocity structure. If all waves are in a continuous microscale breaking state we would therefore expect to only see very thin diffusion sub-layers. Consequently, distinct population boundaries would be evident between the incipient and microscale breaking cases. In reality, microscale breaking waves are constantly collapsing and reforming into a breaking state. Therefore, the microscale breaking cases are likely to consist of two data populations, one with a very thin diffusion sub-layer thicknesses and one similar to that for the incipient case.

In Experiment 7 (incipient case, f24u39ak24) there is relatively few data points indicating a diffusion sub-layer thickness of less than 30μm (Figure 4.28). In Experiment 8 (microscale case, f31u39ak28) 28% of the measurements indicate a diffusion sub-layer thickness of less than 30μm (Figure 4.29). Based on the Peirson and Banner (2003) model it is possible that the measurements of a diffusion sub-layer of less than 30μm are associated with microscale breaking subduction events. The role of microscale breaking in thinning the diffusion sub-layer is discussed further in Chapter 5.

Detached surface layers of dissolved gas rich water observed by Woodrow and Duke (2001) and Takehara and Etoh (2002) were also evident in our experiments (Figure 4.31). Detached surface layers of oxygen rich water were observed in all experiments, from the flat water case (approximately 24% of images) to the microscale breaking case (approximately 30% of images). Woodrow and Duke (2001) attribute the detached surface layer to measured increases in gas flux, however the relatively small increase in detached surface layer events between the flat water and microscale breaking experiments cannot
account for the large increase in measured gas fluxes, nor will such detached layers directly impact the concentration gradient at the interface.

4.8 Validity of LIF processing method

The detection and understanding of optical distortions or errors in the LIF technique has been discussed in detail in Section 4.4. In Section 4.5 it was shown that the optical errors has historically led to the incorrect application of Equation 4.12. In Section 4.6 it was noted that the mean of the gas transfer velocities (in each experiment) is a constant over the entire duration of the experiment. That is, the gas transfer velocity does not increase or decrease with the duration of the experiment and is independent of time. This observation is important in supporting the validity of the data and the processing techniques. Also flux estimates by the LIF method are in strong agreement with the bulk measurement estimates.

As a further validity check, the gas transfer velocity data derived from the LIF images was directly compared with LIF dissolved oxygen concentration profiles.

The 95 percentile bulk dissolved oxygen concentration was directly measured from the concentration profile of each LIF image and the depth recorded. The 95 percentile dissolved oxygen concentration is defined as:

\[
\hat{C}(z) = 0.95 = 1 - \frac{C(z) - C_B}{C_I - C_B} = \hat{C}_{95\%}
\]

[4.14]

and \(z_{95\%}\) is the distance below the surface at which \(C(z)\) satisfies Equation 4.14. The mean and median (value in brackets) \(z_{95\%}\) for each experiment is tabulated in Table 2.2.

With the exception of Experiment 2 (Low wave f34u21ak18) the 95 percentile dissolved oxygen concentration was closest to the surface on the leeward limb of the waves. Also, with the exception of Experiment 4 (microscale f34u57ak32) the 95 percentile dissolved oxygen concentration was closer to the surface at the wave crests than in the wave troughs. This observation is in stark contrast to the LIF gas transfer velocity measurements that
indicate the highest mean gas fluxes are in the wave troughs and the lowest mean gas fluxes are at the wave crests.

The LIF gas transfer velocity data and the 95 percentile dissolved oxygen concentration data highlight the complexities of the hydrodynamic behaviour beneath wind driven waves. From the PIV experiments it was shown that the highest tangential stresses were measured near the crests of the waves and the lowest tangential stresses were measured in the wave troughs. Deacon (1997) conceptualised this model and concluded that the corresponding greater turbulence at the wave crests would result in higher gas fluxes at this wave phase locale. The data from the LIF and PIV experiments would seem to indicate that, at depth, the turbulence has a significant role in mixing of the water column. However, very close to the surface, where viscosity dominates, the influence of wave orbital straining would appear to have a more pronounced influence on the gas transfer velocity than the underlying turbulence. Hence, the 95 percentile dissolved oxygen concentration is closer to the surface at the wave crests than the wave troughs (presumably due to turbulence), but the mean gas transfer velocity in the wave troughs is greater than the mean gas transfer velocity at the wave crests (due to wave orbital straining of the aqueous diffusion sub-layer).

Whilst the measured depth at which the 95 percentile dissolved oxygen concentration occurs contributes to the understanding of hydrodynamic behaviour beneath waves, it cannot be used as a reliable indicator of the gas transfer velocity across the interface. Any dimensionless dissolved oxygen concentration measurement that is used for this purpose would need to be undertaken immediately adjacent to the surface where molecular rather than turbulent diffusion is the dominant process.

Given that in most LIF images a dissolved oxygen concentration gradient was still evident at a depth of 100μm, each LIF image was analysed to determine the dimensionless dissolved oxygen concentration at \( z = 100\mu m \) \( \left( C_{100\mu m} \right) \). Mean values for each experiment are presented in Table 2.2. Median values for each experiment were almost identical to the mean.
The mean dimensionless dissolved oxygen concentration values \( \hat{C}_{100\mu m} \) for each experiment are consistent with the mean gas transfer velocity measured by LIF (Table 2.2). This is highlighted, for example, in Experiments 7 and 8 where the highest mean gas transfer velocities were measured in the wave troughs and the lowest mean gas transfer velocities were measured at the wave crests. For these two experiments the highest mean dimensionless dissolved oxygen concentration values were measured in the wave troughs and the lowest mean dimensionless dissolved oxygen concentration values were measured at the wave crests. Similar observations are also made between all other experiments. These results provide further evidence that the data processing procedure to measure the concentration profile and estimate the gas flux from the dissolved oxygen concentration gradient is robust and reliable.

A log-normal plot of the measured mean dimensionless dissolved oxygen concentration values \( \hat{C}_{100\mu m} \) against the calculated mean gas transfer velocity derived by LIF for each experiment is presented in Figure 4.32. The relationship between \( \hat{C}_{100\mu m} \) and \( k_{\text{vlif}} \) is well correlated and can be expressed as:

\[
k_v = 3.44 \times 10^{-6} \times e^{(3.59 \hat{C}_{100\mu m})} \tag{4.15}
\]

### 4.9 Concluding remarks

Optical distortions have previously prevented non-intrusive measurements of dissolved oxygen concentration profiles by LIF to within 200μm of the air-water interface. It has been shown that by careful experimental design, reliable measurements can be obtained within 28μm of moving air-water interfaces. Consideration of previously unidentified optical distortions in LIF imagery due to non-linear effects has been presented that is critical for robust LIF data processing and experimental design.

Phase resolved gas flux measurements have now been accomplished along wind forced microscale waves and indicate that the highest mean gas fluxes are located in the wave troughs. The local mean oxygen fluxes as determined by LIF techniques can be reconciled...
to within 40% of those obtained by bulk measurement in the water. These data provide a new perspective on wind-wave enhancement of low solubility gas transfer across the air-water interface.

In Chapter 5 the relative contributions of specific hydrodynamic mechanisms to the gas transfer velocity are developed using the PIV, LIF and bulk gas transfer velocity experimental data.
Figure 4.1 UV light sheet generation. A series of UV fused silica lenses were used to contract and focus the light sheet to approximately 6mm wide x 0.4mm thick at the water surface.
Figure 4.2  Several of the optical components used to shape the laser illumination sheet. 2x300mm focal length plano-convex cylindrical lens and a 45° incidence angle 337nm nitrogen gas unpolarised flat mirror. The 600mm focal length plano-convex spherical lens that is closest to the laser is out of view.
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Figure 4.5  Upper panel; small test chamber used to optimise PBA concentration for experimental arrangement. Lower panel: optimum PBA concentration is approximately $7 \times 10^{-6}$ M. On rising limb PBA concentration is too low; on falling limb PBA concentration is too high.
Figure 4.6  Stern-Vollmer relationship (Equation 4.2) between dissolved oxygen concentration and PBA fluorescence intensity. Solid line is for quenching rate constant as determined in this study (0.0272L/mg). Small dashed red line is for quenching rate constant used by Münsterer et al. (1995) and Herlina and Jirka (2004). Long dashed green line is for quenching rate constant used by Lee (2002).
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Figure 4.8  Light rays causing potential optical distortions adjacent to air-water interfaces in fluorescent images. Camera angle and laser sheet thickness are critical in minimising optical distortions.
Figure 4.9 Optical distortion of fluorescent images due to surface optical blurring and non-linear intensity/concentration profile. In all panels, $C_f=10\text{mg/L}$ and $C_B=2\text{mg/L}$, thick solid line is actual profile, thin solid line $T_w=0.4\text{mm}$, thin dashed line $T_w=0.8\text{mm}$, solid circle indicates maximum depth of surface optical blurring. Figures 3a and 3b. $\theta=8^\circ$, $t=0.1\text{s}$. Figures 3c and 3d. $\theta=12^\circ$, $t=0.1\text{s}$, thick dashed line is linear extrapolation to air-water interface from commencement of surface optical blurring. Figures 3e and 3f. $\theta=8^\circ$, $t=0.5\text{s}$. Note $t$ is the time from commencement of aeration.
Figure 4.10 Typical flat water LIF image. The air-water interface is clearly visible as a dark band (low fluorescence) due to the presence of high dissolved oxygen concentration near the surface.
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Figure 4.13  Single column of fluorescent data corrected for Lambert-Beers decay. The uniform fluorescent intensity below a depth of approximately 800 pixels verifies the adopted Lambert-Beers decay corrections.
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Figure 4.16 Experiment 1 (*Flat water* f00u21ak0) transfer velocity computed for individual images as measured by the LIF technique. Upper panel shows values as a function of time, lower panel shows probability density distribution. Horizontal line represents mean transfer velocity.
Figure 4.17  Experiment 2 (Low wave $f_34u21ak18$) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
Figure 4.18  Experiment 3 (*Incipient f34u21ak27*) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
Figure 4.19  Experiment 4 (Microscale f34u57ak32) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
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Figure 4.21  Experiment 6 (Low wave f21u39ak10) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
Figure 4.22  Experiment 7 (Incipient f24u39ak24) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
Figure 4.23  Experiment 8 (Microscale f3u39ak28) transfer velocity computed for individual images as measured by the LIF technique. Upper panels show values as a function of time, lower panels show probability density distributions. Panels a and c, solid black line wave trough, dashed red line wave crest, horizontal lines represent mean transfer velocity. Panels b and d, solid black line leeward wave face, dashed red line windward wave face.
Figure 4.24  Experiment 2 (Low wave f34u21ak18) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.25  Experiment 3 (*Incipient f34u21ak27*) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.26  Experiment 4 (*Microscale* f34u57ak32) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.27  Experiment 6 (*Low wave f21u39ak10*) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.28  Experiment 7 (Incipient f24u39ak24) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.29  Experiment 8 (Microscale f31u39ak28) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°).
Figure 4.30  Dependence of gas transfer velocity with friction velocity as measured by various researchers and compiled by Komori et al. (1993) with all data normalised to a Schmidt number of 600. Bulk transfer velocity for the eight experimental wind-wave cases investigated in this study (large blue and pink diamonds) is also included in the plot following being normalised to a Schmidt number of 600 using Equation 2.4. Solid line shows the Deacon (1977) model with a Schmidt number dependency to the exponent -2/3. Dashed line shows the Jähne et al. (1987) model with a Schmidt number dependency to the exponent -1/2. The blue diamonds represent the *ripple, low wave and incipient* cases and these data closely follow the Jähne et al. (1987) model.
Figure 4.31  LIF images with wave propagating from left to right. Upper panel: shows layer detaching from surface and its reflected image. Lower panel: dark bands below the surface are zones of oxygen enriched water that have detached from surface.
Figure 4.32 A log-normal plot of the measured mean dimensionless dissolved oxygen concentration values ($\hat{C}_{100\mu m}$) against the calculated mean gas transfer velocity derived by LIF for each experiment.
5. HYDRODYNAMIC PARTITIONING OF THE GAS FLUX CONTRIBUTION

The coupled PIV and LIF datasets of this investigation are the first wave phase resolved microphysical measurements within the aqueous viscous and mass diffusion sub-layers. The uniqueness of the dataset presents the opportunity to quantify enhanced gas flux by specific near-surface hydrodynamic processes.

For example, in Chapter 3 the measured surface layer kinematics indicate the highest tangential stresses near the crests of the waves. This is consistent with the findings of Banner and Peirson (1998) and conventional boundary layer theory suggests that the highest gas transfer velocities are also at this location (Deacon 1977). However, in this investigation (Chapter 4) the highest mean gas transfer velocities were measured in the wave troughs, indicating that other wave phase locked hydrodynamic processes must be contributing to thinning of the mass diffusion sub-layer.

In this chapter the contributions to enhanced gas flux by specific surface hydrodynamic features are developed and quantified for the experiments conducted herein. The partitioning is accomplished by theoretical considerations and use of the PIV data and gas transfer velocity data obtained from both the LIF and bulk dissolved oxygen experiments. The hydrodynamic partitioning is progressed further by first considering a conceptual gas transfer model/s.

5.1 Conceptual gas transfer model

Gas exchange across the air-water interface is a complex process, involving disruption of the aqueous diffusion sub-layer through both tangential stresses and wave motion. The relative contributions to enhanced gas flux by:

- Wind-induced turbulence within the viscous sub-layer (Deacon 1977 and Jähne et al. 1987).
- Gravity wave orbital straining (Witting 1971).

- Parasitic capillary ripples (Szeri 1997).

- Subduction at the toe of the spilling region for microscale breaking waves (Peirson and Banner 2003).

are developed with reference to the microphysical datasets obtained within the aqueous viscous and mass diffusion sub-layers.

The preliminary conceptual gas transfer models are presented as a series of diagrams in Figures 5.1 and 5.2 and have been developed from both the literature review and initial observations and conclusions drawn from the PIV and LIF experiments. The diagrams represent the hydrodynamic processes for the water surface descriptors used throughout the text, namely:

- Flat water.

- Ripple.

- Waves of small steepness (Low wave).

- Incipient breaking.

- Microscale breaking.

In the flat water case, before the onset of waves and form drag, the tangential stress is equal to the total wind stress. The tangential stress contributes to the entire formation of the surface wind drift current. Thinning of the diffusion sub-layer is due to momentum flux from the wind (Figure 5.1).
In the *ripple* case (Figure 5.1), vorticity due to surface curvature becomes widespread with alternating vorticity direction at the crests and troughs of the ripples (Longuet-Higgins 1992).

As waves develop the surface wind drift current becomes modulated with the wave form (Figures 3.9 and 3.13). Concomitantly, the tangential stress near the wave crests is higher than in the wave troughs. Greater unsteadiness in the surface wind drift current is also observed at the crests of the waves. Disturbance of the mass diffusion sub-layer due to tangential stresses is therefore more dominant near the wave crests.

Wave orbital velocities impart a cyclic convergence/divergence at the surface that impacts on the aqueous diffusion sub-layer (Figure 3.12 and 3.16). As the wave steepness increases, the convergence/divergence strengthens in magnitude. Mean convergence is experienced on the leeward face and mean divergence on the windward face of waves. Therefore, a general thinning of the mass diffusion sub-layer is experienced between the wave crest and the following wave trough. A general thickening of the mass diffusion sub-layer is experienced between the wave trough and the following wave crest.

The *incipient breaking* condition (Figure 5.2) is reached when the waves are as steep as possible without breaking into a microscale breaking state. These waves are characterised by well-developed parasitic capillaries leeward of the wave crests. The parasitic capillaries are possibly associated with a highly localised vorticity structure (MacIntyre, 1971 and Szeri, 1997) that may also disrupt or thin the mass diffusion sub-layer, although Peirson and Banner (2003) did not detect systematic high vorticity in their PIV experiments that could be attributed to the parasitic capillaries.

At the onset of *microscale breaking* (Figure 5.2) a further hydrodynamic mechanism (subduction at the toe of the spilling region) is triggered that disrupts the mass diffusion sub-layer. This mechanism was first measured by Peirson and Banner (2003) and is responsible for the significant increase in gas flux at the onset of microscale breaking.
In summary,

- For the flat water case thinning of the mass diffusion sub-layer is due only to the wind-induced tangential stress.
- For the ripple case thinning of the mass diffusion sub-layer is caused by the wind-induced tangential stress and the onset of some form drag that generates small capillary ripples across the entire free surface.
- For the low wave case thinning of the mass diffusion sub-layer is caused by the wind-induced tangential stress and the gravity wave orbital straining.
- For the incipient breaking case thinning of the mass diffusion sub-layer is caused by the wind-induced tangential stress, gravity wave orbital straining and vorticity generated from the parasitic capillary waves.
- For the microscale breaking case thinning of the mass diffusion sub-layer is caused by the wind-induced tangential stress, gravity wave orbital straining, vorticity generated by the parasitic capillary waves and subduction at the toe of the spilling region.

5.1.1 Data partitioning
The methodology used in the following sections of this chapter to undertake hydrodynamic partitioning of the gas flux contribution is outlined below and is based on the conceptual model/s presented in the previous section of this chapter.

1. Theoretical review of gas flux enhancement due to gravity wave orbital straining. Comparisons are then made between the theoretical enhancement and the LIF measured enhancement between the wave crests and wave troughs.
2. The LIF and bulk gas transfer velocity data are compared to estimate the enhancement due to the development of the parasitic capillary waves on the leeward faces of the waves for the incipient breaking experiments.

3. The theoretical gravity wave orbital straining gas flux enhancement and the measured gas flux enhancement due to parasitic capillary ripples is deducted from the measured bulk gas transfer velocity data and a wind-induced turbulence model is developed based on a Schmidt number dependency to the exponent \(-\frac{1}{2}\). The microscale breaking data is excluded from this analysis.

4. Gas flux enhancement due to gravity wave orbital straining, wind-induced turbulence and parasitic capillaries is deducted from the microscale breaking bulk transfer velocity data to estimate gas flux enhancement due to subduction at the toe of the spilling region. This is compared and verified with the LIF data.

5.2 Gravity wave orbital straining

The theoretical gravity wave orbital straining investigations conducted by Witting (1971) on thermal boundary layers were summarised in Section 1.2.2.5. For plane progressive irrotational waves Witting (1971) reports that gravity wave orbital straining can enhance the average heat flux \(\bar{Q}\) by factors of no more than 1.38 where the maximum wave steepness \(ak\) is 0.446. In general, waves will collapse well before attaining a steepness of 0.446. For experiments conducted in this study the maximum mean wave steepness \(ak\) is 0.32. Banner and Peirson (1998) reported a maximum mean wave steepness of 0.29 for their investigations of microscale breaking waves. The work by Witting (1971) does not lend itself to a simplistic derivation of enhancement at other wave steepness values.

However, Witting’s (1971) thermal boundary layer model can be readily extended to the mass diffusion sub-layer using fifth order Stokes’ wave theory (Skjelbreia and Hendrickson 1961). Consistent with Witting’s (1971) definition of the thermal boundary layer, the stream function \(\psi\) is the depth of the mass diffusion sub-layer at which the dissolved oxygen concentration is constant.
Witting (1971) adopts an “equivalent slab” analogy (Section 1.2.2.5), based on a mean sub-layer thickness. A key assumption in the development of the gravity wave orbital straining gas flux enhancement model is that the diffusion sub-layer thickness at the wave crests is adopted as the reference sub-layer thickness. This recognises that as waves develop, the tangential stress becomes intensified at the wave crests. The reference locality at the wave crest is based on the assumption that the thickness of the diffusion sub-layer is in part, controlled by the wind induced tangential stresses. The PIV measurements (Section 3.4.2) show that the highest mean tangential stresses are near the wave crests. Consequently, gas flux enhancement by gravity wave orbital straining is potentially much higher than previously anticipated.

5.2.1 Orbital straining theoretical flux enhancement

For two dimensional irrotational flows the stream function $\psi$ and the velocity potential $\phi$ can be related by the Cauchy-Riemann conditional equations:

$$u = \frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial z} \tag{5.1}$$

$$w = \frac{\partial \phi}{\partial z} = -\frac{\partial \psi}{\partial x} \tag{5.2}$$

In a frame of reference moving with the wave, that is moving at the wave speed $c$, the stream function may be expressed as:

$$\psi = \int \left( u - c \right) \, dz \tag{5.3}$$

From linear wave theory:
\[
    u = \frac{ga_k \cosh k(z + d)}{\sigma \cosh kd} \cos kx \tag{5.4}
\]

and by substitution of Equation 5.4 into Equation 5.3 we may solve for \( z \) implicitly such that:

\[
    z = \frac{1}{c} \left[ \frac{ga \sinh k(z + d)}{\sigma \cosh kd} \cos kx - \psi - \frac{ga}{\sigma} \cos kx \right] \tag{5.5}
\]

Alternatively, if non-linear wave effects are included by, say, fifth order Stokes wave theory:

\[
    u = \frac{c\left[ A_1 \cosh k(z + d) \cos kx + A_2 \cosh 2k(z + d)2 \cos 2kx + \right.}{A_1 \cosh 3k(z + d)3 \cos 3kx + A_4 \cosh 4k(z + d)4 \cos 4kx +} + \frac{A_5 \cosh 5k(z + d)5 \cos 5kx}{A_4 \cosh 4k(z + d)4 \cos 4kx +} \tag{5.6}
\]

where the determination of coefficients \( A_1 \) to \( A_5 \) is provided by (Skjelbreia and Hendrickson 1961). Substitution of Equation 5.6 into Equation 5.3 and solving for \( z \) implicitly gives:

\[
    z = -\frac{\psi}{c} - \frac{1}{k} \left[ A_1 \sinh kd \cos kx + A_2 \sinh 2kd \cos 2kx + \right. \\
    \left. \frac{A_4 \sinh 3kd \cos 3kx + A_4 \sinh 4kd \cos 4kx}{A_5 \sinh 5kd \cos 5kx +} \right] \\
    + \frac{1}{k} \left[ A_4 \sinh k(z + d) \cos kx + A_2 \sinh h2k(z + d) \cos 2kx + \right. \\
    \left. \frac{A_4 \sinh 3k(z + d) \cos 3kx + A_4 \sinh 4k(z + d) \cos 4kx}{A_5 \sinh 5k(z + d) \cos 5kx +} \right] \tag{5.7}
\]

Streamlines at selected values of \( \psi \) are plotted in Figures 5.3 and 5.4 for both the linear and fifth order Stokes wave theories for a wave steepness \( ak \) of 0.32 (the maximum wave steepness measured in the experiments conducted herein). The fifth order Stokes waves have a noticeable sharper crest and an extended trough region in comparison to those calculated using linear wave theory. The streamlines have similar features to their respective surface profiles. For both linear and fifth order Stokes waves there is a notable
reduction in streamline depth between the crests and troughs of waves. Consequently, under gravity wave orbital straining, the mass diffusion sub-layer is thickest at the wave crests and thinnest at the wave troughs. Adopting the wave crest as a reference start location, progressive thinning of the mass diffusion sub-layer occurs along the windward limb of the wave. Thickening of the mass diffusion sub-layer occurs along the leeward limb between the wave trough and the wave crest. The plots of the phase related normalised gas transfer velocity in Figures 5.3 and 5.4 show an approximate doubling locally of the gas transfer velocity between the wave crests and wave troughs for a high wave steepness.

Figure 5.5 provides a comparison between the streamline depths at the crests and troughs of waves for both linear and fifth order Stokes theory. At low wave steepness differences between the two theories are negligible. However, as wave steepness increases, streamline truncations predicted by the two theories diverge. Peirson and Banner (2003) and in this study (Figures 3.9, 3.13, 3.17 and 3.21) show that the free surface of microscale breaking waves are similar in profile to that predicted by fifth order Stokes theory, although an asymmetry between the windward and leeward limbs of the waves also occurs (Section 3.3). Further analysis herein is based on fifth order Stokes theory.

Adopting the mass diffusion sub-layer thickness at the wave crest as a reference, the reduction in the mass diffusion sub-layer thickness at the wave trough is plotted against wave steepness in Figure 5.6. At a maximum wave steepness $ak = 0.32$ the mass diffusion sub-layer thickness at the trough has been thinned by a factor of 1.80.

The effective enhancement $W$ of gas flux due to gravity wave orbital straining has been computed and is shown in Figure 5.7. In the presence of waves there is also a small increase in surface area that contributes to the effective enhancement (Jähne and Haußeker 1998). The surface area of the wave $S$ is given by:

$$S = \lambda \int_0^\lambda \sqrt{1 + (d\eta/dx)^2} \, dx \quad [5.8]$$
where for fifth order Stokes waves:

\[ \eta = A_1 \cos kx + A_2 \cos 2kx + A_3 \cos 3kx + A_4 \cos 4kx + A_5 \cos 5kx \]  \[5.9\]

and integrating using Simpson’s rule, the effective enhancement due to the increased surface area and the effective enhancement due to the combined effects of orbital straining and increased surface area are presented in Figure 5.7. For the maximum wave steepness \( ak = 0.446 \) adopted by Witting (1971) the effective enhancement now becomes 1.71. This is substantially higher than the effective enhancement of 1.38 reported by Witting (1971) and is due to the crest mass diffusion sub-layer thickness being adopted as the phase reference position. At the maximum wave steepness in this study \( ak = 0.32 \) the theoretical effective gas flux enhancement due to gravity wave orbital straining is 1.45 which is equivalent to an increase in mean gas transfer velocity of 31%.

Fitting a second order polynomial to the data in Figure 5.7, the effective enhancement of the gas transfer velocity for orbital straining and increased free surface area is:

\[ W = 1.00 + 0.97ak + 1.41(ak)^2 \]  \[5.10\]

The effective enhancement due to the increased surface area is small in comparison to that of the orbital straining, but is included for completeness. Both the increased surface area and the zones of surface convergence and divergence caused by gravity wave orbital straining have been dismissed as having only minor roles in gas flux enhancement by many investigators including Deacon (1981), Csanady (1990) and Jähne and Haußecker (1998), but this analysis shows that it is a potentially significant effect.

McKenna and McGillis (2004) also demonstrate a gas transfer velocity dependence on surface divergence for grid-stirred turbulence and non-breaking mechanically generated surface waves.
5.2.2 Comparison with experimental results

The role of gravity wave orbital straining is compared with the gas transfer velocity measured by the bulk method and the gas transfer velocity as measured at the wave crests and wave troughs by the LIF technique.

In drawing comparisons between the gas transfer velocity data for the bulk method, effective enhancement from both orbital straining and the increased surface area need to be considered. When comparing the LIF gas transfer velocity data at discrete phase locations, effective enhancement is directly related to orbital straining only (i.e., the increase in surface area does not come into consideration).

5.2.2.1 Bulk gas transfer velocity

Experiments 1 to 3 (flat water f00u21ak0, low wave f34u21ak18 and incipient breaking f34u21ak27) were undertaken at the same wind speed. In Experiment 4 (microscale breaking f34u57ak32) the same wave frequency was maintained, however a higher wind speed was required to force the water surface into a microscale breaking state.

Experiments 5 to 8 (ripple f63u42ak00, low wave f21u39ak10, incipient breaking f24u39ak24 and microscale breaking f31u39ak28) were undertaken at the same wind speed and the wave frequency was varied to force the water surface between the different regimes.

It is of some benefit to compare the measured gas transfer velocity data sets where an increase in wave steepness has been achieved for the same given wind speed. Transfer velocity data for each experiment are presented in Table 5.1 together with the theoretical enhancement due to wave orbital straining and increased water surface area. The obvious difficulty with such a comparison is that the friction velocity increases with wave steepness, despite a constant wind speed.

The last column in Table 5.1 estimates the theoretical enhancement due to gravity wave orbital straining based on adopting the crest as the phase reference point. Clearly the
theoretical enhancement for each of the wave cases in this study indicates the role of gravity wave orbital straining is significant. In Experiment 4 (microscale breaking f34u57ak32) the theoretical enhancement to gas flux due to orbital straining is approximately 31%.

In Table 5.1 the measured enhancement factor for Experiments 2 and 3 are referenced to Experiment 1, whilst Experiments 6, 7 and 8 are referenced to Experiment 5. The measured enhancement factors are considerably higher than the corresponding theoretical orbital straining enhancement factor. This suggests that at the onset of waves, the enhanced gas flux cannot be solely attributed to wave orbital straining.

For wind-forced microscale breaking waves, Peirson and Banner (2003) showed that the mean surface divergence on the leeward faces of the waves is relatively weak and the mean surface velocity field can be well approximated by a 5th order Stokes estimate with a superimposed, weakly modulated surface drift. Computations of the mean divergence using a 5th order Stokes description of the surface velocity for the wave forms of the present study shows differences of only about 10% from the simple expression:

\[
\langle |\Gamma| \rangle = 4akf
\]  

[5.11]

where \( |\Gamma| \) is the magnitude of the local surface divergence and the angle brackets denote spatial averaging. Gas transfer velocity data from this study is presented in Figure 5.8 as a function of the square root of the divergence magnitude. The collapse of the non-breaking wave data is modest with levels of transfer velocity observed for non-breaking waves similar to those observed by McKenna and McGillis (2004). A significant difference in gas transfer velocity between non-breaking waves and microscale breaking wave conditions is evident in Figure 5.8.
Table 5.1  Average gas transfer velocity as measured in the bulk and the theoretical enhancement due to orbital straining and increased free surface area.

<table>
<thead>
<tr>
<th>Surface descriptor</th>
<th>Experiment</th>
<th>Wave steepness $a_k$</th>
<th>Wind speed $v_{10cm}$ (m/s)</th>
<th>Friction velocity $u'_f$ (m/s)</th>
<th>Transfer velocity $k_{v_{bulk}}$ (m/s) x10^6</th>
<th>Measured enhancement factor$^{(1)}$</th>
<th>Theoretical enhancement factor W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat water</td>
<td>1</td>
<td>0</td>
<td>2.1</td>
<td>0.12</td>
<td>7.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Low wave</td>
<td>2</td>
<td>0.18</td>
<td>2.1</td>
<td>0.13</td>
<td>13.8</td>
<td>1.8</td>
<td>1.22 (18%)</td>
</tr>
<tr>
<td>Incipient</td>
<td>3</td>
<td>0.27</td>
<td>2.1</td>
<td>0.22</td>
<td>24.0</td>
<td>3.2</td>
<td>1.36 (26%)</td>
</tr>
<tr>
<td>Microscale</td>
<td>4</td>
<td>0.32</td>
<td>5.7</td>
<td>0.52</td>
<td>88.6</td>
<td>n/a (11.7)</td>
<td>1.45 (31%)</td>
</tr>
<tr>
<td>Ripple</td>
<td>5</td>
<td>-</td>
<td>4.2</td>
<td>0.18</td>
<td>16.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Low wave</td>
<td>6</td>
<td>0.10</td>
<td>3.9</td>
<td>0.24</td>
<td>26.2</td>
<td>1.6</td>
<td>1.11 (10%)</td>
</tr>
<tr>
<td>Incipient</td>
<td>7</td>
<td>0.24</td>
<td>3.9</td>
<td>0.32</td>
<td>32.2</td>
<td>2.0</td>
<td>1.31 (24%)</td>
</tr>
<tr>
<td>Microscale</td>
<td>8</td>
<td>0.28</td>
<td>3.9</td>
<td>0.42</td>
<td>63.4</td>
<td>4.0</td>
<td>1.38 (28%)</td>
</tr>
</tbody>
</table>

$^{(1)}$ The measured enhancement for Experiments 2 and 3 is relative to Experiment 1. The measured enhancement factor for Experiments 6, 7 and 8 is relative to Experiment 5.

* A higher wind speed was used for Experiment 4 to force the water surface to a microscale breaking condition. The figure in brackets is the enhancement referenced to Experiment 1, although it has no physical meaning other than to show the relatively high increase in transfer velocity between the flat water and microscale breaking cases.
5.2.2.2  **LIF gas transfer velocity**

The LIF data provides compelling evidence of the role of gravity wave orbital straining on the gas transfer velocity. With the exception of Experiment 2 (*low wave f34u21ak18*) the measured gas transfer velocity in the wave troughs is higher than that at the wave crests. This notable finding contradicts conventional theories in which the highest gas fluxes are thought to occur in the more turbulent regions near the wave crests. Conventional theories have historically dismissed orbital straining as too weak to significantly influence gas transfer (Deacon 1981, Csanady 1990). In Experiment 2 (*low wave f34u21ak18*), the gas transfer velocity at the wave crests and troughs are statistically equivalent. Comparisons between the measured gas transfer velocity at the wave crests and the wave troughs and the theoretical thinning due to gravity wave orbital straining are presented in Table 5.2.

From Figure 5.6 the theoretical thinning of the diffusion sub-layer between the crest and trough and/or the enhancement of the gas transfer velocity may be estimated. The theoretical crest/trough ratios derived from Figure 5.6 and used as a multiplier to directly compare the gas transfer velocity probability density distributions at the wave crests and wave troughs are presented in Table 5.2. These comparisons are also plotted in Figures 5.9 and 5.10.

Experiments 6, 7 and 8 demonstrate good agreement between measured and theoretical diffusion sub-layer thinning from orbital straining between the wave crest and the wave trough. For these experiments measurements are within 10% of predicted values for irrotational waves. The probability density distributions (Figure 5.10) for the wave crests and the wave troughs are in close agreement when multiplied by the theoretical crest/trough ratio. This suggests that on the windward face of the waves, enhanced gas transfer velocity is caused almost solely by gravity wave orbital straining. For Experiments 2 to 4 measurements are within 44% of predicted values.
Table 5.2 Gas transfer velocity as measured at the wave crests and wave troughs by the LIF method and the theoretical enhancement due to orbital straining.

<table>
<thead>
<tr>
<th>Surface descriptor</th>
<th>Experiment</th>
<th>Wave steepness ak</th>
<th>Wind speed $v_{10cm}$ (m/s)</th>
<th>Transfer velocity $v_{lif}$ (m/s) crest $\times 10^6$</th>
<th>Transfer velocity $v_{lif}$ (m/s) trough $\times 10^6$</th>
<th>Measured trough/crest ratio</th>
<th>Theoretical trough/crest ratio</th>
<th>% theoretical contribution to measured trough thinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low wave 2 (f34u21ak18)</td>
<td>0.18</td>
<td>2.1</td>
<td>23.8</td>
<td>23.6</td>
<td>0.99</td>
<td>1.43</td>
<td>144%</td>
<td></td>
</tr>
<tr>
<td>Incipient 3 (f34u21ak27)</td>
<td>0.27</td>
<td>2.1</td>
<td>21.2</td>
<td>58.0</td>
<td>2.74</td>
<td>1.67</td>
<td>61%</td>
<td></td>
</tr>
<tr>
<td>Microscale 4 (f34u57ak32)</td>
<td>0.32</td>
<td>5.7</td>
<td>45.6</td>
<td>138</td>
<td>3.03</td>
<td>1.80</td>
<td>59%</td>
<td></td>
</tr>
<tr>
<td>Low wave 6 (f21u39ak10)</td>
<td>0.10</td>
<td>3.9</td>
<td>17.0</td>
<td>20.1</td>
<td>1.18</td>
<td>1.23</td>
<td>104%</td>
<td></td>
</tr>
<tr>
<td>Incipient 7 (f24u39ak24)</td>
<td>0.24</td>
<td>3.9</td>
<td>19.5</td>
<td>28.1</td>
<td>1.44</td>
<td>1.59</td>
<td>110%</td>
<td></td>
</tr>
<tr>
<td>Microscale 8 (f31u39ak28)</td>
<td>0.28</td>
<td>3.9</td>
<td>39.4</td>
<td>70.3</td>
<td>1.78</td>
<td>1.69</td>
<td>95%</td>
<td></td>
</tr>
</tbody>
</table>

* derived from Figure 5.5
LIF gas transfer velocity measurements on the leeward and windward limbs of the waves for all experiments are bounded by the mean gas transfer velocity at the wave troughs (upper limit) and the mean gas transfer velocity at the wave crests (lower limit). These data support the conclusion that wave orbital straining has a significant role in the enhancement of gas transfer velocity.

5.2.3 Summary of enhancement to gas transfer velocity by gravity wave orbital straining

Both the bulk oxygen and LIF experiments indicate that gravity wave orbital straining cannot be neglected in the overall gas transfer budget. The measured gas transfer velocity data at the wave crests and wave troughs support the theoretical derivation indicating higher gas fluxes in the troughs of the waves. The contribution of wave orbital straining and increased water surface area to enhancement of gas transfer velocity has not been previously quantified against actual measurements. This is the first such undertaking and suggests that the contribution can be significant.

By adopting the wave crests as the reference phase location, it is shown theoretically that effective gas transfer velocity enhancement can be as high as 1.45 or 31% for the experiments conducted in this study. The mass diffusion sub-layer can be thinned by a factor up to 1.80 times by gravity wave orbital straining between the wave crests and the wave troughs (Table 5.2).

McKenna and McGillis (2004) also show a good correlation between gas transfer velocity and mean surface divergence.

5.3 Capillary ripples

MacIntyre (1971) has theoretically shown that localised transfer velocities may be enhanced up to 3.5 times in the presence of capillary ripples. Others such as Szeri (1997) and Witting (1971) have also theoretically indicated that gas fluxes increase in the presence of capillary ripples.
Saylor and Handler (1999) undertook a series of laboratory based experiments and showed that a surface covered in capillary waves could achieve a gas flux equivalent to a wind/wave tunnel experiment with a wind of 10m/s (i.e. equivalent to a surface covered in microscale breaking waves). However, the experiments of Saylor and Handler (1999) generate the capillaries using a vibrating table which imparts energy through the entire water column, rather than being a hydrodynamic feature that has its generation origin at the air-water interface. Also, Saylor and Handler (1999) do not consider the possibility that microscale breaking may be active during their experiments.

5.3.1 Comparisons with experimental data

In Experiments 2 and 6 (*low wave* f34u21ak18, f21u39ak10) parasitic capillary ripples on the leeward face of the gravity waves were not observable. By maintaining the same wind speed and increasing the wave height (Experiment 2) or increasing the wave frequency (Experiment 6) the waves steepen and transition into the incipient wave category. In Experiments 3 and 7 (*incipient wave* f34u21ak27, f24u39ak24) well defined parasitic capillary ripples are present on the leeward face of the gravity waves.

Therefore the influence of capillary ripples on gas transfer velocity enhancement can be quantified between Experiment 2 (f34u21ak18) and Experiment 3 (f34u21ak27) and likewise between Experiment 6 (f21u39ak10) and Experiment 7 (f24u39ak24). Whilst this can be undertaken for both the bulk and LIF data, the LIF data provides more relevant phase specific detail.

The capillary ripples are located between the LIF phase measurement locations at the wave crest and the mid point of the leeward limb. If capillary ripples can significantly enhance gas fluxes then:

- an increase in gas transfer velocity would be expected between the crest transfer velocity data in Experiments 2 and 3 and likewise between Experiments 6 and 7;
• an increase in gas transfer velocity would be expected between the leeward limb and the crest transfer velocity data for both Experiments 3 and 7 (incipient waves).

The crest gas transfer velocity probability density distribution for each of these experiments is plotted in Figure 5.11. The distributions between Experiments 2 and 3 show comparable populations and a similar outcome is evident between Experiments 6 and 7. Between Experiment 2 (low wave f34u21ak18) and Experiment 3 (incipient wave f34u21ak27) there is a small decrease (11%) in the transfer velocity measured at the wave crests, whilst in Experiment 6 (low wave f21u39ak10) and Experiment 7 (incipient wave f24u39ak24) there is a small increase (15%) in the transfer velocity measured at the wave crests. Comparisons of the wave crest gas transfer velocity data show no compelling evidence of enhancement due to the parasitic capillary waves.

The gas transfer velocity probability density distribution for the leeward limb and crest in Experiments 3 and 7 (incipient waves) is plotted in Figure 5.12. In this plot the gas transfer velocity data on the leeward limb has been adjusted for orbital straining to give an equivalent gas transfer velocity at the wave crest. The adjusted data set is remarkably similar to the measured gas transfer velocity at the wave crest. In both experiments the adjusted leeward limb 50 percentile gas transfer velocity is within 2.5% of the measured value at the wave crest. This provides convincing evidence that direct enhancement of gas transfer velocity by parasitic capillary ripples is small.

5.3.2 Summary of enhancement to gas transfer velocity by parasitic capillary ripples

The LIF experiments are the first that quantify the enhancement to gas transfer velocity as a direct result of parasitic capillary ripples. The theoretical approaches of MacIntyre (1971), Szeri (1997) and Witting (1971) suggest that the gas transfer velocity may be significantly enhanced by the direct influence of parasitic capillary ripples. However, the measurements undertaken as part of this study indicate that the direct enhancement in gas transfer velocity due to parasitic capillary ripples is small.
5.4 Wind induced turbulence within the viscous sub-layer

The PIV data presented in Chapter 3 shows that the tangential stress near the wave crests is higher than in the wave troughs. Greater variability in the surface wind drift current is also observed at the crests of the waves. These observations support the notion that thinning of the mass diffusion sub-layer due to wind stress is more dominant near the wave crests.

5.4.1 Solid Wall

At relatively low wind speeds Deacon (1977) found that the gas transfer velocity varied with a Schmidt number exponent of -2/3:

\[ k_v = \frac{1}{12.2} \cdot \text{Sc}^{-\frac{2}{3}} u^* \] \[ [1.27] \]

The formulation and verification of Equation 1.27 was based on Reichardt’s solid wall velocity profile and laboratory data from Hoover and Berkshire (1969) and Liss (1973). As previously noted in section 1.2.2.3 the Deacon model substantially under-predicts gas transfer at wind speeds greater than 3.5m/s and the onset of waves.

Experiment 1 (f00u21ak0) is the only flat water experiment conducted in this investigation. The Deacon model under-estimates the theoretical transfer velocity for Experiment 1 by a factor of approximately 30% (Figure 5.13). Similarly, the Deacon model appears as a lower bound for the majority of the data compiled by Komori et al. (1993) and plotted in Figure 5.13.

5.4.2 Free Surface

The Deacon model is based on solid wall boundary layer theory and presents a lower bound for the transfer velocity data. For the free surface condition, surface parallel velocity fluctuations are possible and Jähne et al. (1987) proposes a transition of the Schmidt number exponent from -2/3 to -1/2 with the onset of waves. The implications are that at a free surface, zones of convergence and divergence may exist. However, even for light winds the surface is still free, and less intense zones of surface convergence and divergence
may be present. Therefore, it would seem reasonable to assume that the Schmidt number exponent is maintained at -1/2 for all non-breaking wave conditions. Jähne et al. (1987) shows:

\[ k_v = \frac{1}{16} Sc^{-\frac{1}{2}} u_{*} \]  \text{[1.31]}

whilst Coantic (1986) also suggests that:

\[ k_v = \frac{1}{13.7} Sc^{-\frac{1}{2}} u_{*} \]  \text{[5.12]}

or

\[ k_v = \frac{1}{8.3} Sc^{-\frac{1}{2}} u_{*} \]  \text{[5.13]}

depending on the data used in his derivation.

Coantic (1986) has shown that the constant in Equations 1.31, 5.12 and 5.13 is sensitive to the data sets used for its derivation. Equation 1.31 is plotted in Figure 5.13 and forms a lower bound for the gas transfer velocity data when the friction velocity exceeds approximately 0.5m/s (i.e. when the water surface is in a fully developed microscale breaking state).

Peirson and Banner (2003) predict subduction of the diffusion sub-layer at the onset of microscale breaking based on their observations of near surface velocity structure. At the subduction location the vertical velocity \( w \neq 0 \) at the surface and, as such, the assumptions used to derive Equations 1.31, 5.12 and 5.13 are not valid for the microscale breaking state.
Using the gas transfer velocity data from the bulk measurements obtained in this study and excluding the microscale breaking cases, the line of best fit based on the Schmidt number exponent of -1/2 is:

\[
k_v = \frac{1}{14.5} S\epsilon^{-\frac{1}{2}} u_w^2 \quad [5.14]
\]

Equation 5.14 is plotted in Figure 5.14 and is consistent with Equations 1.31 and 5.12. Equation 5.14 includes the enhancement partitions associated with the wind induced turbulence within the viscous sub-layer, capillary ripples and gravity wave orbital straining. From Section 5.3 we can assume gas transfer enhancement due the capillary ripples is negligible. Adjusting the bulk measurements to remove the enhancement associated with the theoretical gravity wave orbital straining (Figure 5.15), the line of best fit now yields:

\[
k_{v, wind} = \frac{1}{17.6} S\epsilon^{-\frac{1}{2}} u_w^2 \quad [5.15]
\]

Equation 5.15 represents the enhancement due only to wind induced turbulence within the viscous sub-layer at a free surface. Equation 5.15 excludes enhancement due to wave hydrodynamics, that is, enhancement due to parasitic capillary waves and wave orbital straining. The validity of Equation 5.15 is reliant on a good linear dependency with the friction velocity. A good liner dependency is demonstrated in Figure 5.15.

### 5.5 Subduction at the toe of the spilling region for microscale breaking waves

Subduction at the toe of the spilling region was first measured using PIV techniques by Peirson and Banner (2003). They observed intense magnitudes of vorticity (>1000s\(^{-1}\)) generated at the toe of the spilling regions of microscale breaking waves (Figure 1.6) and proposed that the toe of the spilling region is a point of highly localised subduction, forcing mixing of the thin diffusion sub-layer to a relatively deep depth.
5.5.1 Bulk gas transfer velocity data

The microscale breaking bulk gas transfer velocity data is introduced in Figure 5.16 with enhancement due to orbital straining removed. The microscale breaking data are located well above the line defining enhancement due only to wind induced turbulence within the viscous sub-layer at a free surface (Equation 5.15). It is postulated that the difference between the plotted bulk gas transfer velocity for the microscale breaking cases and Equation 5.15 is due to subduction at the toe of the spilling region of the microscale breaking waves.

In Table 5.3 the contributions of the gas flux from wave orbital straining, capillary ripples, wind shear and subduction at the toe of the spilling region of microscale breaking waves is presented for each of the eight experiments conducted in this study. The measured bulk gas transfer velocity normalised to a Schmidt number of 600 is presented in the third column of Table 5.3. The fourth column represents the theoretical contribution of orbital straining to the measured bulk gas transfer velocity based on the wave steepness (Equation 5.10). The fifth column is included for completeness and represents the contribution to the measured bulk gas transfer velocity from the parasitic capillary ripples on the leeward faces of the incipient and microscale breaking wave states. In Section 5.3 it was deduced that the contribution of the parasitic capillary ripples to enhanced gas flux was negligible. The sixth column of Table 5.3 represents the contribution from wind induced turbulence based on Equation 5.15. The final column of Table 5.3 is the gas flux deficit between the first four data columns in Table 5.3 and represents the gas transfer velocity enhancement due to subduction at the toe of the spilling region. The experiments in Table 5.3 are ordered from lowest to highest gas transfer velocity.

The enhancement due to subduction at the toe of the spilling region for microscale breaking waves is plotted in Figure 5.17. The data scatter about the origin (dashed line) for the non-microscale breaking wave cases is a general indicator of the error sensitivity. Clearly there is a significant enhancement at the onset of microscale breaking. This is supported in Figure 5.13 from the data compiled by Komori et al. (1993) where almost all the
experimental data lies well above the line defined by Equation 1.31 at friction velocities exceeding 0.5 m/s.

Table 5.3 Summary of estimated gas transfer velocity contributions from gravity wave orbital straining, capillary ripples, wind induced shear and microscale breaking subduction events based on the bulk gas transfer velocity data.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Surface descriptor</th>
<th>Total $k_{vbulk}^{2/3}$ x10^6</th>
<th>Orbital straining (m/s) x10^6</th>
<th>Capillary ripple (m/s) x10^6</th>
<th>Wind induced shear (m/s) x10^6</th>
<th>Toe subduction contribution (m/s) x10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (f00u21ak0)</td>
<td>Flat water</td>
<td>7.06</td>
<td>-</td>
<td>-</td>
<td>9.75</td>
<td>-2.69</td>
</tr>
<tr>
<td>2 (f34u21ak18)</td>
<td>Low wave</td>
<td>12.9</td>
<td>2.3</td>
<td>-</td>
<td>10.5</td>
<td>0.1</td>
</tr>
<tr>
<td>5 (f63u42ak00)</td>
<td>Ripple</td>
<td>15.3</td>
<td>-</td>
<td>-</td>
<td>14.5</td>
<td>0.8</td>
</tr>
<tr>
<td>3 (f34u21ak27)</td>
<td>Incipient</td>
<td>22.5</td>
<td>5.6</td>
<td>-</td>
<td>17.6</td>
<td>-0.7</td>
</tr>
<tr>
<td>6 (f21u39ak10)</td>
<td>Low wave</td>
<td>25.2</td>
<td>2.5</td>
<td>-</td>
<td>19.3</td>
<td>3.4</td>
</tr>
<tr>
<td>7 (f24u39ak24)</td>
<td>Incipient</td>
<td>31.9</td>
<td>7.6</td>
<td>-</td>
<td>25.6</td>
<td>-1.3</td>
</tr>
<tr>
<td>8 (f31u39ak28)</td>
<td>Microscale</td>
<td>63.5</td>
<td>17.5 (28%)</td>
<td>-</td>
<td>33.8 (53%)</td>
<td>12.2 (19%)</td>
</tr>
<tr>
<td>4 (f34u57ak32)</td>
<td>Microscale</td>
<td>84.9</td>
<td>26.4 (31%)</td>
<td>-</td>
<td>41.9 (49%)</td>
<td>16.6 (20%)</td>
</tr>
</tbody>
</table>

From Table 5.3, for the microscale breaking cases, approximately 50% of the total gas flux may be attributed to wind induced turbulence, 30% due to gravity wave orbital straining and 20% due to subduction at the toe of the crest spilling region.

5.5.2 LIF gas transfer velocity data

In the previous section the enhancement due to subduction at the toe of the spilling region for microscale breaking waves was determined using the average bulk gas transfer velocity. Comparisons are now made with the LIF data.

5.5.2.1 Experiments 7 and 8

From Experiments 7 and 8 a robust LIF data set is available for determination of the enhancement due to subduction at the toe of the spilling region. In Experiment 7 (Incipient f24u39ak24) and Experiment 8 (microscale f31u39ak28), 589 and 451 LIF images were accepted for processing to determine instantaneous transfer velocities. These data are reproduced from Chapter 4 in Figures 5.18 and 5.19.
Peirson and Banner (2003) predicted subduction of the aqueous diffusion sub-layer at the onset of microscale breaking from their observations of near surface velocity structure. If all waves were in a continuous microscale breaking state then only very thin diffusion sub-layers would be observed. Consequently, distinct population boundaries would be evident between the incipient and microscale breaking cases. From observations during this investigation, microscale breaking waves are constantly collapsing and reforming into a breaking state. Therefore, the microscale breaking cases should consist of two data populations, one with a very thin mass diffusion sub-layer thicknesses and one similar to that for the incipient case.

In Experiment 7 (Incipient f2u3ak24) there are relatively few data points with a transfer velocity greater than 90x10^{-6}m/s in the wave trough. Whilst in Experiment 8 (microscale f31u39ak28) there is a considerable population of data with transfer velocities exceeding this threshold (Figures 5.18 and 5.19). In Experiment 8 transfer velocity data exceeding 90x10^{-6}m/s in the trough are assumed to result from subduction at the toe of the spilling region. Based on the theoretical enhancement due to gravity wave orbital straining (Figure 5.6), threshold values may be deduced for the other wave phase locations. At the wave crest the threshold value is 60x10^{-6}m/s and on the leeward and windward limbs is 78x10^{-6}m/s. These threshold values are plotted in Figure 5.18 and show relatively good agreement with the LIF data. In Table 5.4 the gas transfer velocity data for Experiment 8 is divided into the two populations, gas transfer velocity data less than the threshold values and gas transfer velocity data exceeding the threshold values at the four discreet phase locations.

The average enhancement due to subduction at the toe of the spilling region based on the four discreet phase locations is 31% and at the crest location is 30%. This is in relatively good agreement with the value of 20% derived from the bulk dissolved oxygen measurements (Section 5.5.1). Subduction events contribute significantly to the total flux. For each subduction event approximately a 3.5 fold increase in transfer velocity is observed.
(k_{vlif} =36.4\times10^{-6}\text{m/s compared with }k_{vlif} =129\times10^{-6}\text{m/s}). Consequently, a small increase in subduction events (18%), results in a notable increase in transfer velocity (31%).

Table 5.4 LIF gas transfer velocity data for Experiment 8 (*microscale* f31u39ak28). Partitioning of the data is based upon the subduction threshold gas transfer velocity value of 60\times10^{-6}, 78\times10^{-6}, 90\times10^{-6} and 78\times10^{-6}\text{m/s at the crest, leeward limb, trough and windward limb of the wave.}

<table>
<thead>
<tr>
<th>Location</th>
<th>Total k_{vlif} (m/s) x10^6</th>
<th>Average k_{vlif} excluding subduction events (m/s) x10^6</th>
<th>Average k_{vlif} of subduction events only (m/s) x10^6</th>
<th>Contribution of subduction events to total k_{vlif}</th>
<th>% occurrence of subduction events</th>
<th>Contribution of subduction events to total k_{vlif}</th>
<th>% occurrence of subduction events</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crest</td>
<td>39.4</td>
<td>27.6</td>
<td>112</td>
<td>30%</td>
<td>14%</td>
<td>14%</td>
<td>14%</td>
</tr>
<tr>
<td>Leeward</td>
<td>47.0</td>
<td>36.7</td>
<td>122</td>
<td>22%</td>
<td>12%</td>
<td>12%</td>
<td>12%</td>
</tr>
<tr>
<td>Trough</td>
<td>70.3</td>
<td>48.0</td>
<td>135</td>
<td>32%</td>
<td>26%</td>
<td>26%</td>
<td>26%</td>
</tr>
<tr>
<td>Windward</td>
<td>56.0</td>
<td>33.3</td>
<td>148</td>
<td>41%</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>mean</td>
<td><strong>53.2</strong></td>
<td><strong>36.4</strong></td>
<td><strong>129</strong></td>
<td><strong>31%</strong></td>
<td><strong>18%</strong></td>
<td><strong>18%</strong></td>
<td><strong>18%</strong></td>
</tr>
</tbody>
</table>

Based on the one dimensional form of Fick’s law (Equation 1.6) a transfer velocity of 112\times10^{-6}\text{m/s (crest subduction average) is equivalent to a time of }0.051\text{s from commencement of aeration (for the boundary conditions adopted in Figure 1.3). For Experiment 8 (*microscale* f31u39ak28) this is equivalent to a distance from the subduction point to the crest of }1/6.3\text{ of the wave length for a wave frequency of }3.1\text{s}^{-1}\text{ (Figure 5.20). In this context the mean value of }112\times10^{-6}\text{m/s appears to be consistent with the general locality at which the toe of the crest spilling region is observed.}

In column 3 of Table 5.4 (non-subduction data) the ratio between the crest and trough transfer velocities (48.0/27.6=1.74) is very close to the theoretical orbital straining ratio of 1.69. In column 4 of Table 5.4 (subduction events) there is a considerable discrepancy between the measured crest and trough transfer velocity ratio (135/112=1.2) and the theoretical orbital straining ratio of 1.69.

There are several processes that occur along the length of the wave, that to date have only been considered independently: 1). Gravity wave orbital straining thins the diffusion sub-
layer relative to the reference thickness at the crest, and 2). A time based molecular diffusion process thickens the diffusion sub-layer along the length of the wave (Figure 1.3). Thickening of the diffusion sub-layer along the length of the wave was included in the Peirson and Banner (2003) model (Figure 1.6). At lower transfer velocities the gravity wave orbital straining appears to be the more dominant process. However, at higher transfer velocities (or large concentration gradients) the two processes appear to have an almost equal influence.

The small measured ratio between the crest and trough transfer velocity (subduction data) suggests that once a subduction event occurs the gas transfer velocity is maintained at a relatively constant value along the full length of the wave. On this basis an upper limit to the gas transfer velocity exists that would be close to the mean value of 129x10^{-6} m/s if all waves are in a continuous microscale breaking state. Although it is also noted that at all four phase locations there are numerous individual measurements between 200x10^{-6} m/s and 300x10^{-6} m/s.

The partitioning in Table 5.3 for the bulk gas transfer velocity data could be developed further with an additional column for the time based molecular diffusion process. At lower transfer velocities (non-subduction) the process is relatively slow and hence, negligible. At high transfer velocities (microscale breaking subduction population) the process is much faster and affects the overall gas flux budget. This would be shown as a negative enhancement over the length of the wave. For Experiment 8 the outcome is then an increase in the estimated contribution to transfer velocity from subduction at the toe of the spilling region for microscale breaking waves in Table 5.3 of 19% to possibly something approaching the contribution shown in Table 5.4 of 31%. Further development of this concept would need to be undertaken with numerical models and is well beyond the scope of this present investigation.
5.5.2.2 Experiments 3 and 4

There is insufficient LIF data for Experiment 4 (microscale f34u57ak32) to make a similarly robust assessment, however for completeness the data has been partitioned adopting a threshold value of 120x10\(^{-6}\) for the transfer velocity at the trough (Table 5.5). The threshold value is based on the LIF data populations for Experiment 3 (Incipient f34u21ak27), however it is noted with caution that Experiment 4 was undertaken using considerably higher wind forcing.

<table>
<thead>
<tr>
<th>Location</th>
<th>Total (k_{vlif}) (m/s) x10(^{6})</th>
<th>Average (k_{vlif}) excluding subduction events (m/s) x10(^{6})</th>
<th>Average (k_{vlif}) of subduction events only (m/s) x10(^{6})</th>
<th>Contribution of subduction events to total (k_{vlif})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crest</td>
<td>45.6</td>
<td>36</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Leeward</td>
<td>84.7</td>
<td>50</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>Trough</td>
<td>138</td>
<td>72</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>Windward</td>
<td>61.5</td>
<td>56</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td><strong>82.5</strong></td>
<td><strong>53.5</strong></td>
<td></td>
<td><strong>35%</strong></td>
</tr>
</tbody>
</table>

As described in Chapter 4, LIF measurements at the wave crest for this strongly wind forced case were difficult. In column 3 of Table 5.5 (non-subduction data) the ratio between the crest and trough gas transfer velocities (72/36=2) is in reasonable agreement to the theoretical ratio of 1.80. There is insufficient subduction data for this experiment to make any firm conclusions, other than, with the exception of the trough, the subduction data is of similar magnitude to that shown in Table 5.4 for Experiment 8. Consequently, some statistical data is not presented in Table 5.5.

The contribution of subduction events as measured by the LIF of 35% is higher than that determined by the bulk dissolved oxygen method (20%). This difference is considered to be due to the time based molecular diffusion process.
5.5.3 Summary of enhancement to gas transfer velocity by subduction at the toe of the spilling region for microscale breaking waves

The estimated enhancement to gas transfer velocity by subduction at the toe of the spilling region for microscale breaking has been approached by two independent methods. Direct analysis of the LIF data indicates that for Experiment 8 (microscale f31u39ak28) the subduction events are responsible for 30% (crest value) of the measured total transfer velocity. Enhancement partitioning of the bulk dissolved oxygen data indicates that subduction events are responsible for 19-20% of the measured total transfer velocity. The difference is most likely due to the time (or wave length) based molecular diffusion process where thickening of the diffusion sub-layer occurs along the length of the wave.

The two independent approaches give similar results. This provides strong support to the estimated gas flux enhancement due to wave orbital straining, capillary ripples and wind induced turbulence within the viscous sub-layer.

5.6 Discussion and Summary

A systematic approach has been adopted using both experimental data and theoretical considerations to quantify the partitioning of the gas flux contribution across the air-water interface based on surface hydrodynamic features defined in the PIV analysis. The first wave phase resolved LIF data sets obtained as part of this study have enabled interpretation of gas transfer velocity enhancement that has not previously been possible.

Gravity wave orbital straining and increased surface area that has previously been dismissed by numerous researchers has been shown to significantly enhance gas transfer velocities. For the maximum wave steepness in this study $ak = 0.32$, enhancement can be as much as 31%. Gas transfer enhancement due to gravity wave orbital straining and increased surface area may be approximated by:

$$ W = 1.00 + 0.97ak + 1.41(ak)^3 $$

[5.10]
Several theoretical studies of capillary ripples have indicated they have the potential to substantially increase gas transfer velocities. For example, MacIntyre (1971) has shown that localised transfer velocities may be increased up to 3.5 times in the presence of capillary ripples. Evidence of enhancement due to the presence of parasitic capillary ripples is not supported by the wave phase resolved LIF data. The direct contribution of capillary waves to gas transfer velocity enhancement appears to be negligible for the experiments conducted herein.

Gas transfer velocity is commonly parameterised in terms of friction velocity and Schmidt number. However, this parameterisation encompasses enhancement due to all surface hydrodynamic features and provides little insight into the microphysical interfacial behaviour. By judicious use of the non-microscale wave breaking data and removal of the gas transfer velocity enhancement due to gravity wave orbital straining and capillary ripples a relationship was developed for enhancement due to wind induced turbulence of the viscous sub-layer. Assuming a Schmidt number exponent to the -1/2 relationship, the transfer velocity due solely to wind induced turbulence of the viscous sub-layer is:

\[
k_{v_{\text{wind}}} = \frac{1}{17.6} Sc^{-\frac{1}{2}} H_s^{w}
\]

Having quantified the transfer velocity or its enhancement due to gravity wave orbital straining, capillary waves and wind induced turbulence of the viscous sub-layer, enhancement due to subduction at the toe of the spilling region for microscale breaking waves may also be derived from the bulk dissolved oxygen experiments. For the experiments conducted herein 19 to 20% of the enhancement was found to be due to these subduction events. An independent analysis of the wave phase resolved LIF data where a measure of the enhancement due to these subduction events can be directly quantified found 30 to 35% of the enhancement was due to such events.
The difference between the bulk dissolved oxygen and LIF estimates of enhancement due to subduction may be apportioned to the time based molecular diffusion process over the length scale of the wave.

5.6.1 A hydrodynamic partitioned gas transfer model

Based on the hydrodynamic partitioning of the gas flux across the air water interface a simple model has been developed. Combining Equations 5.10 and 5.15 the gas flux model is:

$$k_v = \frac{1}{17.9} \text{Sc}^{-\frac{1}{2}} u^*_w \left(1.00 + 0.97ak + 1.41(ak)^2\right)$$  \[5.16\]

for water surfaces up to and including incipient breaking. At the onset of microscale breaking an additional term is introduced to include the enhancement due to subduction events. Equation 5.16 then becomes:

$$k_v = [1 - e] \times \left(\frac{1}{17.9} \text{Sc}^{-\frac{1}{2}} u^*_w \left(1.00 + 0.97ak + 1.41(ak)^2\right)\right) + \left[e \times 1.3 \times 10^{-6}\right]$$ \[5.17\]

where: $e$ is an efficiency coefficient based on subduction events causing a destruction of the mass diffusion sub-layer.

Assuming a Schmidt number dependency for the subduction events, Equation 5.17 can be expressed as:

$$k_v = [1 - e] \times \left(\frac{1}{17.9} \text{Sc}^{-\frac{1}{2}} u^*_w \left(1.00 + 0.97ak + 1.41(ak)^2\right)\right) + \left[e \times 3.2 \times 10^{-3} \times \text{Sc}^{-\frac{1}{2}}\right]$$ \[5.18\]

Alternatively, taking the microscale breaking model (Equation 1.37) of Peirson and Banner (2003) and applying this to the subduction contribution in Equation 5.17 yields:
\[ k_v = [1-e] \times \left[ \frac{1}{17.9} Sc^{0.2} u^{*} \left( 0.01 + 0.97 ak + 1.41 (ak)^2 \right) \right] + \left[ e \times (1.5 \rightarrow 1.6) \right] \sqrt{Df} \]  

[5.19]

The measured bulk gas transfer velocity for the eight wind-wave cases investigated in this study are plotted in Figure 5.21 together with the estimated gas transfer velocity based on the model defined by Equation 5.18. The model assumes a quasi steady state system. In Equation 5.16 gravity wave orbital straining dominates the time based molecular diffusion thickening of the diffusion sub-layer. In Equation 5.18 (for subduction events), thinning of the diffusion sub-layer by gravity wave orbital straining and the time based molecular diffusion thickening of the diffusion sub-layer have similar but opposite magnitudes.

A numerical model encompassing wind-wave hydrodynamic features is required to refine Equations 5.16 and 5.18. Such an exercise is beyond the scope of the present study. However, for the first time a model has been developed that encompasses all of the hydrodynamic process responsible for gas transfer enhancement across the air-water interface. More importantly, these processes have been quantified for the first time against actual microphysical measurements of the dissolved oxygen concentration profile in the diffusion sub-layer.

Equation 5.17 suggest that an upper transfer velocity limit must exist that is close to 130x10\(^{-6}\)m/s. Komori et al. (1993) shows experimental data (Figure 5.13) that exceeds this upper limit, possibly because other processes such as wave breaking and spray are initiated. The value of 130x10\(^{-6}\)m/s is based on the average gas transfer velocity at the four wave phase locations for subduction events in Experiment 8 (microscale f31u39ak28). At each of the four wave phase locations there are numerous individual measurements between 200x10\(^{-6}\) and 300x10\(^{-6}\)m/s.

It is possible that the value of 130x10\(^{-6}\)m/s also varies with friction velocity. Hence, there is some uncertainty in the value of this constant, at friction velocities exceeding the value of
the upper limit of experiments conducted herein of 0.5m/s. Caution should be applied in using Equations 5.17 and 5.18 beyond friction velocities exceeding 0.5m/s.
The development of a conceptual gas transfer model. The flat water, ripple and waves of small steepness (low wave) cases are shown in this figure. The models are based on the PIV and LIF data and observations during each of the experiments. The simplest model is the flat water, with each subsequent model of a more complex nature with the inclusion of additional hydrodynamic features.
Figure 5.2  A continuation of the development of a conceptual gas transfer model from Figure 5.1. The incipient breaking and microscale breaking wave cases are shown in this figure. The models are based on the PIV and LIF data and observations during each of the experiments. The simplest model is the flat water, with each subsequent model of a more complex nature with the inclusion of additional hydrodynamic features.
Figure 5.3  Upper panel: normalised low amplitude linear wave theory water profile (black line) for the maximum wave steepness $\alpha_k=0.32$ in this study. Streamlines at given $\varphi$ (coloured lines) indicate a thinning of the mass diffusion sub-layer between the wave crest and the wave trough. Lower panel: normalised gas transfer velocity. Wave orbital straining causes an enhancement in the gas transfer velocity with the highest magnitudes in the wave troughs.
Figure 5.4  Upper panel: normalised 5th order Stokes wave theory water profile (black line) for the maximum wave steepness $ak=0.32$ in this study. Streamlines at given $\psi$ (coloured lines) indicate a thinning of the mass diffusion sub-layer between the wave crest and the wave trough. Lower panel: normalised gas transfer velocity. Wave orbital straining causes an enhancement in the gas transfer velocity with the highest magnitudes in the wave troughs.
Figure 5.5  Wave crest streamline depth and wave trough streamline depth for both linear and fifth order Stokes’ waves. As the waves become progressively steeper the two theories diverge.
Figure 5.6  

Ratio of wave crest and wave trough streamlines for fifth order Stokes’ wave theory. Multiplication of transfer velocity at wave crest by crest/trough ratio yields gas transfer velocity in wave trough resulting from gravity wave orbital straining.
Effective enhancement due to increased surface area (green line) and gravity wave orbital straining (blue line). Effective enhancement due to the combined increased surface area and gravity wave orbital straining is shown by the black line. At the maximum wave steepness in this study $a_k=0.32$ the theoretical effective gas flux enhancement due to gravity wave orbital straining is 1.45 which is equivalent to an increase in mean gas transfer velocity of 31%.

Figure 5.7  

\[ W = 1.00 + 0.97a_k + 1.41(a_k)^2 \]
Figure 5.8  Gas transfer velocities as a function of the estimated square root of the divergence magnitude. The significantly higher gas transfer velocities (>60x10^{-6} m/s) are associated with microscale breaking waves.
Figure 5.9  Probability exceedance distributions of transfer velocity for: (a) Experiment 2 \( \text{low wave } f34u21ak18 \), (b) Experiment 3 \( \text{incipient } f34u21ak27 \) and (c) Experiment 4 \( \text{microscale } f34u57ak32 \). Solid black line is wave trough, dashed red line wave crest and dashed blue line is wave crest values multiplied by the adjustment implied by 5\(^{th}\) order Stokes theory. Error bars are shown at the 50 percentile exceedance.
Figure 5.10  Probability exceedance distributions of transfer velocity for: (a) Experiment 6 (low wave f21u39ak10), (b) Experiment 7 (incipient f24u39ak24) and (c) Experiment 8 (microscale f31u39ak28). Solid black line is wave trough, dashed red line wave crest and dashed blue line is wave crest values multiplied by the adjustment implied by 5th order Stokes theory. Error bars are shown at the 50 percentile exceedance.
Figure 5.11  Probability exceedance distributions of transfer velocity at the wave crests for: (a) Experiment 2 (low wave) solid black line and Experiment 3 (incipient) red dashed line and (b) Experiment 6 (low wave) solid black line and Experiment 7 (incipient) red dashed line. Distributions in panel (a) are similar indicating capillary ripples have only a minor influence on transfer velocity. Similar observations are made in panel (b). Error bars are shown at the 50 percentile exceedance.
Figure 5.12  Probability exceedance distributions of transfer velocity at the wave crests (red dashed line) and the leeward limb (solid black line) for: (a) Experiment 3 (*incipient* f34u21ak27) and (b) Experiment 7 (*incipient* f24u39ak24). Dashed blue line represents gas transfer velocity on leeward limb with orbital straining applied to the crest phase position. Distributions in both panel (a) and panel (b) are similar indicating capillary ripples have only a minor influence on gas transfer velocity.
Figure 5.13  Dependence of gas transfer velocity with friction velocity as measured by various researchers and compiled by Komori et al. (1993) with all data normalised to a Schmidt number of 600. Bulk transfer velocity for the eight experimental wind-wave cases investigated in this study (blue triangles) is also included in the plot following being normalised to a Schmidt number of 600 using Equation 2.4. Solid line shows the Deacon (1977) model with a Schmidt number dependency to the exponent -2/3 (Equation 1.27). Dashed line shows the Jähne et al. (1987) model with a Schmidt number dependency to the exponent -1/2 (Equation 1.31).
Figure 5.14  Dependence of gas transfer velocity with friction velocity as measured in this study (blue triangles). The microscale breaking data from his study has been excluded from the plot. All data has been normalised to a Schmidt number of 600 using Equation 2.4. Solid black line shows the Deacon (1977) model with a Schmidt number dependency to the exponent -2/3 (Equation 1.27). Dashed line shows the Jähne et al. (1987) model with a Schmidt number dependency to the exponent -1/2 (Equation 1.31). Thick solid blue line shows the line of best fit using a Schmidt number dependency to the exponent -1/2 for the data from this study, excluding the microscale breaking experiments (Equation 5.14).
Figure 5.15  As per caption for Figure 5.13. The data from this study has been adjusted to remove gas transfer velocity enhancement due to gravity wave orbital straining (green squares). Thick solid green line now shows the line of best fit to the adjusted data using a Schmidt number dependency to the exponent -1/2, excluding the microscale breaking experiments (Equation 5.15). Equation 5.15 represents transfer velocity enhancement due to wind induced turbulence within the viscous sub-layer only.
Figure 5.16  As per caption for Figure 5.14 with the inclusion of the microscale breaking data (light blue circles). The microscale breaking data has been adjusted to remove enhancement from gravity wave orbital straining. The difference between the thick solid green line (Equation 5.15) and the microscale breaking data is due to enhancement by subduction at the toe of the spilling region for microscale breaking waves.
Figure 5.17  Partitioned enhancement due to subduction at the toe of the spilling region of microscale breaking waves for the data from this study. A significant contribution is evident when the waves transition to microscale breaking.
Figure 5.18  Experiment 7 (incipient f24u39ak24) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°). The estimated threshold value for subduction events is shown as the black dashed lines.
Figure 5.19  Experiment 8 (microscale f31u39ak28) transfer velocity and diffusion sub-layer thickness computed for individual LIF images and plotted at wave phase position. Wave travels from left to right. Wave trough (black symbols, ±180°), wave crest (red symbols, 0°), windward limb (blue symbols, -90°) and leeward limb (green symbols, 90°). The estimated threshold value for subduction events is shown as the black dashed lines.
Figure 5.20  Based on the one dimensional form of Fick’s law (Equation 1.6) a transfer velocity of $112 \times 10^{-6}$ m/s (crest subduction average) is equivalent to a time of 0.051s from commencement of aeration (for the boundary conditions adopted in Figure 1.3). For Experiment 8 (*microscale* f31u39ak28) this is equivalent to a distance from the subduction point to the crest of 1/6.3 of the wave length for a wave period of 0.32s.
Figure 5.21  Bulk gas transfer velocity vs. friction velocity in air for the eight experimental wind-wave cases investigated in this study (black crosses) and bulk gas transfer velocity as estimated by Equation 5.19 (light blue stars).
6. CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

A series of detailed laboratory experiments investigating low solubility gas transfer across wind-forced wavy air-water interfaces has been reported in this thesis. The study examines the dependence of gas flux on the microphysical interfacial wind momentum exchange and the complex wave coupled hydrodynamics. Hydrodynamic behaviour within the aqueous viscous sub-layer has a prominent role in the gas exchange process and was examined using a particle image velocimetry (PIV) system. For a range of carefully selected wind-wave conditions the surface distribution of tangential stress and the kinematics of the surface skin flow were investigated along the entire wave length.

Major technical advances in the development of a Laser Induced Fluorescent (LIF) system led to the first wave phase resolved gas flux measurements. Previously unidentified optical distortions in LIF imagery due to non-linear effects were mathematically described, yielding the first reliable dissolved oxygen concentration profiles to within 28μm of the air-water interface. The unique PIV and LIF data sets were used to quantify the relative contributions to gas flux from wind shear, wave orbital straining, increased surface area of the waves, parasitic capillary ripples and microscale breaking.

**Tangential Stress**

- For the flat water case (before the onset of waves and form drag) the measured tangential stress is equal to the total wind stress.

- For the wind ruffled, mechanically generated wave cases investigated, only 20% of the total stress is due to the tangential component, the remaining 80% is due to form drag. This is consistent with the findings of Banner (1990). Banner and Peirson (1998) found a much higher proportion of tangential stress but this appears to be due to the lower mean steepness and much greater wave field variability of natural wind waves in comparison to wind-forced mechanical waves. The wave coherent tangential stress accounts for less than 4% of the total wind stress.
The mean tangential stress measurements indicate a general peak at a wave phase location of between -70° and 0° (i.e. on the windward side of the wave crest).

**Wave Kinematics**

- In a frame of reference travelling with the wave, transport in the aqueous surface layer is rearward along the entire length of the wave, except for the strongly wind forced microscale breaking case, where the measured surface velocity at the crest of the waves is similar in magnitude to the wave speed.

- The measured mean wind drift current for the incipient and microscale breaking cases are $\langle u_s \rangle / u^* = 0.22 \pm 0.03$ in the wave troughs, increasing to $\langle u_s \rangle / u^* = 0.35 \pm 0.03$ at the wave crests. These results for near-uniform fields of wind forced waves are in good agreement with Peirson and Banner (2003), who examined random fields of wind-generated microscale waves.

- A mean surface convergence was measured on the leeward face and a mean surface divergence was measured on the windward face of waves. The measured mean surface convergence/divergence was consistent with 5th order Stokes wave theory, however, significantly larger instantaneous measurements of surface convergence/divergence were observed.

**Gas Flux**

- Gas flux estimates by the LIF method are within 30% of the bulk measurement method, with the exception of Experiments 2 and 3. For Experiments 2 and 3 the LIF method overestimates the flux by 65% and 41% respectively. The area represented by the LIF measurements is relatively small (3x10^-5 %) in comparison to the total surface area over which gas exchange occurs in the wind-wave tank. These results are a significant improvement on estimates by Woodrow and Duke...
(2001) who reported differences of up to 140% between LIF and bulk measurements.

- The first phase resolved gas flux measurements along wind forced waves have been achieved and indicate the highest mean gas fluxes are located in the wave troughs. This finding demonstrated the importance of wave orbital straining in gas flux enhancement; a wave coupled hydrodynamic process that has previously been considered negligible.

- The relative contributions to gas flux from wind shear, wave orbital straining, increased surface area of the waves, parasitic capillary ripples and microscale breaking were quantified with respect to friction velocity, wave steepness and the frequency of microscale wave breaking. The parasitic capillary ripples are shown to have a negligible role in gas enhancement. A hydrodynamically partitioned model is developed to estimate the gas flux based on both wind and wave characteristics.

- For microscale breaking waves the highly localised subduction at the toe of the spilling region on the leeward face of the wave crests was shown to substantially reduce the thickness of the diffusion sub-layer, resulting in a significant increase in gas flux when waves transitioned from the incipient breaking to the microscale breaking wave form.

- Detached surface layers of dissolved gas rich water observed by Woodrow and Duke (2001) and Takehara and Etoh (2002) were also evident during this study. Woodrow and Duke (2001) attribute the detached surface layers to measured increases in gas flux, however the relatively small increase in detached surface layer events between the flat water and microscale breaking experiments cannot account for the large increase in measured gas fluxes.
Future Work

Developments in the Laser Induced Fluorescent (LIF) system has led to the first reliable measurements of dissolved oxygen concentration profiles to within 28μm of the air-water interface. This will lead to exciting and challenging investigations such as, gas transfer across stratified water layers as well as benthic related studies.

Whilst standalone LIF studies may provide new insights into gas flux enhancement, this study has shown the benefit of incorporating investigations of the microphysical hydrodynamic behaviour to fully understand the mechanisms driving the enhancement process. This will usually require microphysical PIV type measurement applications.
7. REFERENCES


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APPENDIX A

Copies of previous publications based on measurements and material developed during the course of this investigation
Measurement of gas transfer across wind-forced wavy air–water interfaces using laser-induced fluorescence

James W. Walker · William L. Peirson

Abstract Optical distortions have previously prevented non-intrusive measurements of dissolved oxygen concentration profiles by Laser induced fluorescence (LIF) to within 200 μm of the air–water interface. It is shown that by careful experimental design, reliable measurements can be obtained within 28 μm of moving air–water interfaces. Consideration of previously unidentified optical distortions in LIF imagery due to non-linear effects is presented that is critical for robust LIF data processing and experimental design. Phase resolved gas flux measurements have now been accomplished along wind forced microscale waves and indicate that the highest mean gas fluxes are located in the wave troughs. The local mean oxygen fluxes as determined by LIF techniques can be reconciled to within 40% of those obtained by bulk measurement in the water. These data provide a new perspective on wind-wave enhancement of low solubility gas transfer across the air–water interface.

1 Introduction

Existing bulk parameterisations of air–water exchange of low solubility gases are based primarily on the intensity of wind forcing or changes in surface colour associated with bubble entrainment (Jähne and Haubecker 1998; Asher et al. 2002). The gases of primary environmental interest (notably oxygen and carbon dioxide) have low solubility. Present low solubility exchange relationships show only limited agreement with available field and laboratory data, with the scatter in gas exchange rate in field and laboratory data greater than one order of magnitude. A microphysical understanding of interfacial behaviour is required to resolve the source(s) of this observed scatter in exchange rate.

For low solubility gases, mass transport is controlled by a combination of molecular and turbulent processes across the diffusion sub-layer, which occupies the upper 200–300 μm of the water column. Enhanced gas exchange across the air–water interface may occur when the diffusion sub-layer is thinned (Lewis and Whitman 1924) or the diffusion sub-layer is disrupted or renewed by the bulk (Danckwerts 1951). To date, the precise mechanisms causing thinning or disruption of the diffusion sub-layer remain unclear.

Various hydrodynamic mechanisms for thinning or disruption of the diffusion sub-layer have been postulated:

- For low wind speed and flat water Deacon (1977) developed a boundary layer model to estimate the enhanced mass flux due to wind-induced turbulence within the viscous sub-layer. However, with the onset of waves, Deacon’s model substantially under predicts observed flux rates, which he attributed to the onset of microscale breaking (Deacon 1981; Banner and Phillips 1974).
- Komori et al. (1993) investigated a surface renewal parameterisation for strongly sheared wavy interfaces, which related the frequency of turbulent eddy structures to observed flux rates.
- MacIntyre (1971) and Szeri (1997) investigated the potential of capillary waves to reduce the thickness of the diffusion sub-layer.
• Jähne et al. (1987) and Csanady (1990) suggest that the effective thickness of the diffusion sub-layer is in part, controlled by zones of surface divergence and convergence. Csanady (1990) directly attributed the formation of convergent and divergent zones to microscale breaking. McKenna and McGillis (2004) show good collapse of flux data in relation to a characterisation of surface divergence when wave activity is small.

• Peirson and Banner (2003) predicted aqueous diffusion sub-layer destruction at the onset of microscale breaking based on their observations of near surface velocity structure. Their predictions are supported by recent bulk measurements of oxygen transfer rate (Peirson et al. 2007).

This contribution describes recent development of a technique capable of directly observing the aqueous diffusion sub-layer and obtaining point measurements of oxygen flux that can be directly related to positions along a wave.

2 Measurement of diffusion sub-layer behaviour

Under controlled experimental conditions, time based bulk measurements of the tracer concentration in the air and water may be used to determine the mean rate of gas exchange (Downing and Truesdale 1955; Liss 1973):

$$k_v = -\frac{F}{(C_I - C_B)}$$

(1)

where $k_v$ is the gas transfer velocity, $F$ is the mass flux of the gas, $C_I$ is the concentration of the dissolved gas at the water interface, and $C_B$ is the concentration of the dissolved gas in the bulk of the water. Bulk measurements characterise overall gas exchange and provide no insight into the primary forcing mechanisms responsible for the thinning or disruption of the aqueous diffusion sub-layer.

Immediately adjacent to the surface, molecular processes dominate and therefore the dissolved oxygen concentration gradient at the surface is proportional to the mass flux $F$ across the air–water interface at that location as described by Fick’s first law:

$$F = -D \frac{\partial C}{\partial z}$$

(2)

where $D$ is the molecular diffusion coefficient, $C$ is the concentration of the dissolved gas and $z$ is the depth below the air–water interface.

Relatively few researchers have obtained reliable dissolved oxygen concentration gradient profiles near the surface due to the small size of the diffusion sub-layer (200–300 μm). Chu and Jirka (1992) developed a polarographic oxygen microprobe to measure dissolved oxygen concentrations within the diffusion sub-layer. This technique allowed profiling at discrete depth intervals of approximately 100 μm adjacent to flatwater surfaces. However, its spatial resolution was still only suitable for identifying a diffusion sub-layer thickness rather than determining a dissolved oxygen concentration gradient.

The first non-intrusive experiments to measure dissolved oxygen concentration profiles in the diffusion sub-layer were undertaken by Wolff and Hanratty (1994) utilising collisional oxygen quenching of pyrenebutyric acid (PBA) illuminated by a laser light sheet. This Laser induced fluorescence (LIF) technique was subsequently developed by Woodrow and Duke (2001). PBA is dissolved in water at low molar concentrations, illuminated by pulsing a UV laser sheet through the water column to excite the PBA molecules, and recording the PBA fluorescence with a digital camera system. Fluorescence lifetime and intensity is reduced in the presence of oxygen and each image is an instantaneous measure of the dissolved oxygen concentration profile at a discrete location. The fluorescent lifetime can be related to the fluorescent intensity and the dissolved oxygen concentration by the Stern–Vollmer equation:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + \alpha C$$

(3)

where $I$ is the fluorescent intensity, $\tau$ is the fluorescent lifetime, $\alpha$ is the quenching rate constant and $C$ is the concentration of the quencher (oxygen). The subscript $0$ denotes values in the absence of a quencher.

Wolff and Hanratty (1994) recorded instantaneous profiles of fluorescent intensity between the surface and a depth of 3 mm. The fluorescent intensity profile was subsequently processed to determine a dissolved oxygen concentration profile over the same water depth for wind forced and flowing water in a tank 11 m long × 0.35 m wide. Woodrow and Duke (2001) investigated flat water and paddle generated wavy interfaces in a tank 1.2 m long × 0.3 m wide with an 11 mm water depth and recorded a reduction in the diffusion sub-layer thickness when small waves were present.

Wolff and Hanratty (1994) and Woodrow and Duke (2001) directed the laser sheet through the base of the tank to the water surface. Due to absorption of the laser light through the water column they were restricted to relatively shallow water depths (<11 mm). Herlina and Jirka (2004) undertook similar experiments in a water depth of 473 mm by directing the laser down through the water surface. However, such application is restricted to relatively weak sub-surface forcing due to refraction effects associated with curvatures arising from strong sub-surface turbulence or wave generation.
For the construction of a concentration profile from LIF imagery it is necessary to identify the spatial coordinates of the water surface. Woodrow and Duke (2001) and Herlina and Jirka (2004) used a symmetry algorithm to identify the location of the water surface. Whilst for their applications a symmetry algorithm was adequate, this method becomes less robust for steep waves or sloping surfaces. Both groups of researchers also observed a measured concentration distortion near the surface (optical blurring) resulting from their experimental set-up. The optical blurring limited the proximity of valid concentration measurements close to the air–water interface.

A relevant parallel study of the transfer of a reactive gas (HCl) across a wind sheared air–water interface was undertaken by Münsterer and Jähne (1998) using fluorescein as the fluorescence indicator. The fluorescent intensity is determined by the pH of the water arising from absorption of the HCl gas. Fluorescein illumination was provided by a 1 W argon ion laser directed from above the water surface. They found that the thickness of the HCl diffusion sub-layer changed rapidly with time and that the fluctuations in the sub-layer thickness were of the same order of magnitude as the mean thickness of the sub-layer. Woodrow and Duke (2001) also observed significant fluctuations in their measurements of the thickness of the diffusion sub-layer.

Takehara and Etoh (2002) used a similar method to Münsterer and Jähne (1998) by substitution of CO₂ for HCl to visualise CO₂ gas transfer at the air–water interface under wind wave conditions in the laboratory. Whilst detached surface layers of CO₂ rich water were observed, measurements were not of sufficient detail to measure the concentration gradient within the diffusion sub-layer.

### 3 Experiment facilities

We have completed detailed investigations of the PBA technique and developed it for practical application to strongly forced laboratory conditions. In this contribution we describe the key apparatus assembled to undertake precise LIF measurements. The present study was conducted in a wind wave tank with an effective length of 4.550 m, width of 0.245 m and total height of 0.610 m and a water depth of 250 mm (Fig. 1). An electro-mechanical flap type paddle was used to produce monochromatic waves. Wind was generated by a fan fitted to the end of the tank. Guide vanes ensured a relatively uniform air flow across the width of the tank and provided a smooth transition from the fan to the water surface. A dissipative beach was installed at the downwind end of the tank to minimise wave reflections. An objective of the study was to reconcile observed gas flux obtained from bulk measurements against localised measurements using LIF.

Air velocity profiles above the water surface were measured using a pitot tube arrangement. The pitot tube was connected to an MKS Baratron pressure transducer (model 223BD) with a range of 0.2 Torr and recorded to a data acquisition computer. Air velocity measurements commenced as close as practical to the water surface (immediately above the crest of the waves) and extended to near the roof of the wind wave tank. The wind friction velocity \( u^* \) was derived from the measured logarithmic portions of the air velocity profiles immediately above the wave crests.

To minimise biological growth and eliminate surface contaminants a recirculating pump with a diatomaceous earth filter and a UV steriliser was fitted to the tank. Water

![Fig. 1](image_url)  
**Fig. 1** The general arrangement of the wind-wave tank. The surface skimming weir ensured a slick free, clean water surface for all experiments. Fetch dependence of waves was minimised by using mechanically generated waves forced by wind.
surface skimming was accomplished by recirculating water from the test chamber across an overflow weir fitted to the outlet chamber. A light wind was applied to ensure that surface material was driven over the overflow weir. Skimming was undertaken over a period of at least 1 h prior to all experiments. Our microscopic observations of the free surface clearly showed any surface contamination present and none was observed during these experiments.

Profile measurements of dissolved oxygen concentration were recorded in the upper 2–3 mm of the water column using an LIF system with the objective of capturing the dissolved oxygen concentration profile in the diffusion sub-layer along the surfaces of wind-forced surfaces.

LIF illumination was provided by a PTI model GL3300 nitrogen laser. The nitrogen laser emits light in the UV spectrum at a wavelength of 337.1 nm and has a pulse width of 600ps. At the point of exiting the laser, the beam has dimensions of 6 mm wide × 3 mm thick. A series of UV fused silica lenses were used to contract and focus the light sheet to approximately 6 mm wide × 0.4 mm thick at a distance of 985 mm from the laser. The lenses consist of a 600 mm focal length plano-convex spherical lens to minimise expansion of the beam exiting the laser followed by a 300 mm focal length plano-convex cylindrical lens to produce the 6 mm wide sheet at the water surface. A second 300 mm focal length plano-convex cylindrical lens was used to form a light sheet of 0.4 mm thickness in the vicinity of the water surface. A 45° incidence angle 337 nm nitrogen gas unpolarised flat mirror was used to reflect the laser sheet up through the base of the wind-wave tank and into the water column.

All experiments were conducted in a total water depth of 250 mm. To minimise absorbance of the UV laser sheet, it was directed through a hollowed cylindrical section (capped with a UV silica lens, 50 mmØ) extending 170 mm into the water column from the base of the tank. The optimum concentration of PBA is a compromise between absorbance and fluorescence and was found to be 7 × 10⁻⁶ M for our configuration. This value is considerably lower than that used by other researchers but permitted use of greater water depths during these experiments.

A Santa Barbara Instrument Group (SBIG) ST-10XME Charged Couple Device (CCD) camera was selected for the LIF visualisation. The CCD detector is a KAF3200ME with relatively high sensitivity in the UV spectrum. PBA fluorescence occurs at wavelengths between 375 and 425 nm. The quantum efficiency of the CCD for these wavelengths varies between 50 and 60%. The camera has a minimum frame capture cycle time of 15 s that is limited by the data transfer from the camera to computer storage.

Random readout noise and dark current are sources of error in the captured images. Dark current is thermally generated in the CCD and can be reduced by cooling. The camera has an internal solid-state thermoelectric cooler for temperature control. For all LIF experimental imagery the camera was cooled to –10°C. Residual charge is another noise source associated with the CCD readout electronics. Double correlated sampling was undertaken during image generation to minimise the residual noise.

A Nikon ED 80–200 mm focal length lens with an extension bellows was used to magnify the image to provide an effective in situ pixel dimension of 4.15 μm high × 4.15 μm wide within the light sheet. Between the Nikon lens and the CCD camera a long pass edge filter was inserted to remove scattered incident laser light. The edge filter provided greater than 99% transmission for light with wavelengths longer than 370 nm and provided greater than 99% blockage of light with wavelengths shorter than 340 nm (nitrogen laser 337.1 nm).

The image capture sequence was: (1) the electro-mechanical camera shutter opened; (2) a trigger signal sent to the UV laser to fire a single pulse; (3) the camera shutter closed, and; (4) the image downloaded to the host computer. The total duration from opening of the camera electro-mechanical shutter, firing of the laser pulse to closing of the camera shutter was 0.12 s. For surface waves, it was important to determine the position along the wave at which LIF images were taken. Consequently a wave probe was mounted in the wind-wave tank adjacent to the UV laser sheet. A second computer recorded the wave data at 150 Hz together with the instant of illumination. So that images could be captured at specified locations along the length of the wave, the wave data was processed in real-time based on determining a height threshold trigger value on either the rising or falling surface water levels.

Images were captured at the crest, trough and mid height of both the rising and falling limbs of the wave. The camera height was adjusted based on the location of the images (e.g. troughs or crest). Thus, the same experiment was conducted at least four times in order to capture images along the four segments of the wave. Images were captured at intervals between 15 and 120 s depending on the experiment duration.

Bulk dissolved oxygen levels in the wind-wave tank were monitored using an Orion model 835A dissolved oxygen meter and flow cell arrangement with data logged to a computer at 5 s intervals. Each experiment commenced following the stripping of dissolved oxygen from the water column using nitrogen sparging.

4 Optical distortions

To measure dissolved oxygen concentration profiles within the diffusion sub-layer of wind-forced waves requires the
camera to be mounted at an oblique angle to the water surface (Fig. 2). This enables the concentration boundary layer immediately adjacent to the water surface to be observed in spite of cross-tank surface slope or the side wall meniscus. However, an oblique camera angle also induces optical distortions. There are two key forms of optical distortion that influence the capture and processing of LIF images.

4.1 Surface optical blurring

Optical distortion occurs immediately adjacent to the surface and is induced by surface reflection (Fig. 2). For example, along ray 2 the observed intensity is obtained from the light path CDF which includes reflections in the water surface. This surface induced optical distortion (surface optical blurring) limits the proximity of valid concentration measurements close to the surface and has been observed by Woodrow and Duke (2001) and Herlina and Jirka (2004).

The depth below the surface over which surface optical blurring occurs can be minimised by careful experimental design. This can be achieved by reducing the thickness of the UV laser sheet and/or reducing the camera angle. The depth below the surface over which surface optical blurring is present ($z_{sob}$) is given by:

$$z_{sob} = \frac{T}{2} \tan \theta$$

where $T$ is the laser waist beam or thickness of the UV laser sheet in the vicinity of the water surface and $\theta$ is the camera angle. For observations adjacent to strongly forced air–water interfaces, Peirson (1997) found an optimal camera angle ($\theta$) of about $8^\circ$. Many real laser illuminations are non-gaussian in intensity distribution, consequently, extensive trial and error optimisation was required to obtain a UV laser sheet with a waist beam of 0.4 mm in the vicinity of the water surface. This enabled surface optical blurring effects to be restricted to the upper 28 $\mu$m ($\approx 7$ pixels) of the water column (Fig. 3a).

4.2 Optical distortion of non-linear intensity/concentration profiles

The second form of optical distortion occurs in the presence of a non-linear concentration and/or fluorescent intensity profile. As shown in Fig. 2, at depth, the recorded intensity is an average of the varying intensities along the line of observation. For example along ray 1 the observed intensity arises from fluorescence along path AB, which is not normal to the fluorescent light sheet. The recorded intensity may be expressed as:

$$I = \frac{I_0}{B - A} \int_A^B I(z)dz$$

where $I$ is the recorded intensity and A and B are depths at the finite bounds of the light sheet as depicted in Fig. 2.

A fundamental assumption in the development of the two film theory (Lewis and Whitman 1924) and the consequent relationship between the transfer velocity $k_v$ and the thickness of the diffusion sub-layer $\delta_d$ (Eq. 6) is that the
concentration profile within the diffusion sub-layer is linear. Two-film theory assumes a quasi steady-state system in which the concentration of the bulk liquid changes over a relatively long period of time and the thickness of the diffusion sub-layer is relatively stable.

\[ k_v = \frac{D}{\delta_d} \]  

Studies by Woodrow and Duke (2001) and Herlina and Jirka (2004) assumed a linear concentration profile near the surface and adopted a linear extrapolation from a location of identified surface optical blurring (point of maximum intensity gradient) to the surface to determine diffusion sub-layer thickness and transfer velocity. However, extrapolated dissolved oxygen concentrations should achieve saturation values at the water surface by Henry’s Law.

Münsterer and Jähne (1998) have shown for wind-forced surfaces that the thickness of the diffusion sub-layer changes rapidly with time. Our LIF data also showed significant fluctuations in the thickness of the diffusion sub-layer. Therefore, in the presence of rapid changes in the concentration profile near the air–water interface, the concentration profile in the diffusion sub-layer cannot be assumed to be linear.

Beyond the depth of surface optical blurring, the oblique viewing of the intensity profile generated by a finite width...
laser sheet illuminating a concentration gradient can potentially compromise the measurement technique. This arises from two processes: the relationship between intensity and concentration is non-linear (Eq. 3); and, the impact of non-linearity in the concentration gradient itself. We consider a local concentration profile which varies as a polynomial of order \( n \) in the vicinity of a reference depth \( h \) and we use superscripts in brackets to denote differentiation with respect to depth \( z \):

\[
C(z) = C_h + C_h^{(1)}(z-h) + C_h^{(2)} \frac{(z-h)^2}{2!} + \cdots + C_h^{(n)} \frac{(z-h)^n}{n!}
\]  

(7)

where:

\[
C_h^{(n)} = \frac{\partial^n C}{\partial z^n}
\]  

(8)

evaluated at depth \( z = h \).

Approximating the Stern–Vollmer equation (Eq. 3) as a Taylor series yields:

\[
I(C(z)) = \frac{I_0}{1 + zC_h} \left( 1 - \frac{z(C(z) - C_h)}{1 + zC_h} + \frac{z^2(C(z) - C_h)^2}{(1 + zC_h)^2} + \text{HOT} \right)
\]  

(9)

Neglecting higher order terms and substitution of Eqs. 7 and 9 into Eq. 5 yields a difference between the mean intensity observed at an angle \( \theta \) for a sheet thickness \( T \) and the intensity at the centerline of the light sheet at depth \( h \) as:

\[
I_{z=h} - I = \frac{I_0 \sqrt{T \tan \theta}}{(1 + zC_h)^2} \sum_{n=1}^{\infty} \frac{(T \tan \theta)^{2n} C_h^{(2n)}}{(2n)! (2n + 1) 2^{2n}}
\]  

\[
+ \frac{I_0 \sqrt{T \tan \theta}}{(1 + zC_h)^2} \sum_{n=1}^{\infty} \sum_{i=1}^{n} \frac{(T \tan \theta)^{2n} C_h^{(n+2i)}}{(n!)^2 (2n+1) 2^{2n+i+1}}
\]  

(10)

The first term on the RHS of Eq. 10 represents the error contribution by the first order term in Eq. 9. If the concentration profile is linear then this term is zero and the errors in the measured intensity are relatively small (second order intensity term only). However, as the concentration profile becomes progressively more non-linear, higher order variations in \( C_h \) make significant contributions to both first and second order intensity terms. For a uniform concentration with depth all terms on the RHS of Eq. 10 equal zero and no optical distortions are induced.

Adopting a one-dimensional error function concentration profile (representative of unsteady aeration) such that:

\[
C(z) = C_1 - (C_1 - C_h) \text{erf} \left( \frac{z}{2\sqrt{Dt}} \right)
\]  

(11)

where \( t \) is the time from commencement of aeration, the sensitivity of valid LIF measurements with respect to camera angle, laser waist beam and transfer velocity as derived from Eq. 10 are plotted in Figs. 3a–f. For smooth water surfaces (low transfer velocity), image distortion is relatively small and a linear extrapolation between the commencement of surface optical blurring to the air–water interface may under some circumstances be a valid approximation. However, for strongly wind forced surfaces a more oblique camera angle (\( \theta = 12^\circ \)) or wider laser beam waist (\( T = 0.8 \) mm) is clearly unsuitable and a linear extrapolation to the surface will systematically predict a surface oxygen concentration well below saturation.

It was not practically feasible to reduce our beam waist below 0.4 mm. Non-linearity in concentration within the diffusion sub-layer increases with increasing gas flux. Therefore to minimise optical distortion effects during data processing, a first order error function solution is fitted to the data from the location of surface optical blurring to the air–water interface. For our experimental arrangement (based on a theoretical sensitivity analysis) this reduces errors in the measured surface flux due to optical distortions to less than 10%.

Note that in Fig. 3, increasing beam waist also increases the apparent thickness of the diffusion sub-layer. Consequently the optical distortion has two critical effects: the measured gradients of the concentration profile are reduced; and the depth of the diffusion sub-layer is artificially extended.

During this study, a very small angle of view has been used (1.7°). Therefore, variation in ray angle across our images is small. Measurements incorporating a horizontal lens axis but much wider angles of view will be subject to increased optical distortions away from the lens axis.

5 Data processing

During each LIF experiment at least 400 images required processing to determine wave phase resolved gas fluxes. Each LIF image consists of 2,184 columns and 1,472 rows (Fig. 4). Image processing was semi-automated by developing a number of user defined Fortran subroutines. Key steps in the data processing are: (1) identification of the air–water interface; (2) illumination compensation using Lambert–Beers decay relationship and conversion of the fluorescent signal to dissolved oxygen concentration using the Stern–Vollmer equation; (3) removal of surface optically blurred data; and (4) determination of near surface dissolved oxygen concentration gradient and gas flux.
5.1 Location of the air–water interface

Each image was stripped to a width of 202 adjacent columns consisting of the region of uniform illumination with the highest fluorescent signal to noise ratio (Fig. 4). A $3 \times 3$ box car smoothing filter was then applied to the data to further improve the signal to noise ratio, reducing the data file width to 200 columns.

The interface in each image was determined by finding the minimum intensity in each of the columns of data. A linear equation was fitted to the row number corresponding to the minimum fluorescent intensity. Given that the width of the fluorescent component of the image being processed was only 0.83 mm (i.e. 200 columns) a linear fit to the surface is more than adequate in most cases.

5.2 Conversion of fluorescent image to concentration profile

Absorption of the laser light through the water column is only a function of the PBA concentration. Prior to each experiment at least ten LIF images were captured for fully saturated, well mixed conditions (to avoid concentration gradients). These images were then processed and the mean Lambert–Beers decay of these images was adopted for laser decay corrections. Each column within the vertical image strip was corrected for Lambert–Beers decay and converted to a dissolved oxygen concentration. The 200 columns of data were averaged into a single column using the surface position in each column as the air–water interface reference depth. A typical measured concentration profile is shown in Fig. 5 and the uniform concentration below a depth of 2 mm verifies the adopted Lambert–Beers decay corrections.

5.3 Removal of surface optical blurred data

The depth below the surface at which the dissolved oxygen concentration gradient is largest is then located. Data above this location is influenced/contaminated by surface optical blurring and is not included in subsequent analysis.

5.4 Local flux

The dissolved oxygen concentration on the aqueous side of the air–water interface is assumed to be at saturation (Lewis and Whitman 1924; Bolin 1960; Deacon 1977). An error function curve is then fitted to the data and the saturated surface and $dC/dz$ determined (Fig. 5).

The transfer velocity was then determined from Eqs. 1 and 2 such that:

$$k_v = \frac{D}{(C_1 - C_B)} \frac{dC}{dz}$$  \hspace{1cm} (12)

$C_B$ was obtained from an average of the lowest 200 rows of concentration data in each image strip. For each data set a number of images were rejected during processing based on conditional criteria. Images were rejected if: (1) the air–water interface could not be clearly identified; (2) the depth below the surface at which optically blurring occurred could not be defined, or; (3) a concentration gradient (diffusion sub-layer) could not be identified. Extreme flux rate values (both high and low) that passed the conditional criteria were also manually checked for acceptance/rejection.
6 Results

The results of three experiments have been analysed in detail to date:

1. A flatwater condition which remains free of any wave motion but with evidence of high frequency motion due to pressure fluctuations in the wind \((U = 2.1 \, \text{m/s})\).

2. An incipient breaking mode in which the waves are as steep as possible without lapsing into a microscale breaking state. These waves are characterised by well-developed parasitic capillaries leeward of the wave crests \((U = 2.1 \, \text{m/s} \text{ and paddle forced waves with a frequency of 3.4 Hz})\).

3. A microscale breaking case in which a confined spilling region is evident immediately leeward of the wave crest \((U = 5.7 \, \text{m/s} \text{ and paddle forced waves with a frequency of 3.4 Hz})\).

Data for each of the three cases is presented in Table 1. An increase in the average transfer velocity \(k_v\) measured in the bulk by the Orion dissolved oxygen probe is evident between the flatwater and incipient breaking experiments (3.2-fold). Given that the same wind speed was applied to both cases, the increases observed in the transfer velocity can be attributed to the presence of the 0.29 s period paddle generated waves. A higher wind speed \((5.7 \, \text{m/s})\) was required to maintain the surface in a microscale breaking regime and corresponded to an average transfer velocity 11.7 times higher than that for the flatwater case.

Flux rates estimated by the LIF method are within 7% of the bulk measurement method for the flatwater and microscale breaking experiments. For the incipient breaking case the LIF method over-estimates flux rates by 41%. However, note that these LIF estimates are based on the arithmetic mean of the flux rates measured at four discrete wave phase locations exhibiting substantial variation about the mean value. The magnitude of the errors is a significant improvement on estimates by Woodrow and Duke (2001) who reported differences of up to 140% between LIF and bulk measurements.

<table>
<thead>
<tr>
<th>Surface state</th>
<th>(U_{10 , \text{cm}}) (m/s)</th>
<th>(F) (Hz)</th>
<th>(u^*) (m/s)</th>
<th>Bulk (k_v \times 10^6) (m/s)</th>
<th>Accepted LIF images</th>
<th>LIF (k_v \times 10^6) (m/s)</th>
<th>(k_v) SD (\times 10^6)</th>
<th>(k_v) difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flatwater</td>
<td>2.1</td>
<td>–</td>
<td>0.12</td>
<td>7.57 ± 0.33</td>
<td>71</td>
<td>7.94 ± 0.61</td>
<td>5.13</td>
<td>5</td>
</tr>
<tr>
<td>Incipient Breaking</td>
<td>2.1</td>
<td>3.4</td>
<td>0.218</td>
<td>24.0 ± 0.9</td>
<td>78</td>
<td>21.2 ± 1.6</td>
<td>14.5</td>
<td>–20</td>
</tr>
<tr>
<td>Crest</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>34.7 ± 1.8 mean</td>
<td>159</td>
<td>34.9 ± 1.7</td>
<td>21.0</td>
<td>56</td>
</tr>
<tr>
<td>Trough</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>58.0 ± 3.0</td>
<td>105</td>
<td>58.0 ± 3.0</td>
<td>30.6</td>
<td>144</td>
</tr>
<tr>
<td>Windward</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>88.6 ± 3.6</td>
<td>129</td>
<td>82.5 ± 11.0 mean</td>
<td>11.8</td>
<td>–10</td>
</tr>
<tr>
<td>Microscale breaking</td>
<td>5.7</td>
<td>3.4</td>
<td>0.418</td>
<td>88.6 ± 3.6</td>
<td>7</td>
<td>45.6 ± 10.4</td>
<td>27.5</td>
<td>–50</td>
</tr>
<tr>
<td>Crest</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>45.6 ± 10.4</td>
<td>22</td>
<td>84.7 ± 12.8</td>
<td>60.2</td>
<td>2</td>
</tr>
<tr>
<td>Trough</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>138 ± 15.1</td>
<td>27</td>
<td>138 ± 15.1</td>
<td>78.5</td>
<td>52</td>
</tr>
<tr>
<td>Windward</td>
<td>2.1</td>
<td>3.4</td>
<td>0.27</td>
<td>61.5 ± 5.6</td>
<td>27</td>
<td>61.5 ± 5.6</td>
<td>29</td>
<td>–31</td>
</tr>
</tbody>
</table>

“±” Are standard errors of the mean
Etoh (2002) were also evident in our experiments. Detached surface layers of oxygen rich water were observed in all experiments, from the flatwater case (24% of images) to the microscale breaking case (30% of images). Woodrow and Duke (2001) attribute the detached surface layer to measured increases in gas flux, however the relatively small increase in detached surface layer events between the flatwater and microscale breaking experiments cannot account for the 11.3-fold increase in gas fluxes.

The gas flux model presented by Peirson and Banner (2003) based on surface flow kinematics beneath microscale breaking waves suggests thinning of the diffusion sub-layer at the wave crests due to subduction at the spilling region. Thereafter the diffusion sub-layer thickens with the passing of the wave crest and increasing residence time at the surface. The LIF data indicates that the diffusion sub-layer thins following the passing of the wave crest and it is postulated that this thinning is due to wave orbital straining. Further experiments are currently being conducted to investigate this mechanism further.

7 Conclusions

A number of notable developments in the LIF technique have been achieved during the course of this investigation. These include:

- By careful selection of the fluorescent tracer concentration, the illuminating optical path length has been sufficiently extended to enable experiments to be conducted for deep water wave conditions for wind sheared wave interfaces.
- A formal mathematical description of optical distortions has been developed and presented.
- Analysis of optical distortions identified that transfer velocities will be under predicted by assuming a linear concentration gradient.
- Analysis has shown that the diffusion sub-layer thickness adjacent to the surface can be over predicted due to optical distortions.

Previous LIF investigations have been limited to reporting dissolved oxygen concentration profiles to within 200 μm of the air–water interface, restricting reliable results to relatively low gas flux experiments. By careful consideration of optical distortions and the design of the UV laser sheet, reliable measurements of the dissolved oxygen profile to within 28 μm of the surface can now be achieved.

Measurements of transfer velocity using LIF and bulk techniques have now been reconciled to within 41%, which is a substantial improvement on previously reported findings. Phase resolved gas flux measurements have been accomplished for high gas flux wind forced microscale waves. Results using the improved experimental technique reveal that the dissolved oxygen concentration gradient is non-linear within the diffusion sub-layer, which has implications on the data processing of LIF images that have not previously been considered.
For the incipient and microscale breaking wave cases, the detached surface layer features do not appear to be a major contributor to the observed increases in gas transfer. The highest gas fluxes were measured in the wave troughs. Wind shear and wave turbulence models suggest that maximum gas fluxes are found in the proximity of the wave crests, however, our data suggests that wave orbital straining also plays a significant role. Appropriate application of LIF techniques now has the potential to determine the fundamental mechanisms causing enhanced gas transfer across air–water interfaces.

References


Defining the Enhancement of Air-Water Interfacial Oxygen Exchange Rate due to Wind-Forced Microscale Waves

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Abstract Over the last few years, compelling evidence has emerged that the exchange of low-solubility gases across air-water interfaces is strongly enhanced by microscale breaking (e.g. Jähne and Haußecker [12], Zappa et al. [28]). Jähne and Haußecker [12] observe that low-solubility gas flux rates are enhanced by up to a factor of 5 in the presence of small scale waves. Investigations using surface infrared imagery [10, 22, 27, 28] have demonstrated a strong correlation between total flux and a proportional area of surface with a high infra-red radiation emission associated with the passage of microscale breaking waves. The mechanisms causing this significant enhancement in exchange rate remain unclear. Zappa et al. [28] proposed that thinning of the aqueous diffusion sublayer by subsurface turbulence in the vicinity of the high infra-red emission region was primarily responsible for this enhancement. Alternate to this is a relationship between the air-water surface exchange rate and the passage rate of wind-forced microscale breaking waves proposed by Peirson and Banner [21]. They have suggested that subduction of the aqueous diffusion sublayer by the microscale wave spilling regions coupled with a weak surface divergence on the upwind faces of the waves primarily determines the microscale-breaking associated flux rate. We have completed a sequence of precise oxygen re-aeration measurements with the specific objective of testing the findings of Peirson and Banner [21]. Specifically, we have compared the flux rates of wind-forced, flat water surfaces in the absence of waves with those in the presence of wind-forced, steep, unbroken waves and wind-forced, microscale breaking waves. With the introduction of steep, unbroken micro-scale waves the surface exchange rate is enhanced by a factor of approximately 2.5. The transition from incipient breaking of the waves to the microscale breaking state induces a significant increase in the associated wind stress [1]. The observed rapid increase in flux rate is approximately proportional to the increase in the wind stress. For the microscale-breaking state, the observed flux rates show good agreement with the predictions of Peirson and Banner [21].

8.1 Introduction

Existing parameterizations of air-sea exchange of low solubility gases, including major greenhouse gases such as carbon dioxide and oxygen, are based primarily on the intensity of wind forcing or changes in surface colour associated with bubble entrainment (so-called whitecap area) (e.g. Monahan [19]). These proposed relationships show only limited agreement with available field and laboratory data, with the scatter in gas exchange rate in laboratory data greater than one order of magnitude. There is now very strong evidence that the microscale breaking wave field is the primary determining factor in gas exchange once wind speeds exceed 4 ms$^{-1}$ and remains the dominant factor at high wind speeds where bubble entrainment becomes widespread (e.g. Zappa et al. [28]).

There have been two broad approaches to developing parameterizations of air-water exchange of low-solubility gases. The first approach has been to characterise transfer velocity in terms of a surface renewal process whereby turbulence adjacent to the interface forces exchange between the aqueous diffusion layer and the bulk. For example, Komori et al. [15] carefully monitored turbulent activity adjacent to a wind-forced air-water interface and related an observed characteristic turbulent time scale to the observed gas flux.

The attractiveness of this approach is that it has the potential to produce a unified parameterization of low-solubility gas flux for open waters independent of whether the surface disturbances enhancing exchange arise from sub-surface generated turbulence or wind-generated waves. The recent study by Brocchini and Peregrine [5] has shown possibility for the development of more generalised descriptions of the relationship between turbulence and surface waves. However, we note that present evidence is that the dominant contribution to wind-forced wave development is pressure asymmetry on the waves themselves (e.g. Banner [1]).

An alternative approach to quantify surface renewal has recently been examined by McKenna and McGillis [18]. They examined oxygen flux in the presence of clean and contaminated surfaces exposed to standing waves and subsurface grid-generated turbulence. Using particle image velocimetry, they measured the root mean square of the surface divergence magnitude and found that it provided good collapse for their measured surface flux rates.

The second approach to developing parameterizations of low-solubility gas flux has been process-based. Deacon [8] developed a boundary layer turbulence model to quantify the increase in gas flux across the interface due to turbulence generated immediately adjacent to the interface. However, Deacon [9] subsequently found that this characterisation significantly underestimated the observed gas flux levels. He anticipated that this observed disparity as due to microscale breaking at the air-sea interface [3].
A sequence of theoretical investigations by Longuet-Higgins and his co-workers (see especially, Longuet-Higgins [16] and Longuet-Higgins [17]) have been directed at understanding the inception of small-scale wave breaking and its potential links with the formation of parasitic capillary waves on the lee-ward faces of the small gravity waves. In particular, he noted the possibility of the formation of surface stagnation at the troughs of the parasitic capillaries with the consequent inception of flow separation. Ostensibly ignoring Longuet-Higgins’s work, Szeri [23] completed a theoretical study of the enhancement of gas flux due to parasitic capillary waves and found that substantial enhancement could be anticipated due thinning of the aqueous diffusion sublayer at the parasitic capillary wave troughs. To formally link Szeri’s findings to wind-forced wave surfaces, the dynamical linkages between parasitic capillaries and the underlying gravity wave will be necessary (e.g. Longuet-Higgins [17]).

Other investigators have followed Deacon’s idea and draw direct linkages between microscale breaking and gas flux. Csanady [7] constructed a surface vortex model to simulate the effects of microscale breaking on surface exchange. He found that strong, localised surface divergence on the upwind face of the waves significantly reduced the thickness of the aqueous diffusion sublayer locally thereby enhancing the transfer rate. The development and application of infrared imagery to the ocean surface has shown that the upwind faces and crest are regions of significant heat flux [10] in general agreement with Csanady’s findings. In spite of the significance differences in Schmidt number between heat and low solubility gases, strong correlations have been found between a surface heat signature and gas transfer velocity [27].

Based on observations of the aqueous flows immediately adjacent to the interface, Peirson and Banner [21] proposed a simple model description of the impact of microscale breaking on gas transfer. Their observations showed relatively weak divergence (\(<10\text{s}^{-1}\)) on the upwind faces of micro-scale breaking wind waves but intense convergence at the toe of the spilling regions of these waves. Assuming complete subduction at the toe of the spilling region, Peirson and Banner produced a simple model of exchange that incorporated their observations of the surface drift current and the probability of microscale breaking.

In this contribution, we describe a process-based investigation of the air-water gas transfer of a low solubility gas for water surfaces exposed to wind. By carefully controlling the wave properties, we have investigated the rates of gas flux that occur in the presence of different characteristic microscale wave states.
8.2 Methodology

A significant difficulty facing air-water flux experimentalists is the fetch dependence of the surface wave state of wind-forced water surfaces and the associated transfer velocities (e.g. Wanninkhof and Bliven [24]). Provided the wind-forcing is sufficient (>4 m/s), microscale breaking waves form at a fetch of approximately 2 m whose frequency and breaking probability decrease with increasing fetch [2].

Fetch-dependency can be alleviated using a circular wind tank (e.g. Jähne et al. [14]). However, the geometry of such facilities generates lateral overturning of both the air and water cavities that is not representative of mean wind-wave interaction on open waters. Wave interaction at the outer tank wall also promotes stem wave formation that is not common on open air-water interfaces.

During this investigation, we have adopted an alternative approach. By carefully triggering of high frequency waves using a paddle at the windward end of a linear tank (see Figure 8.1) and coupling these monochromatic wave fields with appropriate levels of wind forcing, we have been able to create wind wave fields with minimal variation in surface wave state with fetch. By varying the degree of wind forcing and surface wave state, we have been able to investigate changes in flux rate due to changes in characteristic surface condition.

The primary difficulty associated with undertaking these experiments is maintaining an approximately consistent set of wave conditions along a fetch of several metres. This is for two reasons: first, monochromatic waves are inherently unstable [4] and form groups as the sidebands develop; secondly, viscosity and breaking dissipate short water waves and consequently the wind energy density input to the waves must match the dissipation rate. Our investigations were undertaken in a small glass-walled tank (0.2 m wide, 0.5 m deep by 9 m length) installed in a purpose-built, temperature-regulated room at the Water Research Laboratory. The water depth in the tank remained approximately 250 mm and the air temperature remained $21 \pm 1$ °C throughout testing. Appropriate flow straightening was installed at the upwind end of the tank to ensure a uniform and symmetric distribution of air flow entering the tank. A small cantilever paddle was installed at the upwind end of the tank of minimal height to avoid disruption to the air flow but avoiding the splashing of generated wave crests over the top of the paddle. The side walls of the tank were insulated with 50 mm polystyrene blocks.

To ensure that the tank water remained clean and free from biological or surface active contaminants, the tank was subdivided into two compartments. The upwind compartment was used for the experiments and carefully separated from the downwind chamber by a sealed dividing wall. When not in active use, a pump system gently circulates flow from a depth of 1 m in the downwind chamber to a depth of 250 mm in the upwind
Figure 8.1. Schematic of wind-wave flume. The surface skimming weir ensured a slick free clean water surface for all experiments. Waves were generated using a combination of the mechanical paddle and wind forcing.

with assistance from a light wind, any surface active material residing on the surface of the upwind chamber is driven over the dividing wall to reside on the surface of the downwind chamber. A high-resolution imaging system similar to that developed by Peirson [20] has shown that the surface remains free of surface contamination. The pump system also incorporates a 5\(\mu\)m particulate filter and an ultraviolet source to inhibit slime growth. Periodically, the entire system is flushed.

Two series of experiments have been completed so far. The first series were undertaken with a total fetch of 4m. We selected identical wave conditions to those examined by Banner [1] and found that we were able to maintain waves in an approximately consistent microscale breaking state along our entire fetch. However, when we reduced the paddle amplitude, lower steepness waves proceeded to grow to a microscale breaking state with fetch. To maintain consistent wave conditions with fetch, we had to decrease the wind speed. To examine the impact of low steepness waves on the oxygen flux rate, we undertook a reference test in the absence of waves.

Capacitance wave probes were positioned in the wind-wave flume at locations: near the wave paddle, in the vicinity of the measurement section and near the dissipative beach. Wave data was logged to a computer and wave energies at each of the three locations calculated. This data was used to verify that mean wave energy did not vary by more than \(\pm 10\%\) about the mean along the fetch.

Unsatisfied with undertaking testing with a varying wind speed, we found that by reducing the fetch slightly (to 3m) we were able to undertake a series of tests with a fixed reference wind speed and paddle frequency with consistent wave conditions along the fetch varying from low steepness to a continuous microscale breaking condition. However, with
the paddle switched off, the fetch became covered with capillary ripples of approximately 30mm wavelength. A summary of the conditions investigated during this study is presented in Table 8.1. In this table, we have characterised the surface into five states:

1. The flat water surface which remains free of any wave formation but with slightly perceptible high-frequency motion due to the pressure fluctuations in the wind.
2. Capillary rippled surface with 30mm waves of length which propagate in the downwind direction.
3. Small-amplitude gravity waves with a slightly rippled surface.
4. An incipient breaking condition in which the waves are as steep as possible without lapsing into a microscale breaking state. Such waves have a smooth steady crest accompanied by well-developed parasitic capillaries leeward of the wave crests.
5. The microscale breaking condition characterised by parasitic capillary waves visible ahead of a distinct jump in the water surface slope and pulsations in the crest due to the unsteady motions associate with breaking.

For our investigations, we selected oxygen as our tracer gas. Bulk dissolved oxygen levels in the wind-wave flume were measured using an Orion model 835A dissolved oxygen meter and flow cell arrangement with data logged to a computer at 5s intervals. Calibration of the dissolved oxygen meter was undertaken using the standard 2 point method. Measurement of the overall transfer rate of oxygen from the air to the water was undertaken by monitoring oxygen levels after initial de-aeration and use of the conventional expression (e.g. Woodrow and Duke [26]):

\[ \ln \frac{C_I - C(t)}{C_I - C(0)} = -\frac{k_v}{h} t \]  

(8.1)

where \( C_I \) is the interfacial concentration derived from Henry’s Law, \( C(t) \) is the bulk concentration at time \( t \), \( C(0) \) is the initial bulk concentration, \( k_v \) is the gas transfer rate (ms\(^{-1}\)), and, \( h \) is the depth. The intakes of pump-through dissolved oxygen probes were at mid-depth within the tank to monitor changes in bulk oxygen concentration with time and thereby derive the transfer rate. The results of our measurements are summarised in Table 8.1.

8.3 Results and Discussion

In the absence of waves, flux rates should be well represented by the Deacon [8] expression. However, repeat measurements for this case showed a systematically higher (\( \sim +35\% \)) transfer rate than predicted. An ancillary
Table 8.1. Summary of measurements obtained during this investigation.

<table>
<thead>
<tr>
<th>Designation</th>
<th>$U$ (m/s)</th>
<th>fp (Hz)</th>
<th>Surface characteristic state</th>
<th>$u_*$ (m/s)</th>
<th>$T_{water}$ (°C)</th>
<th>$k_{v,O_2}$ (m/hr)</th>
<th>Prediction Method</th>
<th>Predicted $k_v$ (m/hr)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>f00u21</td>
<td>2.10</td>
<td>0.00</td>
<td>Flat water</td>
<td>0.121</td>
<td>19.7</td>
<td>0.032</td>
<td>Deacon [8]</td>
<td>0.021</td>
<td>-35.70%</td>
</tr>
<tr>
<td>f34u21</td>
<td>2.10</td>
<td>3.40</td>
<td>low steepness waves</td>
<td>0.130</td>
<td>19.0</td>
<td>0.054</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f34u30</td>
<td>3.00</td>
<td>3.40</td>
<td>incipient breaking microscale breaking</td>
<td>0.218</td>
<td>18.8</td>
<td>0.086</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f34u57</td>
<td>5.70</td>
<td>3.40</td>
<td>microscale breaking</td>
<td>0.418</td>
<td>18.0</td>
<td>0.324</td>
<td>Peirson and Banner [21]</td>
<td>0.351</td>
<td>8.50%</td>
</tr>
<tr>
<td>f29u21</td>
<td>2.10</td>
<td>2.90</td>
<td>low steepness waves</td>
<td>0.103</td>
<td>18.7</td>
<td>0.061</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f29u36</td>
<td>3.60</td>
<td>2.90</td>
<td>incipient breaking microscale breaking</td>
<td>0.263</td>
<td>18.7</td>
<td>0.115</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f29u57</td>
<td>5.70</td>
<td>2.90</td>
<td>microscale breaking</td>
<td>0.467</td>
<td>18.4</td>
<td>0.396</td>
<td>Peirson and Banner [21]</td>
<td>0.325</td>
<td>-18.00%</td>
</tr>
<tr>
<td>f00u32</td>
<td>3.20</td>
<td>0.00</td>
<td>capillary ripples</td>
<td>0.260</td>
<td>18.4</td>
<td>0.068</td>
<td>Peirson and Banner [21]</td>
<td>0.336</td>
<td>29.50%</td>
</tr>
<tr>
<td>f21u32</td>
<td>3.20</td>
<td>2.10</td>
<td>low steepness waves</td>
<td>0.270</td>
<td>18.8</td>
<td>0.112</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f21u32</td>
<td>3.20</td>
<td>2.40</td>
<td>incipient breaking microscale breaking</td>
<td>0.24</td>
<td>18.8</td>
<td>0.126</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f21u32</td>
<td>3.20</td>
<td>3.10</td>
<td>microscale breaking</td>
<td>0.340</td>
<td>18.4</td>
<td>0.259</td>
<td>Peirson and Banner [21]</td>
<td>0.336</td>
<td>29.50%</td>
</tr>
</tbody>
</table>
observation was that after application of wind and waves, the water temperature decreased to the stable value as indicated in Table 8.1, whilst air temperature in the entire facility remained the same. This is indicative of the evaporative heat flux taking place at the surface eventually achieving balance with input heat fluxes through the surface, walls and base of the tank. Consequently, the stable temperature of the water must be dependent on the rate of overall heat transfer taking place within the facility.

Other investigators (Woodrow and Duke [25], Figure 16) have observed directly plumes of oxygen-rich water leaving wind-forced free surfaces. The evaporatively-induced temperature instability at the interface could be a source of surface convergence, generating vertical transport and transfer rates systematically higher than Deacon’s predictions. The difference between the measured flat water flux rate and the estimated value is comparable with the enhancement that occurs with the application of small amplitude waves.

At present, we have no direct particle image velocimetry observations with which to compare our data in the form of McKenna and McGillis [18]. However, for wind-forced, microscale breaking waves, Peirson and Banner [21] showed that the mean surface divergence on the up-wind faces of wind-forced microscale breaking waves is relatively weak and the mean surface velocity field can be well approximated by a 5th order Stokes estimate with a superimposed, weakly modulated surface drift. Computations of the mean divergence using a 5th order Stokes description of the surface velocity for the wave forms of the present study shows differences of only about 10% from the simple expression:

\[ \langle |\Gamma| \rangle = 4akf \]  

(8.2)

where \( |\Gamma| \) is the magnitude of the local surface divergence, the angle brackets denote spatial averaging, \( ak \) is the mean wave steepness and \( f \) is the wave frequency. Figure 8.2 presents our data plotted as a function of square root of the divergence magnitude evaluated using Equation (8.2). The collapse of the non-breaking wave data is modest with levels of transfer velocity observed for non-breaking waves are similar to those observed by McKenna and McGillis [18]. Figure 8.2 highlights the significant differences in transfer velocity between non-breaking waves and microscale breaking wave conditions.

Whilst the transfer rates at the incipient breaking limit are higher than for those of lower mean wave steepness, there is no observable jump in transfer that suggests strong flux enhancement due to parasitic capillary presence.

The most significant increases in transfer velocity can be observed to be associated with the transition from incipient to microscale breaking. Consistent with the observations of Banner [1], there is a also substantial jump in the momentum flux as exhibited by the increases in the friction
velocity $u_{*a}$. This observation highlights the importance of the microscale breaking process to the air-water gas exchange process.

Shown in Table 8.1 are the predictions of Peirson and Banner [21] for these conditions. The predictions are reasonable in views of the substantial jump in transfer rate associated with the transition to microscale breaking and the simplicity of the theoretical approach. The predicted values assume 100% breaking occurrence and minimal impact of the wind-drift current. The formation of wave groups along the wave tank may have reduced the breaking probabilities at the downwind end of the test chamber to about 80%. These two factors allow scope to reduce the predicted values by about 20% but no scope to increase them.

The measured values have been converted to equivalent CO$_2$ flux rates at 20°C (with a maximum 5% error due to Schmidt number exponent uncertainties). The present results are shown in the context of laboratory data assembled from other studies by Komori et al. [15] and reproduced here in Figure 8.3. In the regime of moderate wind forcing ($u_{*a} < 0.5$m/s), the present data span the range of observed flux rates and suggest regimes of surface wave impact on low solubility gas transfer. The results of our investigations to date indicate that a process-related categorisation of low solubility air-water gas exchange processes may be possible. As shown in Figure 8.3, very low exchange rates occur in the absence of any wave activity. The presence of small scale wave activity in the absence of any micro-scale breaking can enhance the exchange rate to the level indicated.
Figure 8.3. Laboratory measured transfer velocities as a function of friction velocity in the air obtained during the present study (solid squares ■) normalised for CO$_2$ at 20°C and shown in comparison with data assembled by Komori et al. [15] (their CO$_2$ data shown as solid circles ●); Jähne [11] CO$_2$ data, left pointing triangles ◀; Broecker et al. [6] CO$_2$ data, downward pointing triangles ▼; Jähne et al. [13] CO$_2$ data, solid diamonds ◆; Wanninkhof and Bliven [24] SF$_6$ data, asterices *. The dashed line shows the Deacon [8] relationship and solid lines and annotation delineate regimes of wave-related transfer velocity indicated by this investigation.

Increasing the probability of microscale wave breaking to 100% results in a maximum transfer rate in the vicinity of 0.09 mm/s under moderate wind forcing. At high wind forcing ($u^* > 0.5$ m/s), exchange can be further enhanced possibly due to spray or bubble generation but a process-based investigation of exchange at high wind forcing remains to be undertaken.

8.4 Conclusions and Recommendations

Careful observations of re-oxygenation have been undertaken in a linear wind-wave interaction tank with minimal surface contamination. A unique characteristic of these experiments is that the wind and paddle-generated wave conditions have been selected to minimise the fetch-dependence of the wind-wave field.

Our observation of transfer rate in the absence of surface waves are systematically a factor of 3 times higher than the predictions of Deacon [8]. A concomitant cooling of the water with the application of light winds indicates significant heat flux, presumably due to evaporation. Density instability induced by evaporative cooling could promote the formation of
localised surface divergences and direct transport away from the interface consistent with the observations of Woodrow and Duke [26]. The potential contribution of direct transport away from the surface war-rants further investigation.

Transfer velocity increases systematically with the steepness of small unbroken waves up to the point of incipient breaking. Our observed increase in transfer velocity appears to be consistent with the levels observed by McKenna and McGillis [18]. Further investigation of the role of surface divergence in the enhancement of transfer velocity due to unbroken waves is presently been undertaken. An increase in total stress of approximately a factor of two is required to support the transition from a continuous incipient breaking to a continuous microscale breaking wave state, consistent with the observations of Banner [1]. However, the associated enhancement of the transfer velocity associated with the transition from incipient to active microscale breaking is approximately a factor of 2 to 3. The measured transfer rates in the presence of microscale breaking are consistent with the predictions of Peirson and Banner [21]. Investigations to determine those processes causing further enhancement of transfer velocity under high wind forcing is recommended.

References


