

FREE-SURFACE TURBULENCE AND AIR–WATER GAS TRANSFER

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ABSTRACT

Concurrent measurements of the two-dimensional free-surface velocity field and bulk gas-transfer velocity for the case of zero-mean-shear mechanically generated turbulence are reported. Laboratory experiments in an oscillating grid-stirred tank have been performed that reveal evidence of the role of surface divergence on air–water gas transfer for varying free-surface rheological and dynamical conditions. Temporal measurements of water-side dissolved oxygen concentration were used to infer the gas-transfer rate, and simultaneous DPIV (digital particle image velocimetry) and PTV (particle tracking velocimetry) measurements provided the velocity field for a small free-surface patch. Additionally, the impact of surfactants on the surface flow and gas transport has been explored. Ensemble-averaged free-surface dynamical quantities such as vorticity and turbulent velocity fluctuations are seen to scale with a bulk flow parameterization for a range of surface conditions. However, such quantities are unable to provide a unique relationship for the transfer velocity under all surface conditions. Rather, the gas-transfer velocity is found to scale with the surface divergence as $k \sim \sqrt{a}$. Estimates of the transfer velocity based on a hydrodynamic model incorporating the present surface divergence data are in agreement with the measured values, confirming that the divergence is a critical parameter involved in the interfacial transport process.

BACKGROUND

Hydrodynamic mechanisms of gas transport across an air–water interface are poorly understood, however, their impact is critically relevant to many environmental and industrial processes. While the specific details have yet to be completely elucidated, it is evident that the enhancement of oceanic gas transport (for water-side rate-

controlled gases) over that which is expected for pure molecular diffusion is governed by several interrelated mechanisms that are dependent on wind and wave conditions. Since many complex physical processes have an impact on gas transfer (e.g., the interaction between the wind-driven surface shear layer and the wave field, near-surface turbulence, the modification of interfacial hydrodynamics by surface films, and breaking waves that can lead to bubble formation and increased mixing), an experiment or model that completely describes the phenomenon is presently out of reach. It is therefore desirable to isolate certain aspects for in-depth study. The present work focuses on the mechanism of surface renewal due to turbulent eddies and its role in gas-transfer enhancement.

Models of Air–Water Gas Transfer

For sparingly and moderately soluble gases (e.g., O₂, CO₂, N₂), the transport across an air–water interface is governed by the water-side mass boundary layer within which diffusional processes dominate. The thickness of this layer, and hence the rate of interfacial transport, will depend on the diffusivity of the gas and the nature and intensity of the flow near the interface. Turbulent fluid motions at the surface act to thin this boundary layer and result in increased air–water exchange. While numerous conceptual models and empirical relationships exist, there is still no clear consensus on the parameterization of the gas-transfer rate. This lack of agreement is fundamentally rooted in our incomplete understanding of the relationship between near-surface processes and air–water transfer. The task is further complicated by the complex nature of the free surface (e.g., surface waves) and the small scales ($\mathcal{O}(50\text{--}100\ \mu\text{m})$) that are involved in the mechanisms of mass transfer. Most gas-transfer models can be generalized as being either conceptual,

eddy diffusivity, or hydrodynamic models (Brumley and Jirka, 1988). Regardless of model type, all attempt to predict the interfacial gas flux, F , due to a concentration difference across the interface,

$$F = k(C_s - C_b) \quad (1)$$

where C_s and C_b are the equilibrium surface and bulk gas concentrations, and k is the liquid-phase gas-transfer velocity, which is a function of the specific hydrodynamical regime and the gas diffusivity. Most parameterizations of the transfer velocity can be reduced to

$$k/U \sim \beta Sc^{-n}, \quad Sc \equiv \nu/D \quad (2)$$

where U is a characteristic velocity and β represents the hydrodynamic dependence, often expressed through a Reynolds number functionality. A fundamental weakness in these models is that all rely upon some empirical parameters or coefficients that have indirect relevance to the actual physical processes involved with the exchange at the interface. Irrespective of the numerous models for gas transfer, it is generally believed that the vertical velocity fluctuations near the surface, w' , which bring fluid to the interface for diffusion, are responsible for gas-transfer enhancement. These velocity fluctuations can be expressed in terms of the surface divergence as

$$w'(z) = -(\nabla_h \cdot \mathbf{v}')_o z + \mathcal{O}(z^2) + \dots \quad (3)$$

where the subscript 'o' indicates evaluation at the free surface, $z = 0$, and ∇_h is the horizontal divergence operator. Relating the transfer velocity to a measure of the surface divergence has yet to be done in an experimental context. Many researchers have sought relationships between k and other flow properties (e.g., wind speed, Liss and Merlivat, 1986; turbulent dissipation, Kitaigorodskii, 1984; turbulent intensity, Chu and Jirka, 1992, Asher and Pankow, 1986; wave slope, Hara et al., 1995; microscale wave breaking, Zappa et al., submitted), yet regardless of the flow regime, mass transfer should ultimately be governed by surface divergence, and other quantities can only serve to act as proxies to the actual physical mechanism responsible. This is evidenced by the wide scatter in the results from such experiments. A major source of this disagreement is due to the presence of surface-active films, which are ubiquitous in the ocean and arguably in the laboratory as well.

Surface Film Effects

The exponential dependence of the transfer velocity on the gas diffusivity is often predicted to be $1/2$ by many models. However, this dependence is only valid for a truly clean free surface. When the surface is contaminated with an adsorbed surfactant, the physics lie somewhere between that of a clean surface and a solid boundary where $k \sim Sc^{-2/3}$. The transfer velocity is further modified through a different hydrodynamic dependence via β . The reason of this variability lies with the abil-

ity of a surface-active substance to alter the free-surface dynamic boundary condition. While an uncontaminated free surface can support zero shear, the same is not true for a surfactant-adsorbed surface. The explanation derives from the Marangoni effect. A surface-active substance is known to lower surface tension. When a free-surface flow exists, surfactant is spatially redistributed setting up gradients in surface tension and therefore surface stresses. These stresses act to oppose the surface flow from which they derive their origin. In addition to resisting the in-plane motions of fluid, the presence of a surface stress generates a highly dissipative viscous boundary layer in which flow dampening takes place (Davies, 1972). The adsorbed film acts to increase the thickness of the viscous sublayer and in turn the diffusive boundary layer, retarding the transfer rate considerably. Experimental studies in both the laboratory and field confirm this behavior (e.g., Broecker et al., 1978; Goldman et al., 1988; Frew et al., 1990).

EXPERIMENTAL METHOD

The use of an oscillating grid-stirred tank for this study has the benefit of generating repeatable levels of turbulence with zero-mean-shear in a closed, gas-tight system. Furthermore, the turbulence produced due to an oscillating grid has been examined extensively, and is discussed as being near-isotropic and quasi-homogeneous in the horizontal plane (Thompson and Turner, 1975; Hopfinger and Toly, 1976; Brumley and Jirka, 1987; De Silva and Fernando, 1994). In this work, experiments were conducted in a tank of dimensions $45.4 \text{ cm} \times 45.4 \text{ cm} \times 57.2 \text{ cm}$ deep. The tank was constructed entirely from polycarbonate, and all joints were chemically bonded using methylene chloride. This avoided spurious contaminants from other types of materials and/or sealants. The system was made gas-tight using a neoprene gasket and tank lid. A 7×7 grid made of $d = 1.27 \text{ cm}$ square cross-section polycarbonate bars having a mesh size $M = 6.35 \text{ cm}$ was used for all the experiments. The resulting grid solidity is 35.3%. The tank walls form planes of symmetry with respect to the grid mesh in order to reduce secondary flow generation as discussed by Fernando and De Silva (1993). This grid geometry is identical to that of Brumley and Jirka (1987). The grid was rigidly attached at its center vertex to a delrin rod that extended through the tank floor. A neoprene bellows sealed at one end to the rod and at the other end to the tank floor provided a flexible watertight seal. The rod and grid were made to oscillate vertically using a closed-loop linear actuator device situated beneath the tank. For all results presented here the water depth was 29.1 cm and the distance from the mean grid position to the free surface, z_s , was 9.53 cm ($1.5M$). Several different stoke, S , and frequency, f , combinations were explored. These are summarized in table 1. We note that conditions A and C correspond to conditions 4 and 3 of Chu and Jirka (1992). Other parameters appearing in table 1 were determined using the empirical expressions of Hopfinger and Toly (1976), who

TABLE 1: GRID CONDITIONS AND CHARACTERISTIC PARAMETERS [†]

Grid condition	S (cm)	f (Hz)	z_s (cm)	L_{HT} (cm)	u_{HT} (cm/s)	Re_{HT}	Re_λ
A	2.40	1.66	9.53	0.95	0.41	78	62
B	5.00	1.00	9.53	0.95	0.74	141	84
C	5.00	1.28	9.53	0.95	0.95	180	95
D	6.50	0.95	9.53	0.95	1.04	198	100
F	9.00	0.70	9.53	0.95	1.25	238	109
G	6.50	0.85	9.53	0.95	0.93	177	94
H	7.87	0.70	9.53	0.95	1.02	195	99

[†]See text for explanation.

found that for a planar grid of square cross-section bars with $d/M = 5$, the r.m.s. horizontal turbulent velocity could be related to the grid parameters as

$$u_{HT} = 0.25M^{0.5}S^{1.5}fz^{-1} \quad (4)$$

where z is the vertical distance from the mean grid position. Furthermore, the longitudinal integral length scale, L_{HT} , was found to increase linearly with distance from the grid:

$$L_{HT} = \alpha z \quad (5)$$

The constant α has been shown to fall in the range 0.1–0.4; here, it was taken as 0.1. The turbulent Reynolds number based on the Hopfinger and Toly values was defined as $Re_{HT} \equiv 2u_{HT}L_{HT}/\nu$ in order to compare with previous results. The Reynolds number based on the Taylor microscale was computed from $Re_\lambda \equiv (50Re_{HT})^{0.5}$. We point out that with (4) and (5), these Reynolds numbers are independent of the coordinate z . For all experiments, commercially available spring water was used. The tank and grid were thoroughly cleaned and rinsed for each experiment. Measurements of O_2 evasion were used to determine the gas-transfer velocity. Bulk dissolved O_2 concentration was measured at 0.1 Hz using a YSI probe located 10 cm from the tank floor. For each experiment, N_2 gas was used to flush the tank headspace to yield a known zero O_2 surface concentration. The transfer velocity was obtained through fitting the bulk dissolved O_2 data to the expression

$$C_b(t) = C_b(0)e^{kt/h} \quad (6)$$

where h is the water depth and $C_s(t)$ has been taken to be zero.

The free-surface velocity field was measured for a small surface patch using the techniques of digital particle image velocimetry and particle tracking velocimetry. The flow was seeded with 20–45 μm neutrally buoyant polystyrene spheres impregnated with fluorescein dye. A dual YAG laser operating in a frequency-doubled mode at 532.5 nm was used to illuminate the flow tracers, which when excited at the laser frequency fluoresce at approximately 576 nm. This feature was exploited using optical filtering of the imaging camera to isolate particle image

return. The laser beam was formed into a light cone with appropriate optics and directed to illuminate a circular patch of the free surface 9 cm in diameter. A digital camera with a 1008×1022 CCD imaging array was employed to record the flow field. The camera was arranged such that it imaged a square 10 cm on a side. Optically filtering the camera eliminated background light due to the laser. It also eliminated all but the strongest particle signals—those at the free surface. In this way any particles illuminated at depth were removed through optical thresholding. Images were captured (30 Hz frame rate) and stored real-time using a PC frame grabbing board. The free-surface flow field was assumed stationary and velocity information was sampled over the course of each experiment to build up a statistical base for analysis. The data presented here are the result of acquiring a pair of video frames every 6 seconds for approximately 10 minutes. Typically, three such video sequences were collected for each experiment. This yielded 600 images, or 300 velocity field realizations, per experiment.

The image data was processed using DPIV and PTV codes developed by McKenna. The DPIV code was used for the flow conditions where strong surface bursting was absent and uniform particle seeding distribution was observed. The DPIV algorithm uses a variance-normalized cross-correlation coefficient in determining mean particle displacements. This measure has been reviewed favorably by Burt et al. (1982). The computation of the coefficient is done in the spatial domain rather than the Fourier domain as the former has been found to be more accurate (Huang et al., 1997). Post-processing of the data involved an outlier detection scheme with linear interpolation used for the removed vectors. All images were subsampled to a domain size of roughly 6 cm square. Use of 32 pixel square interrogation windows resulted in a spatial resolution of 6 mm (twice Nyquist). For the more energetic surface conditions where significant bursting took place, the particle seeding density was often nonuniform, eliminating the possibility of standard DPIV cross-correlation processing. Instead, a particle tracking algorithm modeled after that of Cowen and Monismith (1997) was used. This is a hybrid technique which uses coarse DPIV results to guide the particle matching. The irregular velocity data was then transformed to a regular grid for processing using a triangle-based cubic interpolation scheme.

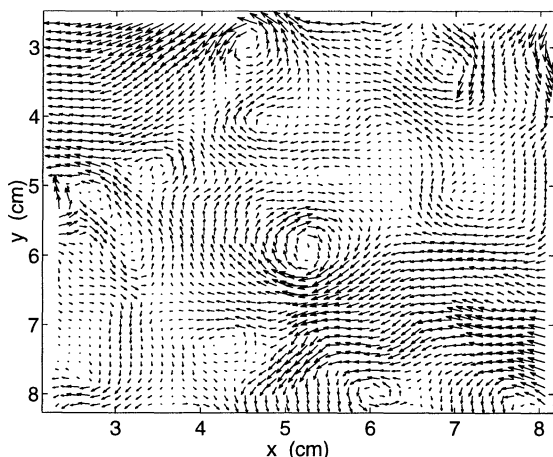


Figure 1: Free-surface velocity field for grid condition G.

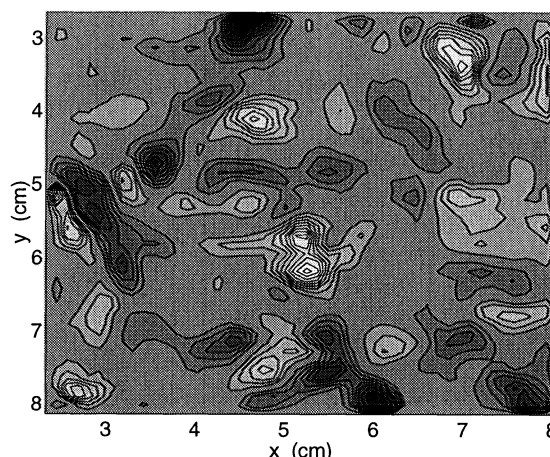


Figure 2: Free-surface normal vorticity field corresponding to figure 1. Contour levels range from -10 s^{-1} to 10 s^{-1} .

RESULTS AND DISCUSSION

Using the DPIV/PTV velocity data, in conjunction with the measurements of the gas-transfer velocity, relationships between the bulk flow and the free-surface flow, and their connections to the observed gas transfer were explored.

Dependence of Free-Surface Flow on Bulk Parameters

To gain insight into the relationships between bulk parameters and free-surface flow properties, various quantities were computed for each instantaneous velocity field, spatial means computed, and ensemble averages taken of all instances acquired. Figure 1 shows a sample free-surface velocity field as measured using DPIV and figure 2 is the corresponding map of the surface normal vorticity, ω . Figures 3 and 4 show the dependence of the r.m.s. turbulent velocity and the surface normal vorticity on Re_{HT} for data from all experimental conditions. There appears to be a direct relationship between the bulk turbulence intensity and its manifestation at the free surface. Surface divergence measurements, on the other hand, did not show such agreement and were not monotonically increasing functions of Re_{HT} . This was determined to be a consequence of inconsistent free-surface conditions (discussed below). This would indicate that in-plane shear and free-surface turbulent intensity is less sensitive to the presence of a surfactant.

Surface Contamination

It became evident that surface contamination played a major role in the observed free-surface behavior. First, it was determined that the flow tracer particles were surface active. This was discovered as a result of performing gas-transfer experiments without surface velocity measurements and the associated addition of particles. For these baseline cases, the surface was vacuumed using an aspirating pipette prior to data collection. Figure 5 shows

the marked reduction of the transfer velocity as a result of particle-borne contamination. As a result, experiments were subsequently performed that used particles that had been flushed continually with clean water. These also appear in figure 5. However, a second aspect of surface contamination also became apparent; the surface condition was not constant during the course of a group of experiments. Such behavior is most probably attributable to surfactant adsorption over time. This is shown by the high k value for the $Re_{HT} = 174$ condition. For the group of washed particle experiments, this case was performed first, then the other three in order of increasing Re_{HT} . The other two groupings, particles present/absent, were both performed in order of increasing Re_{HT} . Therefore, we would expect the trends to be steeper had there not been surfactant adsorption during the experiments. Both of these points are non-trivial for free-surface experimental studies using particle flow tracers. It is clear that careful selection of particles and/or proper treatment of particles is necessary in order to avoid adventitious surface contamination. The data of figure 5 illustrate the inability of a bulk parameterization to accurately predict the gas-transfer rate. While trends are captured, absolute magnitudes are inconsistent. Use of free-surface quantities such as vorticity and r.m.s velocity also fall short, as they are closely linked to the bulk flow. The fact that the transfer velocity is an excellent predictor of the degree of surface contamination supports the idea of surface divergence being instrumental in interfacial mass transfer since the divergence is directly modified by the presence of surface films.

Gas Transfer–Surface Divergence Relationship

Figure 5 is typical of results for air–water gas-transfer experiments. For a given hydrodynamic forcing, the gas-transfer velocity can be a multi-valued function de-

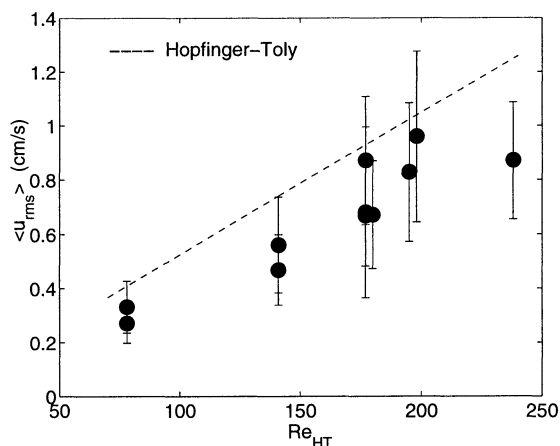


Figure 3: Dependence of surface r.m.s. turbulent velocity fluctuations on bulk parameterization. All surface conditions included.

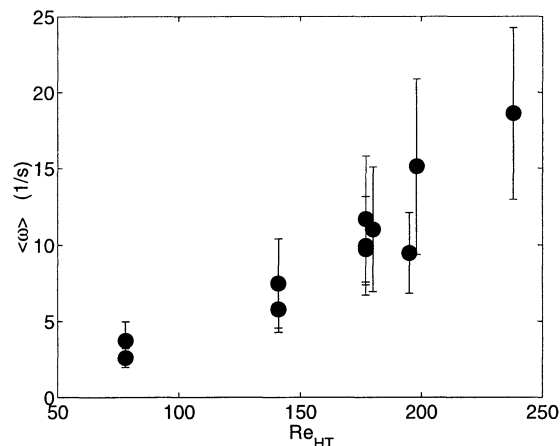


Figure 4: Dependence of surface normal vorticity on bulk parameterization. All surface conditions included.

pending on the surface rheology. Bulk parameterizations of the transfer velocity cannot be expected to be successful on the grounds already mentioned. Several researchers have proposed that the transfer velocity should scale as the square root of the divergence (Ledwell, 1984; Csanady, 1990; Brumley and Jirka, 1988). Chan and Scriven (1970) proposed a relationship for k in terms of the divergence as a result of studying the problem for pure stagnation flow:

$$k(\tau) = \sqrt{\frac{2a}{\pi}} \frac{D^n}{\sqrt{1 - e^{-2a\tau}}} \quad (7)$$

where a is the surface divergence and τ is a characteristic renewal time. To test this hypothesis, we plot k as a function of the measured surface divergence in figure 6. The divergence was estimated as an ensemble average of the square root of the mean surface divergence magnitude for each velocity field. Values of k based on (7) are also shown. The time τ was estimated from the outer time scale, $2L_{HT}/u_{HT}$. Values of the exponent n were determined to best fit the data. The resulting values for n are consistent with the surface cleanliness and are in agreement with what has been found in the past for realistic water surfaces (Jähne et al., 1987).

SUMMARY

Measurements of the free-surface velocity field and gas transfer have added to our understanding of the relationships between near-surface turbulence and air-water gas exchange. It was found that while free-surface dynamical quantities such as the velocity fluctuations and normal vorticity are closely linked to the bulk turbulent flow, they are unable to provide a unique relationship for the gas-transfer velocity. One source of this inadequacy is due to surfactant effects. Results indicated a

strong surface film presence due to flow tracer particles used for the velocity measurements. Surface divergence was found to capture the effects of surface films and is shown to be an excellent indicator of gas transport for a variety of surface conditions. Despite its simplicity, a hydrodynamic model assuming pure stagnation flow seems to describe the gas-transfer velocity-surface divergence relationship quite well.

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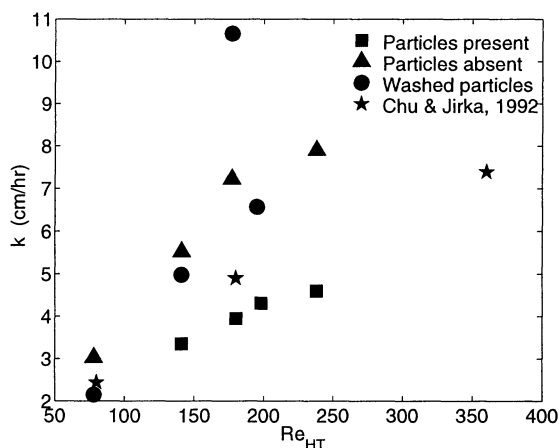


Figure 5: Dependence of gas-transfer velocity on tracer particle contamination. Chu and Jirka values are scaled to match the present data using the ratio z_s/M . Uncertainty in k is less than 10%.

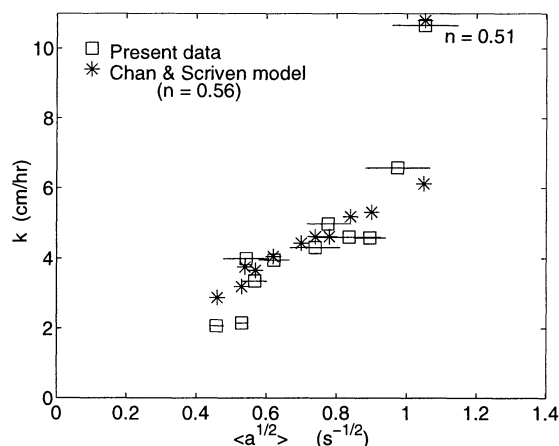


Figure 6: Dependence of gas-transfer velocity on surface divergence, a , for all surface conditions studied. Chan and Scriven model from equation (7) also shown with values for n indicated.

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