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A Structure Function Model Recovers the Many Formulations for Air-Water Gas Transfer Velocity

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Abstract Two ideas regarding the structure of turbulence near a clear air-water interface are used to derive a Waterside gas transfer velocity \( k_L \) for sparingly and slightly soluble gases. The first is that \( k_L \) is proportional to the turnover velocity described by the vertical structure function velocity \( D_{ww}(r) \), where \( r \) is the separation distance between two points. The second is that the scalar exchange between the air-water interface and the waterside turbulence can be suitably described by a length scale proportional to the Batchelor scale \( l_B = \eta \Sc^{-1/2} \), where \( \Sc \) is the molecular Schmidt number and \( \eta \) is the Kolmogorov microscale defining the smallest scale of turbulent eddies impacted by fluid viscosity. Using an approximate solution to the von Kármán-Howarth equation predicting \( D_{ww}(r) \) in the inertial and viscous regimes, prior formulations for \( k_L \) are recovered including (i) \( k_L = \sqrt{2/15 \Sc^{-1/2} \nu} \), \( \nu \) is the Kolmogorov velocity defined by the Reynolds number \( \nu \eta \eta / \nu \), \( \nu \) is the Kolmogorov viscosity of water; (ii) surface divergence formulations; (iii) \( k_L \propto Sc^{-1/2} u_t \), \( u_t \) is the waterside friction velocity; (iv) \( k_L \propto Sc^{-1/2} \nu/\nu \), for Keulegan numbers exceeding a threshold needed for long-wave generation, where the proportionality constant varies with wave age, \( g \) is the gravitational acceleration; and (v) \( k_L = \sqrt{2/15 \Sc^{-1/2}} (v g \beta_o q_o)^{1/4} \) in free convection, where \( q_o \) is the surface heat flux and \( \beta_o \) is the thermal expansion of water. The work demonstrates that the aforementioned \( k_L \) formulations can be recovered from a single structure function model derived for locally homogeneous and isotropic turbulence.

Plain Language Summary The problem considered here is a theoretical prediction of mass transfer across and air-water interface. This interfacial transfer phenomenon is featured prominently in global carbon balances, methane, nitrous oxides, dimethyl sulfide, and other gases. It is used to assess the metabolic health of aquatic ecosystems and to determine evasion rates of volatile organic compounds from lakes, estuaries, reservoirs, and large water treatment plants. The novelty of the approach is to link a bulk quantity reflecting the efficiency of swirling motions near the air-water interface to the sizes of eddies and their energetic content responsible for the aforementioned swirling motion. The proposed approach is shown to recover a number of equations describing gas transport across interfaces that summarize a large corpus of experiments and simulations.

1. Introduction

The imprint of air flow over interfaces of water, sand, and snow reflects the transfer of momentum, energy, and matter and has fascinated scientists and general observers alike (Cornish, 1909). The quantitative description of this imprint, especially in the air-water system, soon followed (Rossby & Montgomery, 1935). More recently, the consequences of this imprint on gas exchange between an open water body and the atmosphere is receiving renewed interest given its significance to a plethora of applications. This interfacial transport phenomenon is featured prominently in global balances of carbon dioxide, methane, nitrous oxides, dimethyl sulfide (DMS), and other gases (Bastviken et al., 2011; Bolin, 1960; Butman & Raymond, 2011; Cole et al., 2010; Garbe et al., 2014; Heiskanen et al., 2014; Huotari et al., 2011; Jähne & Haußècker, 1998; Liu et al., 2016; Mammarella et al., 2015; Rantakari et al., 2015; Raymond et al., 2013; Raymond & Cole, 2001; Upstill-Goddard, 2006; Wanninkhof et al., 2009; Wüst & Lorke, 2003). Regionally and locally, gas transport across the air-water interface is used as a water quality index (e.g., dissolved oxygen and aeration rates) and is often needed when determining evasion rates of volatile pollutants from lakes, estuaries, or even large water treatment plants (Chu & Jirka, 2003; Frost & Upstill-Goddard, 1999; Koopmans & Berg, 2015; Liss et al., 2014; Prata et al., 2017). Given their
Gas fluxes of a slightly or sparingly soluble scalar \( c \) across a clear air-water interface are commonly determined from the waterside bulk equation given as

\[
F_c = k_i \Delta C,
\]

where \( \Delta C = C_s - C_e \), \( C_s \) is the mean liquid phase saturation concentration at the surface (determined from Henry’s law and gas-phase concentration), \( C_e \) is the mean concentration of the exchanging gas in the bulk liquid phase, and \( k_i \) is the liquid phase mass-transfer velocity (labeled as piston velocity in some literature) describing the turbulent transport efficiency near the interface, the subject here. A large corpus of field and laboratory experiments agree that (Lamont & Scott, 1970; Lorke & Peeters, 2006; Zappa et al., 2007)

\[
k_i = \alpha Sc^{-\alpha} \nu_k,
\]

\( \nu_k = (\nu \epsilon)^{1/4} \) is the Kolmogorov velocity scale formed by the Kolmogorov length \( \eta = (\nu \epsilon)^{1/4} \) and time \( \tau_e = (\nu \epsilon)^{1/2} \) scales so as to ensure a Kolmogorov Reynolds number \( Re_k = \eta \nu_k / \nu = 1 \) (Pope, 2000; Tennekes & Lumley, 1972), \( Sc = v / D_m \) is the molecular Schmidt number, \( v \) is the mean turbulent kinetic energy (TKE) dissipation rate, \( \nu \) is the kinematic viscosity, \( D_m \) is the molecular diffusivity of scalar \( c \), and \( \alpha \approx 0.4 \) is a constant determined from experiments (Zappa et al., 2007). Equation (2) appears to hold across a wide range of marine and coastal systems (Zappa et al., 2007) with \( \alpha = 0.4 \), though variations reported in the literature are by no means small \( (\alpha = 0.17 – 0.63) \), as discussed elsewhere (Tokoro et al., 2008; Vachon et al., 2010). Some studies amended \( \alpha \) with a log(\( \epsilon \)) multiplier or a Reynolds number dependency (Wang et al., 2015), while others suggested that these amendments may be due to changes in exponent \( n \) with surface wind conditions (Esters et al., 2017). When the most efficient waterside momentum transporting eddy scales with Kolmogorov variables (labeled as microeddies), then dimensional considerations alone recover equation (2) for \( n = 1/2 \) without invoking complex transport schemes (Lorke & Peeters, 2006) such as surface renewal (Lamont & Scott, 1970; Soloviev, 2007).

A number of theories and experiments also suggest that the air-water gas transfer velocity is given by (Csanady, 1990)

\[
k_i = \beta Sc^{-\beta} u_*,
\]

where \( u_* \) is the waterside friction velocity related to the interfacial stress \( \tau_o \) using \( u_*^2 = \tau_o / \rho \), where \( \rho \) is the water density. Based on laboratory experiments and comparisons with many data sets, the inferred \( \beta \approx 1/16 – 1/9 \). Experimental support for equation (3) across a wide range of \( Sc \) and \( u_* \) has been discussed elsewhere (Honda, 1998; Jähne & Haußeller, 1998; Lorke & Peeters, 2006; Prata et al., 2017). Equation (3) has also been derived from two entirely different perspectives. One assumes that equations (2) and (3) are identical (Lorke & Peeters, 2006) depending on the choice of how \( \epsilon \) is linked to \( u_* \) (e.g., law-of-the-wall), whereas another assumes equation (3) is linked to moderate wind speed conditions associated with momentum transport by rollers (or circulation zones) on breaking wavelets (Csanady, 1990; Soloviev & Schlüssel, 1994). The mathematical form of equation (3) is also consistent with theories for smooth-wall boundary layers albeit with \( n = 2/3 \) and \( \beta = 0.083 \) predicted when assuming a unity turbulent Schmidt number (Deacon, 1977). This agreement opened up the possibility of simple transposition of the law-of-the-wall derived for smooth solid boundaries to air-water interfaces. Reductions from \( n = 2/3 \) to \( n = 1/2 \) (for clear air-water interfaces) are juxtaposition to finite vertical velocity gradients associated with increased surface roughness or mean squared amplitude fluctuations of the water interface (Jähne & Haußeller, 1998). As pointed out elsewhere, the analogy between a solid smooth wall (no slip, \( n = 2/3 \)) and a free surface (finite vertical velocity gradient, \( n = 1/2 \)) cannot be entirely correct (Csanady, 1978; Lamont & Scott, 1970). In fact, finite vertical velocity gradients invited the use of what is termed as surface divergence methods. These methods predict (Banerjee et al., 2004)

\[
k_i = c_s Sc^{-1/2} \sqrt{\nu \Lambda_o},
\]

where \( c_s \) is a similarity constant and \( \Lambda_o \) is the surface divergence of the horizontal velocity components determined from the turbulent vertical velocity \( w' \) by
\[ \Lambda_g = \sqrt{\frac{\partial w'}{\partial z}}. \]  

for an incompressible flow, where \( \partial w'/\partial z \) is to be evaluated at the air-water interface, \( z \) is distance from the interface, overline is time averaging, and primes are turbulent fluctuations.

For high wind speeds, the problem becomes far more complicated and general formulations for \( k_L \) remain in scarcity and high demand. In such conditions, long surface wave breaking occurs and suppresses the short wavelets, thereby altering the \( k_L \) formulation. A surface renewal theory by Soloviev and Schlüssel (1994) based on an assumed log-normal renewal times of eddies predicted that

\[ k_L = \gamma \frac{\text{Sc}^{-1/2}}{u_w} \left( \frac{\text{Sc}^{-1/2}}{u_w} \right)^{1/2}. \]

where \( g \) is the gravitational acceleration and \( \gamma \) is related to wave age, peak angular frequency of wind waves, and a critical parameter for the onset of wave breaking (Soloviev, 2007; Zhao & Toba, 2001). The log-normal renewal time assumption is now supported by laboratory studies, infrared surface temperature measurements, and Direct Numerical Simulations (DNS) studies (Garbe et al., 2004; Kermani & Shen, 2009; Rao et al., 2017). Interestingly, equation (6) predicts a declining \( k_L \) with increasing \( U_w \), which reflects the fact that more of the surface stress is used to support waves instead of waterside turbulence generation. However, if wave breaking that follows enhances \( \epsilon \) on the waterside, then equation (2) may still provide a realistic estimate of \( k_L \) as discussed elsewhere (Kitaigorodskii, 1984). Within the confines of equation (6), the role of bubbles and wave breaking must overcompensate for such decline with increasing \( u_w \) if \( k_L \) increases beyond its linear value given by equation (3) as reported by experiments (Jähne & Haugstecker, 1998). Wave breaking leads to a cascade of other events such as bubble-mediated transfer of scalars where Henry’s law must also be amended when determining \( C_s \). These amendments, which also vary with wind speed, surfactants, and water temperature, have been discussed elsewhere (Memery & Merlivat, 1985; Woolf & Thorpe, 1991) and their effects on \( k_L \) are not considered. Notwithstanding these limitations, few field experiments used DMS to explore the \( k_L \) dependency on mean wind speed at 10 m above the air-water interface (\( U_{10} \)). DMS is not impacted by bubble-mediated transfer and is thus an ideal tracer for exploring \( k_L \) in the absence of bubbles at high \( U_{10} \). Few experiments support the decline of \( k_L \) for DMS with increasing \( U_{10} \) (Bell et al., 2013, 2017; Huebert et al., 2004), while others do not offer such strong evidence (Bigdeli et al., 2018). Some laboratory studies suggest a saturation behavior of \( k_L \) with \( u_w \) at very high \( u_w \) (Komori et al., 1993; Vlahos & Monahan, 2009).

The goal here is not to propose a new formulation for \( k_L \) or compare various \( k_L \) formulations with data. Instead, a new interpretation rooted in a link between \( k_L \) and the spectral shape of turbulence is proposed without resorting to surface renewal schemes. This link assumes that \( k_L \) is a scale-dependent turnover velocity (instead of a piston velocity) and all the aforementioned formulations reviewed here (including their associated constants) reflect different scales over which the spectrum is integrated (Katul & Liu, 2017a). Hence, all the aforementioned \( k_L \) formulations maybe recovered from an accepted structure function shape describing turbulence at high Reynolds numbers on the waterside. In essence, the interpretation of \( k_L \) proposed here (in the absence of waves or wavelets) is shown to be a hybrid between the original theory proposed by Lamont and Scott (1970) and the dimensional considerations of Lorke and Peeters (2006). It maintains the spectral energetic content in eddies originally employed by Lamont and Scott (1970) but without utilizing surface renewal schemes. However, the effective eddy size over which the energy content is being evaluated is derived from dimensional considerations analogous to those used by Lorke and Peeters (2006). When small wavelets or waves are present, the choices of these length scales are determined entirely from plausibility considerations and ad hoc arguments. Nonetheless, by showing connections between established \( k_L \) formulations and the structure function for vertical velocity, the work here offers a different perspective about links between eddy sizes, their energetics, and \( k_L \) beyond surface renewal theory. Also, it allows for a single expression to be derived that interpolates between all the aforementioned prior formulations. Last, it is envisaged that progress in this area can contribute to analogous problems in surface hydrology such as water vapor transfer from rough surfaces into a turbulent atmosphere as may occur during evaporation from bare soil or vegetated systems (Brutsaert, 1975; Haghhighi & Or, 2013; Katul & Liu, 2017b; Shahraeeni et al., 2012).

2. Theory
2.1. Background and Definitions
For slightly and sparingly soluble gases, the small \( D_m \) implies that the resistance to mass transfer in air is negligible compared to its water counterpart (Bolin, 1960). It is well known that when \( \text{Sc} > 1 \), scalar transport near
interfaces is assumed to be conducted by eddies commensurate in size to the Batchelor scale $l_B = Sc^{−1/2} \eta$ (Batchelor, 1959; Hill, 1978; Lorke & Peeters, 2006). The $l_B$ is viewed as the smallest length scales of turbulent tracer fluctuations. This length scale can be derived in multiple ways—but the textbook versions associate this length scale to controls over a diffusive time scale $t_m$ characterizing a diffusive length scale $l_D = \sqrt{D_m t_m}$. When $Sc > 1$, then water viscosity restricts $t_m$ and $t_m$ is given by $\tau_k$ resulting in

$$l_D \propto \sqrt{\frac{\nu}{Sc}} \left( \frac{\nu_D}{\tau_k} \right)^{1/2},$$

thereby recovering $l_D = l_B = Sc^{−1/2} \eta$. With this background, and based on dimensional considerations alone, Lorke and Peeters (2006; hereafter referred to as LP06) showed that for $Sc > 1$, the viscous sublayer thickness ($\delta_v \propto \nu / u_*$) exceeds that of the molecular diffusive layer of scalar $c$ ($\delta_D \propto D_m / u_*$) and the Batchelor scaling restricts the path length over which scalar transport must occur. Hence, $k_l \propto D_m / \min (\delta_v, \delta_D)$. Because $\delta_v > \delta_D$, $k_l$ is dominated by concentration differences along $\delta_v$ and $k_l \sim D_m / \delta_v$. This result is virtually identical to the classical thin-film theory (Fortescue & Pearson, 1967; Lewis & Whitman, 1924). With $\delta_v \propto l_B$, $k_l \propto D_m / \delta_v$. thereby recovering equation (2). LP06 also provides some arguments about expected sizes of $\delta_D = 2\pi l_B$ and $\delta_v = 8.6 / u_*$ based on what is known about variations in turbulent statistics (eddy diffusivity) in the viscous (and buffer) regions of wall-bounded flows.

### 2.2. Surface Renewal Schemes: Large- and Micro-Eddy Models

In air-water mass-transfer studies, several limitations of classical thin-film theory have been addressed via surface renewal schemes. Surface renewals are viewed as approximations to upwellings of eddies in which water flows toward the interface and is then deflected parallel to the interface. As these elements deflect by the air-water surface, flow occurs along the surface leading to a finite $\partial u / \partial x + \partial v / \partial y$ and subsequently plunges back into the body of the water. Here $u$ and $v$ are the velocity components along the longitudinal (or $x$) and lateral (or $y$) directions, respectively. Fresh water elements are then transported very close to the surface so that mass is only transferred by molecular diffusion at the surface. The assumption of instantaneous water element transport, often invoked in surface renewal analysis, is hydrodynamically unrealistic but corrections to it do not alter much gas transfer velocity formulations. Eddies associated with upwellings and contact with the interface are effective in mass transfer across an interface as shown using conditional sampling methods (Komori et al., 1990). Near an air-water interface, DNS also reveal a rich turbulent regime where inertial, pressure, and viscous coupling all play a role (Herlina & Wissink, 2014). Likewise, rapidly acquired thermal infrared images suggest that thermal signatures of the contact durations of eddies with the air-water interface follows a log-normal distribution in agreement with a number of fully developed turbulence theories (Garbe et al., 2004). Hence, the main difference between wall-bounded flow and flow near air-water interfaces is the flow pattern associated with upwelling events close to the surface. In the case of wall-bounded flows, the boundary conditions on this flow are $w = 0$ and $\partial w / \partial z = 0$ resulting in $\partial u / \partial x + \partial v / \partial y = 0$ (no surface divergence). For those boundary conditions, the viscous sublayer cannot be readily penetrated by eddies. In the case of air-water interface, $w = 0$ but $\partial w / \partial z$ is finite (and large) at the interface. Laboratory experiment measuring the waterside $w(z)$ at a small distance away from the air-water interface and $\partial u / \partial x + \partial v / \partial y$ at the interface suggest that (Brumley & Jirka, 1987)

$$w(z) = -\left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right)_{\tau_k=0} z^*,$$

where $z^*$ was shown to be commensurate with $\eta$, though by no means this view is widely accepted and larger eddies have been postulated to impact $w(z)$. As discussed elsewhere (Katul & Liu, 2017a, 2017b; Komori et al., 1990), surface renewal theory predicts

$$k_l \propto \sqrt{\frac{D_m \sigma_z}{L_b}},$$

where $\sigma_z$ is a characteristic turbulent velocity and $L_b$ is a length scale describing the upwelling eddy sizes penetrating the viscous sublayer and efficiently exchanging mass with the air-water interface via molecular
Figure 1. The Kolmogorov microscale \( \eta \) and the Batchelor scale \( l_B \) for \( S_c > 1 \) below the air-water interface. Microeddies are assumed to be isotropic of size \( r \) moving scalars to and from the interface from regions with constant concentration \( C_s \) (labeled as bulk region) to the surface characterized by an interface concentration \( C_i \). The turnover velocity is defined by the magnitude of the relative velocity difference between two points \( |\Delta w'(r)| = |w'(x + r) - w'(x)| = \sqrt{D_{ww}(r)} \) separated by \( r = 2l_B \) as shown. The \( k_L = \sqrt{D_{ww}(r)} \).

diffusion. Two types of models have been proposed to estimate \( \sigma \) and \( L_i \): the so-called microeddy approach (Lamont & Scott, 1970) and the energy-containing eddy approach (Fortescue & Pearson, 1967; Komori et al., 1990). Unlike wall-bounded surfaces, the air-water interface allow eddies of various sizes to make contact with the interface for finite durations (the basis of surface renewal). The problem then is what type of eddies dictate the values of \( \sigma \) and \( L_i \)? In the energy-containing eddy approach, \( \sigma_i \propto \sqrt{\varepsilon_{Re}}, \) where \( \varepsilon_{Re} \) is the TKE and \( L_i \) is the integral length scale of the flow away from the interface. In the microeddy approach, these velocity and length scales are given by their Kolmogorov values (\( \sigma = \sqrt{\nu} \) and \( L_i = \eta \)), thereby recovering equation (2) with \( n = 1/2 \). As a bridge between the microeddy and energetic-eddy approaches, a Reynolds number \( Ret = \sigma_L/\nu \gg 1 \) is first defined to ensure a turbulent state at the macroscopic level near the interface. Next, it is assumed that the bulk TKE dissipation \( \varepsilon \propto \sigma^2/L_i \), thereby resulting in \( \eta/L_i \propto Ret^{-3/4} \), or \( L_i \propto Ret^{3/4} \eta \) (Fortescue & Pearson, 1967; Tennekes & Lumley, 1972). Replacing these estimates in equation (10), the energy-containing eddy approach yields

\[
k_L \propto Ret^{-1/4} \left[ Sc^{-1/2} \nu \right].
\]

This result is analogous to equation (2) (i.e., the microeddy approach) but with \( \alpha \) decreasing as \( Ret^{-1/4} \) with increasing \( Ret \). DNS and experimental support (laboratory and field) for this finding are discussed elsewhere (Herlina & Wissink, 2014; Komori et al., 1990; Wang et al., 2015), at least for moderate \( Ret \). Clearly, in the limit of very large \( Ret \), \( k_L \) may become unrealistically small suggestive that \( \alpha \) must become independent of \( Ret \). The independence of \( \alpha \) from \( Ret \) is analogous to how the Darcy-Weisbach friction-factor becomes independent from the bulk Reynolds number at very high bulk Reynolds numbers in pipe and open channel flows. A number of studies demonstrated that \( \alpha \) becomes constant independent of \( Ret \) for very large \( Ret \) (i.e., consistent with the microeddy approach) but depends on \( Ret^{-1/4} \) for moderate \( Ret \) (Theofanous et al., 1976; i.e., consistent with the energetic-eddy approach). Using laboratory experiments and DNS, the crossover between these two mass-transfer regimes (i.e., energetic eddy to microeddy) was determined to be around \( Ret \approx 500 \) (Herlina & Wissink, 2014; Theofanous et al., 1976). In fact, the DNS results visually reveal large-eddy penetration up to the interface of near-isotropic eddies originating from the bulk fluid at moderate \( Ret < 500 \) and across a wide range of \( Sc \) values. Also, the same DNS and laboratory studies confirm the \( Sc^{-1/2} \) scaling in equation (11), at least for clear interfaces. For the microeddy approach, surface tension effects (or the Weber number) are no longer relevant to \( k_L \) formulations.

2.3. The Structure Function Approach

Noting that \( F_e \) is related to the watershed mean concentration difference between the air-water interface and the bulk layer at some \( \delta \) below the water surface, then \( F_e = w_{70} \Delta C \) and \( k_L \) is interpreted as an effective turnover turbulent velocity \( |w_{70}| \) instead of a piston velocity (Katul & Liu, 2017a) as shown in Figure 1.

The magnitude of this velocity is \( \sqrt{w_{70}^2} \), where \( w_{70}^2 \) is the mean squared vertical velocity of eddies of size \( r = \delta \) given by

\[
w_{70}^2 = \frac{|w'(x + r) - w'(x)|^2}{D_{ww}(r)},
\]

where \( w' \) is the turbulent vertical velocity as before, \( x \) is an arbitrary position, \( r \) is separation distance assumed to represent mean eddy sizes, and \( D_{ww}(r) \) is the second-order structure function of the turbulent vertical velocity. The large \( Sc \) assumption implies that as eddies turn fluid elements, the loss of scalar mass by molecular diffusion from those fluid elements can be ignored over the smallest time scales commensurate with \( \tau_s \). The inference of \( w_{70}^2 \) may be achieved via the scale-wise integration of the spectrum of \( w'(E_{ww}(k), k \) is wavenumber). However, the physical space or structure function representation for \( |w_{70}| \) is preferred for two reasons: (1) The structure function already integrates spectral energy content across scales — as given by the approximate expression (Davidson, 2015; Katul et al., 2016)

\[
r \frac{dD_{ww}(r)}{dr} \sim kE_{ww}(k).
\]
and (2) at \( r = 0 \) and as \( r \to \infty \), the bounds on the structure function are unambiguous and given by
\[
D_{\text{ww}}(0) = 0 \quad \text{and} \quad D_{\text{ww}}(\infty) = 2 \sigma^2_w \text{, where} \quad \sigma_w = \sqrt{\langle w^2 \rangle} \text{ is the vertical velocity standard deviation.} \quad \text{For} \quad E_{\text{ww}}(k),
\]
how those bounds are approached is more problematic. In the case of non-flat water surfaces associated with equations (6) and (3), the choice \( \tau_w \text{ must be viewed as ad hoc but plausible.} \quad \text{The simplest model for} \quad D_{\text{ww}}(r) \text{ is the Kolmogorov inertial subrange scaling (or K41) for locally homogeneous and isotropic turbulence (Kolmogorov, 1941) adjusted by a viscous cutoff given by}
\[
\frac{D_{\text{ww}}(r)}{C_\alpha(r^2)^{2/3}} = 1 - \frac{1}{\zeta} \text{Daw}_r(\zeta),
\]
where \( C_\alpha \text{ is the Kolmogorov constant,} \quad \zeta = \theta(r/\eta)^{2/3} \text{,} \quad \theta = (10C_\alpha)^{-1/2} \text{, and the Dawson function is given by}
\[
\text{Daw}_r(\zeta) = \exp(-\zeta^2) \int_{0}^\zeta \exp(p^2)dp \approx \zeta - \frac{2}{3} \zeta^3 + \cdots.
\]
This expression is an approximate solution to the von Kármán-Howarth equation (von Kármán & Howarth, 1938) derived elsewhere (Katul et al., 2015). When this expression is converted to the spectral domain, it recovers the spectral bottleneck reported at the crossover from inertial to dissipation (Katul et al., 2015). This bottleneck is commonly identified by a bump when the compensated spectrum \( k^{5/3}E_{\text{ww}}(k) \) is plotted against \( k \text{ in the vicinity of} \quad k_l \approx 0.1 \text{ and has been the subject of active research (Davidson, 2015; Dobler et al., 2003; Donzis & Sreenivasan, 2010; Frisch et al., 2013, 2008; Herring et al., 1982; Hill, 1978; Katul et al., 2015; Meyers & Meneveau, 2008). The assumed spectrum by Lamont and Scott (1970) exhibits an inertial subrange adjusted with a power-law viscous cutoff based on the Kovasznay spectrum. Such a spectrum does not exhibit any bottlenecks, which is not consistent with DNS (Meyers & Meneveau, 2008) or high Reynolds number laboratory experiments (Saddoughi & Veeravalli, 1994). As earlier noted, \( k_l = \sqrt{D_{\text{ww}}(r)} \text{ and } D_{\text{ww}}(r) \text{ depend on the scale-wise integrated spectrum in equation (13); hence, not all spectral features are required to reproduce} \quad D_{\text{ww}}(r) \text{ from } E_{\text{ww}}(k). \text{ That is, despite the shortcoming of the spectral shape for } E_{\text{ww}}(k) \text{ used by Lamont and Scott (1970), the outcome for } k_l \text{ may be reasonably insensitive to the presence of the aforementioned bottleneck. For } r/\eta > 10, \quad D_{\text{ww}}(r) = C_\alpha(r^2)^{2/3} \text{ and the effects of viscous cutoff on } D_{\text{ww}}(r) \text{ can be ignored. However, the majority of conditions to be considered here deal with cases where the viscous effects on } D_{\text{ww}}(r) \text{ are significant (at least in the microeddy dominated } R_e). \text{ Setting } r = 2(D_{\text{ww}}tm)^{1/2} = 2(\nu Sc^{-1}tm)^{1/2} \text{ (instead of } l_B \text{) and considering only the two-term expansion of the Dawson function yields}
\[
D_{\text{ww}}(r) = w^2_{10} = \frac{2}{15} Sc^{-1}(\epsilon tm),
\]
where the factor 2 is discussed in Appendix A as well as further rationale for selecting the Batchelor scale for \( r \text{ (in the microeddy regime where } R_e > > 500). \text{ The linearity in } \epsilon tm \text{ here bares resemblance to the Lagrangian structure function in the inertial subrange (Monin & Yaglom, 1975; Ouellette et al., 2006; Yeung, 2002) but with two exceptions: (1) the constant } 2/15 \text{ is independent of the Kolmogorov constant, and (2) the dependency of } k_l^2 \text{ on } Sc^{-1} \text{ arises because scalar molecular diffusion dictates the effective eddy sizes transporting scalar c. \text{ The derivation of equation (16) also makes no specific assumption about the boundary conditions (e.g., the law-of-the-wall). In fact, the structure function shape assumed here applies universally to all locally homogeneous and isotropic turbulence, which is appropriate for eddy sizes much smaller than the integral length scale of the flow (i.e., microeddies). The indirect effect of such boundary conditions will be incorporated into models of } \epsilon \text{ and estimates of } tm. \text{ The predicted } k_l \sim Sc^{-1/2} \text{ is consistent with all prior surface renewal theories and surface divergence arguments. In essence, assuming a } k_l = \sqrt{D_{\text{ww}}(r)} \text{ implies a finite } |dw'/dz| \sim \sqrt{|w'(z+r) - w'(z)|^2/r \text{ at } r \sim l_B \text{ near the interface } (z \rightarrow 0). \text{ It has been shown theoretically (Csanady, 1990; Hasse, 1980; Lamont & Scott, 1970), experimentally (Hondzo, 1998; Jähne & HaußBecker, 1998), and using DNS (Fredriksson et al., 2016; Takagaki et al., 2016) that a finite } dw'/dz \text{ at the interface is responsible for } k_l \sim Sc^{-1/2}, \text{ whereas a } dw/dz \sim 0 \text{ invariably leads to a } k_l \sim Sc^{-2/3}. \text{ The } k_l \sim Sc^{-1/2} \text{ is sufficiently prevalent for clear air-water interfaces that when relating } k_l \text{ across different gases or conditions (e.g., } Sc = 600) \text{ or when inferring } k_l \text{ from surface temperature measurements, conventional practice is to set } n = 1/2 \text{ not } 2/3 \text{ (Asher et al., 2004; Csanady, 1990; Jähne & HaußBecker, 1998). An obvious critique here that also applies to surface renewal, eddy penetration, and surface divergence theories (Csanady, 1990) is the absence of a rigorous link between molecular diffusion at the water surface and eddy transport below the water surface. The structure function approach simply packs them into } l_B.\)
Notwithstanding this critique, it is shown next that the multiple formulations for \( k_i \) reviewed in section 1 can be recovered with appropriate choices of \( t_m \), and models for \( \epsilon \) where needed (instead of \( \sigma_i \) and \( L_i \) in the surface renewal formation of equation (10). The simplest model for \( \epsilon \) may be derived from an idealized stationary and planar-homogeneous TKE budget with no mean vertical velocity where production and dissipation rates of TKE are in balance. For this idealized state,

\[
\epsilon = -\overline{u'w'} \frac{dU}{dz} + \beta_0 q_o = u_+^2 \frac{dU}{dz} (1 - R_{f_i}) \; ; \; R_{f_i} = \frac{\beta_0 q_o}{\overline{u'w'} (dU/dz)} ; \; u_+^2 = -\overline{u'w'} = \frac{\tau_w}{\rho},
\]

where \( dU/dz \) is the waterside mean velocity gradient, \( \beta_0 \) is the thermal expansion coefficient of water that varies with absolute water temperature \( T \), \( R_{f_i} \) is a flux Richardson number, and \( q_o \) is the surface kinematic vertical heat flux (positive upward) assumed to be the main mechanism responsible for buoyancy generation or destruction of TKE (i.e., salinity effects or air entrainment on the water density gradients are ignored). Stable and unstable stratification occur when \( q_o < 0 \) (downward heat flux, \( R_{f_i} > 0 \)) and \( q_o > 0 \) (upward heat flux, \( R_{f_i} < 0 \)), respectively. The two generic terms (mechanical production and buoyant production/dissipation) impacting \( \epsilon \) appear to be sufficient to recover a wide range of field conditions as discussed elsewhere (Macintyre et al., 2010; Tedford et al., 2014). In stable stratification, an \( \epsilon > 0 \) (i.e., turbulence is still active) requires \( 0 < R_{f_i} < 1 \), though a maximum value of about \( R_{f_i,max} = 0.2 - 0.25 \) has been derived that ensures well-developed turbulence and K41 scaling to hold (Katul et al., 2014; Li et al., 2015). However, the \( R_{f_i,max} = 0.2 - 0.25 \) is not connected with laminarization of the flow (Galperin et al., 2007; Grachev et al., 2013; Li et al., 2016; Zilitinkevich et al., 2008). The \( q_o \) may be inferred as a residual of the air-side energy balance considerations. It is the outcome of an imbalance between the net long-wave radiation at the interface and the sum of sensible and latent heat fluxes into the atmosphere. The effects of shortwave radiation are ignored if its attenuation in water over a small distance \( \sim 2\delta \) is small. In what follows, it is assumed that \( |R_{f_i}| < 1 \) for the estimation of \( \epsilon \) and \( dU/dz \) unless stated otherwise. This assumption is mainly employed for comparisons with laboratory studies and published expressions in nonstratified conditions. The expected effects of \( R_{f_i} \) on \( k_i \) are discussed separately. It is worth noting that DNS and numerous experiments on smooth-wall boundary layers (with \( |R_{f_i}| < 1 \)) suggest that TKE production and dissipation near the wall are not in balance and production may exceed dissipation by a factor of 1.7 (McColl et al., 2016; Pope, 2000). This imbalance has obvious consequences on equation (17) but not appreciably on \( k_i \). A \( k_i \sim \epsilon^{1/3} \) means that a factor of 1.7 in dissipation rate overestimate from TKE production translates to a factor of 1.14 adjustment to \( k_i \). Before linking models of \( k_i \) with \( u_* \), the case where \( k_i \) varies with \( \epsilon \) only is first considered.

### 2.4. Recovering \( k_i = \alpha Sc^{-1/2} (\nu e)^{1/4} \) (Abstract, i and v)

This \( k_i \) formulation is directly recovered when setting \( t_m = \tau_x \). That is,

\[
k_i = |w_{30}| = \sqrt{\frac{2}{15}} Sc^{-1/2} \sqrt{\frac{\epsilon}{\nu e}} = \sqrt{\frac{2}{15}} Sc^{-1/2} (\nu e)^{1/4}.
\]

The finding that \( k_i \sim Sc^{-1/2} (\nu e)^{1/4} \) has been discussed elsewhere (Katul & Liu, 2017a). However, the analysis here goes further by proposing \( \alpha = \sqrt{2/15} = 0.37 \), which is reasonably close to the value \( \alpha = 0.42 \) reported by Zappa et al. (2007) and, more recently, by Esters et al. (2017) for open ocean when setting \( n = 1/2 \). Another multisite study reported a 0.39 < \( \alpha < 0.43 \) (Vachon et al., 2010) and noted the sensitivity of their inferred \( \alpha \) to the method and depth used when estimating \( \epsilon \). Also, the predicted \( \alpha \) here agrees with recent DNS analysis (Fredriksson et al., 2016) estimating an \( \alpha = 0.39 \) for the free slip case at the air-water interface. The original work of Lamont and Scott (1970) also reported an \( \alpha = 0.4 \). Kitaigorodskii (1984) derived equation (18) for temperature (without the constant \( \sqrt{2/15} \)) and further proposed that it is applicable for wavy surfaces experiencing wave breaking. The wave-breaking component primarily impacts \( \epsilon \), not the gas transfer law for \( k_i \), a point to be discussed later on.

As a bridge to the energetic-eddy hypothesis for moderate \( Re_e \), it is worth noting that equation (16) can directly recover the \( \alpha \) dependency on \( Re_e \). The ratio of the turnover time scale of large eddies \( (=L_i/\sigma_i) \) to microeddies \( (=\tau_x) \) is \( \sim Re_e^{1/2} \) (Tennekes & Lumley, 1972). Setting \( t_m = \tau_x Re_e^{1/2} \) (i.e., large-eddy formulation) instead of \( t_m = \tau_x \) (microeddy formulation) yields \( k_i \sim S_c^{-1/2} \sqrt{\epsilon \tau_x Re_e^{1/2}} \). That is, \( k_i \) from a microeddy formulation is reduced below the \( k_i \) arising from energetic-eddy considerations by a factor of \( Re_e^{1/4} \). The subunity dependence on \( Re_e \) by \( k_i \) means that when \( Re_e \) increases from 100 to 10,000, alterations in \( k_i \) are about a factor of 3.
In the limit of large $-Ri_f$ (i.e., approaching free convection limit), the above expression yields

$$k_L = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \nu g \beta \rho \right)^{1/4}.$$  \hspace{1cm} (19)

which can be expressed in dimensionless numbers as

$$k_L = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \nu g \beta \rho \right)^{1/4}.$$  \hspace{1cm} (20)

where $Pr = \nu / \alpha_f$ is the molecular Prandtl number, $\alpha_f$ is the molecular diffusivity of heat in water, and $h_c$ is the thickness of the convective layer derived from a constant $\alpha_f \propto \Delta T / h_c$, where $\Delta T$ is the temperature difference between the surface and the waterside well-mixed layer, and $Ra = (h_c^2)(g \beta \rho)(\Delta T) / (\nu \alpha_f)$ is the Rayleigh number. Equation (19) agrees with predictions from a surface renewal model (Soloviev & Schlüssel, 1994) that assumes the mean renewal time is proportional to $\nu / (\alpha_f g \rho)$ (Foster, 1971). Moreover, equation (19) is in agreement with DNS runs (Fredriksson et al., 2016) that reported an expression, given by

$$k_L = 0.39Sc^{-1/2} \left( \nu \beta \rho \right)^{1/4}.$$  \hspace{1cm} (21)

that fits their free convective runs.

### 2.5. Recovering the Surface Divergence Formulation (Abstract, ii)

Recovering equation (4) from (18) can be readily achieved for isotropic turbulence when noting that (Tennekes & Lumley, 1972)

$$\epsilon = 15 \nu \left( \frac{\partial w'}{\partial z} \right)^2.$$  \hspace{1cm} (22)

Inserting equation (22) into (18) leads to

$$k_L = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \nu \Lambda_0 \right).$$  \hspace{1cm} (23)

which is identical to equation (4) when $C_s = \sqrt{2}/(15^{1/4}) \approx 0.7$. This estimate is in acceptable agreement with the recent DNS studies reported by Fredriksson et al. (2016), where $C_s = 0.57$ was determined from fitting to DNS using surface state variables. It also agrees with estimates by Ledwell (1984) who reported $C_s = 0.64$ and by McCreary et al. (1986) who reported $C_s = 0.71$.

In what follows, the $k_L = \left[ D_{mw}(r) \right]^{1/2}$ interpretation is still employed. However, the explanation of $\sqrt{Sc^{-1}(e \tau_m)}$ must be expanded. From dimensional considerations alone, this quantity $\sqrt{Sc^{-1}e \tau_m}$ is simply the energy content in eddies with characteristic durations $\tau_m$ acting on the mean scalar concentration difference $\Delta C$ when supplied by a constant turbulent energy rate given by $\epsilon$. Hence, $\tau_m$ may now be impacted by eddies operating on time scales much larger than $\tau_x$. Because the canonical form of $k_L$ does not change under those conditions (i.e., $\propto \sqrt{Sc^{-1}(e \tau_m)}$), the factor $2/15$ is retained and proportionality constants are determined relative to this original form so as to facilitate an interpolation scheme between all the aforementioned formulations listed in the abstract (via $\tau_m$ and $\epsilon$).

### 2.6. Recovering $k_L = \beta Sc^{-1/2} u_*$ (Abstract, iii)

The consistency between equation (16) and the analysis in Csanady (1990) is now considered. The work by Csanady (1990) suggest that for moderate wind speeds, the intense momentum flux exchange is caused by viscous surface stress variations associated with rollers (i.e., circulation zones) on breaking wavelets. The vertical motion is assumed inviscid and spawned from a viscous boundary layer (meaning that its initial surface vorticity scales with $u_*/\nu$ and is not altered appreciably in time) on the upwind side of the wavelet. The circulation time around the roller then scales with $\nu / (u_*^2)$. It follows that $\tau_m = C_m \nu / u_*^2$ instead of $\tau_x$, where $C_m$ is a similarity constant. A naive argument would suggest that

$$k_L = |w_{70}| = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \epsilon C_m \frac{\nu}{u_*^2} \right)^{1/2}.$$  \hspace{1cm} (24)
The evaluation of $\epsilon$ must now be conducted at some distance from a flat interface to reflect the position of wavelets. When setting $\epsilon = u_*^2/(\delta_v)$ (Brutsaert, 1965) and $\delta_v \propto \nu/u_*$ (Lorke & Peeters, 2006; i.e., the expected thickness of the viscous layer for momentum not scalars is $\delta_v \approx 10\nu/u_*$),

$$k_l = |w_{10}| = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \frac{u_*^3}{10\nu u_*^4 C_m} \right)^{1/2}. \quad (25)$$

That is,

$$k_l = |w_{10}| = \sqrt{\frac{2}{15}} \frac{C_m}{10} Sc^{-1/2} u_* \quad (26)$$

Field experiments reporting $\epsilon$ profiles below a nonflat water surface suggest some independence of $z$ as the water surface is approached (Wang et al., 2015). Based on the model of Soloviev and Schlüssel (1994), we estimated a $C_m = 0.4$ resulting in a $\beta = 0.073$. This $\beta$ value is smaller than the one estimated by LP06 ($\beta = 1/9 = 0.11$) from the law-of-the-wall over a smooth surface but is in better agreement with the empirical fit to many data sets reported by Jähne and Haußecker (1998; $\beta = 1/16 = 0.065$) and others (Munnich & Flothmann, 1975). In fact,

$$k_l = \frac{1}{16} Sc^{-1/2} u_* \quad (27)$$

was used to estimate the $k_l$ component in the absence of wave-breaking in many field studies focused on the effects of wave breaking on $k_l$ (Shuqing & Dongliang, 2016). The arguments leading to equation (26) are indeed naive for two reasons: (1) the $r = 2(D_m t_m)^{1/2} = 2(\nu Sc^{-1} t_m)^{1/2}$ are based on scalar transport into a fluid parcel at a flat interface being entirely driven by molecular diffusion with viscosity restricting the diffusion time scale (i.e., momentum transporting eddies are commensurate to $\eta$, (2) the evaluation of $\epsilon$ at $\delta_v$ (instead of distance $r$ from the interface) is within the viscous boundary layer and is assumed to represent the overall bulk dissipation rate in this entire region (i.e., variation of $\epsilon$ with $z$ from the interface are not too significant for quantities that vary as $\epsilon^{1/4}$ such as $k_l$). Defining a Reynolds number $Re_v = u_\epsilon \delta_v/\nu$, then $\eta/\delta_v = Re_v^{-3/4}$. For $\delta_v = 10\nu/u_*$, $\eta/\delta_v \approx (10)^{-3/4} \approx 0.2$ or $\delta_v \approx 5\eta$, consistent with the viscous boundary layer thickness. Moreover, the structure function $r \sim Sc^{-1/2} \delta_v \sim 5Sc^{-1/2} \eta$ remains well below the crossover from inertial to viscous scales for $Sc >> 1$ (i.e., the assumed structure function shape is correct).

It is instructive to compare this formulation with a case where $t_m = C_m u_\epsilon \nu/g$ (Csanady, 2001) and $\epsilon = u_*^2/\nu (\kappa z_\kappa)$ (Brutsaert, 1965), with $\kappa = 0.4$ being the von Kármán constant and $z_\kappa$ is the momentum roughness length. In the absence of wave breaking, the momentum roughness length may be estimated by $z_\kappa = a_w u_*^2 g^{-1}$ (Charnock, 1955), which can be used in the determination of the waterside $\epsilon$ to yield

$$k_l = |w_{10}| = \sqrt{\frac{2}{15}} Sc^{-1/2} \left( \frac{u_*^3}{\kappa a_w u_*^2 g} \frac{C_w}{g} \right)^{1/2} \quad (28)$$

A number of reviews have already pointed out that Charnock’s equation does not hold for calm conditions or extreme high winds with wave breaking (Wüst & Lorke, 2003). Hence, within the confines of Charnock’s equation, $k_l$ reduces to

$$k_l = |w_{10}| = \sqrt{\frac{2}{15}} \frac{C_w}{\kappa a_w} Sc^{-1/2} u_* \quad (29)$$

This result is analogous to equation (26). The value of $\beta$ is further explored. With $C_w \approx 0.18 \times C_m$ (Soloviev & Schlüssel, 1994) and a waterside $a_w = 0.011 \times (\rho/\rho_a)$ yields a $\beta = 0.03$, which is a factor 2 smaller than $\beta = 0.073$ derived from arguments by Csanady (1990). Here the air-side Charnock constant ($\kappa = 0.011$) is converted to its waterside counterpart assuming continuity of the dynamic surface stress ($\rho_a u_*^2 \kappa_{a_w} = \rho u_*^2$) where $\rho_a$ and $u_*|_{a_w}$ are the air-side density and friction velocity. This continuity is considered next in the presence of waves and wave breaking at large wind speeds. However, the interpretation of $k_l \propto \sqrt{Sc^{-1}(\epsilon t_m)}$ must now be viewed strictly as an outcome of dimensional considerations as (1) $t_m$ deviates appreciably from $t_\tau$ and (2) the uncertainty in $\epsilon$ and $u_*$ determination are large. Nonetheless, this consideration does permit a unified model for $k_l$ that spans all the expressions listed in the abstract. This is the main reason this line of inquiry is being pursued (while mindful of all the model limitations and extrapolations at this stage).
When surface long waves formed by large wind speeds break down, the surface stress $\tau_o$ produced by the wind must be reduced to accommodate the energy carried by waves and the energy used to produce water-side turbulence as related to the tangential stress $\tau_w$. This partitioning is achieved by using the Keulegan number $Ke = u^2/(g \nu)$ so that

$$\tau_w = \frac{\tau_o}{1 + Ke/Ke_c},$$

(30)

where $Ke_c \approx 0.18$ is a critical Keulegan number that determines the crossover from wavelet- to long-wave breaking (Csanady, 2001; Soloviev & Schlüssel, 1994; Soloviev, 2007). Assuming that the waterside friction velocity responsible for the formation of long surface waves. Starting with the definition of $\tau_w = C_w u^2 / \gamma$ and repeating the above analysis with $tm = C_w u^2 / g$ yields

$$k_l = |w_{1O}| = \sqrt{\frac{2}{15} \frac{C_w}{\kappa a_w} S_c^{-1/2} \frac{u^2}{\sqrt{1 + Ke/Ke_c}}}.$$

(31)

When $Ke << Ke_c$, then equation (29) is recovered. However, for $Ke > Ke_c$ (long-wave breaking), then equation (31) becomes

$$k_l = |w_{1O}| = \sqrt{\frac{2}{15} \frac{Ke_c C_w}{\kappa a_w} S_c^{-1/2} \sqrt{g^2 / u^2}}.$$

(32)

which is identical to equation (6) with $\gamma = 0.03 Ke_c^{1/2}$. The connection between $Ke$ and the critical number for wind-wave breaking is now highlighted using arguments similar to Soloviev (2007). As discussed by Zhao and Toba (2001), a dimensionless number $R_B$ empirically characterizing the onset of wind-wave breaking is

$$R_B = \frac{u^2 |_p}{\nu_o \alpha_p} = 1000,$$

(33)

where $\nu_o$ is the air viscosity, $\alpha_p = g / (A_w u^2 |_p)$ is the peak angular frequency of wind waves, and $A_w$ is the wave age (defined as wave speed normalized by $u^2 |_p$). This threshold $R_B$ and $\alpha_p$ have received significant theoretical attention and experimental support (Melville & Rapp, 1985; Shuiqing & Dongliang, 2016; Zhao et al., 2003). Specifying a critical $Ke_c = (u^2 |_p)^2 / (g \nu) = 3.25$ may be inferred. This wave age corresponds to the early stages of surface long-wave development ($A_w \approx 4$) as discussed elsewhere (Csanady, 2001). As earlier noted, the arguments leading to equation (6) miss the enhanced dissipation rate due to wave breaking, which was not explicitly considered by Soloviev and Schlüssel (1994). However, the point here is that when forcing equation (16) with constraints similar to those used in surface renewal theories for long surface waves, their main $k_l$ predictions (Soloviev & Schlüssel, 1994) can be recovered from the structure function model proposed here.

2.7. Recovering $k_l = \gamma S_c^{-1/2} (g v / u^2)^{1/2}$ (Abstract, iv)

Combining all the aforementioned estimates of $\epsilon$ and $tm$, a single model for $k_l$ that accommodates thermal stratification, wavelets and waves can be derived. Thermal stratification (i.e., $Ri_f$) is introduced by $\gamma$ in equation (17). The $Ke$ is introduced by considering the mechanical production term in equation (17) assuming only the turbulent stress (not the mean velocity gradient) is modified by equation (30). This combination of assumptions can be expressed in a Csanady-form as

$$k_l = \sqrt{\frac{2}{15} \sqrt{\frac{1 - Ri_f}{1 + Ke/Ke_c} \left( \frac{dU}{dz} \right) S_c^{-1/2} u^2}}.$$

(35)
Here $dU/dz$ is the mean vorticity and $t_m$ is an effective turnover time scale. If the effect of thermal stratification on $dU/dz$ is ignored for simplicity, then $dU/dz = u_*/\delta$ and

$$k_1 = \sqrt{\frac{2}{15}} \left[ \frac{1}{1 + Ke/K_c} \right]^{-1/2} \frac{Sc^{1/2}}{u_*},$$

and where $A_c = u_*t_m/\delta$ is a constant when $Ke/K_c < 1$. This condition is analogous to the modified turbulent interface law proposed by Csanady (1978). When $Ke/K_c < 1$, then $\delta = 10v/u_*$ (thickness of the viscous sublayer) and $t_m = C_{nv}/u_*^2$ so that $A_c = u_*t_m/\delta = C_m/10$ (with $C_m = 0.4$). That is, the presence of wavelets do not disturb appreciably $\delta$ from its viscous-sublayer estimate.

When $Ke/K_c > 1$, as may be expected for very high wind speeds, then long waves form and $\delta$ now scales with wave properties such as wave age. In the naive case of a wave height scaling as $h = a'(t)^n$, where $C_m = C_c$, $u_*$ is constant. This unified formulation recovers the comprehensive surface renewal model of Soloviev and Schlüssel (1994) with the aforementioned caveats of decline in $k_1$ with increasing $u_*$ for $Ke/K_c > 1$. None of the experiments support a decline in $k_1$ for such conditions (Ho et al., 2006; Wanninkhof et al., 2009). For such conditions, bubble transport becomes a significant contributor to $k_1$ and is not considered here. Renewal formulations correcting for the role of bubbles assume that $k_1$ is a linear superposition of a hydrodynamic term (i.e., analogous to predictions from equation (36)) and a bubble transport term that is separately modeled as proposed elsewhere (Soloviev & Schlüssel, 1994). The hydrodynamic contributions to $k_1$ by such surface renewal schemes exhibit a decline with increased mean wind speed at very large wind speeds.

### 3. Model Limitation

The limitations of the approach are now reviewed. The work here only focused on clear water surfaces with no surfactants. Surfactants introduce finite interfacial stresses at the air-water interface that then create a highly dissipative viscous layer (i.e., the air-water interface begins to resemble a solid wall in the limit of high viscous damping). As such, surfactants are expected to retard gas exchange significantly across the air-water interface. Notwithstanding this complication, a number of studies suggest that the effects of surfactants can be accommodated by varying the exponent $n$ in $k_1 \propto Sc^{-n}$ as discussed elsewhere (McKenna & McGillis, 2004). Notably, it was shown that

$$n \approx \frac{2}{3} \left( \frac{1}{6} \right) \exp(-2\Lambda),$$

where $\Lambda$ is the ratio of the Marangoni stress (related to surfactant concentration) to a virtual viscous stress due to a rigid wall. That is, $\Lambda$ provides a dimensionless number that assess to what degree the surface resembles an immobile boundary. For $\Lambda = 0$ (clean surface), $n = 1/2$ (as predicted by surface renewal and structure function approaches). However, as $\Lambda \rightarrow 1$ (Marangoni stress is comparable to the viscous stress in wall-bounded flows with $\partial \nu/\partial z \rightarrow 0$), $n \rightarrow 2/3$, which is the canonical value for wall-bounded flow; Csanady, 2001; Deacon, 1977. Another limitation is that the formulations here did not consider bubble contributions to $k_1$, which are expected to be significant for large wind speed and long-wave conditions.

The approach is entirely anchored to the von Kármán-Howarth equation describing $D_{aww}(r)$. This equation and approximate solutions to it are based on locally homogeneous and isotropic turbulence. This assumption is clearly violated near the air-water interface at large scales ($r/\eta > 1$), though it may be reasonable for small eddy sizes ($r \approx 2\eta$). Another limitation is the absence of a rigorous link between molecular diffusion at the water surface and eddy transport just below the water surface. The structure function approach here packs them into $l_B$ or their effect on $t_m$. This scaling appears reasonable when $Sc > 1$, as discussed elsewhere (Lorke & Peeters, 2006). However, finite $D_{aww}(r)$ in $r^2$ as $r \sim l_B$ implies that $\partial \nu'/\partial z$ must be finite near the interface. A consequence of a finite $\partial \nu'/\partial z$ is that the approach must lead to $k_1 \sim Sc^{-1/2}$ and cannot predict other scaling exponents (e.g., $k_1 \sim Sc^{-2/3}$). At the most generic level, the structure function approach provides a link between $k_1$, $\epsilon$, and a diffusion time $t_m$ (i.e., $k_1 \propto (t_m)^{1/2}$). To recover prior formulations, choices for $t_m$ and models for $\epsilon$ are needed and those choices also introduce their own limitations. The simplest model for $\epsilon$ may be derived from an idealized stationary and planar-homogeneous TKE budget with no mean vertical velocity and where production and dissipation rates of TKE are in balance. This assumption, while common to many air-sea gas exchange studies, misses important nonlocal TKE transport mechanisms associated with...
Figure 2. Summary of assumptions about $t_m$ and $\epsilon$ used to arrive at equations (i)–(iv) presented in the abstract. The main term is derived from approximations to the von Kármán-Howarth equation that accounts for a balance between energy transfer across scales, vortex stretching and viscous diffusion. Expressions for $tm > \tau_K$ must be viewed as ad hoc but plausible. Dimensional considerations alone would suggest that $kL \propto \sqrt{\epsilon_t}$, where $tm$ may be interpreted as turnover time.

turbulence and mean advective terms. These mechanisms result in $\epsilon$ being underestimated when inferred from production and buoyancy terms alone. The fact that $kL \sim \epsilon^{1/4}$ also means that a factor of 2 adjustments to inferred $\epsilon$ translates to only a factor of 1.18 adjustment to $kL$. The choices made about $tm$ have been discussed at length for almost flat surfaces and small waves. For almost flat surfaces, the choice $tm = \tau_K$ (i.e., the Kolmogorov time scale) recovers prior results with the added foresight for the associated similarity constants. For the energetic-eddy hypothesis, the $tm = Re_1^{1/2} \tau_K$ also recovers the $\alpha$ dependency on Reynolds numbers for $Re_1 < 500$ supported by DNS and experiments. For wavy surfaces, the results derived here must be viewed with caution given that $tm$ may be much larger than $\tau_K$ and other constraints on eddy sizes beyond $r = 2(Dmtm)^{1/2}$ must be factored in. When extrapolating to such wavy surfaces, the quantity $(\epsilon tm^{1/2})$ was broadly interpreted as energy content in eddies of turnover duration $tm$ supplied by an energy rate $\epsilon$. The consistency between this outcome and prior formulations derived from detailed surface renewal schemes or other dynamical considerations (Csanady, 1990) certainly warrants further inquiry, a topic best left for future work.

4. Conclusion

The work here shows how multiple $kL$ expressions can be derived from a single expression (i.e., equation (16)). This equation is derived using the shape of the vertical velocity structure function for locally homogeneous and isotropic turbulence near the air-water interface. It shows that all five $kL$ expressions listed in the abstract are recovered by choosing an appropriate diffusion time scale and estimates of the TKE dissipation rate as summarized in Figure 2. In particular, when the diffusion time scale is set to the Kolmogorov time scale, $kL = \sqrt{2/15Sc^{-1/2}(ve)^{1/4}}$. In the presence of wavelets, the diffusion time $tm = C_m\nu/u_*$ and $kL = \sqrt{2/15Sc_0/10Sc^{-1/2}u_0}$, where $C_m = 0.4$ was determined from independent experiments. In the presence of long waves and when $tm$ scales with $u_* g$ as expected from Charnock’s equation, $kL \propto Sc^{-1/2} \sqrt{gy/u_*}$. The latter condition further requires a Keulegan number exceeding a critical value of 0.18 to ensure the generation of long surface waves. It is noted that while these results agree with prior surface renewal theories (Soloviev, 2007; Soloviev & Schlüssel, 1994), they emerge from the assumed shape of the vertical velocity structure function. Last, the effect of buoyancy is explicitly included and the limits associated with free convection recovered.

Appendix A: Linkage Between Eddy Size and the Batchelor Scale

The rational for selecting eddy size $r \approx 2l_B$ is presented, where $l_B = \sqrt{Dm/\tau_K}$ is the Batchelor scale, $\tau_K$ is the Kolmogorov microscale representing the turnover time of this eddy, and $Dm$ is the molecular diffusion...
coefficient. For this effective eddy of size $r$ to allow efficient mass exchange between the air-water interface and the bulk region, its size must span the thickness of the diffusive layer $\delta_D$ (i.e., $r \approx \delta_D$). Dimensional analysis presented in section 2 already suggested that $\delta_D \propto \sqrt{D_m \tau_c}$ or $\delta_D \approx r \propto l_B$. The premise here is that within the diffusive layer, mass transport over a turnover time period $\tau_c$ is primarily dominated by molecular diffusion. Dimensional analysis alone cannot provide the value of the proportionality constant. To do so requires an estimate of $\delta_D$ by other means such as the diffusion equation applied within the diffusive layer. The diffusive layer is bounded by the air-water interface characterized by concentration $C_s$ and a bulk region characterized by concentration $C_v$. Mass transport within the diffusive layer is governed by

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial z^2}, \quad (A1)$$

where $t$ is time and $z$ is depth from the air-water interface. This equation is subject to two boundary conditions:

$$C(t, 0) = C_s; C(t, z \to \infty) = C_v. \quad (A2)$$

Using the Boltzmann transform

$$\xi = \frac{z}{2 \sqrt{D_m t}}, \quad (A3)$$

reduces the diffusion equation into a second-order ordinary differential equation given by

$$-2\xi \frac{dC}{d\xi} = D_m \frac{d^2C}{d\xi^2}. \quad (A4)$$

Imposing the two boundary conditions yields

$$\frac{C(\xi) - C_s}{C_v - C_s} = \text{erf}(\xi), \quad (A5)$$

where the erf(.) is the error function. The diffusive distance $z$ that would have occurred over $t = \tau_c$ can be determined from

$$\frac{C(\xi) - C_s}{C_v - C_s} = \text{erf}\left(\frac{z}{2l_B}\right). \quad (A6)$$

If delineation of boundary layer thickness (i.e., $z = \delta_D$) is based on 90% attainment of relative concentration change, then

$$\text{erf}\left(\frac{\delta_D}{2l_B}\right) = 0.9, \quad (A7)$$

resulting in $r = \delta_D \approx 1.16(2l_B)$, which, for simplicity, was selected as $\delta_D = r = (2l_B)$ in the main text. It is to be noted that a 95% and a 99% attainment of bulk concentrations would have yielded $\delta_D \approx 1.36(2l_B)$ and $\delta_D \approx 1.82(2l_B)$. With these stricter definitions of boundary layer thickness, the similarity coefficient $\alpha$ in equation (2) increases to $\alpha = \sqrt{1.38 \times (2/15)} = 0.43$ and $\alpha = \sqrt{1.82 \times (2/15)} = 0.49$, respectively.

References


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