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Coupled renewal model of ocean viscous sublayer, thermal skin effect and interfacial gas transfer velocity

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Abstract

A previously developed renewal model included parameterizations for the thermal skin effect and interfacial gas transfer velocity. The more readily available cool skin data were used for an adjustment of the gas transfer parameterization. In this work, the renewal concept is extended to include the velocity difference across the viscous sublayer and to account for the stage of surface wave development. As a result, the empirical coefficients that enter the renewal model have been specified more accurately using laboratory data on the surface wind drift current. In addition, the coefficient linking the cool skin and gas transfer parameterization formulas has been determined from the probability distribution function for renewal events. A comparison of the upgraded renewal model with the thermal skin data collected during the *COARE* and more recent field programs and with gas transfer data collected during *GasEx-01* experiment suggests that the renewal model can be a useful tool for producing a physically based parameterization for the interfacial CO_2 transfer velocity. Model uncertainties associated with the effect of surface films are discussed.

Keywords: Air–water interface; Boundary layers; Surface properties; Air–water exchanges

1. Introduction

In renewal models, the properties of molecular sublayers depend on the surface *renewal time*. The renewal time is then related to the environmental parameters controlling the properties of molecular sublayers.

The renewal model infers an intermittent transport of properties across the aqueous surface molecular sublayers. Howard (1966) formulated a phenomenological theory of free convection at large Rayleigh numbers, which represented the convection as a cyclic process: The thermal boundary layer forms by diffusion, grows until it is thick enough to develop convective instability, and is destroyed by convection, which in turn dies down once the boundary layer is destroyed. Then the cycle begins again. In a series of laboratory experiments Kim et al. (1971) found that the turbulent momentum transport and production in a sheared wall layer in the regime of forced convection also take place intermittently in time and space through small-scale bursting motions.

The first application of the renewal concept for modeling the cool skin of the ocean belongs to Liu and Businger (1975) who developed a method for calculation of average temperature profiles in molecular sublayers by assuming that the sublayers undergo cyclic growth and subsequent destruction. Their model, however, contained an unrealistic probability distribution function for the regime of forced convection. Kudryavtsev and

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Luchnik (1979) refined the renewal concept by introducing a more realistic probability distribution function for the regime of forced convection. Kudrayvtsev and Soloviev (1985) quantified the transition from free to forced convection in the cool skin by introducing the *surface Richardson number* Rf_0. Later, Soloviev and Schlüssel (1994) introduced an additional determining parameter, the *Keulegan number* (*Ke*), which effectively extended the renewal model to higher wind speeds. These authors also developed a coupled parameterization for the temperature difference across the cool skin of the ocean and for the air–sea gas transfer velocity. The more readily available cool skin data were then used for an adjustment of the gas transfer parameterization. Extensions of the renewal model included the effects of solar radiation (Soloviev and Schlüssel, 1996) and rainfall (Schlüssel et al., 1997).

The model constants in Soloviev and Schlüssel (1994) were estimated using the observational data available at that time. More accurate data on the surface wind drift current and ocean thermal skin effect has become available since the time of that publication.

In this paper the renewal concept is further extended to include the current velocity difference across the viscous sublayer and to account for the stage of the surface wave development. This helps to specify more accurately the empirical constants that enter the renewal model using the results of recent laboratory studies. The upgraded renewal model then appears to be in a reasonable agreement with the gas exchange results over the ocean.

The paper is organized as follows. Section 2 describes the development of a coupled renewal model for velocity difference across the aqueous viscous sublayer, thermal skin effect, and interfacial gas transfer velocity. In Section 3 the coupled renewal model is validated with the laboratory data on viscous sublayer and field data on the thermal skin effect and gas transfer velocity. Section 4 is the discussion of the applicability of the renewal model for parameterizing the air–sea CO_2 exchange. Section 5 is a summary of the results and conclusions.

2. Coupled renewal model

A surface renewal model tracks a fluid element adjacent to the sea surface. At an initial moment fluid element has uniform properties, which are equal to the corresponding bulk-water values. As the fluid element is exposed to the interface, molecular diffusion processes modify its properties. Under assumption of horizontal homogeneity, no insolation and no rain, one-dimensional molecular diffusion laws for the tangential component of velocity u, temperature T, and the gas concentration C are as follows (Soloviev and Lukas, 2006):

$$\frac{\partial u}{\partial t}=\frac{\partial}{\partial z}\left(\nu\frac{\partial u}{\partial z}\right), \quad (1)$$

$$\frac{\partial T}{\partial t}=\frac{\partial}{\partial z}\left(\kappa_T\frac{\partial T}{\partial z}\right), \quad (2)$$

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial z}\left(\mu\frac{\partial C}{\partial z}\right), \quad (3)$$

where ν, κ_T, and μ are the molecular kinematic viscosity and thermal and gas diffusivity, respectively, and vertical coordinate z (directed upwards) is related to the instantaneous position of the sea surface.

Error-function solutions of Eqs. (1)–(3) lead to the following formulas for the velocity and temperature differences and for the interfacial component of the gas flux (G_i):

$$\Delta u(t)=2\pi^{-1/2}(t/\nu)^{1/2}\tau_t/\rho, \quad (4)$$

$$\Delta T(t)=-2\pi^{-1/2}(t/\kappa)^{1/2}Q_0/(c_p\rho), \quad (5)$$

$$G_i(t)=\pi^{-1/2}(t/\mu)^{-1/2}\Delta C, \quad (6)$$

where $\Delta u(t)=u_0(t)-u_w$, $\Delta T(t)=T_0(t)-T_w$, $\Delta C=C_w-C_0$; C is the effective gas concentration; τ_t is the tangential component of the wind stress, Q_0 is the surface heat flux, c_p and ρ are the specific heat capacity and density of water; ν, κ_T, and μ are molecular coefficients of kinematic viscosity, thermal and gas diffusivity; t is the elapsed time. $\pi=3.14$; indices 0 and w denote surface and bulk-water values, respectively;

In Eqs. (4)–(5) the evolutions of the velocity and temperature differences are considered under conditions of constant tangential stress τ_t and constant surface heat flux Q_0. The latter is a sum of net longwave irradiance I_L, sensible Q_T heat flux, and latent Q_E heat flux. (No solar radiation effects are considered in this paper.)

Wind-induced surface current constitutes only a tiny part of the total velocity difference between air and sea (about 2%). The condition of constant momentum flux rather than constant velocity difference is therefore appropriate in Eq. (4).

The dependence of the net longwave irradiance I_L and latent heat flux Q_E on the temperature difference due to the cool skin is typically within several % (Paulson and Simpson, 1981). Only Q_T may appreciably depend on the thermal skin effects. Usually, $|I_L+Q_E|\gg|Q_T|$, which means that the net surface flux Q_0 does not depend strongly on the cool skin presence. As a result, the condition of constant heat flux is justified in Eq. (5).

The condition of constant concentration difference accepted in Eq. (6) is appropriate for water-side limited gases (like CO_2, Rn, SF_6, He). The aqueous diffusion sublayer provides the main resistance to the gas transfer and thereby contains the main gas concentration difference across the air–sea interface.

Following the approach of Kudryavtsev and Luchnik (1979), the average velocity and temperature difference across the aqueous viscous and thermal sublayers and the average surface gas flux at the air–sea interface are defined as follows:

$$\overline{\Delta u} = \int_0^\infty p(t)t^{-1}\left(\int_0^t \Delta u(t')\mathrm{d}t'\right)\mathrm{d}t, \tag{7}$$

$$\overline{\Delta T} = \int_0^\infty p(t)t^{-1}\left(\int_0^t \Delta T(t')\mathrm{d}t'\right)\mathrm{d}t, \tag{8}$$

$$\overline{G_i} = \int_0^\infty p(t)t^{-1}\left(\int_0^t G_i(t')\mathrm{d}t'\right)\mathrm{d}t, \tag{9}$$

where $p(t)$ is the probability density for time periods t of bursting motions below the sea surface. This is the probability of local destruction of the molecular sublayers in a time interval (t, t+dt), where t is the elapsed time since the previous destruction.

Rao et al. (1971) and Garbe et al. (2002) found that the time between bursts is distributed according to a lognormal law. The probability density for such a process is given by

$$p(t) = \pi^{-1/2}(\sigma_i t)^{-1}\exp[-(\ln t - m)^2/\sigma^2], t > 0. \tag{10}$$

where m is the mean value and σ^2 is the variance for the logarithm of the random variable t. With probability density (10) integrals on the right side of Eqs (7)–(9) lead to the following relations:

$$\overline{\Delta u} = (4\pi^{-1/2}/3)\exp(-\sigma^2/16)(t_*/v)^{1/2}\tau_t/\rho, \tag{11}$$

$$\overline{\Delta T} = -(4\pi^{-1/2}/3)\exp(-\sigma^2/16)(t_*/\kappa_T)^{1/2}Q_0/(c_p\rho), \tag{12}$$

$$K_i = 2\pi^{-1/2}\exp(3\sigma^2/16)(t_*/\mu)^{-1/2}, \tag{13}$$

where K_i is the interfacial gas transfer velocity (piston velocity) defined as $K_i = \overline{G_i}/\Delta C$, and $t_* = \exp(m+\sigma^2/4)$ is the average time between bursts, which has been referred to as the renewal time. This implies that bursting events affect the viscous, thermal, and diffusion molecular sublayers in the same manner, and the quantities m and σ^2 in Eqs. (11)–(13) are the same.

The renewal time is defined with the formula proposed by Soloviev and Schlüssel (1996):

$$t_* = \frac{9_i\pi_i v}{16u_*^2}\exp(\sigma^2/8)\Lambda_0^2(1-a_0^3\Lambda_0^4 Rf_0)^{-1/2} \times (1+Ke/Ke_{\mathrm{cr}}), \tag{14}$$

where the surface Richardson number Rf_0 and the Keulegan number Ke are

$$Rf_0 = \frac{\alpha_T g_i v}{c_p \rho u_*^4}\left(Q_E + Q_T + I_L + \frac{\beta_S S_0 c_p}{\alpha_T L}Q_E\right), \tag{15}$$

$$Ke = u_*^3/(g_i v), \tag{16}$$

and Λ_0, a_0, and Ke_{cr} are dimensionless constants; S_0 is the sea surface salinity; α_T and β_S are the coefficients of thermal expansion and saline contraction. The friction velocity in water u_* is defined via the total wind stress τ_0 as follows: $u_* = (\tau_0/\rho)^{1/2}$.

The surface Richardson number (Rf_0) proposed by Kudrayvtsev and Soloviev (1985) is the surface asymptote of the flux Richardson number, which is a criterion for the transition from free to forced convection; while, the Keulegan number (Ke) defined by Csanady (1978) is a criterion for the transition to large-scale wave breaking. (See Soloviev and Schlüssel, 1994 for more details.)

An interpretation of the Ke-number dependence in Eq. (14) is that under high wind-speed conditions the tangential stress τ_t relates to the total wind stress τ_0 according to the following formula (Soloviev and Schlüssel, 1996):

$$\tau_t = \tau_0(1 + Ke/Ke_{\mathrm{cr}})^{-1}. \tag{17}$$

where Ke_{cr} is the critical value of the Keulegan number.

Inserting the renewal time formulation (14) into (11)–(13) and taking into account Eq. (17) and the definition of the friction velocity $u_* = (\tau_0/\rho)^{1/2}$ leads to the following coupled set of parametric formulas:

$$\Delta\bar{u}/u_* = \Lambda_0(1-a_0^3\Lambda_0^4 Rf_0)^{-1/4}, \tag{18}$$

$$\Delta\overline{T}/T_* = -\Lambda_0 Pr^{1/2}(1-a_0^3\Lambda_0^4 Rf_0)^{-1/4} \times (1+Ke/Ke_{\mathrm{cr}})^{1/2}, \tag{19}$$

$$K_\mu/u_* = \Lambda_0\Lambda_0^{-1}\mathrm{Sc}^{-1/2}(1-a_0^3\Lambda_0^4 Rf_0)^{1/4} \times t(1+Ke/Ke_{\mathrm{cr}})^{-1/2}, \tag{20}$$

Table 1
Parameter σ from the laboratory results of Garbe et al. (2002) and the computation of coefficient A_0

Wind speed, m s^{-1}	σ	A_0
2.0	1.39	1.08
4.2	0.8	0.92
8.0	0.7	0.89

where $T_* = Q_0/(c_p \rho u_*)$, $Pr = \nu/\kappa_T$, and $\mathrm{Sc} = \nu/\mu$, and dimensionless coefficient A_0 is expressed through parameter σ of lognormal distribution (14) as

$$A_0 = (8\pi^{-1}/3)\exp(\sigma^2/8). \tag{21}$$

Calculation of A_0 according to Eq. (21) with σ determined from the Garbe et al. (2002) laboratory experiment is presented in Table 1. The numeric value of A_0 appears to be close to unity and only slightly changing with wind speed. Taking, for certainty, $\sigma = 0.8$, the estimate further used in this paper, will be: $A_0 = 0.92$.

Zhao and Toba (2001) proposed a parameter $R_B = u_{*a}^2/(\nu_a \omega_p)$ with a critical value of $R_B = 10^3$ for the onset of wind–wave breaking. Parameter R_B can be rewritten as

$$R_B = A_w u_*^3/(g\nu_a), \tag{22}$$

where A_w is the wave age defined as $A_w = g/(\omega_p u_{*a})$, ω_p is the peak angular frequency of wind waves, u_{*a} is the friction velocity in the air. The Keulegan number thus appears to be connected to the Zhao and Toba (2001) nondimensional parameter R_B:

$$Ke = \frac{u_*^3}{g_i \nu} = \frac{u_{*a}^3 \beta}{g \nu_a}\frac{\nu_a}{\nu}\left(\frac{\rho_a}{\rho}\right)^{3/2}\frac{1}{A_w} = R_B \frac{\nu_a}{\nu}\left(\frac{\rho_a}{\rho}\right)^{3/2}\frac{1}{A_w}. \tag{23}$$

A tentative estimate of $Ke_{cr} \approx 0.18$ was derived by Soloviev and Schlüssel (1994) from indirect data—the critical wind speed, $U_{10} \approx 10$ m s^{-1}, at which, according to the visual Beaufort scale, long-wave breaking sets in. From Eq. (23), it follows that critical value $R_B = 10^3$ corresponds to $Ke_{cr} = 0.18$ at wave age $A_w = 3.25$, which corresponds to an early stage of wave development.

Numeric values of the model constants, Λ_0 and a_0, entering formulas (18)–(20) are determined from comparison with relevant laboratory data in the next section.

3. Comparison with laboratory data

It is remarkable that according to Eq. (18) the dimensionless ratio $\overline{\Delta u}/u_*$ does not depend on the Keulegan number, which means that constant Λ_0 can conveniently be estimated from the experimental data on the surface wind drift current. The ratio, $\overline{\Delta u}/u_*$, is closely related to the so-called wind drift coefficient, u_0/U_{10}, where u_0 is the averaged current velocity at the sea surface relative to the background ocean current, and U_{10} is the wind speed at 10 m height. The current velocity at the sea surface includes the Stokes drift, which is relatively small (between 5 and 20% of the wind drift current). The difference between the current velocity at the sea surface u_0 and the Stokes surface drift u_S is the wind-induced surface drift:

$$u_{wd} = u_0 - u_S. \tag{24}$$

The ratio between wind-induced surface drift u_{wd} and water friction velocity u_* as measured by Wu (1975) with surface drifters varied between 11 and 20. Wu (1975) concluded that $\langle u_{wd}/u_* \rangle \approx 17.0$ and has no obvious systematic dependence upon friction velocity. Phillips and Banner (1974) laboratory experiment indicated that $\langle u_{wd}/u_* \rangle \approx 16.1$. Techniques involving surface drifters have, however, been found to introduce a bias in the surface velocity measurements (Zhang and Harrison, 2004).

Values of u_{wd}/u_* derived from particle image velocimetry and from infrared imaging also demonstrate no obvious dependence on the friction velocity but consistently indicate smaller surface drift currents than those derived from drifter measurements (Zhang and Harrison, 2004). The wind-induced velocities derived from the infrared images and surface drifters are shown in

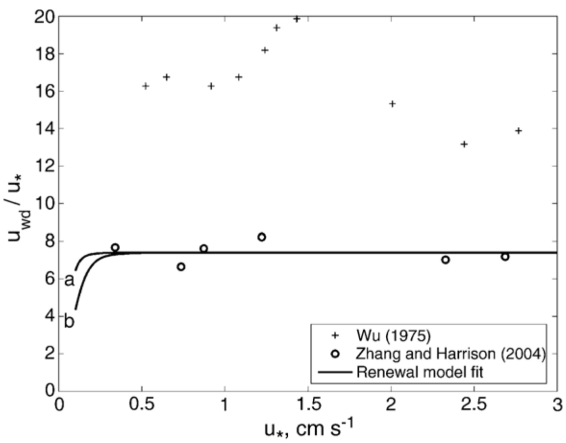

Fig. 1. Nondimensional wind-induced surface current in the laboratory tank as a function of wind friction velocity derived from surface drifters (Wu, 1975) and infrared imaging (Zhang and Harrison, 2004) in comparison with the renewal model at $\Lambda_0 = 7.4$ for two surface cooling rates: (a) $Q_0 = 20$ W m^{-2}, and (b) $Q_0 = 200$ W m^{-2}.

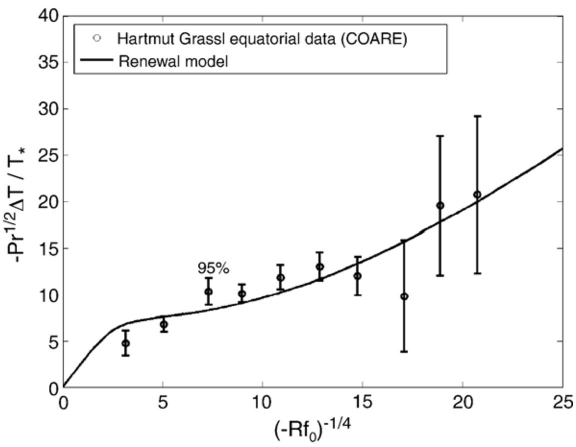

Fig. 2. Nighttime cool skin data of Hartmut Grassl obtained in the western equatorial Pacific during COARE in comparison with renewal model for developed seas ($A_w = 15$).

Fig. 1. Discarding the drifter measurements and averaging over all friction velocities results in $\langle u_{wd}/u_* \rangle \approx 7.4$. Based on these laboratory results we accept an estimate $\Lambda_0 \approx 7.4$. This is in fact an upper estimate, because it does not take into account the existence of relatively small current velocity difference across the turbulent layer (*i.e.*, below the viscous sublayer).

Model constant Λ_0 is linked to the coefficient λ that was historically introduced by Saunders (1967) in the following way:

$$\lambda = Pr^{-1/2}\Lambda_0. \tag{25}$$

From the determination of $\Lambda_0 \approx 7.4$ and Prandtl number $Pr \approx 7.5$ (at atmospheric pressure, 20 °C temperature, and 35 psu salinity), from relation (25) it follows that $\lambda \approx 2.7$, which is much lower than previously accepted values but close enough to the direct measurement of the cool skin by a micro-wire sensor (Ward and Donelan, 2006).

A fit of parameterization (18) at $\Lambda_0 \approx 7.4$ to the results of the Zhang and Harrison (2004) is shown in Fig. 1. Note that in Eq. (18) the term $(1 - a_0^3 \Lambda_0^4 Rf_0)^{-1/4}$ relating to buoyancy effects is of importance under low wind-speed conditions only. Fig. 1 shows parameterization (18) for two values of the net surface heat flux Q_0.

The low wind-speed asymptote for Eq. (19) is $\overline{\Delta T} = -a_0^{3/4}\left(\frac{\nu}{-\alpha_T g \kappa_T^2}\right)^{1/4}\left(\frac{Q_0}{c_p \rho}\right)^{3/4}$, which coincides with the Katsaros et al. (1977) formula obtained for calm weather conditions. The commonly accepted estimate following from laboratory experiments with free convection is $a_0 = 0.25$ (Fedorov and Ginzburg, 1988).

Nondimensional constants a_0 and Λ_0 are related to the critical surface Richardson number Rf_{cr} introduced by Soloviev and Schlüssel (1994) in the following way: $Rf_{cr} = -a_0^{-3}\Lambda_0^{-4}$. For $a_0 = 0.25$ and $\Lambda_0 \approx 7.4$, this results in $Rf_{cr} = -2 \times 10^{-2}$, which is different from $Rf_{cr} = -1.5 \times 10^{-4}$ used in Soloviev and Schlüssel (1994). This difference is explained by a stronger contribution of the *Ke*-number dependence under moderate wind-speed conditions when defined with formula (23) and Zhao and Toba (2001) results.

4. Validation with cool skin data

During COARE Hartmut Grassl collected substantial statistics on the temperature difference across the cool skin in the western equatorial Pacific. Fig. 2 shows parameterization (19) plotted for $a_0 = 0.25$, $\Lambda_0 \approx 7.4$, and $A_w = 15$ in comparison with the COARE data set. The wave age of $A_w = 15$ corresponds to developed wind waves, which are often observed in the open ocean. There is a reasonable agreement between the COARE data and this renewal type parameterization.

Fig. 3a shows the data set collected in the western tropical and subtropical Pacific from the R/V *Mirai* with

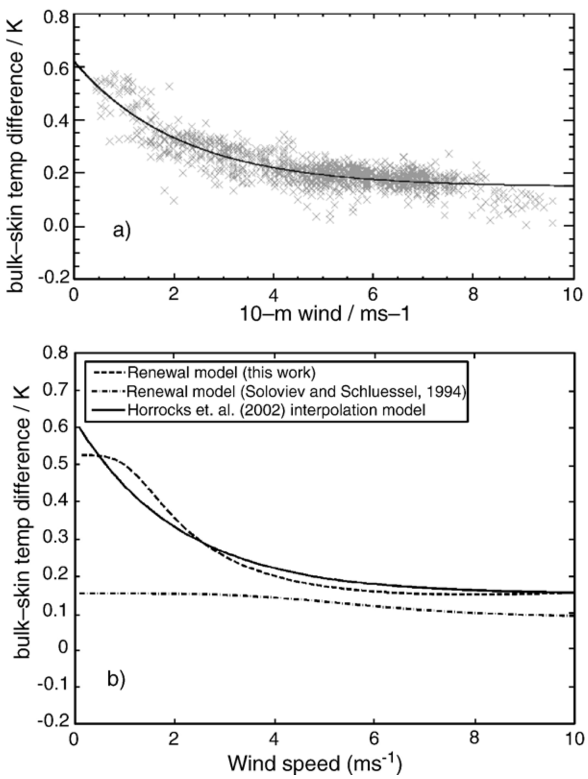

Fig. 3. (a) Nighttime bulk minus skin SST difference plotted against measured wind speeds during the R/V *Mirai* cruise (Horrocks et al., 2002). The curve is the best fit to empirical formula (26). (b) Three different models of the cools skin.

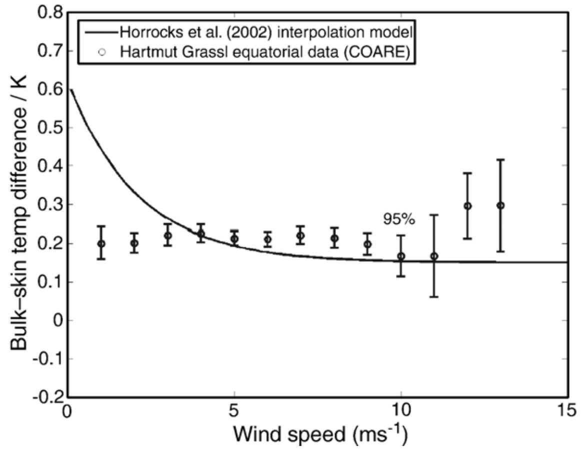

Fig. 4. Nighttime bulk minus skin SST difference plotted against measured wind speeds during the COARE campaign by Hartmut Grassl cruise in comparison with empirical formula (26).

a scanning infrared sea surface temperature radiometer SISTeR (Horrocks et al., 2002). In Fig. 3a this data set is fitted with an empirical formula

$$\Delta T = a + b\exp(-U_{10}/U_0), \tag{26}$$

which was originally proposed by Craig Donlon, Here, ΔT is the bulk minus surface temperature difference, U_{10} is the wind speed at 10 m height, and a, b, and U_0 were found by Horrocks et al. (2002) to have values of 0.15, 0.47, and 2.1 respectively. There is a good agreement between this empirical parameterization and the R/V *Mirai* data.

Fig. 3b compares three parameterizations of the thermal skin effect: 1) empirical formula (26); 2) the original renewal model with the empirical constants specified by Soloviev and Schlüssel (1994); 3) the renewal model (19) with the empirical constants specified in this work. In describing the R/V *Mirai* data set, both Eqs (26) and (19) apparently have reasonably good performance, while the original model of Soloviev and Schlüssel (1994) deviates appreciably from this data set.

In a companion paper Donlon et al. (2002) analyzed the data from six cruises obtained in the tropical and subtropical regions of the Pacific and Atlantic Oceans including the data shown in Fig. 3a. They found good correlation between parametric formula (26) and observations for wind speed above 3 m s^{-1}, though with somewhat bigger scatter than in the subset shown Fig. 3a.

Performance of formula (26) at wind speeds below 3 m s^{-1} is less certain. In fact, parameterization (26) when compared to the COARE data set of Hartmut Grassl (Fig. 4) shows significant deviation at wind speeds below 3 m s^{-1}. This difference is not surprising, because after all formula (26) is purely empirical and has a little chance to be universally applicable.

Models based on the essential physics of the air–sea interface (*e.g.*, renewal and boundary layer models) have a better chance to describe diverse ocean environments. In particular, renewal type parameterization (19), which is an upgraded version of the original model of Soloviev and Schlüssel (1994), agrees reasonably well with both the R/V *Mirai* and the COARE data sets.

5. Implications for gas transfer parameterization

Fig. 5a compares results of direct, eddy-correlation measurements of the CO_2 air–sea flux during *GasEx-01* with renewal model (20). The bubble-mediated contribution to the gas transfer velocity for CO_2 according to

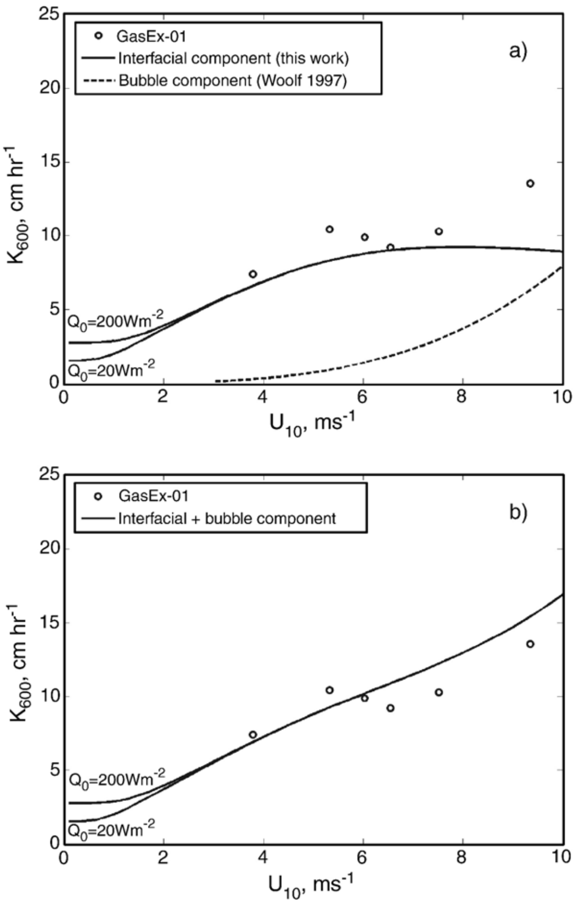

Fig. 5. (a) Comparison of the renewal type (interfacial) parameterization (20) for 2 values of the surface heat flux Q_0 with direct measurements of the CO_2 transfer velocity during *GasEx-2001* (Hare et al., 2004). Woolf's (1997) parameterization of the bubble-mediated component for clean bubbles is shown with a dashed line. (b) Sum of the interfacial and bubble mediated parameterizations in comparison with the *GasEx-2001* data.

the model of Woolf (1997) is also shown. The resultant curve demonstrated in Fig. 5b suggests a good agreement between model and observations encouraging further exploration of the applicability of the renewal model for parameterization of the air–sea gas exchange.

Fig. 6 shows a summary of gas transfer results over the ocean. The theoretical dependencies correspond to the sum of an interfacial component (renewal model (20) and the Woolf (1997) bubble-mediated component.

Both theoretical relationships and field data are color-coded. Blue color indicates low solubility gases (SF_6 and ^3He); red color indicates higher solubility gases (Rn and CO_2). Under high wind-speed conditions, theoretical curves for different gases deviate but appear to be consistent with the available data.

The possibility of coupling the parameterizations for viscous, thermal, and diffusion sublayers is based on the idea that they all are governed by similar laws. The more readily available surface wind drift and cool skin data are then used for an adjustment of the gas transfer parameterization. A difference between the interfacial gas and heat transfer has been observed in the laboratory experiment of Atmane et al. (2004). This difference has been ascribed to the effect of surface films, which is most pronounced at low wind speeds.

The Atmane et al. (2004) experiment was, however, solely based on the controlled heat flux method for estimating gas transfer velocity. According to the laboratory test of Richardson et al. (2000), this indirect method can in fact exhibit significant differences between the heat and gas exchange data. At the same time, the version of this method developed by the same team of investigators (Garbe et al., 2002) but employing the properties of the "natural" cool skin on the ocean surface does not seem to reveal appreciable difference in the process of the interfacial gas and heat exchange.

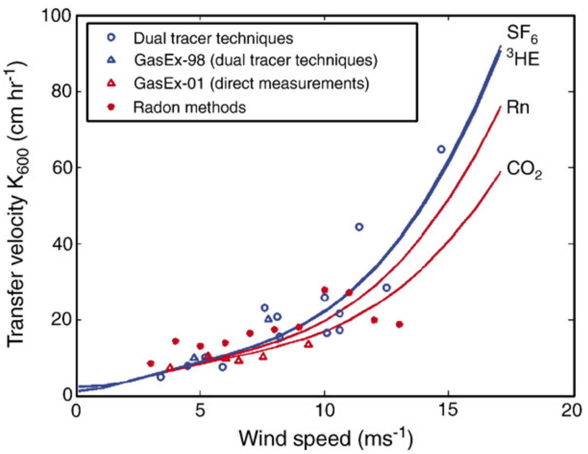

Fig. 6. Renewal model in comparison with the gas transfer results over the ocean using the dual tracer and radon techniques as well as direct measurements. The continuous lines are the theoretical relationships for the gases involved in the corresponding measurement techniques (SF_6 and ^3He, Rn). The theoretical dependence for CO_2 is also shown. The dual tracer data are from Wanninkhof et al. (1997), Asher and Wanninkhof (1998), and Nightingale et al. (2000). The radon data are from Peng et al. (1974, 1979), and Cember (1989). The *GasEx-98* data are from Wanninkhof and McGillis (1999), and the *GasEx-01* data are from Hare et al. (2004).

The effect of surface films of the air–sea exchange processes, which is primarily important under low wind-speed conditions, is far from complete understanding (Frew, 1997). At this point, there is no sufficient data to address adequately this issue. If future experiments will reveal significant differences in the effect of surface films on the different types of molecular sublayers, then parameterizations (18)–(20) will need to be decoupled in their low wind-speed portions. This would require the introduction of an additional parameter, possibly including a Schmidt and Prandtl number dependence similar to that proposed by Asher et al. (2005).

6. Conclusions

Since the publication of the Soloviev and Schlüssel (1994) renewal model, new laboratory and experimental data have been emerging. Including the viscous sublayer component into the renewal model has extended the scope of experimental data available for the model validation, which has resulted in a better specification of model constant Λ_0. Specification of the critical surface Richardson number Rf_{cr} via a free-convection constant a_0 has resulted in a better description of various cool skin data sets. In addition, linking the critical Keulegan number Ke_{cr} to the Zhao and Toba (2001) threshold on whitecapping has provided an avenue for incorporating the wave age parameter into the renewal model. After updating the values of constants the renewal model is now in reasonably good agreement with recent data from three different types of the aqueous molecular sublayer. It is worth to stress that the data used to determine values of model parameters are independent of those used to test the model.

Finally, the comparison of the renewal model with the cool skin data collected by Hartmut Grassl during the COARE field campaign and by Tim Nightingale during the R/V *Mirai* cruise (Horrocks et al., 2002) and gas transfer data collected during gas exchange experiments (Wanninkhof and McGillis, 1999; Hare et al., 2004) suggests that the renewal model can be a useful tool for producing a physically based parameterization of the thermal skin effects and the interfacial component of gas transfer velocity. In particular, the analysis shown in

Fig. 6 can offer an explanation of the difference between the Wanninkhof (1992) and Liss and Merlivat (1986) empirical parameterizations for gas transfer velocity. The former was derived from dual-tracer data (using low solubility gases SF_6 and ^3He), while the latter was derived from a laboratory experiment with a better soluble gas (CO_2).

A competing, physically based model is the *boundary layer* model, which does not explicitly include intermittency of exchange processes near the surface. Instead, it identifies the connection between the interfacial gas transfer velocity and the dissipation of the turbulent kinetic energy directly (Kitaigorodskii and Donelan, 1984; Soloviev et al., 2007-this issue) or indirectly via the Kolmogorov's internal scale of turbulence (Wick et al., 1996; Fairall et al., 2000; Hare et al., 2004). Though each approach has its own advantages and disadvantages, both have been fruitful. Moreover, they have been "cross-pollinating" each other. In particular, the boundary layer models have accepted the surface Richardson number as a determining parameter, which was first introduced in the renewal model. At the same time the renewal model has replaced constant Rf_{cr} with parameter a_0, which was first introduced in the boundary layer model. Furthermore, since these two types of models are based on equivalent physical principles of the boundary layer turbulence, they should lead to quite similar final parameterizations.

A potential advantage of physically based versus empirical parameterizations is that the former can potentially provide global coverage, while the latter will require adjustment of their empirical coefficients for specific climatic regions, seasons, and, perhaps, even for single weather events. At the same time it is still a long way for producing robust parameterization scheme for air–sea gas exchange providing global coverage (*i.e.*, consistent with remote sensing methods). The main uncertainties are in the effect of surface films and bubbles on the air–sea exchanges.

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