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Gas exchange across the air–sea interface

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ABSTRACT

The physics of gas exchange at the air–sea interface are reviewed. In order to describe the transfer of gases in the liquid near the boundary, a molecular plus eddy diffusivity concept is used, which has been found useful for smooth flow over solid surfaces. From consideration of the boundary conditions a similar dependence of eddy diffusivity on distance from the interface can be derived for the flow beneath a gas/liquid interface, at least in the absence of waves. The influence of waves is then discussed. It is evident from scale considerations that the effect of gravity waves is small. It is known from wind tunnel work that capillary waves enhance gas transfer considerably. The existing hypotheses are apparently not sufficient to explain the observations. Examination of field data is even more frustrating since the data do not show the expected increase of gas exchange with wind speed.

1. Introduction

Hitherto the transport of gases to and from the oceans via the atmosphere has been mainly inferred from global source strength estimates, so that the calculated fluxes are subject to considerable uncertainty.

Alternatively, transfer of any gas across the air–sea interface can be estimated from the product of its concentration difference across the interface and an appropriate transfer velocity. Such calculations would be greatly improved if the transfer velocity could be related to the existing wealth of meteorological data. However, before this can be done, a better understanding of the processes at the interface is necessary.

The ocean and atmosphere are considered as a coupled system in which gas fluxes pass, on average, continuously through the interface. The layers adjacent to the interface are viewed as regions of molecular transport (viscous sublayer). For gases with high solubility and/or rapid chemical reactivity in the aqueous phase (e.g. H_2O, SO_2, NH_3) the main resistance to transfer is in the gas phase, while for most other gases (e.g. O_2, N_2, CO_2) the main resistance is in the liquid phase. For simplicity of discussion, we will consider only the latter case.

The model concepts are taken either from fluid dynamics of flows above a solid surface or from physical chemistry. They are commonly known as:

(i) film model, i.e. a layer of molecular transport at the interface, bordering on the bulk fluid side with a region of fully turbulent transport (Whitman, 1923), or more refined, with a smooth transition from molecular to turbulent transport, reviewed by Deacon (1977), or
(ii) surface renewal model, where the fluid, which is at rest at the interface, is removed into the bulk at random intervals (Higbie, 1935; Danckwerts, 1951).

The surface renewal model is probably applicable to the case of little mechanical mixing but unstable stratification, e.g. by cooling of the sea surface due to evaporation and radiation under conditions of vanishing wind speed and low insolation. The film model or notion of a viscous

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sublayer is based on measurements of flow above a flat solid surface, where addition of molecular plus turbulent transport gives a good description. This description has also been used to describe the heat flow through the interfacial layer of the ocean (Hasse, 1971).

Caution has often been voiced, since in order to use the latter theory inferences from the theory of flow over a smooth, solid, flat plate must be made for the flow at the moving sea surface, especially for application in the liquid phase, since in this case the fluid borders the atmosphere, a gas with a factor of 10^{-3} smaller density. Therefore, the boundary conditions at a fluid interface are discussed in the next section as well as their consequences for turbulent transport near the interface. In Section 3 effects of waves on gas transfer are discussed. In Section 4 recent field observations of gas transfer across the air–sea interface are compared with predictions from model considerations.

2. Boundary conditions and model considerations

2.1. *The model*

Models like those employing the film or surface renewal concepts are macroscopic descriptions, which account for the microphysical process of turbulence only in a bulk sense. In the following, a molecular plus eddy diffusivity approach is used. The boundary conditions are used to obtain the variation of eddy diffusivity with distance from the interface—the eddy diffusivity decreasing as the interface is approached. This does not mean that there is really a layer of purely molecular transport but rather that the eddies are rare and contribute little to the total transport. The model is evidently a steady-state model. The effects of surface waves have to be considered separately (see Section 3).

Reichardt (1951) investigated aerodynamically smooth flow of a fluid above a solid, flat surface and obtained a good description of the flow profile by assuming that the effective viscosity ν_{eff} is given by the sum of molecular (ν) plus turbulent (K_t) viscosity,

$$\nu_{\text{eff}} = \nu + K_t.$$

Invoking considerations of continuity, he found that the eddy diffusivity should vary with the third (or even higher) power of z, where z is the distance from the wall. Monin and Yaglom (1965) obtained a related result for the flow profile also at a smooth solid, flat wall. For large distances from the wall, $K_t = u_* kz$ after Prandtl (with k von Karman's constant). Thus according to Reichardt (1951)

$$\nu_{\text{eff}} = \nu + k\nu\left(z^+ - z_1 \tanh \frac{z^+}{z_1}\right)$$

where $z^+ = zu_*/\nu$; u_* is the friction velocity in the fluid; $z_1 = 11$ is an empirical constant determined by Reichardt to fit the velocity profile. This formulation can be used for other properties if the molecular viscosity is replaced by the appropriate molecular diffusivity (D) and if it is assumed that the turbulent transfer is independent of the property exchanged. (If this is not the case, a turbulent Schmidt number would have to be included in front of the von Karman constant k in the following equation.) Then

$$D_{\text{eff}} = D + k\nu\left(z^+ - z_1 \tanh \frac{z^+}{z_1}\right).$$

Calculation of transfer velocities is then straightforward (see Deacon, 1977 and Hasse, 1971). This is similar to the film model, but avoids the unrealistic notion of a purely viscous layer near a fully turbulent layer and the necessity of having different thicknesses for the diffusive sublayer depending on the molecular diffusivity of the property.

It should be noted that this model does not have an adjustable constant. The only empirical constant ($z_1 = 11$) was determined from flow above smooth solid surfaces in wind tunnels and is used unchanged for transport of both heat and gases at sea.

2.2. *Boundary conditions and eddy diffusivity*

While Reichardt's model was originally developed for aerodynamically smooth flow of a fluid at a fixed, flat wall, it is now applied to the flow at a liquid–gas interface, i.e. to a free surface. Intuitively, it seems that the smooth flow model is more likely to apply to the viscous sublayer in the air above the water than to the water at the air–water interface, since the air, due to its low density, will not appear as a fixed wall to the water.

Yet the assumption of a sublayer of molecular transport in the water has been successfully employed in the case of the similar problem of heat flux through the sea surface (Hasse, 1971) for open sea conditions. This was made plausible by the consideration that the turbulent movements of the fluid near the interface will be similar to the movements at a fixed wall, since the boundary conditions are the same, i.e. fluid elements may not penetrate the interface. One point in the argument was found difficult to understand, namely—if capillary waves can disturb the surface against surface tension, why can't the turbulence of the water do the same? The main difference is that a fluid particle in turbulent motion perpendicular to the interface has to take the energy necessary to deform the surface against surface tension from its own kinetic energy. However, in the case of capillary waves there is a periodic exchange between the kinetic energy of ordered wave motion and the work against surface tension. The kinetic energy was originally provided over a relatively long period of time from turbulent motions in the atmosphere and/or from instabilities in the larger waves, both of which provide a much larger reservoir than that available to an individual turbulent motion. Therefore, turbulent motions perpendicular to the interface are restricted, as they are at a fixed wall.

Although this argument is reasonable, the implications for the transport processes near and at the interface are not that straightforward due to the presence of waves. We will therefore consider first conditions at a liquid–gas interface without waves.

In this section we advance the idea that the boundary conditions in the liquid at a liquid–gas (water–air) interface without waves are similar to those for a fluid at a solid surface. The main argument is that eddy motions perpendicular to the interface are zero at the interface due to surface tension. To have a fluid particle with a nonzero normal component of motion at the interface, we would have to create new surface. The energy for this—in the absence of other forces—could come only from the kinetic energy of the fluid particle. It can be shown from simple calculations, that the energy necessary to create new surface is several orders of magnitude larger than the turbulent kinetic energy available at the interface.

We envisage a fluid particle (of characteristic length r) moving with turbulent motion towards the interface. It is assumed that r is of the order of the viscous boundary layer thickness or smaller, since we are dealing with turbulent motions of fluid particles within the vicous boundary layer. Hence

$$r \sim 5\nu/u_*.$$

In order for the boundary conditions to be different from those at a solid surface, it is sufficient for the fluid particle to be able to deform the surface locally. For the order-of-magnitude calculation, we require the whole mass of the fluid particle to move just outside of the original boundary, but still having a coherent surface with the main fluid (Fig. 1). The increase of surface area relative to the volume of the fluid is then of order $3/r$, and depends only marginally on the actual geometry. The kinetic energy of turbulent motion perpendicular to the surface per unit volume can be assumed to be proportional to $\rho_w u_{*w}^2$ (where ρ is density; the index w indicates variables in the liquid). Hence the ratio η of the work used to increase the surface area to the kinetic energy of the fluid particles is

$$\eta = \frac{T\,\Delta\,\text{area}}{\rho_w u_{*w}^2\,\text{volume}} = \frac{T}{\rho_w u_{*w}^2}\,\frac{3}{r} = \frac{3}{5}\,\frac{T}{\rho_w \nu u_{*w}}$$

where T is surface tension. For a 5 m/s wind speed, $\eta \sim 6 \cdot 10^3$. The ratio becomes smaller with higher wind speeds, but larger for smaller fluid particles. We may therefore assume the velocity component w perpendicular to the interface to be zero at the interface.

For the lateral components of eddy motions, we have as a boundary condition the two-dimensional continuity equation for incompressible flow

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0,$$

since deviation from this would imply creation of new surface, which is not possible with the energy available from the turbulence. Hence, together with

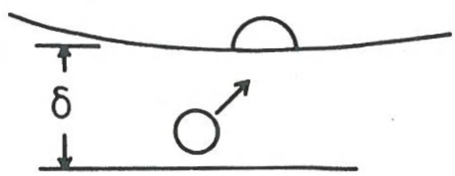

Fig. 1. Sketch of a fluid particle moving through the viscous sublayer and finally deforming the interface.

the three-dimensional continuity equation, it follows that

$$\frac{\partial w}{\partial z} = 0$$

at the interface. If we write

$$w(z) = w(0) + \frac{\partial w}{\partial z} \cdot z + \frac{1}{2} \cdot \frac{\partial^2 w}{\partial z^2} \cdot z^2 + \ldots$$

we have $w(z) \sim z^2$. This is based on the continuity equation which is valid in incompressible flow for mean or fluctuating velocities. Hence, it also follows that on the average $\sigma_w \sim z^2$ near the interface, with σ the standard deviation.

From this, one may derive the variation of K_t with z near the interface with the arguments of Prandtl's (1932) mixing-length theory. Consider a conservative property χ. We assume σ_χ proportional $\partial\chi/\partial z$, where the coefficient of proportionality has the dimension of a length. Since the only relevant length scale near the boundary in the turbulent flow is the distance from the interface,

$$\sigma_\chi \sim z \cdot \frac{\partial \chi}{\partial z}.$$

Hence (with correlation coefficient R and the primes denoting fluctuating variables)

$$K_t \cdot \frac{\partial \chi}{\partial z} = \overline{\chi' w'} = R\sigma_w \sigma_\chi = \text{const} \cdot R \cdot z^2 \cdot z \cdot \frac{\partial \chi}{\partial z}$$

plus terms of higher order. Accordingly near the interface $K_t \sim z^3$ plus terms of higher order. It is therefore reasonable to use the smooth transition from molecular to turbulent flow, as formulated by Reichardt, in this case also, since it predicts the correct power of z (for small z) at a fluid–gas interface without waves.

A note of caution may be appropriate. Although it has been argued that the boundary conditions at the liquid–gas interface would necessitate the same power law at this interface as at a solid wall, this inference is modified by the presence of waves. Application of these ideas in Section 4 is only a test to see how far the model may be extended.

The ocean has many modes of motion and only a few are discussed in any detail below. For example, effects of stability probably dominate at low wind speeds (Katsaros et al., 1978). Other processes which may produce turbulence in the bulk water below the interface, such as shear flow instability or breaking of internal waves, have not been mentioned. Effects of waves are discussed below, but even so the division into gravity waves (large scales) and capillary waves (small scales) is artificial as there is a continuous spectrum of surface waves.

One guideline for discussion has been scale considerations. Processes which have scales comparable to the thickness of the viscous sublayer are thought to be potentially important, while those with a large disparity of scales are thought to be probably less effective. The latter argument is not necessarily true with strongly nonlinear processes.

3. Influence of waves on gas transfer

In Section 2, the boundary conditions for a level fluid gas interface were reviewed. We now consider effects caused by the presence of waves at the interface. In general, we expect several types of wave influence (both capillary and gravity) on gas exchange; they may be roughly classed as follows:

(1) Increase of surface area.
(2) Variations in boundary layer thickness connected with wave motion.
(3) Boundary conditions formulated for level, not curved interface.
(4) Variations in the thickness of the viscous boundary layer caused by variations in momentum transfer between ocean and atmosphere.
(5) Nonlinear effects, e.g. interactions between wave motion and turbulence within the water and hence dissipation of wave energy into turbulence.

Due to their different scales, the effects will be different for gravity and capillary waves; we will treat gravity waves first.

3.1. *Effect of gravity waves*

(Numbers refer to the above listing of possible influences of waves on gas exchange.)

(1) Compared to a level surface, the increase in surface area due to waves is of order S^2, where S is the wave steepness, defined as the ratio of wave height to wave length. Since a typical steepness is 1/17, the area of enlargement is only of order 1%. Even in the case of gravity

waves of limiting slope the surface area enlargement is only a few per cent.

(2) Assume that the boundary layer is stretched or compressed with the orbital motions of the waves. When averaged over a wave length, only the quadratic term in wave steepness is left, which provides an effect of the same order as just calculated and thus may be neglected. The notion of thinning and thickening of the viscous sublayer with wave motion is a film-type concept, where the viscous sublayer is treated as a fluid layer which remains coherent (like a rubber cloth). It is questionable if this is a good description, since the concept of a viscous sublayer does not describe a property of the fluid, but rather the absence of a process within the fluid. Molecular transport exists everywhere in the liquid. The viscous sublayer is distinguished from the bulk of the fluid only in that turbulence is hindered by the presence of the wall from being an effective transport agent. Dilation and compression of the fluid would not directly restrict penetration of the viscous sublayer by eddy motions. The turbulence near the interface is influenced mainly by continuity constraints near the interface, i.e. we would not expect a direct influence on gas exchange from wave coherent fluid sheet motions. There could, however, be an indirect influence since the production of turbulence is influenced by changes of the shear. Also, eddies which decay within the viscous sublayer would probably be influenced by fluid sheet motion, so that their dissipation rate may be increased (more rapid dissipation of turbulence would lead to less effective gas exchange).

Combined effect of (1) and (2)

Effects mentioned under (1) and (2) are not independent; enlargement of the surface area, for instance, would parallel thinning of the fluid layer. Witting (1971) has calculated the combined effect for different wave types. He assumed that thinning of the viscous sublayer (the rubber cloth model) would increase gas transfer, which is doubtful. But even so for the combined effect of (1) and (2) in the limiting case of a gravity wave at the verge of breaking (maximum wave steepness), the calculated increase was only 38%. Since at a given time not all gravity waves are near breaking, the average effect will certainly be considerably smaller.

(3) The boundary conditions have been discussed for a level fluid–gas interface. Of course, the sea surface is not a level surface, but compared with the thickness of the viscous sublayer (fractions of a millimetre) the surface curvature induced by gravity waves is negligible, except at the moment of breaking. In the case of breaking waves, a steady-state gas flux model is not applicable at breaking locations, but is probably applicable elsewhere. On average the influence of curvature is therefore not expected to alter the boundary conditions and hence of the $K_t \sim z^3$ behaviour.

(4) For application of the Reichardt model, we need to know the friction velocity in the water. Gravity waves may take up momentum through coherent pressure and wave fields. It is estimated that on average 5 to 20% of the total momentum flux from the atmosphere to the sea is taken up by gravity waves, except at short fetches (Hasselmann et al., 1973; Snyder et al., 1978). This part of the stress may effectively bypass the interface. Since we describe the turbulent diffusivity in the water with the aid of u_{*w}, and obtain this term from atmospheric data by continuity of stress through the interface, we may assume an error in the determination of the transfer velocity of order zero to 10%. For the time being, this seems to be a small and, therefore, permissible error.

(5) Gravity waves dissipate mainly through breaking and/or transfer of energy to capillary waves. Effects of the latter will be discussed in the next subsection. It is evident that breaking of waves is important in bubble production and in this way may influence gas transfer. Aside from the generation of capillary waves and bubbles, it is not evident to what extent breaking of waves with its violent overturning, splashing and general commotion contributes locally to gas transfer. Since for moderate sea states the area covered with breaking waves is a small percentage of the total area, a considerable effect would be necessary for this to become important on the average.

Phillips (1977, chap. 3.9) has pointed to small-scale wave breaking, which does not enclose bubbles and is less spectacular than white capping, but is also producing unsteady eddy motion, and should be important to momentum, heat and gas transfer since it occurs under all wind speeds. Banner and Melville (1976) found a considerable increase of momentum transfer by small-scale breaking, artificially induced in a wind–water tunnel. Plant and Wright (1977) showed that Phillips' explanation of short wave breaking induced by augmented wind drift in the viscous sublayer is not in agreement with observations. Since the physical process is not clear, it cannot be judged what the importance of small-scale breaking is to momentum and/or gas transfer.

Other nonlinear effects of gravity waves which would enhance or modify production of turbulence and thus further gas exchange are assumed to be small (this is based on the ad hoc argument that the lifetime of gravity waves is fairly long and the wave motions span a considerable depth compared with the thickness of the viscous sublayer).

In conclusion we expect that the effects of gravity waves (aside from being a source of capillary waves) will be small except under high wind conditions with wave breaking, bubble formations and spray blown from the crests of the waves. Thus, except for high wind speeds, it seems permissible to use the Reichardt model with the continuity of stress assumption.

3.2. *Effects of capillary waves*

Experimental wind–wave tunnel studies of gas exchange usually show an increase in transfer velocity with wind speed. The relationship between transfer velocity and wind speed is evidently not linear. This may at least partly be explained by the limited length of wind tunnels, but it has also been observed that the rate of change of transfer velocity with wind speed markedly increases with the onset of capillary waves. Recently, Jähne et al. (1979) have reported gas exchange results obtained using a circular wind–water tunnel, an experimental setup with essentially unlimited fetch. They reported linear variations of transfer velocity with wind speed, whose magnitude differed from conditions with and without capillary waves. The rate of increase when capillary waves were present was considerably greater than when they were absent.

The present state of knowledge is inadequate concerning the life cycle of capillary waves, their interplay with turbulence and their actual forms at sea. Therefore a discussion of the effect of capillary waves must, of necessity, be speculative and of a preliminary nature. For ease of discussion, we will follow points (1) through (5) used in the previous section.

(1) Capillary waves increase the surface area of the water. For a certain type of capillary wave (a two-dimensional wave superimposed on a homogeneous flow) with sharp troughs and rounded crests a theoretical upper limit to the increase in surface area has been calculated (Crapper, 1957). On the other hand, it is not known if the capillaries ever reach the "theoretical" limit (they may become unstable long before reaching the state). Also, observations indicate that the capillaries occur mainly on the forward slope of the longer waves. Therefore, the increase in total area caused by capillaries may be of order 50% or less. According to the reviewer of this article, it is impossible to visualize capillary waves ever increasing the sea surface area by more than a fairly small fraction of 50%.

(2) Thinning and thickening of the viscous sublayer by wave motion is unlikely to be important (but see item 5 below) since, in the absence of experimental evidence for the occurrence of very steep capillary waves at sea, it seems reasonable to assume that values of wave steepness S will be less than one. The area increase and the corresponding decrease of the interfacial layer thickness will be of the order S^2. For the case of pure two-dimensional capillary waves on homogeneous flow, the streamlines were determined by Crapper (1957) (see Fig. 2). MacIntyre (1971) has calculated the effect of surface sheet dilation for sinusoidal and Crapper waves: The effect becomes large for Crapper waves with large wave steepnesses—it is doubtful whether these are stable enough to cover an appreciable percentage of the sea surface and so have a noticeable average effect on the gas flux.

As discussed in Section 3.1 for the case of gravity waves, it is not evident that thinning of the fluid sheets at the interface per se would directly further gas exchange since no corresponding thinning of the viscous sublayer is necessarily implied.

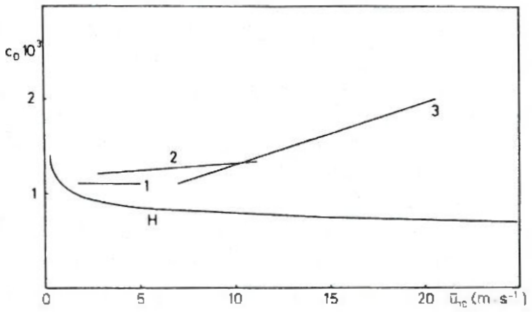

Fig. 2. Roughness of the sea surface. Comparison between measured drag coefficients $c_D = u_*^2/\bar{u}_{10m}^2$ (numbered lines) and hydrodynamical smooth flow (curve marked *H*). The implication is that the increase of momentum flow compared to smooth flow is brought about by "form" drag of gravity waves and ripples. The average value at moderate wind speeds is fairly well known both form direct and profile measurements, while the value at high wind speeds is based on few direct measurements. Results are taken from (1) Dittmer (1977), (2) Brocks and Krügermeyer (1972), (3) Smith and Banke (1975).

Combined effect of (1) and (2)

Again, the effects are not independent, since increase of surface area is coupled with thinning of the fluid sheet. Using a "rubber cloth" type of assumption, Witting (1971) has calculated the combined effect on heat flow for a Crapper capillary wave. The effect is seemingly very strong, indicating a ninefold increase in heat flow compared with a level surface. Even accepting the rubber cloth assumption, the magnitude of the effect will certainly be less in nature. Firstly, the largest effect was calculated for the limiting wave height (the extreme shape in Fig. 2) and it is not known if this shape can ever be reached or if the capillary waves become unstable long before this. Secondly, the effect is wavelength dependent, the maximum amplification being reached only for a wave of length 1.7 cm, the wavelength of minimum phase speed, commonly taken as the border between capillary waves and gravity waves, which means that the effects of gravity and surface tension are about equally important. Since gravity waves have sharp crests and rounded troughs and capillary waves round crests and sharp troughs, it is fairly unlikely that a wave of 1.7 cm wavelength has the limiting shape of a pure capillary wave. For other reasonable assumptions, (shorter waves, lesser steepness) the calculated increase of heat flux was much less than a factor of 9. In reality, effects (1) and (2) probably combine to produce an increase in gas flux compared with a level surface by a factor of 2 or so.

(3) Boundary conditions formulated for a level, uncurved interface. In section 2.2 it has been argued that the boundary conditions at a fluid interface are similar to those at a fixed wall. In deriving the depth dependence of turbulence intensity, a level surface has also been assumed. The corresponding exercise for a curved fluid–gas interface has not yet been done to our knowledge. But even if another power of z would be applicable at locations of strong curvature, leading to more favourable conditions for gas exchange, the total area covered by such locations would be small and therefore the average effect on gas exchange small also. Since penetration of the viscous sublayer by turbulence is hindered by continuity constraints, qualitatively, deeper penetration would be facilitated by convex curvature of the interface (in a trough) whereas concave curvature (at a crest) would hinder deeper penetration. Only inasmuch as favourable and adverse influences do not average out need a net effect be considered. Again it may be assumed that the net effect is of order S^2.

(4) The roughness length z_0 of the sea surface is of order 2×10^{-4} m (e.g. Kraus, 1972). According to Prandtl (1932), the height of the roughness elements at a solid surface is approximately $30z_0$, i.e. of order 1 cm for the value of z_0 given above. This has repeatedly led to the simplistic speculation that capillary waves act as the roughness elements in momentum transfer. An alternative line of argument is based on the observation that at moderate wind speeds (say up to 14 m/s) the drag coefficient is only 10 to 40% higher than that for smooth flow over a flat, solid surface (Fig. 3). The increase of momentum transfer compared with smooth flow could be explained by the momentum transfer to the waves while the main part would be transferred by molecular action. It is not really known which or to what extent either of these arguments is correct even as a bulk

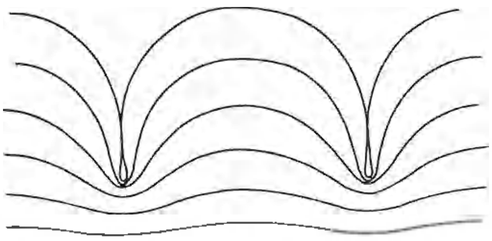

Fig. 3. Streamlines of capillary waves of finite amplitude—from Crapper (1957). Each of the lower streamlines can be taken as the surface of a capillary wave of lesser steepness (by permission of Cambridge University Press).

description. But assuming that capillary waves take up momentum from the atmosphere and lose it to the currents over the depth range of orbital motions, this would mean that a certain percentage of stress bypasses the viscous sublayer, and the sublayer thickness has to be calculated considering a correspondingly smaller fraction of the total stress. That is, the gas exchange would be less effective in the presence of capillary waves, which is contrary to what is observed.

(5) This subsection on nonlinear processes is more speculative, since both experimental evidence and theoretical development are lacking. If we picture a shear layer at the interface at which capillary waves are being generated, it is difficult to conceive that the shear and capillary wave motion will not interact. Such interactions would produce turbulence from the capillary wave energy rather than dissipate the wave energy directly by molecular action. The turbulence near the interface would maintain the shear layer. A related non-linear effect would be instability of the capillary waves, which again would probably produce turbulence.

The significance of such production of turbulence by capillary waves may be seen in the following. In ordinary boundary layer dynamics, the friction velocity is treated as the relevant velocity scale. If influences of stability near the interface and effects from pressure gradients are ignored, friction velocity and distance from the wall are the scales which determine the velocity profile, the production of turbulence and hence the turbulent exchanges. With capillary waves interacting and transporting momentum, the velocity profile and production of turbulence may be changed. In addition, the energy of turbulence need not be produced locally or advected from the bulk of the fluid, but can be transferred from the turbulence of the air into the interfacial layers via uptake by and decay of capillary waves. Production of turbulence near the interface, where advection of turbulence from the bulk of the fluid is hindered, would certainly enhance gas exchange considerably.

Since details of the life cycles of capillary waves are unknown, there is no way to predict the depth dependence of the turbulence and stress. The ad hoc hypothesis is that the distance from the interface is the decisive parameter and therefore the turbulent stress profile will not be too different from that at a solid surface. This at least explains why application of the Reichardt formulation produces a reasonable description of the heat flux through the sea–air interface for open sea data, where capillary waves are ubiquitous (of course, the extrapolation from momentum transfer to heat transfer is far less dubious than to gas exchange, since the ratio of the molecular diffusivities is about 10 in the first case and about 600 in the latter).

3.3. *Discussion of wave effects*

A heretofore unused argument is that effects 1, 2, 3 discussed above would not only increase gas transfer but also momentum exchange. Since momentum exchange is referred to a level surface, if the ordinary determination of the friction velocity is used, and this friction velocity is applied in the gas transfer model calculations, the biases caused by the three effects approximately cancel. Take, for example, the "rubber cloth" assumption that the viscous sublayer would be thinned by the waves. If this viscous sublayer would be thinned at some places, not only the gas but also the momentum exchange would be facilitated. Since the momentum flux, as measured at the 10 m level, is given, a thinning of the viscous sublayer must be balanced by a thickening at other places such that the momentum exchange through the interface equals the flux through the 10 m level. Only inasmuch as there are nonlinearities involved which would affect gas and momentum transfer differently is it really necessary to account for (1) through (3).

It is therefore believed that the key to an understanding of gas exchange processes is the nonlinear interactions between capillary waves and flow characteristics at the interface. It is known (see Bradshaw, 1973) that streamwise curvature enhances turbulence considerably. Since curvature is strong in capillary waves, a significant effect on turbulent flow and hence viscous sublayer thickness is likely.

In summary, increase of the surface area and periodic reduction in the thickness of fluid layers as a consequence of (quasi steady-state) capillary wave motion could account for an increase in gas flux of up to a maximum of a factor of two, compared with that from a level surface. The rather spectacular increase of gas exchange observed in wind tunnels with the onset of capillary waves has yet to receive a full explanation.

4. Observations

Peng et al. (1979) reported radon deficiency measurements at about 100 stations well distributed over the Atlantic and Pacific oceans. Their method gives the gas transfer velocity with a time constant of about 2.6 days, depending on wind speed (under calm conditions, 3.8 days). The observations may be compared with theoretical predictions of transfer velocities versus wind speed. Since it is not really possible to include effects of the different processes discussed above, the calculation has been done for a level surface with the theory given in Section 2.

From the instantaneous wind speed and with the aid of a mean drag coefficient $c_D = 1.3 \times 10^{-3}$, a friction velocity at the gas side of the interface has been calculated. Continuity of momentum flux at the interface yields the value of friction velocity to be used in Reichardt's formula. The result of the calculation depends (through the densities and the diffusivity) somewhat on the water temperature, as shown by the two lines in Fig. 4.

It is evident that the data do not show the expected increase of the transfer velocity with wind speed, and this conclusion is not altered if the average wind speed for the two previous days of the cruise is used (not shown) instead of the in-

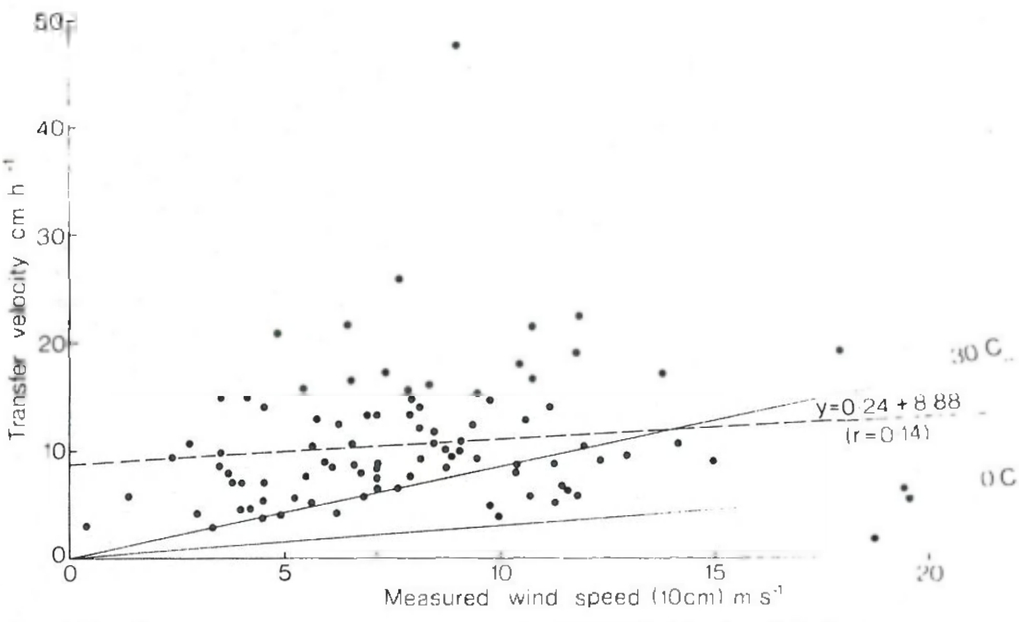

Fig. 4. Transfer velocity (cm h^{-1}) as determined on the GEOSECS Atlantic and Pacific cruises by the Radon Deficiency Method (Peng et al., 1979) plotted against the measured wind speed (m s^{-1}) at the time the samples were collected. Wind speeds at nominal 10 m height have been reduced to 10 cm height with the aid of the logarithmic wind profile for better comparison with wind tunnel results. Full line, predictions based on the molecular plus eddy diffusivity approaches of Deacon (1977) and Hasse (1971) at the temperatures stated, using the temperature dependence of diffusivity after Himmelblau (1964). Broken line is the least squares fit through the data points.

stantaneous value. The apparent absence of an effect of wind on the transfer velocity, as evidenced by the large scatter of the data points in Fig. 4 which leads to the low slope of the least squares line and the low correlation coefficient between the variables, is very surprising. It seems physically unrealistic to find little or no effect of wind speed on the rate of gas transfer and all the wind tunnel studies show clear positive relationships. The absence of a wind speed effect in the field data may be due to experimental imperfections (e.g. Jähne et al., 1979; Broecker et al., 1978). Even so the radon data will still be useful for obtaining global average values for the transfer velocity (see Peng et al., 1979).

Recently Roether et al. (1978) have improved the radon method to allow a more rapid collection of data. The preliminary results of a recent field experiment (Kromer, 1979) are on average in reasonable agreements with the Peng et al. (1979) data. The mean difference is hardly significant and may be further reduced by making reasonable assumptions about the radon production in the mixed layer, since the radium content in the mixed layer was not measured but extrapolated from the assumed radium–radon equilibrium below the thermocline. But even though there are nearly 4 weeks of frequent data, no dependence of the transfer velocity on wind speed could be detected. An attempt to make a "standing crop" analysis failed with an assumed bi-linear wind speed dependence. It is evident from the given time traces that any similar assumption (exponential, square law) would not produce a better description. A final evaluation must be left until the accompanying hydrographic data are analysed.

5. Discussion

The results of the field experiments are frustating in that they fail to show a clear dependence on wind speed. Most of the processes which appear to be important for gas exchange ought to depend in one way or the other on turbulence or wave energy and hence, at least indirectly, on mean wind speed.

So far, we have not considered the effect of bubbles on gas exchange. Bubbles can take up gas from the fluid, rise to the surface and burst, thus bypassing the layer of slow diffusive transport at the interface. Bubbles could be generated by trapping of air by capillary waves, although obviously a much more effective process is the breaking of waves which produces patches of bubbles—the white caps. Both mechanisms of bubble generation should produce increasing numbers of bubbles with increasing wind speed.

Another hitherto unmentioned process is the effect of surface films on gas transfer. Surface active material arising from natural biological processes and man-made activities is ubiquitous. It is also known that surfactant films do not remain coherent at wind speeds of about force three and above. Therefore they are assumed not to influence gas exchange directly. Even at lower speeds, since the films on the open sea are not homogeneous, their efficiency as a barrier to gas molecules is probably low. But it is known (e.g. Garrett, 1969) that surface films damp capillary waves. The physics or physiochemistry of how surface films act in damping capillary waves and how this influences turbulence and thus indirectly gas exchange is unknown. There is at least a chance that the surface active material dispersed by wave action in the bulk of the water is still active enough to influence important transfer mechanisms even if it is not able to build films or visibly influence the smaller waves. Even the fact that is has been possible to correlate wind speed with microwave backscatter from the ocean, which shows that the spectral energy of waves in the centimetre region is correlated with wind speed, does not preclude an influence of surfactants on higher frequency waves or Fourier components.

In conclusion it might be said that the results of field experiments should be sufficient to calculate global gas exchange fluxes between the ocean and the atmosphere within a factor of two or three. There remain several difficulties with the theory; for example the theory of damping of capillary waves (see Phillips, 1977) contains the kinematic viscosity only and is independent of the surface tension, while experimental investigations of wave damping reveal a clear dependence on surface tension (Garrett, 1969). It is safe to say that the physics of gas exchange processes remain largely unresolved.

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ГАЗООБМЕН ЧЕРЕЗ ПОВЕРХНОСТЬ РАЗДЕЛА ОКЕАН-АТМОСФЕРА

Дается обзор физических процессов газообмена через поверхность раздела океан–атмосфера. Для описания переноса газов в жидкость вблизи границы раздела используется концепция молекулярной плюс турбулентной диффузии, что оказалось полезным при гладком обтекании твердых поверхностей. Найдено, что хотя граничные условия на свободной границе раздела отличаются, они ведут к существенно такой же зависимости коэффициента турбулентной диффузии от расстояния до стенки, по крайней мере, для поверхности раздела жидкость-газ без волн. Затем обсуждается влияние волн. Из масштабного анализа очевидно, что влияние гравитационных волн мало. Из исследовании в аэродинамических трубах известно, что капилярные волны значительно усиливают газообмен. Существующие гипотезы представляются недостаточными для объяснения этих наблюдений. Анализ данных полевых измерений даже усугубляет ситуацию, поскольки эти данные не выявляют ожидаемого усиления газообмена с увеличением скорости ветра.