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On the mechanism of gas exchange at the air–sea interface

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ABSTRACT

Experimental evidence from work in wind–water tunnels has pointed to an influence of capillary waves on gas exchange for liquid-phase-controlled gases. These experiments are often interpreted in terms of some surface renewal model. Here it is proposed that capillary waves are not likely to be the reason for surface renewal because of the disparity of time scales. Also, the balance of energy of turbulence in wind–water tunnels is different from that in the open sea due to side and bottom friction in the experimental facilities. It is pointed out that in wind–water tunnels, secondary flows must exist, that would produce forced surface renewal.

1. Introduction

The mechanism of gas exchange at the air–sea interface has often been discussed in this journal: Deacon (1977), Hasse and Liss (1980), Holmén and Liss (1984). Jähne et al. (1987) have reviewed the present hypotheses or "models" and the experimental evidence. An extensive list of references is given in Coantic (1986). Gas exchange, especially where the limiting layer of molecular diffusion is on the liquid side of the interface, is of increasing interest because of the climatic relevance of gases such as CO_2. Certainly, it is important to know the mechanisms and the related process rates of gas exchange at the air–sea interface, in order to calculate, e.g., CO_2-uptake by the oceans. However, the existing experimental evidence from field and laboratory studies is remarkably inconsistent. In Hasse and Liss (1980), we tried to use physical reasoning in order to give some insight and guidelines for extrapolation or parameterization. In the present paper, we point to two arguments that apparently have not been used in the discussion of liquid-phase-controlled gas exchange, but which might be useful for interpretation of experimental results and their extrapolation to applications.

In the following, only liquid-phase-controlled gas transfer at the gas–water interface is considered. We will disregard the stagnant film model as being not very realistic. Then there are essentially two models available to describe gas exchange: the "surface renewal" model (SR) and the "boundary layer" model (BL). In short, the SR-model assumes that lumps of fluid are randomly removed from the interface and are replaced by fluid from the bulk water. Hence, molecular transport, driven by the concentration difference between air and water, repeatedly starts at irregular intervals and is disrupted before equilibrium is reached. The exchange rate in this model is governed by an empirical coefficient with dimension time, that can be taken as an average life-time of fluid in the sublayer of molecular diffusion. Turbulence is not explicitly present in the model, but it is implied that the bulk of the water is reasonably well-mixed and so has a homogeneous gas concentration. The BL-model originates from the assertion of continuity of the surface proper. This results from the fact that the energy of turbulence is not sufficient to disrupt the surface against surface tension (Hasse and Liss, 1980). As a consequence of the two- and three-dimensional continuity conditions at the surface, turbulence intensity decreases towards the interface. Hence, in the layer very close to the interface, molecular transfer takes over from turbulent transfer. In this model, an empirical constant, relating momentum boundary layer thickness to the ratio viscosity ν over friction

velocity u_*, is taken from wind tunnel work over solid surfaces.

Both models might be used to describe the heat flux through the interfacial layer and the related temperature difference between the interface and the bulk water (e.g., Liu and Businger, 1975; Hasse, 1971). Assuming that passive properties are transported by the same mechanism as heat, experimental determinations of the heat exchange at the air–sea interface should give an estimate of gas exchange when the molecular thermal conductivity is replaced by the appropriate molecular diffusivity. However, the diffusivity of gases is much less than the thermal conductivity, and the different power laws for extrapolation to other diffusivities for the two models yield different predictions, see, e.g., Deacon (1977) and Holmén and Liss (1984). Consequently, we need to know what model is appropriate in order to extrapolate for gas transfer. Unfortunately, experiments so far have been inconclusive (Holmén and Liss, 1984). Also, there is disagreement between open sea and wind tunnel results. One of the more striking examples is the rather pronounced increase of the gas exchange rate at a certain wind speed when capillary waves first appear. Jähne et al. (1979) used a circular wind–water tunnel, where the rotation of the fluid and perhaps bottom and side friction inhibited capillary waves below wind speeds of about 5 m/s. At sea, capillary waves or wavelets are commonly observed at Beaufort 1, corresponding to about 2 m/s wind speed. While it is obvious that the results of wind–water tunnel work cannot be applied at sea without a better understanding of the dominant physics, the observations point to a mechanism correlated with the appearance of capillary waves. It is tempting to conclude that capillary waves promote surface renewal and thereby increase heat and gas transfer.

It is the purpose of the present paper to show that the surface renewal model is not compatible with an intensification of gas exchange by capillary waves.

2. Capillary waves and the surface renewal model

The theory for the surface renewal model relates the average flux at the surface Q_o to the driving concentration difference $c_s - c_b$ by

$$Q_o = c\rho D(c_s - c_b)(D t_*)^{-1/2}, \quad (1)$$

where D is the diffusivity, $(D t_*)^{1/2}$ is a penetration depth, ρ density, and c an auxiliary constant (e.g., c is specific heat if eq. (1) is used for heat flux, and c_s, c_b represent temperatures). The coefficient t_* is a characteristic renewal time. It is evident that t_* is a kind of short-hand for the complicated physics of the exchange processes. There is no reason to assume that t_* is constant. At present, there is also no simple way to relate t_* to other characteristic variables of the problem. Certainly, the scaling length for any property could be related to the scaling length for momentum ν/u_*, where ν is kinematic viscosity and u_* friction velocity. But aside from the fact that the relationship is not known, it is not trivial to relate the exchange of passive admixtures to that of momentum, since momentum can be transferred by wave coherent pressure forces (see, e.g., Hasse, 1986). The SR-model predicts that heat and passive admixtures are exchanged by the same mechanism. Hence, one may derive an estimate of t_* from a knowledge of heat flux at the air–sea interface. For typical open sea values of heat flux and surface minus bulk water temperature difference (taken from Hasse, 1971), and 6 m/s wind speed, one obtains

$$t_* \sim 10 \text{ s}.$$

This estimate is in good agreement with Ewing and McAlister (1960), who found re-establishment times between 5 s and 40 s for the cool skin of the ocean.

Considering the renewal time t_* to be of order 10 s, and the frequencies of capillary waves to be of order 10 Hz, it is evident that there is a disparity of scales by a factor of order 100. The simple notion of capillary waves triggering the surface renewal cannot be correct. Some tens or hundreds of capillary waves would pass through the lump of fluid before it is renewed. In any case, it is not likely that capillary waves would normally trigger surface renewal, since wave motions are orderly.

The characteristic time scale of surface film adjustment and the periods of capillary waves have been known for some time. It is the intention of the present paper to draw attention to their *disparity*: the surface renewal model is not

able to explain the enhancement of gas transfer by capillary waves in a simple way.

A reviewer of the present paper has mentioned that although a single capillary wave probably does not "trigger" surface renewal, it is nevertheless plausible that groups of waves influence the process of gas transfer. However, we would still need to explain how a longer wave train of fairly orderly motions induces surface renewal. In any case, the wave train argument is not applicable for the situation in wind–water tunnels where one typically runs stationary experiments either with capillary waves or without.

3. Laboratory versus field experiments

It might be appropriate to explain why results of laboratory experiments are so different from those in the open sea. The difference is found in the budget of kinetic energy of turbulence. In deep water, turbulent energy is produced mechanically (via shear stress) or by buoyancy, and is dissipated by the internal friction of the fluid motions. In a wind–water tunnel, there is additional friction at the side walls and at the bottom. Also, developing boundary layers have to be considered. Necessarily, the budget of kinetic energy of turbulence in the laboratory is not related in the same way to the friction velocity as it is in the open sea. Since mixing in the liquid depends on the energy of turbulence, the transfer velocity or the renewal time of the SR-model is not necessarily comparable between laboratory and field experiments.

Still, it is hard to argue for the BL-model when carefully conducted laboratory experiments result in power laws (the exponent n) more in favour of the SR-model. It is the opinion of the present author that the results of laboratory experiments should not be used to decide between SR- and BL-models. The nature of the laboratory experiments forces some type of surface renewal. Wind–water tunnel experiments, because of side and bottom friction and reflection of waves at the side walls, exhibit secondary flows. As soon as there is a lateral component of the secondary flow, this, together with the limited cross section, pumps bulk water to the surface, a process which is equivalent to an enforced surface water renewal. The typical tunnel sizes and flow velocities yield "renewal" times of the right order of magnitude. For a numerical example, assume a wind–water tunnel width of 20 cm, an air speed of 10 m/s corresponding to a downstream water velocity of 3 cm/s and half as large a lateral speed of secondary flow in the water. This results in a renewal time of order 13 s. It is evident that depending on the flow characteristics of a specific facility, secondary flows may enforce a surface renewal not characteristic of open ocean conditions.

Unfortunately, the importance of secondary flows in studies of gas exchange as biasing towards the SR-model has not been fully recognized. It is strongly recommended that the secondary flow characteristics in experimental facilities be determined and considered when results are discussed.

4. Boundary conditions

The reason for a rather large variety of hypotheses for gas transfer at the air–sea interface is disagreement on how micrometeorological experience obtained over a solid surface is to be applied at a fluid interface. Authors often assume intuitively that for gas-phase-controlled transfer the air–water interface may be treated like a solid wall because of the much larger density of water compared to air. Conversely, to many authors, it is questionable how the interface should be treated in the case of the liquid-phase-controlled gas exchange: do water waves serve as roughness elements to the flow in the water? This question is senseless: waves comprise very orderly motion, and the apparent roughness is part of the orderly smooth motion. Waves, as long as they are linear, do not mix (see, e.g., Phillips (1977)).

The only way to transfer knowledge from solid surfaces to a fluid interface is to use the appropriate boundary condition at the fluid interface and repeat derivations with the changed boundary conditions. It has been argued by Hasse and Liss (1980) that the appropriate boundary condition at a liquid interface is the two-dimensional continuity equation for flows in the local, momentary fluid surface proper:

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

where u, v are the x, y velocity components in a surface-following, orthogonal coordinate system, where z is perpendicular to the local, momentary surface. The argument is based on the concept of surface tension: energy is necessary to create new surface, but fluid particles may be moved within the surface without loss or gain of energy as long as the local area of the surface is not changed. The energy of a turbulence element is not sufficient to locally create new surface (Hasse and Liss, 1980). This is not in contradiction with the existence of capillary waves, since in capillary waves, energy is periodically converted between kinetic energy of wave motion and work of motion under the influence of surface tension. Similarly, for natural convection, the buoyancy force is small compared to surface tension, so that the surface remains coherent. Buoyancy may lead to confluent streaks, as observed by Woodcock (1941) on a pond during a cool night.

5. Conclusion

The surface renewal model is, in its simplicity, an appealing concept to depict how the air–sea exchange of heat and admixtures may be effected. However, if we accept the idea that surface renewal implies work to create new surface, we need to explain where the necessary energy comes from. The disparity between renewal time and periods of capillary waves shows that the latter do not provide a simple explanation.

On the other hand, it is likely that the apparent success of the surface renewal model in laboratory experiments is an artefact of secondary flows, not applicable to the open sea.

We conclude that the surface renewal model cannot be taken as established in order to calculate gas exchange rates based on extrapolation from observed rates of heat exchange. For the time being, the boundary layer model appears to be physically more realistic and should be used to estimate gas exchange rates.

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REFERENCES

Coantic, M. 1986. A model for gas transfer across air–water interfaces with capillary waves. *J. Geophys. Res. 91 C3*, 3925–3943.

Deacon, E. L. 1977. Gas transfer to and across an air–water interface. *Tellus 29*, 363–374.

Ewing, G. and McAlister, E. D. 1960. On the thermal boundary layer of the ocean. *Science 131*, 1374–1376.

Hasse, L. 1971. The sea surface temperature deviation and the heat flow at the sea–air interface. *Bound. Lay. Met. 1*, 368–379.

Hasse, L. 1986. On Charnock's relation for the roughness at sea. In: *Oceanic whitecaps* (eds. E. C. Monahan and G. MacNiocaill). Dordrecht/Holland: D. Reidel Publ. Comp., 49–56.

Hasse, L. and Liss, P. S. 1980. Gas exchange across the air–sea interface. *Tellus 32*, 470–481.

Holmén, K. and Liss, P. 1984. Models for air–water gas transfer: an experimental investigation. *Tellus 36B*, 92–100.

Jähne, B., Münnich, K. O. and Siegenthaler, U. 1979. Measurements of gas exchange and momentum transfer in a circular wind water tunnel. *Tellus 31*, 321–329.

Jähne, B., Münnich, K. O., Bösinger, R., Dutzi, A., Huber, W. and Libner, P. 1987. On the parameters influencing air–water gas exchange. *J. Geophys. Res. 92 C2*, 1937–1949.

Kitaigorodskii, S. A. 1984. On the fluid dynamical theory of turbulent gas transfer across an air sea interface in the presence of breaking wind waves. *J. Phys. Oc. 14*, 960–972.

Liu, W. T. and Businger, J. A. 1975. Temperature profile in the molecular sublayer near the interface of a fluid in turbulent motion. *Geophys. Res. Letters 2(9)*, 403–404.

Phillips, O. M. 1977. *The dynamics of the upper ocean.* Cambridge: University Press, 2nd edition. 336 pp.

Woodcock, A. H. 1941. Surface cooling and streaming in shallow fresh and salt waters. *J. Marine Res. 4*, 153–161.