J. Fluid Mech. (1997), vol. 332, pp. 341–358

Capillary waves and air–sea gas transfer

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(Received 22 September 1995 and in revised form 9 September 1996)

The effects of capillary waves are considered on the transfer of gas into (or out of) solution through a gas–liquid interface. The bulk liquid is assumed to be otherwise motionless in the analysis of a preliminary problem; in this problem, a concentration boundary layer is developed as a consequence of a first-order chemical reaction that is assumed to deplete the dissolved gas in the liquid. The reaction rate determines the asymptotic thickness of the concentration boundary layer. It is shown that gas transfer through the concentration boundary layer is most enhanced by the presence of capillary waves when there is vigorous removal of dissolved gases by chemical reaction – i.e. when the reaction is fast and the boundary layer is thin. The results of this theory are then measured against gas transfer through a turbulent, sheared interface in the context of a surface renewal model. Here it is the exchange, from time to time, of fluid between the interface and the bulk that leads to the development of a thin concentration boundary layer when the bulk fluid is not saturated with dissolved gas. Capillary waves are shown to thicken the concentration boundary layer at the interface and to increase the rate of gas transfer.

1. Introduction

The oceans are a vast reservoir of dissolved gases – a fact that is of increasing importance in the modelling of global climate change. A substantial proportion of the dissolved gases in the oceans have crossed the wavy sheared surfactant-covered ocean surface in a way that is rather poorly understood. As reviewed by Liss (1983), it is known that the flux of gas through the ocean surface increases dramatically when there are capillary waves on the interface. In this paper we shall attempt to cast some light on the transport of gases through such a dynamic interface. Our goal is to explore fundamental aspects of transport, as well as to estimate the importance of capillary waves in air–sea gas transfer by offering an improvement to a currently accepted model.

There has been considerable recent interest in transport problems in the presence of wavy motion of a fluid. One group of researchers, including Aranson *et al.* (1991), Gollub and coworkers (Ramshankar, Berlin & Gollub 1990; Ramshankar & Gollub 1991; Mesquita, Kane & Gollub 1992), and also Feng & Wiggins (1995) has studied the transport of impurities by modulated capillary waves that lead to chaotic particle paths in the flow. These works are concentrated on developing a statistical understanding of the 'effective diffusivity' of such microscopically chaotic flow fields. Their focus has been on horizontal transport of a passively advected tracer.

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A second group of researchers has considered the more general problem of transport associated with cellular or periodic flows. A homogenization technique is pursued, in which the focus is on synthesizing the details of small-scale analyses of transport via convection-enhanced diffusion across streamlines in the flow. The result is that the original convection–diffusion equation is approximated at long times and over large scales by a simple diffusion equation with an anisotropic ‘effective diffusivity’. This technique has been applied by Knobloch & Merryfield (1992) to several periodic flows with no mean, and extended recently in a variational setting by Fannjiang & Papanicolaou (1994).

We are interested in convection-enhanced diffusion in a situation in which one is forced to account for a boundary condition. Therefore the homogenization technique, which depends on an infinitely repeated flow field, cannot be applied. Our goal is to describe the critical *vertical* transport through the wavy interface. The influence of chaotic particle trajectories on this process is of interest, especially in view of resonant triad interactions, instabilities, etc.; however it is clear that simpler transport problems should be approached first.

We shall begin with an analysis of a model problem that recalls the work of Witting (1971). In that paper, the author developed a theory for the asymptotic enhancement of transport of heat by capillary waves in an otherwise undisturbed fluid. Witting regarded the thickness of the concentration boundary layer as given, then proceeded to find the rate of heat transfer through the boundary layer. The capillary wave profiles used in Witting’s work are the exact solutions due to Crapper (1957). Witting found that the flux of heat may be enhanced up to nine times by capillary waves of limiting steepness.

The influence of capillary waves on the vertical flux of gas through an interface was also considered by MacIntyre (1971). In that paper, the author made an ingenious estimate of the mean effect of the steepening and shallowing of gradients in concentration associated with the passing of a wave. However, the thickness of the concentration boundary layer was also fixed *a priori* – independently of whether or not waves were present. The dependence of the results on the thickness of the surface layer is not known, as MacIntyre presented relative results comparing transport through rippled surfaces to transport through flat surfaces.

In the first part of this paper, we consider the transport of gas through an otherwise planar interface disturbed by a wave of a given wavenumber. We shall assume that the dissolved gas is either produced within the liquid below the interface and is transported through the surface to the gas above, or else that the gas crosses the interface, passes into solution and is there consumed in some chemical reaction. The motivations for including the chemical reaction are many. The chemical reaction will lead to a concentration boundary layer at the interface, with a thickness that is determined in terms of the reaction rate as a part of the solution of the problem. This represents an important generalization of the work of Witting and of MacIntyre. By tuning the reaction rate, we can explore the effect of capillary waves on the diffusive transport of dissolved gases at different depths. Of course, a very substantial number of air–sea gas exchanges involve chemical reaction, as described by Liss (1983). However, the most important consequence of chemical reaction in this work is as an artifice to engender a concentration boundary layer in the theory. For simplicity, we shall assume that the rate of production or consumption of the dissolved gas in the liquid is linear in the concentration of dissolved gases – a first-order reaction. We concentrate on the case of invasion of dissolved gases for the majority of the paper; as we show in the Appendix, the escape of gases produced by the chemical reaction is very similar. The goal is to determine the effect of capillary waves on gas transfer through the interface, and on the thickness of the concentration boundary layer.

The theory provides fundamental background for use in a treatment of the more difficult problem of air–sea gas transfer. In a realistic situation, where the sea surface is disturbed by waves of every wavelength and is sheared by winds, it is the turbulence in the water that controls the rate of gas transfer. This understanding lead Danckwerts (1951) to propose the surface renewal model of air–sea gas transfer at turbulent conditions. In this model, well-stirred bulk water is assumed to be exchanged frequently with the interface. It is the rapid invasion of dissolved gases into fresh patches of surface water that leads to the enhancement of gas transfer. In this paper, we shall propose a modification of the surface renewal model that incorporates the consequences of capillary waves that we develop in the preliminary theory. This will serve as a point of departure for investigating the relative magnitudes of gas transfer enhancement by capillary waves and by near-surface turbulence.

2. Preliminary theory

We consider the transport problem in deep water under an interface disturbed by a two-dimensional nonlinear monochromatic (Crapper) capillary wave. In the case of removal of dissolved gas in the liquid via chemical reaction, the convection–diffusion equation for the dissolved gas in the liquid is

$$\frac{\partial C}{\partial t^*} + \boldsymbol{u}^* \cdot \nabla^* C = D\nabla^{*2} C - r^* C, \tag{2.1}$$

where C is the concentration of dissolved gas (e.g. mass fraction), $\boldsymbol{u}^*$ is the velocity vector in the liquid, D^* is the diffusivity of the gas in the liquid, and $r^* > 0$ is the reaction rate. An asterisk indicates a dimensional variable. In the case of a clean surface, the boundary condition at the interface is simply Henry's Law, which states that the mass fraction of the gas in the liquid immediately under the interface is proportional to the partial pressure of the gas above the interface.

The principal difficulty associated with obtaining a solution to the transport problem is that the domain occupied by the liquid has a moving boundary at precisely the location where the interesting phenomena occur. We address this difficulty by passing to streamline coordinates for the liquid under the wavy surface. This crucial step has the double advantage of recasting the problem on a flat spatial domain (so that the boundary condition is satisfied at a constant-coordinate line), and of exposing the driving force behind convection-enhanced diffusion. The latter, of course, is the alternate approach and divergence of two given material points in the fluid due to the passage of waves on the surface. In the steadily translating frame moving with the wave, path-lines correspond exactly to streamlines; hence the approach and divergence of streamlines gives information on the approach and divergence of material points. We return to this point below.

Based on physical considerations, it is clear that whatever motions in the fluid that can be attributed to the passage of the wave will decay rapidly with depth. Therefore, we expect that the concentration field, which inherits its dependence on the horizontal coordinate from the boundary condition (if surfactants are present), or from the field equation, will become 'homogenized' with depth. In other words, we expect that there will be a thin layer near the surface of the fluid within which there are appreciable horizontal variations in concentration, but that with depth, the dependence on the horizontal coordinate will be very much weaker.

Similar physical arguments were recently advanced by Fyrillas & Szeri (1994, 1995, 1996) in order to develop a perturbation method to determine the gas and/or soluble surfactant concentration field outside a slowly dissolving or growing bubble undergoing rapid volume oscillations. In those papers, it is found that the transport problem can be split into two simpler problems by virtue of the linearity of the convection–diffusion equation in the concentration field. The problem is split into (i) an oscillatory problem for the rapidly oscillating part of the concentration field associated with the oscillating boundary condition and with the convection-enhanced diffusion, and (ii) a smooth problem for the slowly evolving concentration field that accounts for the 'homogenized' effect. The oscillatory problem is solved to leading order by the method of matched asymptotic expansions; by requiring that the outer limit of the inner approximation should be zero, the solution to the oscillatory problem emerges as non-zero only in a thin layer outside the bubble. This, however, places a restriction on that part of the boundary condition that is ascribed to the oscillatory problem. In this way, the splitting is 'defined'. The remainder of the boundary condition is satisfied by the smooth problem, which is solved by the method of multiple scales in time. The product of the analysis is (i) a rational technique for defining the splitting of such a problem, (ii) an expression for the smooth and oscillatory parts of the concentration field, and (iii) expressions for the bubble growth rate via rectified diffusion.

In the present paper, we shall use similar notions to address the transport problem for a gas through a wavy interface. We shall define an oscillatory problem and a smooth problem. The oscillatory problem can be solved by the method of matched asymptotic expansions with the added requirement that the inner approximation match zero (the outer approximation of the oscillatory problem). In this paper we shall have no need of an oscillatory solution, as the boundary condition to be satisfied by the concentration field will emerge as translation-invariant. The horizontal variations in the concentration field come into the theory at higher order. The smooth problem satisfies the translation-invariant boundary condition, with a solution that is obtained by the method of multiple scales in time.

We shall be concerned throughout this paper with a wave that is translating with speed c^* on an otherwise undisturbed interface. In the coordinate system that translates with the wave, the interface and velocity field appear steady. If the spatial coordinates are x^* along the interface, here assumed to be planar in the mean, and z^* measured vertically upward from the mean surface, the velocity of the fluid is $-c^*$ in the x^*-direction, as $z^* \to -\infty$. We use the asterisk to indicate dimensional variables. We write the equation of the surface in the form $z^* = \eta^*(k^*x^*)$. The (radian) frequency of the wave is ω^*, and $k^* = 2\pi/\lambda^*$ is the wavenumber.

It is convenient to define dimensionless variables using the length scale k^{*-1} and the time scale ω^{*-1}; hence we define $x^* = x/k^*$, $z^* = z/k^*$, and $t = \omega^* t^*$. The transport equation becomes

$$\frac{\partial C}{\partial t} + \boldsymbol{u} \cdot \nabla C = \frac{1}{\mathscr{P}} \nabla^2 C - \frac{\mathscr{R}}{\mathscr{P}} C, \tag{2.2}$$

where $\mathscr{P} \equiv \omega^*/D^*k^{*2}$ is the Péclet number, and $\mathscr{R} \equiv r^*/D^*k^{*2}$ is the dimensionless reaction rate. The parameter $\mathscr{R}$ can be interpreted as the ratio of the time scale for diffusion through $\lambda^*/(2\pi)$ to the time scale of the reaction. $\mathscr{P}$ is the time scale for diffusion through $\lambda^*/(2\pi)$ divided by the time scale for convection.

2.1. *Formulation*

In the uniformly translating reference frame in which the waves appear motionless, it is possible to define a stream function and velocity potential through the relations

$$u = \frac{\partial \psi}{\partial z} = -\frac{\partial \phi}{\partial x}, \quad w = -\frac{\partial \psi}{\partial x} = -\frac{\partial \phi}{\partial z}. \tag{2.3}$$

If the surface is at $z = \eta(x)$, these equations serve to define ϕ and ψ for $z \leqslant \eta(x)$, the domain occupied by the fluid. Moreover, because the definition of ψ leaves it determined only to within an arbitrary constant, we set $\psi = 0$ on the interface. Hence $\psi \to \infty$ as $z \to -\infty$. We note that $u \to -1$ and $w \to 0$ as $\psi \to \infty$.

Now, we follow Witting (1971) and recast the transport equation into (ϕ, ψ)-coordinates, in order that the equation will be satisfied in the simpler half-space $\psi > 0$. Hereafter, we consider the mass fraction of dissolved gas C to be a function of t, ϕ and ψ. In order to perform the transformation of the convection–diffusion equation to streamline coordinates, we use standard methods of multivariable calculus to write the derivatives with respect to (x, z) as derivatives with respect to (ϕ, ψ) using the chain rule.

The differentiation of the defining relations $x = x(\phi, \psi)$ and $z = z(\phi, \psi)$ with respect to x and z yields equations that relate the various derivatives; solution of these equations leads to

$$\frac{\partial x}{\partial \phi} = Ju = -J\frac{\partial \phi}{\partial x} = J\frac{\partial \psi}{\partial z}, \quad \frac{\partial x}{\partial \psi} = Jw = -J\frac{\partial \phi}{\partial z} = -J\frac{\partial \psi}{\partial x},$$

and to

$$\frac{\partial z}{\partial \phi} = Jw = -J\frac{\partial \phi}{\partial z} = -J\frac{\partial \psi}{\partial x}, \quad \frac{\partial z}{\partial \psi} = -Ju = J\frac{\partial \phi}{\partial x} = -J\frac{\partial \psi}{\partial z}.$$

Here we have used the notation for the Jacobian

$$J = \{x, z\} \equiv \frac{\partial x}{\partial \phi}\frac{\partial z}{\partial \psi} - \frac{\partial x}{\partial \psi}\frac{\partial z}{\partial \phi} = \frac{-1}{u^2 + w^2}.$$

Finally, this procedure yields expressions for the partial derivatives we require:

$$\frac{\partial}{\partial x} = \frac{1}{J}\{\cdot, z\}, \quad \frac{\partial}{\partial z} = \frac{1}{J}\{x, \cdot\}.$$

We make use of these results to compute

$$u\frac{\partial C}{\partial x} + w\frac{\partial C}{\partial z} = \frac{1}{J}\frac{\partial C}{\partial \phi}, \tag{2.4}$$

and

$$\nabla^2 C = \frac{-1}{J}\tilde{\nabla}^2 C \equiv \frac{-1}{J}\left[\frac{\partial^2 C}{\partial \phi^2} + \frac{\partial^2 C}{\partial \psi^2}\right].$$

We note that because $\phi + \mathrm{i}\psi = f(x + \mathrm{i}z)$ is analytic, and has a derivative that is nowhere zero in the liquid, f has a unique analytic inverse. This latter statement is proved in Carrier, Krook & Pearson (1983).

The transport problem becomes, in dimensionless streamline coordinates,

$$\frac{\partial C}{\partial t} + \frac{1}{J}\frac{\partial C}{\partial \phi} = -\frac{1}{\mathscr{P}J}\tilde{\nabla}^2 C - \frac{\mathscr{R}}{\mathscr{P}}C. \tag{2.5}$$

Witting (1971) has obtained this same equation in his analysis of thermal boundary layers and capillary waves, but without the chemical reaction term – i.e. with $\mathscr{R} \equiv 0$.

Witting proceeded to solve the asymptotic problem (with $\partial/\partial t \equiv 0$) using a Fourier series approach. The sines and cosines in his expansions are functions of ϕ and the coefficients are functions of ψ. Witting treated both Dirichlet and Neumann boundary conditions on the surface, and fixed the bulk temperature on a specific stream surface ψ_0 below the surface.

The boundary condition on the concentration field of dissolved gas in the fluid is obtained by application of Henry's Law, which states that the concentration in the fluid separated from a gas by a plane interface is proportional to the partial pressure of the gas above the fluid. Thus, for a clean surface, we have

$$C(t, \phi, \psi = 0) = C_s, \tag{2.6}$$

where C_s is the saturation concentration at the given partial pressure – a Dirichlet boundary condition.

Hence, our problem is similar to the one treated by Witting except in two important respects. First, the thickness of the concentration boundary layer will arise naturally as a part of the solution to our problem, whereas Witting fixed (arbitrarily) the thickness of the thermal boundary layer. Secondly, we shall treat the unsteady problem, while Witting considered only the steady problem. In fact, it is elimination of $\mathscr{R}$ and of the time derivative that allows Witting to pursue a Fourier series solution, because in this case J drops out of (2.5). Because we shall keep both terms that Witting dropped, we shall have to pursue a perturbation analysis. This analysis will yield a procedure for averaging the problem along the wave direction.

Typical values for the variables associated with a capillary wave at an air–water interface are as follows. The frequency of the wave $f_w^* = 50\,\text{Hz} = \omega^*/(2\pi)$, the wavenumber is 11 cm^{-1}, and the diffusivity is 2×10^{-5} $\text{cm}^2\ \text{s}^{-1}$. This yields a Péclet number of 130 000; hence the two terms on the right-hand side of (2.5) are divided by a very large number. This suggests that it may be fruitful to explore the limit of infinite Péclet number.

Although the limit $\mathscr{P} \to \infty$ is singular, it does provide important clues for the large, but finite $\mathscr{P}$ problem. If we set $\mathscr{P}$ to ∞, the right-hand side of the transport equation (2.5) becomes 0. The boundary condition and equation admit a solution which is steady, and independent of ϕ. This corresponds to C being a material field, which happens to be constant on streamlines. If C (owing to initial conditions) depends on ϕ as well as on ψ, then C must also depend on t in such a way as to account for the (generally) differential speeds of particles along different streamlines in the flow. Hence, when $\mathscr{P}$ is large, but finite, we expect that the dominant effect will be the (convection-enhanced) diffusion of C across streamlines.

In the smooth problem we seek the homogenized response of the concentration field (C_{sm}) to the translation-invariant boundary condition. The governing equation is

$$\frac{\partial C_{sm}}{\partial t} + \frac{1}{J}\frac{\partial C_{sm}}{\partial \phi} = -\frac{1}{\mathscr{P}J}\tilde{\nabla}^2 C_{sm} - \frac{\mathscr{R}}{\mathscr{P}} C_{sm},$$

together with the boundary condition $C_{sm}(t, \phi, \psi = 0) = C_s$. We shall determine the response on a slow time scale to the rapid steepening and shallowing of concentration gradients that occurs as a consequence of the wavy motion. This is most easily accomplished if we define a slow time scale explicitly and use the method of multiple scales. Therefore, we define $\lambda = t/\mathscr{P}$. Next, we expand the smooth concentration field in the form

$$C_{sm}(t, \phi, \psi; \mathscr{P}) = C_{sm}^0(t, \lambda, \phi, \psi) + \mathscr{P}^{-1} C_{sm}^1(t, \lambda, \phi, \psi) + \cdots.$$

Then to order zero in the small parameter $\mathscr{P}^{-1}$, we have the equation

$$\frac{\partial C^0_{sm}}{\partial t} + \frac{1}{J}\frac{\partial C^0_{sm}}{\partial \phi} = 0.$$

This admits the solution $C^0_{sm}(t, \lambda, \phi, \psi) = C^0_{sm}(\lambda, \psi)$, assuming a translation-invariant initial condition. This is simply the mathematical version of our earlier assertion, "when $\mathscr{P}$ is large, the concentration field is very nearly a time independent material field". To the next order in the small parameter $\mathscr{P}^{-1}$, the equation to be satisfied is

$$\frac{\partial C^1_{sm}}{\partial t} + \frac{1}{J}\frac{\partial C^1_{sm}}{\partial \phi} = -\frac{\partial C^0_{sm}}{\partial \lambda} - \mathscr{R}C^0_{sm} - \frac{1}{J}\tilde{\nabla}^2 C^0_{sm}. \tag{2.7}$$

Again, the boundary condition

$$C^0_{sm}|_{\psi=0} = C_s, \qquad C^1_{sm}|_{\psi=0} = 0,$$

and differential equation admit a t-independent solution; therefore we suppose $\partial C^1_{sm}/\partial t = 0$. In order to eliminate secular behaviour, we must insist that the average with respect to ϕ of J times (2.7) is zero. This yields a second equation to be satisfied by C^0_{sm},

$$\langle J \rangle_\phi \frac{\partial C^0_{sm}}{\partial \lambda} = -\langle J \rangle_\phi \mathscr{R} C^0_{sm} - \frac{\partial^2 C^0_{sm}}{\partial \psi^2}, \tag{2.8}$$

where the average is defined by

$$\langle \cdot \rangle_\phi \equiv \frac{1}{2\pi}\int_0^{2\pi} (\cdot)\mathrm{d}\phi.$$

Solution of (2.8) yields the leading-order concentration field, which is independent of t and ϕ. Equation (2.8) describes the evolution of the concentration field via convection-enhanced diffusion and chemical reaction on the diffusive time scale. Because the boundary condition (2.6) is translation-invariant, the oscillatory problem at leading order is a homogeneous partial differential equation with a homogeneous boundary condition – with solution zero.

The flux of gas per unit area evaluated on the surface is, in dimensional variables $-D^* \boldsymbol{e}_n \cdot \nabla^* C$ evaluated on $z^* = \eta^*$. The vector $\boldsymbol{e}_n$ is the outward unit normal at the fluid surface. The flux per unit area, rendered dimensionless by dividing by k^* and D^*, is $F = \boldsymbol{e}_n \cdot \nabla C$ evaluated on $\psi = 0$. The normal vector to the surface is most easily obtained from the gradient of the stream function:

$$\boldsymbol{e}_n = \frac{-\nabla\psi}{\|\nabla\psi\|} = \left[\frac{w}{(u^2+w^2)^{1/2}}\boldsymbol{e}_x - \frac{u}{(u^2+w^2)^{1/2}}\boldsymbol{e}_z\right]_{\psi=0}. \tag{2.9}$$

The gradient of the concentration field may be written

$$\nabla C = \frac{1}{J}\{C, z\}\boldsymbol{e}_x + \frac{1}{J}\{x, C\}\boldsymbol{e}_z.$$

Hence we obtain

$$[\boldsymbol{e}_n \cdot \nabla C]_{\psi=0} = \left[-(u^2+w^2)^{1/2}\frac{\partial C}{\partial \psi}\right]_{\psi=0}.$$

The flux emerges as

$$F = \left(u^2+w^2\right)^{1/2}\frac{\partial C}{\partial \psi}\bigg|_{\psi=0}.$$

Next we average this over the arclength; this is simplified by use of the relation $ds = d\phi/(u^2 + w^2)^{1/2}$, where s is the arclength. The smooth concentration field is independent of ϕ to leading order. Hence, when we average the flux per unit area we obtain

$$\langle F \rangle_\phi = \frac{\partial C^0_{sm}}{\partial \psi}|_{\psi=0} + O\left(\mathscr{P}^{-1}\right). \tag{2.10}$$

2.2. *Gas transport through flat and wavy interfaces*

If the interface is flat, then $u = -1$ and $w = 0$. The *slowest* rate of gas transport will be that which obtains asymptotically in time (i.e. when $\lambda \to \infty$). Hence, we consider the problem for the long-time asymptotic concentration field, indicated by an overbar:

$$\frac{d^2 \bar{C}^0_{sm}}{d\psi^2} - \mathscr{R}\bar{C}^0_{sm} = 0,$$

with the boundary condition $\bar{C}^0_{sm}(\psi = 0) = C_s$. The solution which decays as $\psi \to \infty$ is $\bar{C}^0_{sm}(\psi) = C_s \exp(-\mathscr{R}^{1/2}\psi)$. Hence the averaged flux per unit area is simply

$$\langle F \rangle_\phi = -\mathscr{R}^{1/2} C_s; \tag{2.11}$$

the negative sign is an indication that the flux is into the liquid. We shall also determine the concentration boundary layer thickness, which we define to be the depth of fluid within which the mass fraction C is at least $0.05C_s$. In the case of a clean, flat interface, the thickness is

$$\delta_c = \frac{\log 20}{\mathscr{R}^{1/2}}. \tag{2.12}$$

Now we investigate the concentration field within the liquid under an interface disturbed by capillary waves. We shall make use of the well-known exact solution of Crapper (1957), which in our variables takes the form

$$x + iz = -\phi - i\psi + \frac{4i}{1 + A\exp(i\phi)\exp(-\psi)} - 4i, \tag{2.13}$$

and

$$u - iw = -\left(\frac{1 + A\exp(i\phi)\exp(-\psi)}{1 - A\exp(i\phi)\exp(-\psi)}\right)^2. \tag{2.14}$$

The constant A is related to the amplitude of the wave a^* – the dimensional vertical distance between crest and trough. If we define a dimensionless amplitude $a = k^*a^* = 2\pi a^*/\lambda^*$, then the constant A may be written

$$A = \frac{4}{a}\left[\left(1 + \frac{a^2}{16}\right)^{1/2} - 1\right].$$

The waves make physical sense only for $a^*/\lambda^* \leqslant 0.730$; this translates to $A \leqslant 0.455$. In figure 1 we show profiles and streamlines of the nonlinear capillary waves. Using this solution, it is possible to compute the required spatial average without approximation

$$\left\langle \frac{1}{u^2 + w^2} \right\rangle_\phi = \frac{A^6 - 19A^4\exp 2\psi - 13A^2\exp 4\psi - \exp 6\psi}{\left(A^2 - \exp 2\psi\right)^3}. \tag{2.15}$$

In order to determine the flux, we must solve (2.8) – again *the long-time asymptotic*

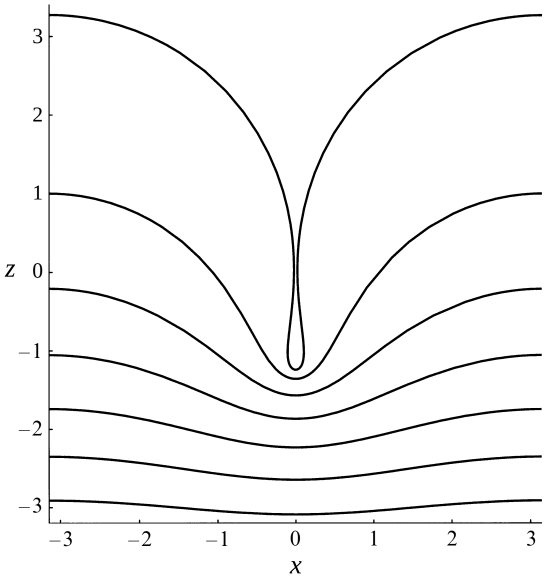

FIGURE 1. A plot of the surface elevation and streamlines of the exact solution for a capillary wave with amplitude $A = 0.45$ – this is very nearly the maximum amplitude that makes physical sense. The subsurface streamlines are surfaces of waves of lesser amplitude.

solution provides the most conservative answer. Therefore we solve

$$\frac{\mathrm{d}^2\bar{C}^0_{sm}}{\mathrm{d}\psi^2} - \mathscr{R}\left\langle \frac{1}{u^2+w^2} \right\rangle_\phi \bar{C}^0_{sm} = 0,$$

making use of (2.15), with the boundary condition $\bar{C}^0_{sm}(\psi = 0) = C_s$. We use a simple shooting method to determine that value of $\partial\bar{C}^0_{sm}/\partial\psi$ at $\psi = 0$ which makes $\bar{C}^0_{sm} \to 0$ as $\psi \to \infty$.

In figure 2 we show the asymptotic, smooth concentration field of dissolved gases in the liquid $\bar{C}^0_{sm}$ for a capillary wave with $A = 0.35$ and reaction rate $\mathscr{R} = 1$. One can readily observe the steepening of the concentration field under the trough of the wave (here at $x = 0$) and the shallowing of the concentration field under the crest of the wave (at $x = \pm\pi$). For reference, in figure 3 we show $\bar{C}^0_{sm}$ in a liquid undisturbed by capillary waves.

It is of central importance in this work to understand why the concentration gradient is steeper under the troughs of the capillary waves – this is why convection enhances the diffusion. As was mentioned before, the concentration field is very nearly a material field as a consequence of the slow diffusive time scale compared to the fast convective time scale. To leading order, our analysis shows that the asymptotic concentration field is a function of ψ only. Hence, wherever streamlines approach one another in physical space, the spatial gradient in concentration (with respect to x and z) will be steeper; where streamlines diverge, spatial gradients of the concentration will be smaller.

From a physical point of view, the steepness of the concentration field under the troughs is a function of the relatively brief time the fluid spends under the troughs compared to the long time the fluid spends under the crests. Hence, smaller-amplitude capillary waves – which are more nearly sinusoidal, have smaller enhancement of diffusion by convection. The time spent under troughs and under crests is more

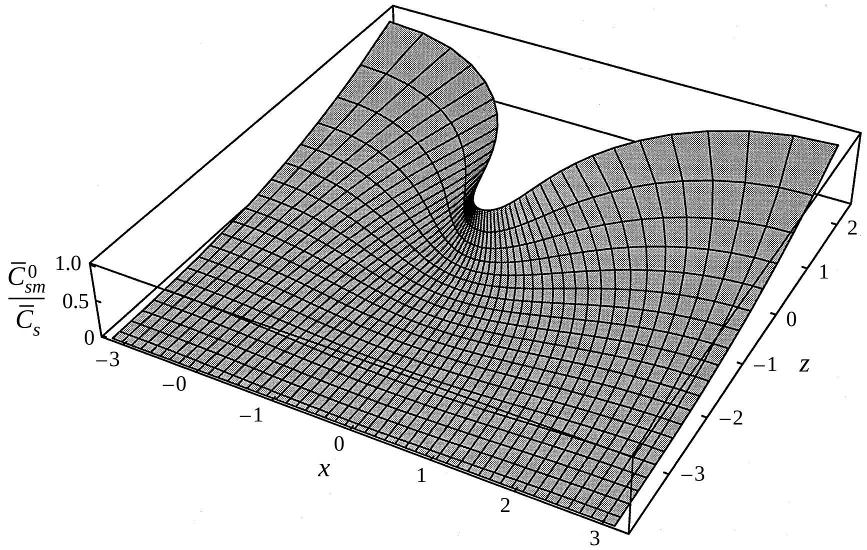

FIGURE 2. The concentration field of dissolved gas, asymptotically in time, in the fluid disturbed by a capillary wave with amplitude $A = 0.35$ and reaction rate $\mathscr{R} = 1$.

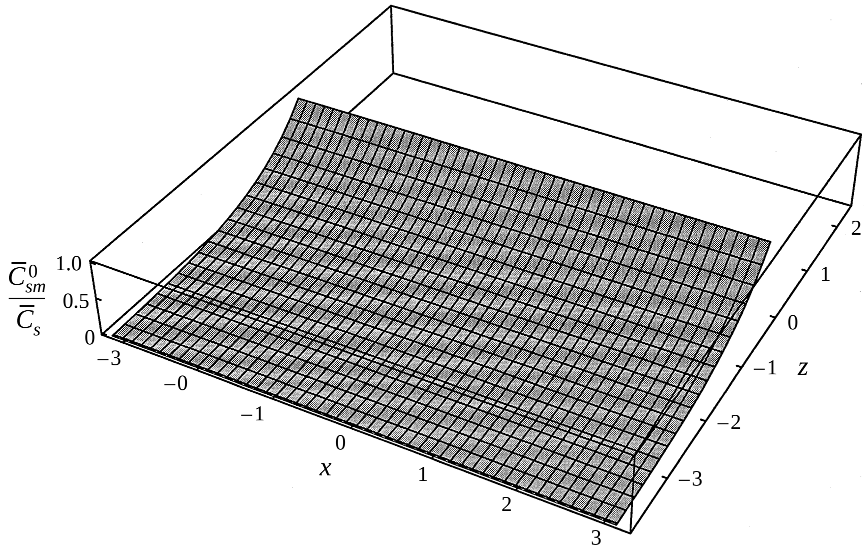

FIGURE 3. The concentration field of dissolved gas, asymptotically in time, in an undisturbed fluid. The reaction rate is $\mathscr{R} = 1$.

nearly balanced. Under large-amplitude capillary waves, the time a fluid point spends under troughs is very much shorter than the time spent under crests. Thus when streamlines converge under the trough of a large-amplitude capillary wave, the concentration gradient is large.

The flux, normalized by the clean surface result (2.11) is plotted in figure 4 for several different wave amplitudes over a broad range of the parameter $10^{-3} \leqslant \mathscr{R} \leqslant 10^3$. One observes that there is a substantial increase in the transport of gas through the interface as a consequence of the presence of capillary waves. This is particularly true

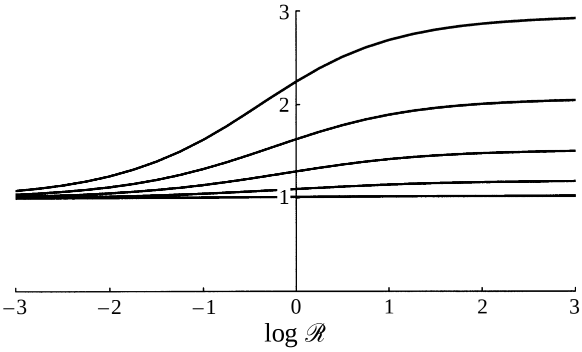

FIGURE 4. Enhancement of transfer of gas through the interface by capillary waves. The curves show the long-time asymptotic average flux of gas into solution through a rippled interface, normalized by the flux of gas into solution through a flat interface, as a function of the dimensionless reaction rate $\mathscr{R}$. The different curves correspond to capillary waves of different amplitudes $A = 0.45$ (uppermost), $A = 0.35$, $A = 0.25$, $A = 0.15$ and $A = 0.05$ (lowest).

for larger-amplitude ripples (i.e. larger A) and for more vigorous removal of dissolved gases via chemical reaction in the fluid (large $\mathscr{R}$). Over the range of reaction rates shown in figure 4 the maximum enhancement of transport is about 3 times the flat interface value.

It is interesting to observe in figure 4 that the flux enhancement appears to level off at both extrema of the domain in $\mathscr{R}$. When $\mathscr{R} \to \infty$, the concentration boundary layer is very thin. Therefore, the fluid within the concentration boundary layer lies very close to the surface, where the convection-enhanced diffusion is at its maximum. When $\mathscr{R} \to 0$, the concentration boundary layer is very thick. In this limit, convection significantly enhances diffusion only in a thin surface sub-layer within the thick concentration boundary layer. The majority of the diffusion is not enhanced by the very weak convection deep beneath the ripples.

The concentration boundary layer thickness is defined as follows. First, we use the (numerical) solution of the transport equation to determine the value of the stream function (say $\tilde{\psi}$) where $C = 0.05C_s$. Next, we determine the dimensionless volume of the fluid per wavelength above this streamline to yield an expression for the concentration boundary layer thickness. In other words, we integrate

$$\frac{1}{2\pi}\int_{x=0}^{x=2\pi}\int_{z=z(\phi,\tilde{\psi})}^{z=z(\phi,0)} \mathrm{d}z\,\mathrm{d}x;$$

upon changing variables in the integral, this becomes

$$\frac{1}{2\pi}\int_{\phi=0}^{\phi=2\pi}\int_{\psi=0}^{\psi=\tilde{\psi}} \frac{1}{u^2+w^2}\mathrm{d}\psi\,\mathrm{d}\phi.$$

This integral may be evaluated without approximation to yield

$$\delta_c = \frac{8A^2}{\left(-1+A^2\right)^2} - \frac{8A^4}{\left(A^2-\mathrm{e}^{2\tilde{\psi}}\right)^2} + \frac{8A^2}{A^2-\mathrm{e}^{2\tilde{\psi}}} + \tilde{\psi}. \tag{2.16}$$

The concentration boundary layer thickness, computed via (2.16) and normalized by the clean surface result (2.12) is plotted in figure 5 for several different wave amplitudes over the range $10^{-3} \leqslant \mathscr{R} \leqslant 10^3$. Clearly, in addition to the increased transport of gas into solution through the wavy interface, there is a significant thickening in the

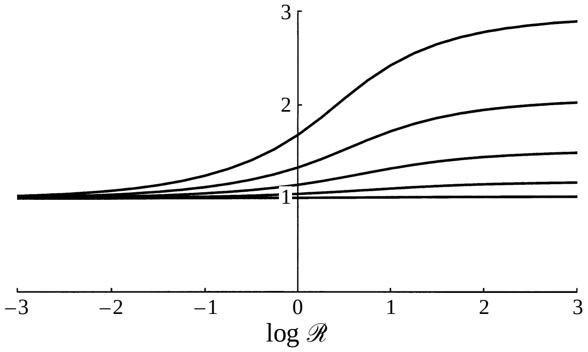

FIGURE 5. Thickening of the concentration boundary layer by capillary waves. The curves show the long-time asymptotic boundary layer thickness under a rippled interface, normalized by the boundary layer thickness under a flat interface, as a function of the dimensionless reaction rate $\mathscr{R}$. The different curves correspond to capillary waves of different amplitudes $A = 0.45$ (uppermost), $A = 0.35$, $A = 0.25$, $A = 0.15$ and $A = 0.05$ (lowest). The boundary layer thickness is the thickness of fluid near the surface within which the concentration is $\geqslant 5\%$ of the saturation concentration – the value at the surface.

concentration boundary layer. This is a clear demonstration that the boundary layer profile of the concentration field is nonlinear. If the profile were linear, enhancement of transport could only occur with a thinning of the boundary layer. Over the ranges of $\mathscr{R}$ and of capillary waves we examined, the increase in thickness of the concentration boundary layer can be as much as three times the boundary layer under a flat interface – for large-amplitude capillary waves and vigorous removal by chemical reaction in the liquid. As was the case with gas transfer enhancement, the thickening of the concentration boundary layer by capillary waves levels off as $\mathscr{R} \to \infty$ and as $\mathscr{R} \to 0$.

Finally, it is worth noting that the enhancement of transport through the wavy compared to the flat interface is not simply a product of the increased surface area available for transport, but rather a more subtle effect of convection-enhanced diffusion. The surface area is proportional to the arclength of the interface:

$$\frac{1}{2\pi}\int_0^{2\pi}\left[\left(\frac{\partial x}{\partial \phi}\right)^2+\left(\frac{\partial z}{\partial \phi}\right)^2\right]^{1/2}_{\psi=0} \mathrm{d}\phi = \frac{1+3A^2}{1-A^2}.$$

This expression achieves its maximum of approximately 2 for waves of limiting amplitude $A = 0.455$. Hence, a simple increase in the surface area available for transport through the wavy surface cannot account for the total amount of enhancement of gas transfer: one must also account for the convection-enhanced diffusion of dissolved gas within the liquid, as we have done.

3. Capillary waves and the surface renewal model

Thus far the present work has been devoted to understanding how to formulate and solve a rather fundamental problem: the consequences for gas transfer of the presence of monochromatic nonlinear capillary waves on the surface of an otherwise undisturbed deep fluid. It is of interest to know how the enhancement of gas transfer across an interface by capillary waves compares with enhancement by other mechanisms. To this end, we shall incorporate our new understanding of the role of capillary waves into one model of air–sea gas transfer that is currently accepted by some researchers – the surface renewal model. Before undertaking this analysis, some discussion of the theory is appropriate.

There is basic agreement among researchers in air–sea gas transfer that under typical windy wavy conditions a concentration boundary layer exists at the free surface due to turbulent mixing near the free surface. There is less agreement, however, on the source of the turbulence. Coantic (1986) and Jähne *et al.* (1987) argue that the waves on the interface are the source of near-surface turbulence. This is through the interaction of capillary waves and shear flow (Coantic) or through turbulent wave dissipation (Jähne *et al.*). McCready & Hanratty (1985), Back & McCready (1988) and more recently Komori, Nagarosa & Murakami (1993) argue that the turbulence in the water side is caused by turbulent gas flow over small-wavelength waves.

Near-surface turbulence is thought to keep the concentration boundary layer thin because it decays as one approaches the free surface. Within the thin concentration boundary layer molecular diffusion is the dominant mode of transport. We have shown that capillary waves can thicken the concentration boundary layer and increase gas transport. Therefore it is of interest to estimate how important is the effect of capillary waves compared to the enhancement of transport by near-surface turbulence – whatever its source.

To explore this issue, we will attempt a modification of the surface renewal model to include the effects of capillary waves. There are a number of shortcomings to the surface renewal model; chief among these may be that the mechanism for generation of near-surface turbulence is overlooked. However, it is useful to consider the model in order to estimate the magnitude of capillary wave enhancement of gas transfer compared to turbulent enhancement. A final reason to undertake this analysis is to exploit the transient dynamics of our perturbation theory for the transport problem. We return to this point later.

The surface renewal model was originated by Danckwerts (1951). Essentially, the model proposes that it is the exchange of fluid between the interface and the bulk that is responsible for the enhanced rates of gas transfer at turbulent air–water interfaces. When fresh bulk liquid alights on the surface, there is a very rapid invasion of dissolved gases down the steep concentration gradient (assuming that the bulk liquid is undersaturated). The rate of gas transfer into a given 'surface patch' slowly decreases, until the next surface renewal event.

The rapid gas transfer to a fresh patch of surface can be understood from the solution of equation (2.1) with $\boldsymbol{u} \equiv 0$ and $\mathscr{R} \equiv 0$. Suppose that on the interface the concentration boundary condition is $C(t^*, x^*, z^* = 0) = C_s$ and in the bulk, the far-field condition is $C(t^*, x^*, z^* \to -\infty) = C_b < C_s$. Then the solution of (2.1) with $\boldsymbol{u} \equiv 0$ and $\mathscr{R} \equiv 0$ is

$$C = C_b + (C_s - C_b)\,\mathrm{erfc}\left(\frac{-z^*}{2(D^* t^*)^{1/2}}\right).$$

The gas flux per unit time per unit surface area is

$$F^* = D\frac{\partial C}{\partial z^*} = (C_s - C_b)\left(\frac{D^*}{\pi t^*}\right)^{1/2}.$$

Hence, if the last surface renewal occurred at $t^* = 0$, then the rate of gas transfer F^* is very large when t^* is small. Danckwerts (1951) proposed that there is a random distribution of surface ages $f(\theta^*) = s^* \exp(-s^*\theta^*)$ where θ^* is the age of the surface and s^* is the fraction of the surface renewed per unit time. To obtain the average flux over the entire surface, one simply averages F^* (with t^* interpreted as θ^*) over the distribution of ages of surface patches:

$$\langle F^* \rangle = (C_s - C_b)\left(\frac{D^*}{\pi}\right)^{1/2} s^* \int_0^\infty \frac{\exp(-s^*\theta^*)}{(\theta^*)^{1/2}}\mathrm{d}\theta^* = \left(Ds^*\right)^{1/2}(C_s - C_b). \tag{3.1}$$

The overall rate of gas transfer is linear in the bulk undersaturation, and depends on the square-root of the gas diffusivity and the rate of surface renewal.

In the surface renewal model there is a concentration boundary layer at the interface that is kept thin by renewal, followed by slow invasion of dissolved gases by molecular diffusion, followed by renewal, etc. Between renewal events, the model assumes that a given surface patch absorbs gas as though it were quiescent and infinitely deep. Recent work on the surface renewal model has therefore focused on measuring the rate of surface renewal (Asher & Pankow 1991; Komori *et al.* 1993), or on proposing alternative distributions of surface ages (Fan, Shen & Chou 1993).

However, it is well-known that the wind-sheared turbulent air–sea interface is heavily populated by capillary waves. These may be observed, for example, in figures 10 and 11 of the paper by Jähne *et al.* (1987). Capillary waves are known to be associated with larger waves. These have been investigated recently by Perlin, Lin & Ting (1993), who found that the high-frequency parasitic capillary waves formed on gravity waves are fairly well-described by the theory of Crapper (1970). In analysing the parasitic capillary waves, Crapper makes use of his earlier exact solution for the form of the nonlinear capillary waves – the same profiles we used in the preliminary theory.

The physical paradigm for surface renewal put forward by Komori *et al.* (1993) describes surface renewal events as occurring intermittently on the windward side of gravity waves. At low or moderate wind speeds, parasitic capillary waves occur on the leeward side and in the troughs of gravity waves. Hence, a case may be made for an interactive effect between surface renewal that gives rise to a fresh patch of bulk fluid on the surface, followed rapidly by capillary waves that enhance the gas transfer into the fresh surface patch at the critical early age of the surface patch.

With these ideas in mind, we propose a modest enhancement of the surface renewal model to include the effects of capillary waves. Danckwerts (1951) and others who followed have assumed that between surface renewal events the liquid absorbs gas as though it were quiescent and infinitely deep. We shall assume that between surface renewal events, the liquid absorbs gas as though it were an otherwise quiescent liquid perturbed by capillary waves on the interface. In this way, we propose to combine the theory developed in the earlier part of the present work, which derives from the work of Witting (1971) and of MacIntyre (1971), with the surface renewal model of Danckwerts (1951). Of course, it is cavalier of us, to say the least, to suppose that between surface renewal events our theory of capillary-wave-enhanced diffusive transport applies – but we believe it to be in the spirit of the surface renewal model. Besides, the goal of this analysis is to estimate how capillary wave enhancement compares to near-surface turbulence enhancement of gas transfer.

The starting point of our modification of the surface renewal model is equation (2.8), which is the averaged problem cast in terms of the time scale $\lambda = \theta/\mathscr{P}$, where θ is the dimensionless age of a surface patch. We shall take the boundary and initial conditions $C^0_{sm}(\lambda, \psi = 0) = C_s$, $C^0_{sm}(\lambda = 0, \psi) = C_b$ and the far-field condition $C^0_{sm}(\lambda, \psi \to \infty) = C_b$, where C_b is the bulk concentration. We shall assume that the wave disturbing the interface is a monochromatic nonlinear Crapper capillary wave, hence we have (2.15). Now, we shall make a further approximation. Because convection-enhanced diffusion acts only for a short time before the next surface renewal, there will be a gradient of C_{sm}^0 with respect to ψ only at small ψ. Therefore, we shall replace $\langle -J\rangle_\phi$, which is a function of depth ψ, by its value at the surface $\psi = 0$, $\langle -J\rangle_{\phi,0}$. Under this approximation, (2.8) has the solution

$$C_{sm}^0 = C_b + (C_s - C_b)\,\mathrm{erfc}\left[\frac{-\psi}{2}\left(\frac{\langle -J\rangle_{\phi,0}}{\lambda}\right)^{1/2}\right].$$

The dimensionless gas flux per unit time per unit surface area is

$$F = \left(\frac{\partial C}{\partial \psi}\right)_{\psi=0} = (C_s - C_b)\left(\frac{\langle -J\rangle_{\phi,0}}{\pi\lambda}\right)^{1/2} = \left(\mathscr{P}\frac{\langle -J\rangle_{\phi,0}}{\pi\theta}\right)^{1/2}(C_s - C_b).$$

Next, following Danckwerts (1951), we average over a random distribution of ages of surface patches to obtain

$$\langle F\rangle = \left(\langle -J\rangle_{\phi,0}\mathscr{P}s\right)^{1/2}(C_s - C_b),$$

where s is the dimensionless rate of surface renewal. In dimensional terms, we have

$$\langle F^*\rangle = \langle -J\rangle_{\phi,0}^{1/2}\left(D^* s^*\right)^{1/2}(C_s - C_b),$$

which may be compared to (3.1) to understand the relative contribution of capillary wave enhancement between surface renewal events. Our modification of the surface renewal theory does not change the fact that the overall gas transfer rate is linear in the bulk undersaturation or that it depends on the square-root of the gas diffusivity and the surface renewal rate. The modification simply introduces a prefactor that accounts for the convection-enhanced diffusion due to capillary waves. The prefactor $\langle -J\rangle_{\phi,0}^{1/2}$ associated with capillary wave enhancement, where

$$\langle -J\rangle_{\phi,0} = \frac{-1 - 13A^2 - 19A^4 + A^6}{(-1 + A)^3(1 + A)^3}, \tag{3.2}$$

is shown in figure 6. It is interesting to note that the prefactor could simply be absorbed into s^* – the fraction of the surface renewed per unit time. This is despite the fact that the capillary waves by themselves cause no surface renewal.

Jähne *et al.* (1987) have noted that the *mean*-square slope of capillary waves on the air–water interface does not normally exceed 0.2. For nonlinear (Crapper) capillary waves, the mean-square slope is

$$\left\langle\left(\frac{\mathrm{d}z}{\mathrm{d}x}\right)^2_{\psi=0}\right\rangle = \frac{8A^2(A^2 - 1)^2}{(1 - 6A^2 + A^4)^2}\left[\frac{1 - 6A^2 + A^4}{(-1 + A^2)^2}\right]^{1/2};$$

hence 0.2 for the mean-square slope corresponds to $A \approx 0.07$, which yields a capillary wave enhancement of $\langle -J\rangle_{\phi,0}^{1/2} \approx 1.04$ or 4%.

However, the theory of Crapper (1970) and the experiments of Perlin *et al.* (1993) have shown that the capillary wave steepness is not uniformly distributed over the entire surface when larger waves are present. Capillary waves at low and moderate wind speeds are far steeper on the leeward sides of gravity waves – this may again be observed in the photographs in figures 10 and 11 of Jähne *et al.* (1987). At fairly low capillary wave amplitudes, say $A = 0.15$, the gas transfer is enhanced by 20%. Such amplitudes are well within the values observed by Perlin *et al.* (1993). These

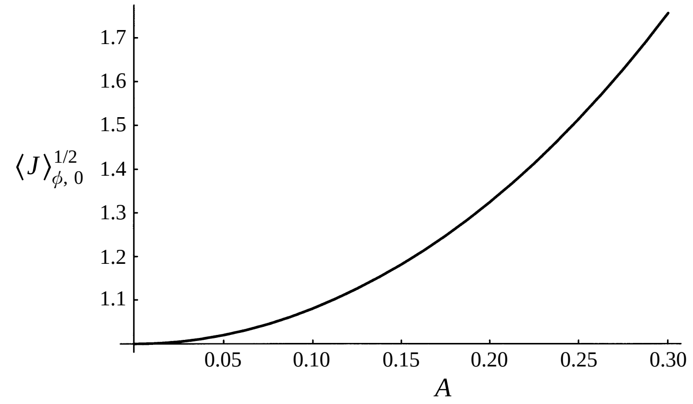

FIGURE 6. The factor by which gas transfer in a surface renewal model is enhanced by capillary waves, as a function of the amplitude of the capillary waves.

observations suggest two points: (i) that the surface slope (squared) averaged over the whole surface may not be the best measure of the amplitudes of the capillary waves of importance in air–sea gas transfer, and (ii) that a deeper understanding may arise from experimental observation of the correlation between the locations of intense near-surface turbulence and of capillary waves.

4. Conclusions

In this paper we considered the effects of capillary waves on air–water gas transfer into both (i) an otherwise quiescent liquid within which the dissolved gas is produced or consumed in a chemical reaction, and (ii) through a turbulent sheared interface in the context of a surface renewal model. The effects of capillary waves derive from the fact that stream surfaces are closer together under troughs and further apart under crests of waves. This leads to an alternate steepening and shallowing of the concentration field – which is very nearly a material field as a consequence of the smallness of molecular diffusivity. Owing to the enhancement of transport under the troughs of capillary waves, the concentration boundary layer is thickened; dissolved gases penetrate more deeply when the gradients are steepened by the waves.

In the preliminary theory of gas transfer into an otherwise undisturbed liquid, the concentration boundary layer is a consequence of a first-order chemical reaction supposed to occur in the liquid. By tuning the reaction rate, it was possible to change the thickness of the concentration boundary layer. This permitted us to explore the enhancement to molecular diffusivity at different depths in the capillary wave. We found that enhancement to molecular diffusivity was greatest for thin concentration boundary layers caused, in this problem, by vigorous removal of dissolved gases by chemical reaction in the liquid. Asymptotically in time (which gives the most conservative figure) the capillary waves were found to enhance transport and to thicken the concentration boundary layer by up to three times. These enhancements of gas transfer are less than the enhancements in the related theories developed by Witting (1971) or by MacIntyre (1971), but those authors assumed a thickness, *a priori*, for the boundary layer rather than permitting the thickness to emerge in the solution of the problem, as we have done.

Finally, we made use of the theory thus developed to propose an enhancement to the surface renewal model of Danckwerts (1951) for the transfer of gas through a sheared turbulent interface. In the original surface renewal model, the liquid absorbs gas into solution as though it were quiescent and of infinite depth between renewal events. This simple model yields rapid invasion of dissolved gas until the next surface renewal event, when bulk fluid is instantaneously exchanged with the interface. Our proposal is to regard the liquid between surface renewals not as wholly quiescent, but rather as disturbed by capillary waves (but otherwise quiescent).

This proposal is made as a consequence of the understanding developed in the preliminary theory. There, we found that asymptotically in time the capillary wave enhancement of gas transfer was greatest through a thin boundary layer. This is a consequence of the fact that convection-enhanced diffusion is most effective at the surface. If one considers the unsteady problem of gas invasion into a fresh surface patch in the surface renewal model, then at an early age the concentration boundary layer is thin.

Hence, with frequent surface renewal, a thin concentration boundary layer is maintained at the interface. This situation is especially amenable to the convection-enhanced diffusion associated with capillary waves. To understand the consequences, we simply solved a suitably spatially averaged unsteady transport problem to obtain the gas flux into a fresh patch of surface as a function of the age of the patch. Next, we followed Danckwerts (1951) and averaged this flux over a random distribution of surface ages. What emerged was a very straightforward modification of the surface renewal model to include the effects of capillary waves.

In the modified surface renewal model, the surface renewal events are thought to take place intermittently on the windward side of gravity waves; such were the observations in the recent experiments of Komori *et al.* (1993). These fresh surface patches are soon after disturbed by capillary waves, which are ubiquitous at high wind speeds (MacIntyre 1971), and present even at still conditions as well-understood parasitic capillary waves (Perlin *et al.* 1993). In the latter paper, the authors show that the solution of Crapper (1970) for the capillary waves is a good approximation especially on the critical leeward side of the gravity waves. Hence we suggest that air–sea gas transfer may be better understood as capillary wave enhancement of molecular diffusion into concentration boundary layers thinned by near-surface turbulence.

The author would like to acknowledge the support of the Office of Naval Research under the Young Investigator Program. The author is grateful to the Referees for their constructive comments, and to M. J. McCready for a very helpful discussion.

Appendix. On the escape of dissolved gases from the liquid

Briefly, we now comment on the case where the dissolved gas is produced in the liquid via chemical reaction, and subsequently escapes through the rippled interface to the free state. If we set $C = 1$ to be the equilibrium concentration of dissolved gases in the liquid, then the convection–diffusion equation is

$$\frac{\partial C}{\partial t^*} + \boldsymbol{u}^* \cdot \nabla^* C = D\nabla^{*2} C + r(1 - C).$$

If we define instead $\hat{C} \equiv C - 1$, it is a simple matter to show that $\hat{C}$ satisfies (2.2) with the boundary condition

$$\hat{C}|_{\psi=0} = C_s - 1.$$

Hence, in the case of a clean interface, the solution to the transport problem when the dissolved gas is produced in the liquid via chemical reaction is simply $(C_s - 1)/C_s$

times the solution of the transport problem when the dissolved gas is destroyed in the liquid via chemical reaction.

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