NONSTATIONARY DIFFUSION NEAR A PERTURBED FREE FLUID SURFACE

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A free surface, both under natural conditions and in instruments of chemical technology and thermal energetics, is mostly perturbed by waves. The natural problem arises: which waves can vary the intensity of diffusion processes in a fluid, and which wave parameters affect most substantially gas exchange between the free surface and the atmosphere?

An effective method of solving the diffusion problem near a free surface was suggested in [1, 2], where the existence was shown of a self-similar solution, obtained within the approximation of a thin diffusion boundary layer. In fact, this approach is based on the introduction of Lagrange coordinates for fluid particles at the surface. In the present study, the method mentioned is generalized to the case of nonstationary diffusion with homogeneous initial and boundary conditions and imposed perturbations of general spatial form. Diffusion is then investigated in detail in traveling and standing plane waves.

Since the diffusion coefficients in the fluid are small for all molecules, most of the resistance to mass transfer is concentrated in the fluid phase, and material diffusion in the gas phase over the fluid must not be considered, assuming for all moments of time $t > 0$ that the concentration at the free surface is given by C_0. The initial concentration of the dissolved gas in the fluid bulk is C_1.

Let the free surface be given by the equation $y = h(x, z, t)$, where y is the vertical, and x and z are the horizontal coordinates. Denoting by the subscript 0 the values of all quantities at the surface $y = h$, we have the kinematic condition

$$v_0 = \partial h/\partial t + (\mathbf{u}_0 \cdot \nabla)h. \tag{1}$$

Here and in the following $\nabla = (\partial/\partial x, \partial/\partial z)$ is the two-dimensional gradient operator, and $\mathbf{u}_0 = (u_0, w_0)$ is the vector of horizontal velocity components at the fluid surface. Integrating the equation of continuity near the free surface, for the vertical velocity component one obtains within the first approximation

$$v = v_0 + (h - y)(\nabla \cdot \mathbf{u}_0). \tag{2}$$

For waves in soft water the horizontal velocity components are constant over the whole layer thickness and equal to their values at the surface; therefore it follows from the equation of continuity that $v = -y(\nabla \cdot \mathbf{u}_0)$ and $v_0 = -h(\nabla \cdot \mathbf{u}_0)$. Combining the latter relation with the kinematic condition (1), we find the conservation equation of fluid mass, known in the theory of soft water:

$$\partial h/\partial t + (\nabla \cdot \mathbf{u}_0 h) = 0. \tag{3}$$

If one now takes into account expressions (1), (2), and transforms the equation of convective diffusion, selected in the boundary-layer approximation, to the new coordinate $y' = h - y$ measured from the free surface, it acquires the form [1, 2]

$$\partial C/\partial t + (\mathbf{u}_0 \cdot \nabla)C - y'(\nabla \cdot \mathbf{u}_0)\partial C/\partial y' = D\partial^2 C/\partial y'^2. \tag{4}$$

In deriving Eq. (4) and everywhere in the following, one also uses the approximation of a weakly curved surface, neglecting terms with x and z derivatives of second order of smallness: $(\nabla h)^2$, $\nabla^2 h$, $(\nabla h \cdot \nabla C)$. This approximation is, obviously, valid for long waves, whose amplitudes are much smaller than the wavelength.

For small diffusion coefficients of gas molecules in viscous fluids ($D \sim 10^{-9}$–10^{-12} m^2/sec), and during the significant time interval ($t \ll h^2/D$), the external boundary of the diffusion boundary layer $\delta \sim (Dt)^{1/2}$ does not reach the bottom of the basin, and the exact boundary condition at the bottom $(\partial C/\partial y')_{y'=h} = 0$ can be neglected, replacing it by the condition $C = C_1$, with $\delta \ll y' < h$. For waves in deep water, when the wave-

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length λ is much smaller than the depth h, the time interval for which Eq. (4) is solved is determined by the condition $\delta(t) \ll \lambda$, upon satisfaction of which the assumption of constancy of the horizontal velocity components over the thickness of the diffusion boundary layer is valid.

So as not to encumber the discussion, in what follows we omit the subscript 0 at the velocity components and the prime of the coordinate y. Equation (4) is augmented by the boundary and initial conditions: $C(y=0) = C_0$, $C(y \gg \delta) = C_1$, $C(t=0) = C_1$. There exists a self-similar solution of Eq. (4), satisfying this boundary condition:

$$\frac{C - C_0}{C_1 - C_0} = \frac{2}{\sqrt{\pi}} \int_0^{y/\delta} \exp(-\eta^2)\, d\eta. \tag{5}$$

The following equation is obtained from (4) for δ, the thickness of the diffusion boundary layer,

$$\partial\delta^2/\partial t + (\mathbf{u}\cdot\nabla)\delta^2 + 2(\nabla\cdot\mathbf{u})\delta^2 = 4D \tag{6}$$

with the initial condition $\delta = 0$ at $t = 0$.

In the approximation adopted the horizontal velocities in the depth of the fluid layer and at the free surface coincide. Any two fluid particles, then, having initially identical coordinates x_0, z_0 but with different distances to the surface y_{01}, y_{02}, will in the following have coinciding horizontal coordinates $x_1 = x_2$, $z_1 = z_2$, and vertical coordinates strictly proportional to each other $y_1/y_2 = y_{01}/y_{02}$. The trajectories of fluid particles are found from the differential equations

$$dx/dt = u(x, z, t), \quad dz/dt = w(x, z, t), \quad dy/dt = -(\nabla\cdot\mathbf{u})y \tag{7}$$

with the initial conditions $x = x_0$, $z = z_0$, $y = y_0$ at $t = 0$. An extracted small fluid region at the free surface with layers adjacent to it from below will be displaced spatially, undergoing only simple deformations in the y direction.

Substituting **u** and $(\nabla \cdot \mathbf{u})$ from (7) into (6), we have

$$\frac{d\delta^2}{dt} - \frac{2}{y}\frac{dy}{dt}\delta^2 = 4D, \tag{8}$$

where the total (substantial) derivative along the fluid particle trajectory on the free surface $d/dt = \partial/\partial t + (\mathbf{u}\cdot\nabla)$ was introduced. Integrating Eq. (8) with account of the initial condition $\delta(t=0) = 0$ gives

$$\delta = \sqrt{4Dy^2(t)\int_0^t \frac{dt'}{y^2(t')}}. \tag{9}$$

For waves in soft water $y \sim h$, as it follows from (3), (7) that $(1/h)dh/dt = -(\nabla\cdot\mathbf{u}) = (1/y)dy/dt$. Then

$$\delta = 2h(t)\sqrt{D\int_0^t \frac{dt'}{h^2(t')}}, \tag{10}$$

whence it is seen that the thickness of the diffusion boundary layer is proportional to the instantaneous thickness of the water layer, while "memory" of former deformations of this layer occurs in form of an integral, computed along a Lagrangian trajectory of surface particles. To determine δ at the given point x, z at the moment of time t, it is required, by inverse integration from t to 0, to determine from Eq. (7) the particle trajectory at the surface [i.e, determine x_0, z_0, $x(t)$, $z(t)$], and then calculate the integral $\int_0^t dt'/h^2(t', x(t'), z(t'))$.

By definition, the local mass flow density is $j = -D(\partial C/\partial y)_0$. By Eqs. (5), (6)

$$j = \frac{2D(C_0 - C_1)}{\sqrt{\pi}\,\delta} = \frac{C_0 - C_1}{\sqrt{\pi}}\left[\frac{\partial\delta}{\partial t} + (\nabla\cdot\mathbf{u}\delta)\right]. \tag{11}$$

After integration over the surface in Eq. (11) the divergent term vanishes due to the periodic boundary conditions in x and z, and the integral mass flow is

$$J = \int_S j dx\, dz = \frac{C_0 - C_1}{\sqrt{\pi}} \int_S \frac{\partial \delta}{\partial t} dx\, dz.$$

The total amount of material diffusing through the surface S at time t is

$$m = \int_0^t J dt = \frac{C_0 - C_1}{\sqrt{\pi}} \int_S \delta dx\, dz = \frac{C_0 - C_1}{\sqrt{\pi}} S \langle \delta \rangle \tag{12}$$

(the angular brackets denote averaging over the spatial variables x and z).

In the waterless case at the same time the mass $m_0 = [(C_0 - C_1)/\pi^{1/2}]S(4Dt)^{1/2}$ diffuses through the area S. The mass-transfer intensification coefficient K is naturally determined by the ratio $m/m_0 = \langle \delta \rangle / \delta_0$. From expressions (9), (12) we have

$$K = \left\langle y(t) \sqrt{\frac{1}{t} \int_0^t \frac{dt'}{y^2(t')}} \right\rangle \xrightarrow[t \to \infty]{} \left\langle y(t) \left(\overline{\frac{1}{y^2}}\right)^{1/2} \right\rangle \tag{13}$$

(the overbar denotes averaging over the time interval t). For a traveling wave it is possible to further simplify the asymptotic (13):

$$K \xrightarrow[t \to \infty]{} \langle y \rangle \left(\overline{\frac{1}{y^2}}\right)^{1/2}.$$

Indeed, in a traveling wave the mean of the Lagrangian coordinate y^{-2} over time with $t \to \infty$ becomes dependent on the coordinates x and z. Therefore the quantity $(\overline{1/y^2})^{1/2}$ is removed from the angular bracket in Eq. (13). Since in a traveling wave a fluid particle passes in a long time all coordinates x in a wave unit cell, the averages over x, z and the mean over t must coincide (i.e., $\langle y \rangle = \overline{y}$).

We show now that from the known Cauchy–Bunyakovskii inequality [3] $(\int f\varphi dt)^2 \leqslant (\int f^2 dt)(\int \varphi^2 dt)$ (in our case $\overline{f\varphi}^2 \leqslant \overline{f^2}\,\overline{\varphi^2}$) it follows that $K_\infty \geq 1$. Choosing $f = \sqrt{y}$, $\varphi = 1/\sqrt{y}$, we have

$$1 = \left(\overline{\sqrt{y} \frac{1}{\sqrt{y}}}\right)^2 \leqslant \overline{y}\left(\overline{\frac{1}{y}}\right) \leqslant \overline{y}\left(\overline{\frac{1}{y^2}}\right)^{1/2} = K_\infty. \tag{14}$$

The last inequality in (14) $(\overline{1/y}) \leqslant (\overline{1/y^2})^{1/2}$ follows from the obvious formula $0 \leqslant \overline{(1/y - (\overline{1/y}))^2}$ after expanding the bracket and extracting the root.

For a standing wave the extraction of $(\overline{y^{-2}})^{1/2}$ from the angular bracket in Eq. (13) is inadmissible, since it is obvious that this time average depends substantially on the coordinates x, z, i.e., on whether the surface particle carries out oscillations (in nodes or antinodes of a standing wave, for example).

The problem of diffusion to the free surface is solved as follows for a traveling plane wave. For a given fluid velocity at the surface $u = u_m \cos[2\pi(x - ct)/\lambda]$ it is necessary to determine the local mass flow density and the mass-transfer intensification coefficient with instantaneous inclusion of the diffusion process at the moment of time $t = 0$. In a coordinate system moving with the wave phase velocity the fluid flow is stationary with velocity $u - c$. The equation for the Lagrange coordinates of the fluid particles in this reference system is

$$\frac{d\xi}{dt} = \frac{u - c}{\lambda} = -\frac{c}{\lambda}(1 - A\cos 2\pi\xi), \tag{15}$$

where $A = u_m/c$; $\xi = (x - ct)/\lambda$. Using (15), we obtain

$$\pi\tau\sqrt{1 - A^2} = \operatorname{arctg}\left(\frac{\operatorname{tg}\pi\xi_0}{\varkappa}\right) - \operatorname{arctg}\left(\frac{\operatorname{tg}\pi\xi}{\varkappa}\right). \tag{16}$$

Here $\tau = tc/\lambda$; $\varkappa = \sqrt{(1 - A)/(1 + A)}$, and $\xi_0 = x_0/\lambda$ is the initial dimensionless coordinate of the fluid particle. Integrating (7), we find

$$y = \frac{\text{const}}{1 - A\cos 2\pi\xi}. \tag{17}$$

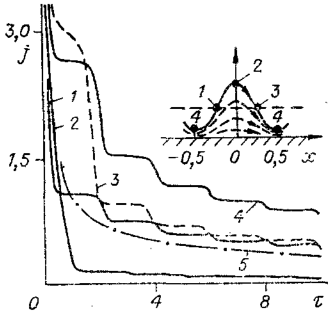

Fig. 1

Substituting (17) into Eq. (9), after calculating the integral with replacement of the variable of integration t by ξ, we write

$$\delta^2 = \left(\frac{4D\lambda}{c}\right)\frac{\xi_0 - \xi - \frac{A}{2\pi}(\sin 2\pi\xi_0 - \sin 2\pi\xi)}{(1 - A\cos 2\pi\xi)^2}, \tag{18}$$

where $4D\lambda/c = 4DT_0 = \delta_0^2$ is the square of the thickness of the diffusion boundary layer, formed after the wave period $T_0 = \lambda/c$ in the waveless case. In what follows we use the dimensionless thickness δ, referred to δ_0. Equations (16) and (18) provide, in parametric form in terms of the parameter ξ_0, the dependence $\delta(\xi, t)$, and, consequently, according to Eq. (11), they determine the local material flow $j(\xi, \tau)$.

In Fig. 1 the curves 1-4 demonstrate the behavior of $j(\xi, \tau)$ as a function of dimensionless time τ for four characteristic points on the wave profile ($\xi = -0.25$; 0; 0.25; 0.5), which for the case under consideration $A = \sqrt{3}/2 = 0.865$ is illustrated above; these four mentioned points are noted on the profile, and the current lines are denoted by primes with depth; line 5 is the local mass flow in the waveless case.

All curves for the case of a traveling wave in Fig. 1 have a characteristic step shape. For the amplitude $A = \sqrt{3}/2$ the step duration in the local mass flow is equal to 2, being the time required for displacement of the fluid particle on the free surface from one wave cell into another (for example, from a trough into an adjacent wave trough). Indeed, the time for this displacement is

$$T = T_0 \int_0^1 \frac{d\xi}{1 - A\cos 2\pi\xi} = \frac{T_0}{\sqrt{1 - A^2}}, \tag{19}$$

and in dimensionless units with $A = \sqrt{3}/2$ we obtain $\tau = 2$.

For large τ it follows from (16) that $\xi_0 = \sqrt{1 - A^2}\tau$. We determine the asymptotic integral mass flow by Eq. (12), where it is necessary to substitute the expression for δ, following from (18) for $\tau \to \infty : \delta = \sqrt{\xi_0}/(1 - A\cos 2\pi\xi)$; we then have, by Eq. (12),

$$K_\infty = (1 - A^2)^{1/4} \int_0^1 \frac{d\xi}{(1 - A\cos 2\pi\xi)} = \frac{1}{(1 - A^2)^{1/4}}. \tag{20}$$

For the amplitude $A = \sqrt{3}/2$ the asymptotic value is $K_\infty = \sqrt{2}$, i.e., for quite large wave amplitude ($A = 0.865$) the diffusion process intensification reaches only 41%. However, with the velocity u_m approaching c (i.e., when $A \to 1$) by Eqs. (19), (20) T and K_∞ tend to infinity. A similar effect is observed in analyzing diffusion on a wavy discharging film [2], and is called "diffusion independent of wave cells." The qualitative explanation is the following: in the case $u_m = c$ the integral (19) diverges, and the fluid particles cannot be displaced from one cell to another during a finite time; consequently, one and the same stationary mass flow distribution is established in each cell; in this case $m \sim t$ and $m_0 \sim \sqrt{t}$, so that with increasing t, $K \sim \sqrt{t} \to \infty$.

We obtain now the solution of the problem of nonstationary diffusion of a standing wave on the surface, the particle velocity in which is given by the formula $u = cA\cos(2\pi x/\lambda)\cos(2\pi t/T_0)$. Introducing the dimensionless variables $\xi = x/\lambda$, $\tau = t/T_0$, we rewrite Eq. (7) in the form

$$d\xi/d\tau = A\cos(2\pi\xi)\cos(2\pi\tau); \tag{21}$$

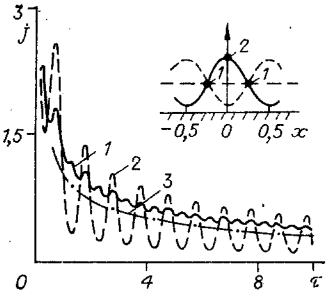

Fig. 2

$$dy/dt = y\,A\,\sin(2\pi\xi)\cos(2\pi\tau). \tag{22}$$

Equations (21), (22) are integrated by the method of separation of variables:

$$\sin 2\pi\xi_0 = \frac{\sin 2\pi\xi - \mathrm{th}\,\varphi}{1 - \sin 2\pi\xi\,\mathrm{th}\,\varphi}; \tag{23}$$

$$y = y_0(\mathrm{ch}\,\varphi + \sin 2\pi\xi_0\,\mathrm{sh}\,\varphi) \tag{24}$$

($\varphi = A\sin 2\pi\tau$). To determine the thickness of the diffusion layer $\delta(x, t)$ we substitute y from (24) into (9), and then replace everywhere $\sin 2\pi\xi_0$ by expression (23). After performing some transformations, we then have for the dimensionless thickness $\delta(\xi, \tau)$

$$\delta^2(\xi, \tau) = \int_0^\tau \frac{d\tau_1}{[\mathrm{ch}(\varphi_1 - \varphi) + \sin 2\pi\xi\,\mathrm{sh}(\varphi_1 - \varphi)]^2} \tag{25}$$

($\varphi_1 = A\sin 2\pi\tau_1$ is the dimensionless variable of integration). The integral in Eq. (25) could not be calculated analytically, but it is easily determined numerically by the Simpson method.

In Fig. 2 we show for the same amplitude $A = \sqrt{3}/2$ the local mass flow $j = 1/\delta$ in a standing wave. Curve 1 was calculated for the points $\xi = 0.25$, $2 - \xi = 0$. These points are the crest and trough (1, 2, respectively, on the wave profile). Curve 3 refers to the waveless case. An interesting feature can be noted of curve 1: while decaying, it oscillates with double frequency. This is explained by the fact that near a node, the fluid surface will be extended when the antinode on the right moves above and when a trough is formed here. Therefore y, the coordinate of the fluid particle near the site, will be contracted with double the frequency. According to Eq. (9), these oscillations generate fluctuations of twice the frequency in $\delta(\xi, \tau)$ and, consequently, in $j(\xi, \tau)$.

By comparing Figs. 1 and 2 it can be concluded that the mass-transfer intensification obtained for a standing wave is substantially smaller than for a traveling wave. Direct calculations of the intensification coefficient $K = \langle\delta\rangle/\sqrt{\tau}$ were carried out by Eq. (13).

Curves 1 and 2 of Fig. 3 show the behavior of the quantity $\Delta K = (K - 1)\cdot 100\%$ for these types of waves with identical amplitude $A = \sqrt{3}/2$. With increasing τ the oscillations noted in Fig. 3 decay, and certain ΔK_∞ values are established (41.2 and 7.8%).

Curves 1 and 2 of Fig. 4 show the dependence of the quantity ΔK_∞ on the wave amplitude for traveling and standing waves, respectively. For traveling waves with $A \to 1$ the fluid velocity at the crests u_{max} approaches the phase velocity c. In this case the fluid surface is partitioned into isolated crest diffusion cells. A stationary diffusion process is established in each such cell with the flow of time, which differs qualitatively from the general case in which the fluid in the wave system drifts from cell to cell ($A < 1$). For standing waves this mechanism is absent, and mass-transfer intensification is generated only by oscillating motions of the fluid. Due to the nonlinear character of the amplitude of diffusing oscillations, the averaging provides a small positive enhancement effect of mass exchange in standing waves. The results of calculations for standing waves can be represented with an error not exceeding 0.5% in the form of the following approximation: $\Delta K_\infty = 0.125A^2\cdot(1 + 0.583A^2)^{-1/2}\cdot 100\%$.

It is clear that wind, being the common reason for wave generation in open basins, is capable of leading to formation of diffusion of independent wave cells due to the loss of the approximate velocity of fluid surface

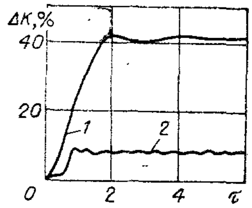

Fig. 3

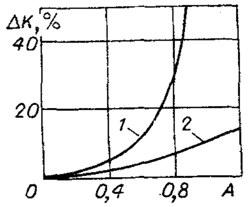

Fig. 4

layers to the wave phase velocity. With increasing wind velocity, however, one must generate wave collapse, and the fluid surface turbulence is enhanced. These regimes require different investigation methods.

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