Distribution of surfactant along the free liquid surface under the action of surface waves

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Abstract

Fluctuations of an insoluble surfactant monolayer along the free liquid surface induced by standing waves are considered theoretically. The energy of the fluctuating interface is assumed to be equal to the total free energy that is a function of surface tension. The dependence of the surface concentration on the surface tension is taken according to the Gibbs adsorption equation. Van der Waals forces between molecules that are present in all condensed matter systems are taken into account in the form of van der Waals energy for a thin film. The obtained theoretical result shows that the longitudinal distribution of the surfactant concentration can be expressed analytically, and that the distribution of concentration changes relative to some reference level has been found to be periodic with a period that is half of the wave period. The maximal concentration is achieved in nodal points of the wave profile.

1 Introduction

Wave motions in small-scale systems may be useful for transport of insoluble, film forming surfactant molecules floating on the free liquid surface. Surface-active agents (surfactants) are used for decreasing surface tension and also for laminarization and hydrophobilization of flows having complex structures. The dynamics of localized surfactant on a thin film has been considered by Gaver and Grotberg [1], who employed the lubrication theory to derive equations that describe the evolution of the film thickness and surfactant concentration. Numerical investigation of patterns of standing waves has been performed by Dolnik et al. [2], who obtained the different wave patterns associated with the aperiodic instability in a two-dimensional reaction-diffusion model. Their results
show the possibility of emerging periodic time sequences of stripes and rhombi, stripes and squares, and stripes, rhombi, and hexagons. The effect of surfactant additives on wave motion of liquid has been investigated for the first time by Levich [3], who demonstrated that the damping effect influences short waves only and the effect of surface-active agent could be manifested only at small Reynolds numbers. In other words, these phenomena take place only for capillary waves or ripples that are mainly determined by the surface tension [4]. The analysis of spontaneous spreading of an insoluble surfactant monolayer has been carried out by Matar and Troian [5], who noted Marangoni forces as the main source of digitation for both small and large wave number disturbances. Evolution equations obtained allowed the sensitivity of spreading surfactant-coated film to small disturbances in the surfactant distribution to be revealed. It should be also noted that the van der Waals forces are playing the significant role in the dynamics of thin films [6] and must be added to the usual contribution from surface tension.

The purpose of the present study is to solve the inverse problem: an attempt is made to obtain the distribution of a surfactant on the surface of liquid that is subjected to the action of standing or progressive high-frequency surface waves.

2 Problem statement

Linarized Navier-Stokes equations (non-linear convective terms are neglected) are (planar motion is considered, the positive direction of z-axis is downwards)

$$\frac{\partial \mathbf{V}}{\partial t} = -\frac{1}{\rho} \nabla p + \nu \Delta \mathbf{V} + g.$$

(1)

The continuity equation is

$$\text{div} \mathbf{V} = 0.$$

(2)

The surface-active material is entrained by a liquid flow, and the linearized equation describing the conservation of this material is [3, 7]

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x} \left( \Gamma v_x \right) = D_s \frac{\partial^2 \Gamma}{\partial x^2},$$

(3)

where $D_s$ is the mass diffusivity of the solute.

Assuming that the surface concentration $\Gamma$, according to Levich [3], can be represented as

$$\Gamma = \Gamma_0 + \Gamma',$$

(4)

where $\Gamma_0$ is the constant surface concentration on the undeformed surface, and $\Gamma' \ll \Gamma_0$ the linearized equation for $\Gamma'$ is

$$\frac{\partial \Gamma'}{\partial t} + \Gamma_0 \frac{\partial \Gamma'}{\partial x} = D_s \frac{\partial^2 \Gamma'}{\partial x^2}.$$

(5)

The problem under consideration is hence reduced to finding the surface-active material distribution that arises on the liquid surface when the free surface is subjected by the action of standing or progressive capillary-gravity waves.
3 Effect of liquid wave motion on surfactant film

As has been noted above, the equation describing the disturbances of concentration of surfactant is taken in the form (5) in which the quantity \( \Gamma' \frac{\partial v_x}{\partial x} \) has been neglected as a second-order infinitesimal. According to Xiao-Lin and Velarde [7], Marangoni stresses corresponding to the tangential stresses balance, can be taken into account with the help of the linearized condition at the open surface:

\[
\left( \frac{\partial \sigma}{\partial \Gamma} \right) \nabla \Gamma' + \rho \nu \left( \nabla v_z + \frac{\partial v_x}{\partial z} \right) = 0 ,
\]

where \( \sigma \) is the surface tension at air-liquid interface and \( \nu \) is the liquid kinematic viscosity. The normal stresses balance, according to these authors, is

\[
p - \rho g \zeta + \sigma_0 \nabla^2 \zeta + 2 \mu_d \frac{\partial v_z}{\partial z} = 0 ,
\]

where \( \mu_d = \rho \nu \) is the dynamic viscosity and \( \sigma_0 \) is a reference value of the air-liquid interfacial tension. According to Privman [8] (pp. 8 and 10), for the average inclination angle

\[
\theta = \arctan \left( \frac{d \zeta}{dx} \right) ,
\]

where \( \zeta \) is the vertical displacement of the free surface, the "macroscopic" energy of fluctuating interface is given by (in 2d case)

\[
E_c = \frac{1}{2} A k T \kappa \int \left( \frac{d \zeta}{dx} \right)^2 dx ,
\]

where \( \kappa = \sigma + \frac{d^2 \sigma}{d \theta^2} \) is the surface stiffness coefficient, \( k = 1.38 \cdot 10^{-16} \) erg-deg\(^{-1}\) is the Boltzmann constant, \( A = 2 \pi/k \), and \( T \) is absolute temperature. The integration is carried out along one wavelength. According to Levich [3], (p. 610), the horizontal and vertical components of the liquid velocity and the pressure are

\[
\begin{align*}
v_x &= (ikF e^{kz} - l Ge^{lz}) e^{ikx + \alpha t} , \\
v_z &= (kF e^{kz} + ik Ge^{lz}) e^{ikx + \alpha t} , \\
p &= -\rho \alpha F e^{kz} e^{ikx + \alpha t} - \rho g z ,
\end{align*}
\]

where \( \alpha = i \omega + \beta \) (\( \beta \) is a complex number whose real part represents the damping coefficient, and the imaginary part, the frequency correction, the full expression for \( \beta \) is given by Levich [3], (p. 615), \( l^2 = k^2 + \alpha/\nu \), and \( \nu \) is the kinematic viscosity. It is supposed that the dampening effect of viscosity in the bulk can be compensated by forced oscillations from some external source. For small amplitude waves, it may be written:
\[ \frac{\partial \xi}{\partial t} \approx v_x \text{ and } \frac{\partial \zeta}{\partial t} \approx v_z, \]  
(11)

where \( v_x \) and \( v_z \) are the horizontal and the vertical velocity components respectively. Then, the displacements of liquid particles are obtained by integrating first and second of equations (10):

\[ \xi = \frac{1}{\alpha} (ikF e^{kz} - lG e^{lz}) e^{ikx + \alpha t}, \]
\[ \zeta = \frac{1}{\alpha} (kF e^{kz} + ikG e^{lz}) e^{ikx + \alpha t}. \]

(12)

The second of equations (12) gives:

\[ \frac{d \zeta}{dx} \bigg|_{x=0} = \frac{ik}{\alpha} (F + iG) e^{ikx + \alpha t}, \]
\[ \left( \frac{d \zeta}{dx} \right)^2 = -\frac{k^4}{\alpha^2} (F + iG)^2 e^{2ikx + 2\alpha t}. \]

(13)

Substituting (13) into (9) allows the expression for energy of curvature to be obtained in the form:

\[ E_c = -\frac{k}{4\pi} \left( \sigma + \frac{d^2 \sigma}{d \theta^2} \right) \int \frac{k^4}{\alpha^2} (kF + iG)^2 e^{2\alpha t} dx, \]

(14)

where \( \theta = \arctan \frac{d \zeta}{dx} \approx \frac{d \zeta}{dx} \). After integrating, (14) becomes

\[ E_c = \frac{ik}{8\pi \alpha^2} (F + iG)^2 e^{2(ikx + \alpha t)} \left( \sigma + \frac{d^2 \sigma}{d \theta^2} \right). \]

(15)

The real part of (15) should be taken for consideration of the energy balance. Because it can be written \( \frac{d \sigma}{d \theta} \approx \frac{d \sigma}{dx} \) and, consequently,

\[ \frac{d^2 \sigma}{d \theta^2} = \frac{d^2 \sigma}{dx^2} \left( \frac{dx}{d \theta} \right)^2 + \frac{d^2 x}{d \theta^2} \frac{d \sigma}{dx}, \]

the expression for the energy of curvature is (the real part of the wave profile at \( z = 0 \) is considered):

\[ E_c = \frac{k^4}{8\pi \alpha^2} \left( \sigma + \frac{d^2 \sigma}{d \theta^2} \right) e^{2\alpha t} \left( -2FG \cos 2kx - F^2 \sin 2kx + G^2 \sin 2kx \right) \]

(16)

Using the estimation of the relation \( F/G \) given by Levich [3], (p. 617):

\[ \frac{F}{G} \approx \sqrt{\frac{\alpha_0}{\nu k^2}} \]

(17)
for the case of very short waves \((\omega_0 \sim 1 \text{ MHz}, \nu \sim 10^{-6} \text{ m}^2\text{s}^{-1}, k \sim 10^5 \text{ m}^{-1})\) gives the possibility to neglect the coefficient \(G\) in comparison with \(F\). Then, taking into account that
\[
\frac{d\theta}{dx} \approx \frac{d^2 \zeta}{dx^2} = -\frac{k^3}{\alpha} (F + iG) e^{ikx + \alpha} \quad \text{and} \quad \frac{d^2 x}{d\theta^2} = -\frac{i \alpha^2}{k^5} e^{-2(ikx + \alpha)} (F + iG)^2,
\]
the expression for considered energy is obtained in the form:
\[
E_c = -\frac{k^4 F^2 \sin 2kx}{8\pi \alpha^2} \left[ \sigma + \frac{d^2 \sigma}{dx^2} \frac{\alpha^2}{k^6} (F + iG)^2 e^{-2(ikx + \alpha)} \right] \quad \text{and, using again the estimation (17), this expression is reduced to}
\]
\[
E_c = -\frac{k^3}{8\alpha^2 \sigma e^{2\alpha t}} F^2 - \frac{d^2 \sigma}{dx^2} \frac{\alpha^2}{k^6} \frac{\sin 4kx}{2} + \frac{d^2 \sigma}{dx^2} \frac{\alpha^2}{k^5} F^2 \sin^2 2kx. \quad (19)
\]
The interacting term of the van der Waals energy per unit area, according to Safran [9], is
\[
E_W = -\pi n_0^2 W_0 \frac{\Gamma}{6D^2} \quad (20)
\]
where \(n_0\) is the volume density, \(W_0\) is related to the Hamaker constant \((W_0 = A_{12} / \pi n_0^2)\) and \(D\) is the thickness of a surfactant film. As Safran [9] notes (p. 140), typically the Hamaker constant is of order \(25kT\). The surface density is expressed as \(n_0 = \Gamma / D\), therefore, the considered energy can be rewritten in the form
\[
E_W = -\pi W_0 \frac{\Gamma^2}{6 D^4}. \quad (21)
\]
According to Evans [10], (p.64),
\[
\Gamma = -\frac{d\sigma}{d\mu_c}, \quad (22)
\]
where \(\mu_c\) is the chemical potential that can (for small separations from the interface) be taken according to Netz [11, 12], when the surface potential is determined in the framework of Debye-Hückel theory (a dielectric constant ratio is sufficiently small):
\[
\mu_c = kT \frac{l_B}{2z}, \quad (23)
\]
where \(l_B = e^2 / 4\pi\varepsilon_0 kT\) is the Bjerrum length defining the distance at which two unit charges interact with thermal energy \(kT\) in the positive half-space [11], \(e\) is the electron charge, \(\varepsilon_0\) is the dielectric constant, and \(z\) is the vertical
coordinate. As has been noted by Netz, the asymptotic results are reduced to the Coulomb interaction.

Vertical displacements of the liquid interface are determined according to Levich \[3\]

\[ \zeta_{z=0} = \frac{k}{\alpha} (F + iG)e^{i(kx + \alpha t)} , \]
i.e., \( z \) should be taken as 0 in the second of eqs. (12).

It can be written \( \Gamma = -\frac{d\sigma}{dx} \), and for small amplitude waves:

\[ \frac{d\mu_c}{dx} = \frac{-i k T_B \alpha}{2(F + iG)} e^{-(ikx + \alpha t)} . \quad (24) \]

Therefore, the expression for the concentration becomes (as before, on the linearized wave surface)

\[ \Gamma = -\frac{2(F + iG)}{ik T_B \alpha} e^{ikx + \alpha t} \frac{d\sigma}{dx} . \quad (25) \]

The real part of \( \Gamma \), taking into account (17), is

\[ \text{Real } \Gamma = -\frac{2Fe^{\alpha t} \sin kx}{k T_B \alpha} \frac{d\sigma}{dx} . \quad (26) \]

Substituting (26) into (21) gives

\[ E_W = -\frac{2\pi W_0}{3} \frac{F^2 e^{2\alpha t} \sin^2 kx}{k^2 T^2 l_B^2 \alpha^2 D^4} \left( \frac{d\sigma}{dx} \right)^2 . \quad (27) \]

The sum of energies of curvature and of van der Waals can be equated to the total free energy corresponding to the Gibbs isotherm \[10\]

\[ E_t = \frac{\delta A}{V_L} RT \ln \left( \frac{p_0}{p} \right) + 2\alpha A , \quad (28) \]

where \( A \) is the surface area that is \( A = 2\pi/k \) \((k \) is the wave number) in 2d case, and \( \delta \) is the thickness of the gap containing \( dA/V_L \) moles of the surfactant. The first term in the right hand part of (28) can be taken equal to 0 because the insoluble surfactant is considered which forms the monolayer on the free liquid surface and, consequently, \( p_0 \approx p \). This leads to the non-linear second order differential equation for determination of the surface tension:

\[ \frac{d^2 \sigma}{dx^2} - \left( \frac{d\sigma}{dx} \right)^2 \frac{8\pi W_0 F^2 k^2}{3k^2 T^2 l_B^2 D^4 \alpha^2} \cot 2kx + \frac{d\sigma}{dx} k \cos 2kx \]

\[ + \sigma \left( 1 - \frac{16\pi \alpha^2 e^{-2\alpha t}}{k^4 F^2 \sin 2kx} \right) \frac{k^6 F^2}{\alpha^2 \cos 2kx} e^{-2\alpha t} = 0 \quad (29) \]
Denoting for convenience \( a = \frac{8\pi}{3} \frac{W_0 F^2 k^2}{k^2 T \ell_b^2 D^4 \alpha^2} \), this equation (taking into account that the last term contains the multiplier that decreases exponentially and at sufficiently large \( t \) it becomes negligible, i.e., considering the asymptotic behavior after the lapse of some time), is rewritten as:

\[
\frac{d^2 \sigma}{dx^2} - a \left( \frac{d\sigma}{dx} \right)^2 \cot 2kx + k \frac{d\sigma}{dx} \cos 2kx = 0.
\]

(30)

The first boundary condition follows from the periodicity of considered function:

\[
\frac{d\sigma}{dx} \bigg|_{x=0} = \frac{d\sigma}{dx} \bigg|_{x=\pi/n}, \quad (n = \text{integer}.
\]

It can immediately be noted that the trivial solution of this equation is \( \sigma = \text{const} \). Moreover, this equation does not explicitly contain the sought-for function \( \sigma \), hence, the solution can be found with the help of the substitution [13]

\[
y = \frac{d\sigma}{dx}
\]

that allows the Bernoulli equation to be obtained:

\[
\frac{dy}{dx} - ay^2 \cot 2kx + ky \cos 2kx = 0.
\]

(31)

This equation reduces to the linear first-order equation by substitution \( u(x) = 1/y \):

\[
\frac{du}{dx} - ku \cos 2kx + a \cot 2kx = 0.
\]

(32)

Its general solution is [13]:

\[
u = e^{-f} \left( \text{const} - a \int e^f \cot 2kx \, dx \right).
\]

(33)

where \( f = -k \int \cos 2kx \, dx = -\frac{1}{2} \sin 2kx \). The arbitrary constant can be supposed equal to 0 without the loss of generality because the distribution of the surface tension is considered relatively to some reference level. Therefore, the solution of (31) is

\[
u = a \exp \left( \frac{\sin 2kx}{2} \right) \int \frac{\cos 2kx}{\sin 2kx} \exp \left( -\frac{\sin 2kx}{2} \right) \, dx =
\]

\[
a \cdot \frac{\exp \left( \frac{\sin 2kx}{2} \right)}{2k} \int \frac{\exp \left( -\frac{\sin 2kx}{2} \right)}{\frac{1}{2} \sin 2kx} \, d \left( \frac{\sin 2kx}{2} \right) =
\]

\[
a \cdot \frac{\exp \left( \frac{\sin 2kx}{2} \right)}{2k} Ei \left( -\frac{\sin 2kx}{2} \right)
\]

(34)
where $Ei(x)$ is the exponential-integral function. There has been used formula (2.325) from Gradstein and Ryzhik [14]. Returning to the substitution for $y$ gives the derivative of the surface tension coefficient

$$\frac{d\sigma}{dx} = y = \frac{1}{u} = \frac{2k}{a} \exp\left(-\frac{\sin 2kx}{2}\right) \frac{Ei\left(-\frac{\sin 2kx}{2}\right)}{Ei\left(-\frac{\sin 2kx}{2}\right)}$$

and the expression for the surface tension

$$\sigma = \frac{2k}{a} \int \frac{\exp\left(-\frac{\sin 2kx}{2}\right) dx}{Ei\left(-\frac{\sin 2kx}{2}\right)}$$.

This integral, in principle, can be calculated but it is not necessary because only the derivative of $\sigma$ is used for determination of the concentration distribution. Again, the dependence of the concentration on the surface tension that is given by the Gibbs adsorption equation (28) can be used and the chemical potential can be taken as before in the form of (23), according to Netz [11]. In the assumption that $z = \zeta$ for small amplitude waves, the chemical potential gets

$$\mu_c = kT \frac{l_B \alpha e^{(ikx + \alpha t)}}{2k} \left( F + iG \right)$$.

Using (26) allows the distribution of concentration disturbances along the free liquid surface to be obtained:

$$\text{Real } \Gamma' = -\frac{2Fe^{\alpha t} \sin kx}{kTl_B \alpha} \frac{d\sigma}{dx} = -\frac{2Fe^{\alpha t}}{kTl_B \alpha} \exp\left(-\frac{\sin 2kx}{2}\right) \frac{2k \sin kx}{aEi\left(-\frac{\sin 2kx}{2}\right)}$$

that gives the sought-for distribution relatively to some reference level. This function in dimensionless form is presented in Fig. 1.

## 4 Concluding remarks

The result obtained shows that the longitudinal distribution of the surfactant concentration under action of small-amplitude surface waves experiences double variations relatively to an initial wave, i.e., the maximal concentration is achieved in nodal points of the wave profile. This result is in good agreement with the effect noted by Moroney et al [15] for standing wave excitation in water containing polystyrene micro spheres where these spheres tend to collect in lines that are one-half of a wave length and parallel to the waterfront. The theoretical solution allows the surfactant distribution along the liquid free surface.
to be evaluated and therefore it may be useful for a comparison with experimental data. As can be seen in Fig. 1, peaks of surfactant concentration are occurred near by nodal points of a wave profile. It should be noted that two half-wave of the surfactant distribution give a quite symmetric pattern. This shows that the total amount of surfactant remains constant in spite of concentration fluctuations, i.e., a condition of conservation of substance is fulfilled.

References


