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BUBBLE MOTION UNDER THE ACTION OF A GRADIENT IN SURFACE-ACTIVE MATERIAL CONCENTRATION

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The problem of bubble motion under the action of a gradient in surface-active material concentration is considered. The bubble drift velocity is determined. The possibility of calculating bubble velocity with simultaneous action of temperature and concentration gradients is considered.

The study of bubble and droplet motion in liquid and gaseous media is important in the solution of many practical technical problems (emulsion theory, solution of droplets, atomization of fuels, fuel placement in reservoirs, bubbling in air regeneration systems aboard spacecraft, etc.).

In most cases the motive force is provided by gravitation, but there are also cases in which droplet or bubble motion is caused by nonuniform surface tension on a boundary [1, 2]. This nonuniformity can develop either because of a nonuniform temperature distribution [3-5], or because of a nonuniform concentration of surface-active material [6].

Below we will study bubble motion under the action of a constant gradient in surface-active material concentration, but in contrast to [6], where the simplifications made to the fundamental equations were purely intuitive, a more formal simplification procedure will be used, based on expansion in the small parameters of the problem. We will assume that mass forces are absent, and that evaporation of the surface-active material into the bubbles does not occur. The motion is steady-state and translational. We place the origin of the coordinate system at the center of the moving bubble.

The distributions of velocity $\bar{v}$, pressure p, and surface-active material concentration are defined by a system of equations

$$\begin{gathered}\frac{\partial \bar{v}}{\partial t}+(\bar{v}\nabla)\bar{v}=-\frac{\nabla p}{\rho}+\nu\Delta\bar{v},\ \nabla\bar{v}=0,\\ \frac{\partial c}{\partial t}+\bar{v}\nabla c=D_v\Delta c.\end{gathered} \tag{1}$$

On the bubble surface at $r=R_L$ the equation for conservation of surface-active material has the form [2, 7]

$$\frac{\partial \Gamma}{\partial t}+\frac{1}{R\sin\theta}\frac{\partial}{\partial\theta}(\Gamma v_\theta\sin\theta)-D_s\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Gamma}{\partial\theta}\right)=D_v\frac{\partial c}{\partial r}\bigg|_{r=R}. \tag{2}$$

Limiting ourselves to the case Re ≪ 1, Pe ≪ 1, we will estimate the order of magnitude of the terms of Eqs. (1), (2), transforming to dimensionless variables and choosing for the length scale the droplet radius R, for velocity $|d\sigma/dc|RE_c/\mu$, for pressure $|d\sigma/dc|E_c$, and for concentration E_cR. Performing this estimate, we find that in the zeroth approximation for small Re and Pe in Eq. (1) the inertial terms may be neglected, while in Eq. (2) (assuming also that $D_V \sim D_S$) the first two operators on the left-hand side may be dropped, these representing the change in surface concentration of the surface-active material with time and the convective transfer of the material along the surface.

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Thus, in Eq. (2) for slow motion (small Pe_s) we may neglect the convective term, while in [6] surface diffusion was neglected without sufficient justification. Moreover, the operator $\partial c/\partial r$ was replaced by the difference operator $\Delta c/\delta$, although the boundary layer scale δ of the problem was undefined. Now, Eqs. (1), (2), again written in dimensioned variables, take on the form

$$0 = -\frac{\nabla p}{\rho} + \nu\Delta\bar{v}, \quad \nabla\bar{v} = 0, \quad D_v\Delta c = 0,$$
$$D_s\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Gamma}{\partial\theta}\right) + D_vR^2\sin\theta\left.\frac{\partial c}{\partial r}\right|_{r=R} = 0. \tag{3}$$

Integration of the last equation of Eq. (3) requires imposition of one more condition, e.g., at the point of influx:

$$\left.\frac{\partial\Gamma}{R\partial\theta}\right|_{\theta=0} = 0. \tag{4}$$

This equation itself contains a new unknown Γ. Therefore, to transform Eq. (3) to a mathematically complete boundary problem, one more equation must be added. For this equation we may choose the expression for surface-active material flow to the surface, expressed in terms of the adsorption and desorption coefficients α and β [8]:

$$\left.\frac{\partial c}{\partial r}\right|_{r=R} = \beta\left(1 - \frac{\Gamma}{\Gamma_\infty}\right)\left.c\right|_{r=R} - \alpha\Gamma. \tag{5}$$

Here Γ_∞ is the maximum adsorption.

Far from the bubble we consider the surface-active material adsorption gradient constant, while on the surface the usual kinematic and dynamic conditions are fulfilled:

$$\bar{v}|_{r\to\infty} = 0, \quad \bar{v}|_{r=R} = U_c\cos\theta,$$
$$\sigma_{r\theta} + \left.\frac{\partial\sigma}{\partial\Gamma}\frac{1}{R}\frac{\partial\Gamma}{\partial\theta}\right|_{r=R} = \left.\sigma'_{r\theta}\right|_{r=R}. \tag{6}$$

In the latter equation we take $\sigma'_{r\theta} \approx 0$ (neglecting the viscosity of the gas). With conservation of total gas volume in the bubble (i.e., in the absence of phase transitions) the total force acting on the bubble will be

$$F = \int(\sigma_{rr}\cos\theta - \sigma_{r\theta}\sin\theta)\,ds|_{r=R} = 0. \tag{7}$$

In the case of a spherical bubble, in place of Eq. (7) we may consider the equivalent condition [1]

$$\left.\sigma_{rr} + \frac{2\sigma}{R}\right|_{r=R} = \left.\sigma'_{rr}\right|_{r=R}, \tag{8}$$

which expresses the equality of normal stresses. Since the gas pressure within the bubble p_0 may be considered constant, and pressure measured with that value as a reference, in Eq. (8) we may take $\sigma'_{rr} = 0$.

If the spherical form is lost during bubble motion, then to determine the new unknown $r = R(\theta)$ both conditions (7) and (8) are required. This fact was not noted in [3, 4], which produced a false result for velocity of thermocapillary motion, in fact, for terms of order $O[M^2]$, where M is the Marangoni number, since in the zeroth approximation in M the bubble is spherical and Eqs. (7), (8) are equivalent, while in the first approximation the properties of the functions obtained for the velocity from condition (8) prove to be such that condition (7) is also fulfilled automatically for a spherical surface. This was shown by the fact that the function $f_1(\theta)$ in the expansion of $r = R(\theta)$ in powers of M proved equal to zero.

Equation (5) in nonlinear. Limiting ourselves to the main point of the problem, we will consider the conditions at which one can take

$$\frac{\Gamma}{\Gamma_\infty} \ll 1. \tag{9}$$

Condition (9) is satisfied for dilute solutions. However, it also imposes a limit on the "surface-active material force" [7, 9]. It follows from the last relationship of Eq. (3) that

$$\frac{D_v R^2 c}{R} \sim D_s \Gamma. \tag{10}$$

The equilibrium values of Γ and c are related by the expression $\Gamma = hc$, where h is the "adsorption depth." Substituting the latter expression in Eq. (10), we obtain the estimate

$$\frac{D_v}{D_s}\,\frac{R}{h}\,\frac{\Gamma}{\Gamma_\infty} \sim \frac{\Gamma}{\Gamma_\infty} \ll 1. \tag{11}$$

Since it was assumed that $D_V \sim D_S$, then for $R \lesssim h$, i.e., for strong or moderate material activity, Eqs. (3), (9) are satisfied simultaneously.

In the zeroth approximation in small values of the parameters Re and Pe, the solution of linear problem (3)-(7) can be obtained by the standard method, with one of conditions (7) or (8) being used in the zeroth approximation, as was noted above. After calculations, we obtain

$$v_r = -\left(\frac{R}{r}\right)^3 \frac{E_c R}{3\mu}\, s\, \frac{d\sigma}{d\Gamma} \cos\theta,$$

$$v_\theta = -\left(\frac{R}{r}\right)^3 \frac{E_c R}{6\mu}\, s\, \frac{d\sigma}{d\Gamma} \sin\theta,$$

$$p = 0, \quad \Gamma = \Gamma_0 + sE_c \cos\theta,$$

$$c = c_0 + \left(1 + \frac{1}{2} A \left(\frac{R}{r}\right)^3\right) E_c r \cos\theta,$$

where the following notation is used:

$$s = \frac{3D_v R^3 \beta}{2\alpha R^2 D_v - D_s (4D_v - 2R\beta)},$$

$$A = \frac{D_v (\alpha R^2 - 2D_s) - 2D_s R\beta}{D_v (\alpha R^2 - 2D_s) + D_s R\beta};$$

Γ_0, c_0 are the surface-active material concentrations corresponding to the instantaneous position of the bubble center. As in the thermocapillary problem, the bubble moves in the direction of the material gradient. The bubble drift velocity is given by

$$U_c = -\frac{E_c}{3\mu}\, s\, \frac{d\sigma}{d\Gamma}. \tag{14}$$

A posteriori verification of solution (12), found with neglect of inertial forces [10], shows that the problem is solved in the Stokes approximation. We note that the expression for U_C is analogous in form to the expression for the zeroth approximation of thermocapillary drift velocity, obtained in [3, 4].

In the presence of both a temperature gradient and a concentration gradient, the total effect of their action on drift velocity can be determined. In fact, in view of the linearity of the problem, the total drift velocity will be equal to the sum of the quantities U_C, as given by Eq. (14), and U_T, calculated in [4].

An interesting physical situation can appear when thermodiffusion is considered. It is well known that a concentration gradient can develop in a solution with initially uniform distribution of material when a temperature gradient is imposed. The total diffusion flux is then given by [11]

$$\bar{I} = -\rho c (1 - c) D_T \operatorname{grad} T - \rho D_v \operatorname{grad} c. \tag{15}$$

If $\sigma = \sigma(\Gamma, T)$, then the change in surface tension has the form

$$\nabla\sigma = \left(\frac{\partial\sigma}{\partial\Gamma}\right) \nabla\Gamma + \left(\frac{\partial\sigma}{\partial T}\right) \nabla T. \tag{16}$$

It is obvious that $(\partial\sigma/\partial\Gamma)\nabla\Gamma = (\partial\sigma/\partial c)\nabla c$. Then Eq. (16) may be written:

$$\nabla\sigma = \left(\frac{\partial\sigma}{\partial c}\right)\nabla c + \left(\frac{\partial\sigma}{\partial T}\right)\nabla T. \quad (17)$$

In the stationary state net diffusion flux is absent, and from Eq. (15) we obtain

$$\Delta c = -\frac{c(1-c)D_T}{D_v}\nabla T. \quad (18)$$

Substituting Eq. (18) in Eq. (17), we have finally

$$\nabla\sigma = \left(\frac{\partial\sigma}{\partial T} - \frac{c(1-c)D_T}{D_v}\frac{\partial\sigma}{\partial c}\right)\nabla T. \quad (19)$$

If both terms in parentheses are of the same order, braking of the thermocapillary drift of the bubble by surface-active materials can be expected. For example, for alcohols [12], the temperature coefficient is equal to $\partial\sigma/\partial T \sim 0.03$ erg/cm^2·deg K, $c(\partial\sigma/\partial c) \sim 10$ erg/cm^2; the Sore coefficient D_T/D_V can reach a magnitude of 10^{-3} deg^{-1} [11].

Thus, both terms in Eq. (19) prove to be of the same order, and a situation is possible in which a bubble becomes completely frozen by the surface-active material gradient developed.

NOTATION

t, time; $\bar{v}$, velocity; T, temperature; U_c, drift velocity; p, pressure; c, volume concentration of surface active material; D_V, D_S, D_T, volume, surface, and thermodiffusion coefficients; μ, ν, dynamic and kinematic viscosity coefficients; ρ, density; Γ, Γ_∞, surface concentration and maximum adsorption of surface-active material; R, bubble radius; r, θ, coordinates; α, β, desorption and adsorption coefficients; σ_{ik}, stress tensor components; σ, surface tension; F, total force; Pe, Re, dimensionless parameters of problem; E_c, constant surface-active material concentration gradient; A, s, constant parameters; $\bar{I}$, total diffusion flow of the surface-active material.

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