CHANGE IN SHAPE OF DROP MOVING DUE TO THE CHEMITHERMOCAPILLARY EFFECT

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It is well known that a fluid drop (bubble), placed in a different fluid (unmixed with it), and found in a temperature field with a constant gradient, drifts in the absence of external forces in the direction of the temperature gradient with constant velocity

$$U=\left|\frac{d\sigma}{dT}\right|\frac{Aa}{\mu_1}\frac{2}{(2+\delta)(2+3\beta)},$$

where σ is the interphase surface tension; T is temperature; $d\sigma/dT$ = const; A, constant temperature gradient at infinity; a, drop radius; μ_1, dynamic viscosity of the external medium; β and δ, ratios of the dynamic viscosities to the fluid thermal conductivities inside and outside the drop, respectively.

The expression first derived for the rate of thermocapillary drift was obtained theoretically and verified experimentally in [1]. Consequently, the thermocapillary drift effect of drops and bubbles was investigated in detail (see, for example, [2-5]). In particular, it was noted that a drop which is more dense than the fluid is expanded while drifting in the direction of motion, and is compressed in the opposite case [3, 5].

Thermocapillary drift occurs due to the Marangoni effect, causing, by the temperature dependence of the surface tension, generation of additional tangential stresses at the surface of a drop (bubble) in an external temperature field. As was first noted in [6], these additional tangential stresses at the drop surface may occur due to the nonuniform temperature distribution, generating proper drop motion in a primarily isothermal medium, when we have at the drop surface exo- or endothermal interphase reactions with participation of material dissolved in the continuous phase. In this case, for certain parameter values it is possible to have generation of a tractive force acting on the drop [6, 7], as well as drift of the drop with constant velocity in a direction dependent on the initial conditions [7]. Similar effects are conveniently called chemithermocapillary. The chemithermocapillary drift rate is [7]

$$U_*=0.049\,D_1a\left[QC_\infty\frac{d\sigma/dT}{\mu_1\lambda_1(1+(3/2)\beta)(2+\delta)}\right]^2,$$

where D_1 is the diffusion coefficient of the reagent in the external fluid; Q, thermal effect of the interphase reaction; C_∞, reagent concentration far from the drop; λ_1, thermal conductivity of the external fluid. This result refers to the case in which the diffusion Peclet number is large: $Pe = U_*a/D_1 \gg 1$, while the thermal Peclet numbers are small: $Pe_{\chi_i} = U_*a/\chi_i \ll 1$ (χ_i are the phase thermal diffusivities).

It was assumed in [7] that the interphase surface tension is large and, therefore, the drop retains its spherical shape. In this case, the balance condition of the normal momentum components at the interphase surface reduced to a nonsubstantial pressure jump, while the balance condition of tangential components would lead to an infinite system of equations, relating the expansion coefficients of the current function in Gegenbauer polynomials in $C_n^{-1/2}$, whose approximate solution provided an expression for the force acting on the drop.

It can be shown, however, that account of the balance of normal stress components at the phase separation surface leads to the conclusion of varying shape of a drop moving due to the chemithermocapillary effect even in the zeroth approximation in the Reynolds number. This deformation under consideration differs from the deformation of a nonreacting drop (bubble) moving in the fluid – ordinary or thermocapillary. Thus, it was shown in [3, 5, 8] that during drop motion in a fluid its shape remains spherical for any Weber numbers in the vanishing approximation in the Reynolds number, since the solution corresponding to this approximation satisfies the balance conditions of both tangential and normal stress components.

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1. We recall the statement of the problem considered in [7]. A drop of a distinct (unmixed) fluid moves in an infinite, homogeneous fluid with constant velocity. At the surface of the drop a chemical reaction takes place with heat release (absorption), the reagent is transported by diffusion from the external fluid, and reacts instantaneously at the interphase surface (the diffusion regime). The Pe value is assumed large, and that of Pe_{χ_i} is assumed to be small (since for most fluids the Lewis number is $L = \chi/D \sim 10^2$). Within the approximations of creeping flow (Re = 0), diffusion boundary layer (Pe ≫ 1), and within the vanishing approximation in small thermal Peclet numbers ($Pe_{\chi_i} = 0$) inside and outside the drop, the fluid equations of motion and the distributions of reagent concentration outside the drop, and of temperatures in both phases, are described by the following equations and boundary conditions in dimensionless variables in a spherical coordinate system, attached to the drop center of mass:

$$E^4\psi_i = 0,\quad E^2 = \partial^2_{rr} + (1-\mu^2)r^{-2}\partial^2_{\mu\mu},\quad \mu \equiv \cos\theta,\ i = 1, 2, \tag{1.1}$$

$$r\to\infty,\quad \psi_1 \to \frac{1}{2}(1-\mu^2)r^2,\quad r = 0,\quad \psi_2/r^2 < \infty,$$
$$r = 1,\ \partial_\mu\psi_1 = \partial_\mu\psi_2 = 0,\ \partial_r\psi_1 = \partial_r\psi_2;$$

$$\frac{\partial(\psi_1, z)}{\partial(r,\mu)} = \frac{1}{\mathrm{Pe}}\frac{\partial^2 z}{\partial r^2},\quad r\to\infty,\quad z\to 0,\quad r = 1,\quad z = 1; \tag{1.2}$$

$$\Delta\varphi_i = 0,\ i = 1, 2,\ r\to\infty,\quad \varphi_1\to 0,\ r = 0,\ \varphi_2 < \infty, \tag{1.3}$$
$$r = 1,\ \varphi_1 = \varphi_2,\ \partial_r\varphi_1 - \delta\partial_r\varphi_2 = \partial_r z;$$

$$(2\partial_r - \partial^2_{rr})(\psi_1 - \beta\psi_2) = \mathrm{Ma}(1-\mu^2)\partial_\mu\varphi_1,\quad r = 1; \tag{1.4}$$

$$-\mathrm{Re}(p_1 - \beta p_2) - 2\partial^2_{r\mu}(\psi_1 - \beta\psi_2) = 2\left(\frac{\mathrm{Re}}{\mathrm{We}} + \mathrm{Ma}\,\varphi_1\right),\quad r = 1. \tag{1.5}$$

Here $\psi_i' = U_\infty a^2\psi_i$ (i = 1 refers to the external fluid, and i = 2 to the fluid inside the drop); $r = r'/a$; $z = (C_\infty - C)/C_\infty$; $\varphi_i = L\theta_*^{-1}(T_i - T_\infty)$; $p_i = p_i'(\rho_i U_\infty^2)^{-1}(\mu_1/\mu_i)$; $\theta_* = QC_\infty\cdot(\rho_1 c_{p_1})^{-1}$; Q, thermal effect of the interphase reaction; $\mathrm{Pe} = U_\infty a/D$, $\mathrm{Re} = U_\infty a/\nu_1$, $\mathrm{We} = \rho_1 U_\infty^2 a/\sigma_\infty$, $\mathrm{Ma} = L^{-1}\theta_*\sigma_\infty^{-1}(d\sigma/dT)\mathrm{Re}/\mathrm{We}$ are the Peclet, Reynolds, and Marangoni numbers; C, reagent concentration in the continuous phase; p_i, ρ_i, and T_i, pressure, density, and temperature; μ_i, ν_i, λ_i, χ_i, and c_p, dynamic and kinematic viscosities, the thermal conductivity and diffusivity, and the specific heat capacity; T_∞, temperature away from the drop; σ_∞, interphase surface tension corresponding to this temperature; U_∞, fluid velocity far from the drop; subscript i = 1 refers to the continuous phase and 2 to the drop; $\beta = \mu_2/\mu_1$; $\delta = \lambda_2/\lambda_1$; $L = \chi_1/D$; the primes denote dimensional quantities; the direction of the polar axis coincides with the drop flow direction at infinity.

Problem (1.1)-(1.5) is solved as follows. Initially one finds the solution of problem (1.1) without singularities in the whole flow region, accurately within the undetermined constants A, A_n (n ≥ 3):

$$\psi_1 = (r^2 + Ar - (A+1)r^{-1})G_2(\mu) + \sum_{n=3}^{\infty} A_n(r^{-n+3} - r^{-n+1})G_n(\mu),$$
$$\psi_2 = (A + 3/2)(r^4 - r^2)G_2(\mu) + \sum_{n=3}^{\infty} A_n(r^{n+2} - r^n)G_n(\mu) \tag{1.6}$$

[$G_n(\mu)$ are Gegenbauer polynomials of order n and degree $-1/2$ ($G_n(\mu) \equiv C_n^{-1/2}(\mu)$)].

Using (1.6), one can find the solutions of problem (1.2), (1.3) which contain the unknown constants A, A_n (n ≥ 3). Substituting these solutions into conditions (1.4), expressing the balance of tangential stresses, we obtain an infinite nonlinear system of equations in A, A_n:

$$A = -\frac{1 + (3/2)\beta}{1+\beta} + \frac{1}{3}\mathrm{Ma}\,B_1(1+\beta)^{-1},\quad A_{n+1} = \frac{n(n+1)\mathrm{Ma}}{(4n+2)(1+\beta)}B_n,$$

$$B_n = -\frac{(n+1/2)}{(n+1+\delta n)}\frac{1}{\varepsilon\sqrt{\pi}}\int_{-1}^{1} f(\mu)\left[\int_{-1}^{\mu} f(\mu)\,d\mu\right]^{-1/2} P_n(\mu)\,d\mu, \tag{1.7}$$

$$f(\mu) = (2A+3)\,G_2(\mu) + \sum_{n=3}^{\infty} 2A_n G_n(\mu), \quad \varepsilon = \mathrm{Pe}^{-1/2}$$

(a more detailed derivation of the system was given in [7]).

Assuming that as We → 0, condition (1.5) reduces within the principal approximation to an equation for the pressure jump at the drop surface, and the problem reduces to a solution of system (1.7) in the constants A, A_n ($n \geq 3$) [7]. If the We value is arbitrary, then in (1.5) it is necessary to include the terms containing the stream ψ_i and temperature φ_1 functions. From (1.6) we find for the pressure [9]

$$\begin{aligned} \mathrm{Re}\, p_1 &= \left(-\pi_1 r + \frac{A}{r^2}\right) P_1(\mu) + \sum_{n=2}^{\infty} \frac{2(2n-1)}{n+1} A_{n+1} r^{-n-1} P_n(\mu), \\ \mathrm{Re}\, p_2 &= (-\pi_2 + 10(A+3/2))\, r P_1(\mu) + \sum_{n=2}^{\infty} \frac{2(2n+3)}{n} A_{n+1} r^n P_n(\mu), \end{aligned} \tag{1.8}$$

where $\pi_i = \rho_i g a^2/(U_\infty \mu_1)$ is the dimensionless hydrostatic pressure; g is the free-fall acceleration (the mass force is the weight function); and Π_0 = const. For uniform motion $\pi_1 - \beta\pi_2 = 3A$. Substituting relationship (1.8) then, with account of this equality into (1.5), we have a new system of equations for the constants A, A_n:

$$A = -\frac{1+(3/2)\beta}{1+\beta} + \frac{1}{3}\mathrm{Ma}\, B_1 (1+\beta)^{-1}, \quad A_{n+1} = \mathrm{Ma}\frac{n(n+1)}{3(n\beta+\beta+n)} B_n, \quad n \geqslant 2 \tag{1.9}$$

[the expression for B_n is the same as in (1.7)].

Equations (1.7) and (1.9) can be satisfied simultaneously only for A. For A_{n+1} ($n \geq 2$), Eqs. (1.7) and (1.9) are incompatible. This implies that the drop shape cannot be assumed to be spherical even within the zeroth approximation in the Reynolds number (the Stokes approximation under conditions of the chemithermocapillary effect): the nonuniformity of temperature distribution over the surface of the drop leads to its deformation and to the appearance of additional harmonics of the stream function. Nevertheless, the constants A_{n+1} ($n \geq 2$) decrease quickly with increasing n, and they can be assumed to be small in comparison with A. Consequently, one can construct an approximate solution of system (1.7), (1.9), neglecting in the expressions for B_n the contribution of the terms proportional to the constants A_n ($n \geq 3$). Thus, in this approximation, $A_n \equiv 0$ ($n \geq 3$), while for A one obtains a nonlinear equation whose solution provides an expression for the force acting on the drop under conditions of the chemithermocapillary effect (see Eq. (15) in [7]). We note that the conditions for the tangential and normal stress components are satisfied simultaneously [the first equations in (1.7) and (1.9)], so that within this approximation the drop can be assumed to be spherical for any We. Nevertheless, it follows from (1.7) and (1.9) that $A_n \neq 0$ ($n \geq 3$). The constants A_n cannot be calculated without taking into account the variation in the drop shape, since the equations for A_n ($n \geq 3$) in systems (1.7), (1.9) are incompatible. However, from the smallness of the constants A_n in comparison with A it follows that the drop deformation is small (of order A_n/A).

Below we construct a refinement of the solution of problem (1.1)-(1.5) obtained in [7], taking into account the higher harmonics in the stream functions (1.6) and the variation in the drop shape.

2. Consider a fluid drop of arbitrary, quite smooth shape, moving in a different fluid (unmixed with it). On the surface of the drop there occurs in the diffusion regime a nonisothermal chemical reaction due to the reagent dissolved in the external fluid. The surface tension of the drop depends on temperature linearly. The Re and Pe_{χ_i} are assumed to be small, and the Pe value — large. We select a spherical coordinate system with an origin coinciding with the center of mass of the drop. The distributions of fluid flow velocity, reagent concentration in the continuous phase, and the temperature distributions outside and inside the drop within the approximations of creeping flow, diffusion boundary layers, and absence of convective thermal conductivity, respectively, are described by the following equations and boundary conditions in dimensionless form:

$$E^4\psi_i = 0,\quad E^2 = \partial^2_{rr} + r^{-2}(1-\mu^2)\,\partial^2_{\mu\mu},$$
$$r\to\infty,\quad \psi_1 \to (1/2)r^2(1-\mu^2),\ r=0,\ \psi_2/r^2<\infty,\ r=R,\ \psi_1=\psi_2=0, \tag{2.1}$$
$$-\partial_r\psi_1 + \frac{R'}{R^2}(1-\mu^2)\,\partial_\mu\psi_1 = -\partial_r\psi_2 + \frac{R'}{R^2}(1-\mu^2)\,\partial_\mu\psi_2;$$

$$\frac{1}{r^2}\frac{\partial(\psi_1, z)}{\partial(r,\mu)} = \mathrm{Pe}^{-1}\Delta z,\quad r\to\infty,\quad z=0,\quad r=R,\quad z=1; \tag{2.2}$$

$$\Delta\varphi_i = 0,\ i=1,2,\ r\to\infty,\quad \varphi_1\to 0,\ r=0,\ \varphi_2<\infty, \tag{2.3}$$
$$r=R,\ \varphi_1=\varphi_2,\ \partial_r\varphi_1 - (R'/R^2)(1-\mu^2)\partial_\mu\varphi_1 -$$
$$-\delta(\partial_r\varphi_2 - (R'/R^2)(1-\mu^2)\partial_\mu\varphi_2) = \partial_n z;$$
$$r=R,\quad 2\left[2\partial^2_{r\mu}\psi - 3R^{-1}\partial_\mu\psi + \mu(1-\mu^2)^{-1}\partial_r\psi\right]^1_2\times \tag{2.4}$$
$$\times(1-\mu^2)R'/R + \left[2\partial_r\psi - R\partial^2_{rr}\psi + R^{-1}(1-\mu^2)\partial^2_{\mu\mu}\psi\right]^1_2\left(1-(1-\mu^2)\left(\frac{R'}{R}\right)^2\right) =$$
$$= R(1-\mu^2)\left(1+(1-\mu^2)\left(\frac{R'}{R}\right)^2\right)^{1/2}\mathrm{Ma}\,(R'\partial_r\varphi + \partial_\mu\varphi);$$
$$r=R,\quad -\mathrm{Re}\,[p]^1_2\left(1+(1-\mu^2)\left(\frac{R'}{R}\right)^2\right) - \frac{2}{R^2}\Big\{\left[\partial^2_{r\mu}\psi - 2R^{-1}\partial_\mu\psi\right]^1_2 -$$
$$-R'R^{-1}\left[2\partial_r\psi - R\partial^2_{rr}\psi + R^{-1}(1-\mu^2)\partial^2_{\mu\mu}\psi\right]^1_2 - \tag{2.5}$$
$$(1-\mu^2)\left(\frac{R'}{R}\right)^2\left[\partial^2_{r\mu}\psi + \mu(1-\mu^2)^{-1}\partial_r\psi - \frac{1}{R}\partial_\mu\psi\right]^1_2\Big\} = \left(1+(1-\mu^2)\left(\frac{R'}{R}\right)^2\right)2h\left(\frac{\mathrm{Re}}{\mathrm{We}} + \mathrm{Ma}\,\varphi\right).$$

Here $R \equiv R(\mu)$ is a function describing the shape of the drop in the spherical coordinate system; $R' \equiv dR/d\mu$; ∂_n, normal derivatives with respect to the drop surface; $h \equiv h(\mu)$, dimensionless curvature of the interphase boundary; $[\cdot]_2{}^1 = (\cdot)_1 - \beta(\cdot)_2$. The boundary conditions in (2.3) express the equality of temperatures and balance of thermal fluxes at the drop surface, and conditions (2.4) and (2.5) express the balance of tangential and normal stresses, respectively. The length scale is the radius a of a sphere, of equal volume with the drop.

The solution of problem (2.1)-(2.5) is constructed similarly to the solution of the problem in [7]. It has been shown in Sec. 1 that the variation in the drop shape can be assumed to be small: $R(\mu) = 1 + \xi(\mu)$, $|\xi(\mu)| \ll 1$, $\xi(\mu) = \sum\limits_{n=0}^{\infty}\chi_n P_n(\mu)$, while $\chi_0 = \chi_1 = 0$; since the fluid is incompressible and the origin of coordinates coincides with the center of mass of the drop. From the conditions satisfied on the spherical surface it follows that, on a weakly deformed surface, $|\partial_\mu\psi| \sim |\xi(\mu)| \ll 1$.

The current functions ψ_i, satisfying the equation $E^4\psi_i = 0$ and the boundary conditions at the origin of coordinates and at infinity, are [9]

$$\psi_1 = (r^2 + B_2r^{-1} + D_2r)\,G_2(\mu) + \sum_{n=3}^{\infty}(B_nr^{-n+1} + D_nr^{-n+3})\,G_n(\mu),$$
$$\psi_2 = (A_2r^2 + C_2r^4)\,G_2(\mu) + \sum_{n=3}^{\infty}(A_nr^n + C_nr^{n+2})\,G_n(\mu). \tag{2.6}$$

The first terms in (2.6) provide, for weak drop deformation, the main contribution to the chemithermocapillary effect and, therefore, we take into account the surface nonsphericity only in these terms, denoted by $\psi_1{}^{(0)}$ and $\psi_2{}^{(0)}$, so that for $r = 1 + \xi(\mu)$ we obtain, accurately within $O(\xi)$,

$$\psi_i(r,\mu) = \psi_i(1,\mu) + \partial_r\psi_i^{(0)}\big|_{r=1}\,\xi(\mu),$$
$$r=1,\quad \partial_r\psi_i^{(0)}\xi(\mu) \sim G_2(\mu)\sum_{n=2}^{\infty}\chi_nP_n(\mu) = \sum_{n=2}^{\infty}\omega_nG_n(\mu), \tag{2.7}$$
$$\omega_n = (1/2)n(n-1)[\chi_{n-2}/(2n-3) - \chi_n/(2n+1)].$$

Substituting (2.6), with account of (2.7), into the boundary conditions of (2.1) for $r = R$, and retaining terms of first order of smallness in $\xi(\mu)$, we determine the conditions on the coefficients in the stream function, using which we find

$$\psi_1 = (r^2 + D_2 r - r^{-1}((D_2+1) - (2D_2+3)\chi_2/5))G_2(\mu) +$$
$$+ \sum_{n=3}^{\infty}[D_n(r^{-n+3} - r^{-n+1}) - \omega_n r^{-n+1}]G_n(\mu),$$
$$\psi_2 = [(D_2 + 3/2 - 3\chi_2/10)(r^4 - r^2) + (D_2 + 3/2)(3\chi_2/5)r^2]G_2(\mu) + \tag{2.8}$$
$$+ \sum_{n=3}^{\infty}[D_n(r^{n+2} - r^n) + \omega_n((n - 2(D_2+1))r^{n+2} - (n - (2D_2+3))r^4)G_n(\mu).$$

We turn to problem (2.2) and consider its solution within the approximation of the diffusion boundary layer [10]:

$$z = \operatorname{erfc}\left(\frac{\psi_1}{2\varepsilon\sqrt{\tau}}\right), \quad \tau = \int_{-1}^{\mu}(R^2 + R'^2)\,\partial_r\psi_1 d\mu, \quad \varepsilon = \mathrm{Pe}^{-1/2} \tag{2.9}$$

[ψ_1 is defined by expression (2.8)]. Differentiating (2.9) normally to the surface of the drop, we obtain an expression which is accurate within terms of first order of smallness in $\xi(\mu)$:

$$\partial_n z = j_0(\mu) + j_1(\mu), \quad j_0(\mu) = -\frac{1}{\varepsilon\sqrt{\pi}}\tau_0^{-1/2}\partial_r\psi_1^{(0)},$$
$$j_1(\mu) = -\frac{1}{\varepsilon\sqrt{\pi}}\tau_0^{-1/2}\left(\partial_r\psi_1^{(1)} + \partial_{rr}^2\psi_1^{(0)}\xi(\mu) + \frac{1}{2\varepsilon\sqrt{\pi}}\tau_0^{-3/2}\partial_r\psi_1^{(0)}\tau_1,\right.$$
$$\tau_0 = \int_{-1}^{\mu}\partial_r\psi_1^{(0)}d\mu, \quad \tau_1 = \int_{-1}^{\mu}[(2\partial_r\psi_1^{(0)} + \partial_{rr}^2\psi_1^{(0)})\xi(\mu) + \partial_r\psi_1^{(1)}]\,d\mu_1, \tag{2.10}$$
$$\psi_1^{(0)} = (r^2 + D_2 r - r^{-1}(D_2+1))G_2(\mu),$$
$$\psi_1^{(1)} = r^{-1}(2D_2+3)\frac{\chi_2}{5}G_2(\mu) + \sum_{n=3}^{\infty}[D_n(r^{-n+3} - r^{-n+1}) - \omega_n r^{-n+1}]G_n(\mu)$$

(the derivative values are taken at r = 1). Expression (2.10) for $\partial_n z$ must be substituted into the boundary condition of equality of thermal fluxes for r = R in (2.3). The solution of problem (2.3) is:

$$\varphi_1 = \sum_{n=0}^{\infty}\alpha_n r^{-n-1}P_n(\mu), \quad \varphi_2 = \sum_{n=0}^{\infty}\beta_n r^n P_n(\mu). \tag{2.11}$$

The basic contribution to the chemithermocapillary effect is provided by the lowest harmonics in (2.11). We denote $\varphi_1^{(0)} \equiv \alpha_0 r^{-1} + \alpha_1 r^{-2}\mu$, $\varphi_2^{(0)} = \beta_0 + \beta_1 r\mu$, and take into account the nonsphericity of the drop surface only in the expression for $\varphi_i^{(0)}$ similarly to the way it was done in the case $\psi_i^{(0)}$, retaining terms of first order of smallness in $\xi(\mu)$. Accurately within $O(\xi(\mu))$, the boundary conditions at r = R in (2.3) are

$$r = 1, \quad \varphi_1^{(0)} + \partial_r\varphi_1^{(0)}\xi(\mu) + \varphi_1^{(1)} = \varphi_2^{(0)} + \partial_r\varphi_2^{(0)}\xi(\mu) + \varphi_2^{(1)},$$
$$\partial_r\varphi_1^{(0)} + \partial_{rr}^2\varphi_1^{(0)}\xi(\mu) + \partial_r\varphi_1^{(1)} - \xi'(\mu)(1-\mu^2)\,\partial_\mu\varphi_1^{(0)} -$$
$$- \delta\left(\partial_r\varphi_2^{(0)} + \partial_{rr}^2\varphi_2^{(0)}\xi(\mu) + \partial_r\varphi_2^{(1)} - \xi'(\mu)(1-\mu^2)\,\partial_\mu\varphi_2^{(0)} = \right. \tag{2.12}$$
$$= j_0(\mu) + j_1(\mu), \quad \varphi_i^{(1)} = \varphi_i - \varphi_i^{(0)}.$$

The expressions for $j_0(\mu)$ and $j_1(\mu)$, determined in (2.10), are expanded in series in Legendre polynomials:

$$j_0(\mu) = \varkappa_0^{(0)} + \varkappa_1^{(0)}\mu + \Sigma_1, \quad j_1(\mu) = \varkappa_0^{(1)} + \varkappa_1^{(1)}\mu + \Sigma_2,$$
$$\varkappa_n^{(p)} = \frac{2n+1}{2}\int_{-1}^{1} j_p P_n(\mu)\,d\mu, \quad p = 0,\ 1,$$
$$\Sigma_1 = \sum_{n=2}^{\infty}\varkappa_n^{(0)}P_n(\mu), \quad \Sigma_2 = \sum_{n=2}^{\infty}\varkappa_n^{(1)}P_n(\mu).$$

Since the coefficients $\kappa_n^{(0)}$ and $\kappa_n^{(1)}$ decrease quickly with increasing n, we assume that $\Sigma_1 \sim O(\xi)$ and $\Sigma_2 \sim o(\xi)$. Using properties of the Legendre polynomials and equating coefficients of polynomials with identical powers, from (2.11) and (2.12) we obtain conditions relating the coefficients α_n, β_n, and κ_n:

$$\begin{gathered}\alpha_0 = \beta_0,\ \alpha_1(1-(4/5)\chi_2) = \beta_1(1+(2/5)\chi_2),\\ -(\alpha_0\chi_2+(6/7)\alpha_1\chi_3+\alpha_2) = (3/7)\beta_1\chi_2+\beta_2,\\ -\left(\alpha_0\chi_3 + 2\alpha_1\left(\frac{k}{2k-1}\chi_{k-1} + \frac{k}{2k+3}\chi_{k+1}\right) + \alpha_k\right) =\\ = \beta_1\left(\frac{k}{2k-1}\chi_{k-1} + \frac{k+1}{2k+1}\chi_{k+1}\right) + \beta_k, \quad k \geqslant 3;\end{gathered} \tag{2.13}$$

$$\begin{gathered}-\alpha_0 = \varkappa_0^{(0)} + \varkappa_0^{(1)}, \quad -2\alpha_1(1-(3/5)\chi_2) - \delta\beta_1(1-(6/5)\chi_2) = \varkappa_1^{(0)}+\varkappa_1^{(1)},\\ 2\alpha_0\chi_2 + (6/7)\alpha_1\chi_3 - 3\alpha_2 - \delta(2\beta_2 - (12/7)\beta_1\chi_3) = \varkappa_2^{(0)},\\ 2\alpha_0\chi_k + \alpha_1\left(\frac{k(k+5)}{2k-1}\chi_{k-1} + \frac{(k+1)(4-k)}{2k+1}\chi_{k+1}\right) -\\ -\delta\left[k\beta_k - \beta_1\left(\chi_{k+1}\frac{(k+1)(k+2)}{2k+3} - \chi_{k-1}\frac{k(k-1)}{2k-1}\right)\right] = \varkappa_k^{(0)}, \quad k \geqslant 3.\end{gathered} \tag{2.14}$$

We note that the coefficients κ_i depend, in turn, on the constants D_i in the stream functions and on χ_i.

We substitute into (2.4) and (2.5) expressions (2.8) for the stream functions and the temperature distributions (2.11) with the coefficients α_i and β_i, satisfying (2.13) and (2.14), taking into account first-order terms in $\xi(\mu)$ and the nonsphericity of the surface only in $\varphi_i^{(0)}$, $\psi_i^{(0)}$, and $p_i^{(0)}$ [$p_i^{(0)}$ are the vanishing and first harmonic pressures in (1.8)]. Equating the coefficients of Legendre polynomials of identical powers, we find an infinite system of equations in D_i and χ_i, while the equations for D_2 and χ_2 are nonlinear, those for D_i and χ_3 ($i \geq 3$) are linear. In this case one uses in (2.5) the relation $h(\mu) = 1 - \xi(\mu) - (1/2)[(1-\mu^2)\xi'(\mu)]'$, $|\xi| \ll 1$ [8].

The system of equations for the coefficients D_i and χ_i is coupled. The following procedure is used to decouple the equations. We neglect the terms χ_i, $i \geq N$, D_k ($k \geq N+1$) in comparison with D_N ($N \geq 2$). This procedure can be justified, since the coefficients χ_k and D_k decrease with increasing k, and the conditions for normal and tangential stress components are satisfied for the first principal harmonic on the nondeformed surface (Sec. 1). Restricting ourselves to second harmonics, we have for D_3 and χ_2 the system of equations

$$\begin{gathered}10D_3(1+\beta) - 6\mathrm{Ma}\chi_2\frac{\varkappa_0^{(0)}}{3+2\delta} = -6\mathrm{Ma}\frac{\varkappa_2^{(0)}}{3+2\delta},\\ -D_3(2+3\beta) + \chi_2\left(4\frac{\mathrm{Re}}{\mathrm{We}} - 2\mathrm{Ma}\frac{5+4\delta}{3+2\delta}\varkappa_0^{(0)}\right) = 2\mathrm{Ma}\frac{\varkappa_2^{(0)}}{3+2\delta},\end{gathered}$$

whose solution is

$$\begin{gathered}\chi_2 = \mathrm{Ma}\,\varkappa_2^{(0)}\Delta^{-1}, \quad D_3 = -12\,\mathrm{Ma}\,\varkappa_2^{(0)}\left(\frac{\mathrm{Re}}{\mathrm{We}} - \mathrm{Ma}\,\varkappa_0^{(0)}\right)\Delta^{-1},\\ \Delta = 20(1+\beta)\frac{\mathrm{Re}}{\mathrm{We}}(3+2\delta) - \mathrm{Ma}\varkappa_0^{(0)}(56+59\beta+40\delta(1+\beta)),\\ \varkappa_0^{(0)} = -\frac{1}{2}\sqrt{\mathrm{Pe}}\sqrt{\frac{3}{\pi}}(D_2+3/2)^{1/2}\int_{-1}^{1}\frac{1-\mu}{\sqrt{2-\mu}}d\mu \approx 0.6\sqrt{\mathrm{Pe}(D_2+3/2)},\\ \varkappa_2^{(0)} = -\frac{5}{4}\sqrt{\mathrm{Pe}}\sqrt{\frac{3}{\pi}}(D_2+3/2)^{1/2}\int_{-1}^{1}\frac{1-\mu}{\sqrt{2-\mu}}P_2(\mu)d\mu \approx 0.07\sqrt{\mathrm{Pe}(D_2+3/2)}.\end{gathered} \tag{2.15}$$

For the fundamental harmonic D_2 we obtain the same equation as in the case of a nondeformed surface [7]:

$$D_2 = -\frac{1+(3/2)\beta}{1+\beta} - \frac{6(2-\sqrt{3})}{5\sqrt{\pi}}\frac{\sqrt{\mathrm{Pe}}}{(1+\beta)(2+\delta)}\left(D_2+\frac{3}{2}\right)^{1/2},$$

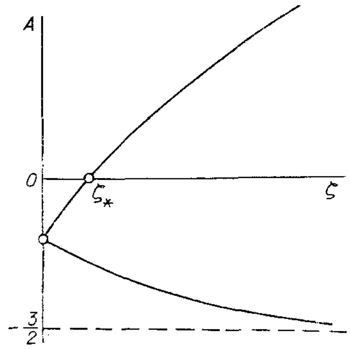

Fig. 1

with the solution

$$D_2^{(1,2)} = -\frac{1+(3/2)\beta}{1+\beta} + \frac{1}{2}\left[\zeta \pm \left(\frac{2\zeta}{1+\beta} + \zeta^2\right)^{1/2}\right], \quad \zeta = \left[\frac{0.18\mathrm{Ma}\sqrt{\mathrm{Pe}}}{(2+\delta)(1+\beta)}\right]^2. \tag{2.16}$$

The dependence of D_2 on ζ (2.16) is shown schematically in Fig. 1. The upper branch corresponds to $\theta_* d\sigma/dT < 0$, and the lower to $\theta_* d\sigma/dT > 0$. It is seen that for $\zeta > \zeta_*$ and $\theta_* d\sigma/dT < 0$ a tractive force is generated, while for $\theta_* d\sigma/dT > 0$ and increasing ζ the resistance force is enhanced and tends to the Stokes force ($D_2 = -3/2$), i.e., the drop behaves as a hard ball. For $\zeta = \zeta_*$, $D_2 = 0$ and the force acting the drop from the side of the surrounding fluid, $F = -4\pi\mu_1 a D_2 U_\infty$ [9], vanishes; in this case, the drop drifts with velocity U_* (see Sec. 1, as well as [7]).

We analyze now the variation in the drop shape. Using the expression for Ma (Sec. 1), (2.15) is conveniently rewritten in the form

$$\begin{gathered}
\chi_2 = \mathrm{Ma}_* I_2 \sqrt{\mathrm{Pe}(D_2 + 3/2)}\,\Delta_*^{-1}, \\
\Delta_* = 20(1+\beta)(3+2\delta) + I_0 \mathrm{Ma}_* \sqrt{\mathrm{Pe}(D_2+3/2)}\,(56 + 59\beta + 40\delta(1+\beta)), \\
\mathrm{Ma}_* = \mathrm{L}^{-1}\frac{\theta_*}{\sigma}\frac{d\sigma}{dT}, \quad I_0 = \frac{1}{2}\sqrt{\frac{3}{\pi}}\int_{-1}^{1}\frac{1-\mu}{\sqrt{2-\mu}}\,d\mu \approx 0.651, \\
I_2 = -\frac{5}{2}\sqrt{\frac{3}{\pi}}\int_{-1}^{1}\frac{1-\mu}{\sqrt{2-\mu}}P_2(\mu)\,d\mu \approx 0.082.
\end{gathered} \tag{2.17}$$

It is seen that if $\sigma \to \infty$, then $\chi_2 \to 0$, i.e., the drop remains spherical. Consider the two limiting cases: $\mathrm{Ma}_* \mathrm{Pe}^{1/2} \ll 1$ and $\mathrm{Ma}_* \mathrm{Pe}^{1/2} \gg 1$. In the first case we have

$$\chi_2 = \frac{I_2 \mathrm{Ma}_* \mathrm{Pe}^{1/2}(D_2+3/2)^{1/2}}{20(1+\beta)(3+2\delta)} = 4.1\cdot 10^{-3}\frac{\mathrm{Ma}_* \mathrm{Pe}^{1/2}(D_2+3/2)^{1/2}}{(1+\beta)(3+2\delta)}.$$

The sign of χ_2 coincides with that of Ma_*. If $\mathrm{Ma}_* < 0$ (the force acting on the drop, less than the Rybchinskii–Hadamard force, is a tractive or vanishing force – drift with constant velocity [7]) then $\chi_2 < 0$ and the drop is displaced in the direction of motion. If $\mathrm{Ma}_* > 0$ (the force acting on the drop is stronger than the Rybchinskii–Hadamard force), the drop extends in the direction of motion. In the drifting state

$$\chi_2 = -1.11\cdot 10^{-3}\frac{a\sigma(\theta_*\sigma^{-1}d\sigma/dT)^2}{\mu_1\chi_1 \mathrm{L}(1+\beta)(1+(3/2)\beta)(2+\delta)(3+2\delta)},$$

i.e., the drop has a shape of an ellipsoid slightly flattened along the drift direction. This is natural, since in the drift state the thermocapillary component of tangential stresses is directed toward the drifting drop; the temperature in the front portion of the drop is higher than on the back side (similarly to thermocapillary drift in the temperature gradient field), and, consequently, the Laplace pressure in the leading portion is less than in the trailing portion, leading to a decreasing drop curvature in its leading portion – surface flattening.

In the second case,

$$\chi_2 = \frac{I_2}{I_0}(56 + 59\beta + 40\delta(1+\beta))^{-1} = \frac{2.26\cdot 10^{-3}}{1 + (59/56)\beta + (5/7)\delta(1+\beta)},$$

whence it follows that the drop always extends in the direction of motion, independently of the sign of Ma_*.

In the intermediate case ($Ma_* Pe^{1/2} \sim 1$), Eq. (2.17) is valid, but if $Ma_* < 0$, the denominator contains a difference of two positive numbers, which can vanish for certain parameter values. Near these values the assumption of weak drop deformation for any We is incorrect.

It is noted that, for typical parameter values for fluids and surface reactions [$L \sim 10^2$, $\sigma \sim 10^1$-10^2 erg/cm², $d\sigma/dT \sim 0.1$ erg/(cm²·K), $\theta_* \sim 1$-100 K), we obtain $Ma_* \sim 10^{-3}$-10^{-4}, so that $Ma_* Pe^{1/2} \ll 1$ in the wide region of variation of $Pe^{1/2} \gg 1$.

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