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THERMOCAPILLARY DRIFT OF A DROP IN THE CASE WHEN THE SURFACE TENSION DEPENDS NON-LINEARLY ON THE TEMPERATURE*

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An approximate analytic solution of the problem of the motion of a spherical drop (or a bubble) in an unbounded viscous incompressible fluid dependent on an external constant temperature gradient is obtained in the quasistationary approximation. The motion is connected with the appearance of tangential stresses at the drop surface caused by the change in the value of the surface tension σ with temperature T (the Marangoni effect), and is directed towards the sections of the external medium heated to a higher temperature when $d\sigma/dT < 0$, and in the opposite direction when $d\sigma/dT > 0$ (thermocapillary drift).

Unlike the case studied earlier in /1-3/ of the linear dependence of the surface tension on temperature, the present paper considers an arbitrary, non-linear dependence (in particular a quadratic dependence characteristic of aqueous solutions of high mol.wt. alcohols, certain metal alloys and nematic liquid crystals /4, 5/).

The velocity and temperture distributions inside and outside the drop are obtained, when there is no gravity, under the assumption that the Reynolds and thermal Peclet numbers are small.

It is shown that the non-linear dependence of the surface tension on temperature may lead to the appearance of equilibrium states in which the centre of mass of the drop is at rest, while the fluid inside and outside it moves in a steady manner. When the conditions are sufficiently general, such states of stable equilibrium correspond to the presence, in the two-phase medium, of a plane of attraction normal to the unperturbed temperature gradient at which the particles of disperse phase concentrate. In practice, this may upset the process of separation of the impurities in conditions of low gravity (for example in the case when bubbles have to be removed from a melt). Analysis of the change in the form of the drop shows that at low Weber numbers a drop in the equilibrium state takes the form of an ellipsoid of revolution flattened in the direction of the outer temperature gradient when $d^2\sigma/dT^2 = \text{const} > 0$, and stretched in this direction in the opposite case.

1. Formulation of the problem. We consider the steady-state motion of a drop of a viscous incompressible liquid in another, mutually immiscible viscous incompressible liquid occupying the whole space. The liquid is at rest at infinity, and a constant temperature gradient is specified. We assume that the densities, viscosities, thermal conductivities and heat capacities of the liquids inside and outside the drop are constant, the surface tension is an arbitrary function of the temperature, the motion of the drop is fairly slow (small Reynolds and Peclet numbers) and, that the drop remains spherical (the deviation from spherical shape will be discussed at the end of Sect.2). The problem is symmetrical about the z axis passing through the centre of the drop in a direction parallel to the outer temperture gradient.

It will be convenient to introduce a reference system attached to the centre of the moving drop (as the problem is then reduced to the analysis of a streamlined plane-parallel flow past a drop, where the velocity of flow has to be determined), and to measure the temperature relative to the unperturbed temperature at a point at which the centre of the drop is found at the given instant. Then the temperature at any point of the space will be given by the expression

$$T_i = T_\infty(x_0) + S_\infty(x - x_0) + T_i' \tag{1.1}$$

Here and henceforth the indices $i = 1, 2$ will refer to the outside liquid and the drop respectively, S_∞ is the magnitude of the given outer temperature gradient away from the drop ($S_\infty > 0$ if the direction of the temperature gradient is the same as the positive direction of the x axis, and $S_\infty < 0$ otherwise), $T_\infty(x_0)$ is the temperature unperturbed by the drop at some point of the x axis with the coordinate x_0, x is the coordinate of the

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point at which the centre of the drop is situated at the given instant, and T_i' is the temperature relative to the unperturbed temperature at the point with coordinate x.

Assuming that the surface tension depends linearly on temperature and using the reference system attached to the centre of the drop, we obtain the steady-state distribution of the velocities and temperature T_i' for the case of a steady drift of the drop /1-3/. When the dependence of the surface tension on temperature is arbitrary, its derivative with respect to temperature, which defines the Marangoni effect, will in general change with the motion of the drop. We shall consider the problem in the quasistationary approximation, when the changes in the velocity field and temperature field T_i' are fairly slow.

Let τ be the characeristic time of change of the velocity field

$$\tau \sim |v\,(\partial v/\partial t)^{-1}| \tag{1.2}$$

Then, provided that the conditions

$$\frac{a^2}{\nu_i\tau} \ll 1, \quad \mathrm{Pe}_i\frac{a^2}{\chi_i\tau} \ll 1 \tag{1.3}$$

hold, the distributions of the velocity and temperature T_i' can be assumed to be quasistationary. Here ν_i, χ_i are the kinematic viscosity coefficient and thermal conductivity, a is the radius of the drop and Pe_i are the thermal Peclet numbers calculated from the characteristic velocity of motion. In what follows, having obtained the quasistationary solution we shall give an estimate for the time τ in terms of the defining parameters of the problem.

Using the assumptions formulated above we can write, in the quasistationary approximation using a spherical system of coordinates in which the radius r is measured from the centre of the drop and the angle θ from the positive direction of the x axis, the equation of the boundary conditions for the velocity and temperature in the form

$$\begin{gathered}
0 = -\nabla p_i + \mu_i \Delta \mathbf{v}_i, \quad \operatorname{div} \mathbf{v}_i = 0, \quad \Delta T_i' = 0 \\
r \to \infty, \quad \mathbf{v}_1 \to U_\infty \cos\theta \mathbf{e}_r - U_\infty \sin\theta \mathbf{e}_\theta, \quad T_1' \to S_\infty r\cos\theta \\
r \to 0, \quad |\mathbf{v}_2| < \infty, \quad |T_2'| < \infty \\
r = a, \quad v_{1r} = v_{2r} = 0, \quad v_{1\theta} = v_{2\theta} \\
\frac{p_2 - p_1}{2} = \mu_2 \frac{\partial v_{2r}}{\partial r} - \mu_1 \frac{\partial v_{1r}}{\partial r} + \frac{\sigma}{a} \\
\mu_1\left(\frac{\partial v_{1\theta}}{\partial r} - \frac{v_{1\theta}}{r}\right) - \mu_2\left(\frac{\partial v_{2\theta}}{\partial r} - \frac{v_{2\theta}}{r}\right) + \frac{1}{a}\frac{d\sigma}{dT}\frac{dT_1'}{d\theta} = 0 \\
T_1' = T_2', \quad \lambda_1 \frac{\partial T_1'}{\partial r} = \lambda_2 \frac{\partial T_2'}{\partial r}
\end{gathered} \tag{1.4}$$

Here U_∞ is the velocity of the incoming flow which has to be determined from the condition that the force acting on the drop ($(U_\infty > 0)$ vanishes if this velocity is directed along the x axis, and $U_\infty < 0$ otherwise), $\mathbf{v}_i$, p_i, ρ_i is the velocity, pressure and density, μ_i, and λ_i are the dynamic viscosity coefficient and thermal conductivity, and $\mathbf{e}_r$ and $\mathbf{e}_\theta$ are unit vectors of the spherical system of coordinates.

All unknown functions as well as U_∞, $d\sigma/dT$, depend parametrically on time, or, which is the same, on the x coordinate of the centre of the drop, since

$$x(t) = x(t_0) - \int_{t_0}^{t} U_\infty(\xi)\,d\xi \tag{1.5}$$

After introducing the stream function and changing to dimensionless coordinates, we can write the equations and boundary conditions (1.4) in the form

$$E^4\psi_i = 0; \quad E^2 = \frac{\partial^2}{\partial r^2} + \frac{1-\mu^2}{r^2}\frac{\partial^2}{\partial \mu^2} \tag{1.6}$$

$$\begin{gathered}
r \to \infty, \quad \psi_1 \to {}^1/_2 r^2(1-\mu^2); \quad r \to 0, \quad \psi_2/r^2 < \infty \\
r = 1, \quad \psi_1 = \psi_2 = 0, \quad \partial\psi_1/\partial r = \partial\psi_2/\partial r
\end{gathered} \tag{1.7}$$

$$r = 1, \quad \left(2\frac{\partial}{\partial r} - \frac{\partial^2}{\partial r^2}\right)(\psi_1 - \beta\psi_2) = M(1-\mu^2)\frac{\partial\varphi_1}{\partial\mu} \tag{1.8}$$

$$\Delta\varphi_i = 0 \tag{1.9}$$

$$\begin{gathered}
r \to \infty, \quad \varphi_1 \to r\mu, \quad r \to 0, \quad |\varphi_2| < \infty \\
r = 1, \quad \varphi_1 = \varphi_2, \quad \partial\varphi_1/\partial r = \delta\partial\varphi_2/\partial r
\end{gathered} \tag{1.10}$$

$$\mu = \cos\theta, \quad v_{ir} = \frac{1}{r^2 \sin\theta}\frac{\partial\psi_i}{\partial\theta}, \quad v_{i\theta} = -\frac{1}{r\sin\theta}\frac{\partial\psi_i}{\partial r}$$

$$\varphi_i = \frac{T_i'}{aS_\infty}, \quad \beta = \frac{\mu_2}{\mu_1}, \quad \delta = \frac{\lambda_2}{\lambda_1}, \quad M = \frac{aS_\infty}{\mu_1 U_\infty}\frac{d\sigma}{dT}$$

Here the velocities and the spatial coordinate are referred, respectively, to the velocity U_∞ and radius of the drop a, with the previous notation used to describe them, M is a dimensionless function of x, and μ (when the surface tension depends linearly on temperature, then M becomes the Marangoni number (apart from the sign)).

2. The velocity and temperature field. The velocity of drift of the drop and distortion of its shape. The solution of Eqs.(1.6) with boundary conditions (1.7) determining the velocity field inside and outside the drop is as follows (e.g. /6/):

$$\psi_1 = \left(r^2 + Ar - \frac{A+1}{r}\right)\frac{1-\mu^2}{2} + \sum_{n=3}^{\infty} A_n\left(r^{-n+3} - r^{-n+1}\right)G_n(\mu)$$
$$\psi_2 = \left(A + \frac{3}{2}\right)(r^4 - r^2)\frac{1-\mu^2}{2} + \sum_{n=3}^{\infty} A_n\left(r^{n+2} - r^n\right)G_n(\mu) \tag{2.1}$$

Here $G_n(\mu)$ is the Gegenbauer function of the first kind, of order n and degree $^1/_2$. The constants $A, A_3, A_4, \ldots$ (depending parametrically on x) will be determined from the boundary condition (1.8) using the solution of Problem (1.9), (1.10) on the temperature distribution.

$$\varphi_1 = \left(r + \frac{1-\delta}{2+\delta}\frac{1}{r^2}\right)\mu, \quad \varphi_2 = \frac{3}{2+\delta}r\mu \tag{2.2}$$

stationary with respect to the Peclet number in the zeroth approximation.

After substituting relations (2.1) and (2.2) into the boundary condition (1.8), the latter takes the form

$$6\left(1 + A + \beta\left(\frac{3}{2} + A\right)\right)G_2(\mu) + \sum_{n=3}^{\infty} A_n(4n-2)(1+\beta)G_n(\mu) =$$
$$\frac{3}{2+\delta}(1-\mu^2)M \tag{2.3}$$

Substituting into (2.3) the expansion of the function $(1-\mu^2)M(x,\mu)$ in series in terms of the Gegenbauer functions (see e.g., /6/)

$$(1-\mu^2)M(x,\mu) = \sum_{n=2}^{\infty}\frac{1}{2}n(n-1)(2n-1)B_n(x)G_n(\mu) \tag{2.4}$$

$$B_n(x) = \int_{-1}^{1} M(x,\mu)G_n(\mu)\,d\mu \tag{2.5}$$

and equating to zero the sum of the coefficients of Gegenbauer functions of like order, we obtain

$$A = \left[\frac{3}{2(2+\delta)}B_2 - \left(1 + \frac{3}{2}\beta\right)\right](1+\beta)^{-1}$$
$$A_n = \frac{3n(n-1)}{4(2+\delta)(1+\beta)}B_n, \quad n = 3, 4, \ldots \tag{2.6}$$

After determining the constants $A, A_3, A_4, \ldots$, the quasistationary velocity field inside and outside the drop becomes completely constructed. The force acting on the drop from the direction of the outer liquid is given by the expression /6/

$$F = -4\pi\mu_1 aAU_\infty$$

or, after substituting relations (2.5) and (2.6) and taking into account the expression for $M(x,\mu)$ (see Sect.1), by the expression

$$F = 4\pi\mu_1 a (1+\beta)^{-1}\left[\left(1+\frac{3}{2}\beta\right)U_\infty(x) - \frac{3}{4(2+\delta)}\frac{aS_\infty}{\mu_1}\int\limits_{-1}^{1}\frac{d\sigma}{dT}(x,\mu)(1-\mu^2)\,d\mu\right] \tag{2.7}$$

The speed of drift of the drop U $(U = -U_\infty)$ is found from the condition that the above force vanishes:

$$U(x) = -\frac{3}{2(2+\delta)(2+3\beta)}\frac{aS_\infty}{\mu_1}\int\limits_{-1}^{1}\frac{d\sigma}{dT}(x,\mu)(1-\mu^2)\,d\mu \tag{2.8}$$

We see that when the relation $\sigma = \sigma(T)$ is decreasing, the drop drifts in the direction of increasing temperature of the external liquid. In the special case of a decreasing linear relation $(d\sigma/dT = \text{const} < 0)$, we obtain from (2.8) the well-known result /1-3/

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

Using expression (2.8) we can obtain from Eq.(1.5) the x coordinate of the centre of mass of the drop as a function of time.

When the rate of flow past the drop is given and the internal viscosity becomes infinitely large $(\beta \to \infty)$, the thermocapillary convection within the drop will be suppressed and (2.7) will yield Stokes's formula for the resistance of a solid sphere, while in the case of infinitely large thermal conductivity of the liquid within the drop $(\delta \to \infty)$ (2.7) will yield the Rybchinskii-Hadamard formula for the resistance of the drop, and the decrease in temperature along its surface as well as the Marangoni effect will both vanish. In both limiting cases the rate of drift of the drop will become zero.

The conditions that the Reynolds and Peclet numbers are both small, adopted in this paper, impose an upper limit on the possible values of the quantities S_∞ and $d\sigma/dT$.

Using the quasistationary solution for the velocity field, we shall estimate the characteristic time τ according to (1.2). We obtain

$$\tau \sim (\mu_1+\mu_2)\,(aS_\infty^2\,|\,d^2\sigma/dT^2|)^{-1} \tag{2.9}$$

i.e. the conditions of quasistationarity (1.3) will hold for a sufficiently slow change in the value of the quantity $d\sigma/dT$ with temperature, and sufficiently small drop size and the values of external temperature gradient.

In formulating Problem (1.6)-(1.10), we have omitted the boundary condition for the normal stresses at the boundary of the drop:

$$r=1,\quad -\frac{\mathrm{We}}{\mathrm{Re}}(p_1-\beta p_2) - 2\frac{\mathrm{We}}{\mathrm{Re}}(\partial^2_{r\mu}\psi_1 - \beta\partial^2_{r\mu}\psi_2) = 2h\,\frac{\sigma(\mu)}{\sigma_0}$$
$$\mathrm{We} = \frac{\rho_1 a U_\infty^2}{\sigma_0},\quad \mathrm{Re} = \frac{aU_\infty}{\nu_1} \tag{2.10}$$

Here σ_0 is the zeroth term in the expansion of the function $\sigma(\mu)$ in terms of Legendre polynomials, We, Re is the Weber and Reynolds number, $h = {}^1/_2 Ha$, H is the curvature of the surface of the drop (for a spherical drop we have $H = 2/a$, $h = 1$), p_1 and p_2 are the dimensionless pressures outside and inside the drop referred to $\mu_1 a^{-1}U_\infty$ and $\mu_2 a^{-1}U_\infty$ respectively, and we can obtain for them the following expession /6/:

$$p_1 = \frac{A}{r^2}\mu + \sum_{n=2}^{\infty}\frac{2(2n-1)}{n+1}A_{n+1}r^{-n-1}P_n(\mu) + p_\infty$$
$$p_2 = 10\left(A+\frac{3}{2}\right)r\mu + \sum_{n=2}^{\infty}\frac{2(2n+3)}{n}A_{n+1}r^nP_n(\mu) + \Pi \tag{2.11}$$

Here p_∞ is the dimensionless pressure away from the drop, Π is a constant, the expressions for $A, A_2, A_3, \ldots$ are given in (2.6), and $P_n(\mu)$ is an n-th order Legendre polynomial.

Substituting into (2.10) the already known solutions (2.1) and (2.11) and taking into account (2.5) and (2.6) and relation

$$\sigma(\mu) = \sigma_0 + \frac{3\mu_1 U_\infty}{2+\delta} \sum_{n=1}^{\infty} B_{n+1}\left(n + \frac{1}{2}\right) P_n(\mu)$$

which can be derived from (2.4), we can show that condition (2.10) is not, in general, satisfied. This means that the shape of the drop cannot remain spherical ($h \neq 1$). However, when the condition $(\mathrm{We}/\mathrm{Re})\, B \ll 1$ is satisfied, where $B = \max_{n\geqslant 2} B_n$, holds, the deviation of the shape from the spherical will be small and Eq.(2.10) will have to be regarded as a boundary condition for the normal stresses referred to the spherical surface ($r = 1$), which will reduce, in the principal approximation, to a Laplacian jump in pressure at the drop surface.

We will seek the shape of the surface in the form

$$R(\mu) = 1 + \varepsilon\xi(\mu) + \ldots, \quad \varepsilon = \mathrm{We}/\mathrm{Re} \tag{2.12}$$

$$\xi(\mu) = \sum_{n=2}^{\infty} \alpha_n P_n(\mu) \tag{2.13}$$

The expansion (2.13) begins with the term with number $n = 2$, since the volume of the drop does not change when its surface is deformed and the origin of coordinates is chosen at its centre of mass.

The dimensionless curvature h can also be represented as an expansion

$$h = 1 + \varepsilon h^{(1)} + \ldots \tag{2.14}$$

and by virtue of the relation

$$h^{(1)} = -\xi - \frac{1}{2}\frac{d}{d\mu}\left((1-\mu^2)\frac{d\xi}{d\mu}\right)$$

it will be

$$h^{(1)} = \sum_{n=2}^{\infty} \gamma_n P_n(\mu), \quad \gamma_n = \frac{(n-1)(n+2)}{2}\alpha_n \tag{2.15}$$

After substituting into (2.10) the relations (2.1), (2.11) and (2.14) and taking into account (2.15), we obtain

$$-p_\infty + \beta\Pi + \left(6 + 3A + 6\beta\left(A + \frac{3}{2}\right)\right)P_1(\mu) +$$
$$\sum_{n=2}^{\infty}\left(6A_{n+1}\frac{n + n\beta + \beta}{n(n+1)} - 2\gamma_n\right)P_n(\mu) =$$
$$2\frac{\mathrm{Re}}{\mathrm{We}} + \frac{6}{2+\delta}\sum_{n=1}^{\infty}\left(n + \frac{1}{2}\right)B_{n+1}P_n(\mu)$$

This yields the constant Π, and taking into account the relations (2.6) we obtain

$$A = 0, \quad \gamma_n = \frac{3(\beta - n\beta - n - 2)}{4(2+\delta)(1+\beta)} B_{n+1} \tag{2.16}$$

The first equation of (2.16) reflects the fact that the force acting on the drop is equal to zero. Substituting the second relation of (2.16) into the second relation of (2.15), we obtain

$$\alpha_n = \frac{3(\beta - n\beta - n - 2)}{2(2+\delta)(1+\beta)(n-1)(n+2)} B_{n+1} \tag{2.17}$$

which, together with (2.12) and (2.13), determines the form of the drop surface.

When $\delta \to \infty$, the drop becomes spherical within the approximation used. When $\beta \to \infty$, the drop remains, in general, non-spherical. This is connected with the fact that although the motion of the liquid within the drop may be very slow, the liquid is very viscous and this leads to the appearance of appreciable stresses and pressure drops and non-sphericity of the shape, with the non-uniformity of the temperature along the surface making an additional contribution to it.

In the special case when the surface tension depends linearly on temperature, we find that $\alpha_n = 0$ $(n = 2, 3, \ldots)$, i.e. the drop, as was to be expected in accordance with the results of /2/, retains its spherical shape within the approximation used.

3. *Quadratic dependence of the surface tension on temperature. The equilibrium plane.* We shall consider a quadratic dependence of the surface tension on temperature

$$\sigma = \sigma_0 + \frac{1}{2}\alpha(T - T_0)^2, \quad \alpha = d^2\sigma/dT^2 = \text{const} \tag{3.1}$$

The characteristic time of change of the velocities (2.9) will be

$$\tau \sim (\mu_1 + \mu_2)(|\alpha| aS_\infty^2)^{-1}$$

We obtain the following expression for the first derivative of the surface tension with respect to temperature, by virtue of the relations (1.1) and (2.2):

$$\frac{d\sigma}{dT}(x, \mu) = \alpha\Big(T(x_0) + S_\infty(x - x_0) - T_0 + \frac{3}{2+\delta}aS_\infty\mu\Big) \tag{3.2}$$

Substitution into (2.8) and integration yields the following expression for the drift velocity:

$$U(x) = \frac{2\alpha aS_\infty^2(x_* - x)}{(2+\delta)(2+3\beta)\mu_1}, \quad x_* = x_0 + \frac{T_0 - T(x_0)}{S_\infty} \tag{3.3}$$

When $x = x_*$, the drift velocity becomes zero, hence we can call the plane $x = x_*$ the equilibrium plane (EP). Indeed, if the centre of the drop at rest lies in this plane, the force exerted on the drop is equal to zero and the drop remains at rest. This state may be found to be unstable.

Qualitative considerations show that when relation (3.1) has a minimum, i.e. when $\alpha > 0$, the EP will represent a plane of attraction and the equilibrium will be stable (the drift velocity outside the EP will always be directed towards the plane). When $\alpha < 0$, the EP will represent a plane of repulsion and the equilibrium will be unstable (the drift velocity will be directed away from the plane).

In order to estimate the time at which the drop reaches the EP (when $\alpha > 0$), we use the relation (1.5) where $U_\infty = -U$, and formula (3.3). We obtain

$$x(t) = x_* + (x(t_0) - x_*)\exp\left[-\frac{2\alpha aS_\infty^2}{(2+\delta)(2+3\beta)\mu_1}(t - t_0)\right]$$

i.e., as we expected, when starting from an arbitrary initial position, the drop will reach the EP after an infinitely long time.

We can transfer the concept of the EP to the case of an arbitrary dependence of the surface tension on temperature. We can also have a single (for the quadratic relation (3.1)), or several EP's, or, as in the case of a linear dependence, there may be no EP's. If the surface tension is independent of the temperature, any plane can serve as the EP.

We can assert that if the first non-zero quantity

$$D_n = \int_{-1}^{1} \frac{d^n\sigma}{dT^n}(x_*, \mu)(1 - \mu^2)\,d\mu, \quad n = 2, 3\ldots$$

has an even number and is positive, then the EP is stable (the drift velocity in a sufficiently small neighbourhood is directed, on both sides of the EP, towards the plane). Otherwise the EP is unstable (the drift velocity in a sufficiently small neighbourhood is directed, on one or both sides of the EP, away from the plane). If the surface tension is independent of the temperature, then $D_n = 0$ $(n = 2, 3\ldots)$ and the EP will be neutrally stable.

In the case of the quadratic dependence (3.1) the EP coincides with the plane of extremal value of the surface tension. When the dependence of the surface tension is arbitrary, the situation is, in general, different. Moreover, the position of the EP, and even its existence, may depend on the size of the drop.

We shall determine, as an example, the velocity of drift of an air bubble in an aqueous solution of n-heptanol. It was shown experimentally in /5/ that at sufficiently large concentrations the surface tension at the solution-air interface depends non-monotonically on temperature, and this dependence can be described in an approximate manner by the quadratic relation (3.1).

Thus for a concentration of $7.6\cdot10^{-3}\,M$ we obtain the relation (3.1) where $\alpha \cong 6.6\cdot10^{-6}$ N/(m · deg²), $T_0 = 39°$ C and an air bubble of radius $a = 10^{-4}$ m will move, in an external temperature field whose gradient is $S_\infty = 50$ deg/m, as follows from (3.3), with a velocity U [m/sec] $\cong 1.3\cdot10^{-3}\,y$ [m]. Here y is the distance between the centre of the drop and the plane at rest. Since the solution was very dilute, its viscosity, within the temperature range in question, was assumed to be equal to the mean viscosity of water ($\mu_1 \cong 0.65\cdot10^{-3}$ kg/m · sec). It was also taken into account that in the case of a bubble $\beta = 0$, $\delta = 0$. At a distance of 0.1m from the EP the bubble will move with a velocity of $1.3\cdot10^{-4}$ m/sec=7.8 mm/min and at a distance of 0.01 m, the velocity will be $1.3\cdot10^{-5}$ m/sec=0.78 mm/min.

It can be confirmed that the conditions of quasistationarity (1.3) and the assumption that the Reynolds and Peclet numbers are both small, also hold. Indeed, for the numerical values quoted above we have (the drift velocity is taken at a distance of 0.1 m from the EP)

$$\mathrm{Re}_1 = \frac{Ua}{\nu_1} \sim 2\cdot10^{-2}, \qquad \mathrm{Pe}_1 = \frac{Ua}{\chi_1} \sim 10^{-1}$$

$$\tau \sim 400\ \mathrm{c}; \qquad \frac{a^2}{\nu_1\tau} \leqslant 10^{-4}, \qquad \mathrm{Pe}_1\frac{a^2}{\chi_1\tau} \leqslant 10^{-4}$$

4. Velocity field and the distortion of the spherical form of the drop at the EP.

We shall consider the flow arising outside and inside the drop when its centre of mass lies in the EP, in the case of a quadratic relation containing a minimum ($\alpha > 0$). Expression (3.2) for the rate of change of surface tension with temperature at the drop surface will now take the form

$$\frac{d\sigma}{dT} = \alpha a S_\infty \frac{3}{2+\delta}\mu$$

and, taking into account (2.1), (2.5) and (2.6), we can write the expressions for the dimensionless stream function as follows:

$$\psi_{*1} = (1 - 1/r^2)(1-\mu^2)\mu, \quad \psi_{*2} = (r^5 - r^3)(1-\mu^2)\mu \tag{4.1}$$

Here the value of the maximum velocity at the drop surface is chosen as the scale of velocity

$$U^\circ = \frac{9\alpha(aS_\infty)^2}{10\mu_1(2+\delta)^2(1+\beta)} \tag{4.2}$$

(the velocity given above is attained at $\theta = \pi/4,\ 3\pi/4$, i.e. at the points of the drop surface equidistant from the EP and the normal to it passing through the centre of mass of the drop).

For example, in the case of an air bubble of radius $a = 10^{-3}$ m in an aqueous solution of n-heptanol of concentration $7.6\cdot10^{-3}\,M$, situated at the EP, with an external temperature gradient $S_\infty = 100$ deg/m, the maximum velocity of flow at the surface will be $U^\circ \cong 2.2\cdot10^{-5}$ m/sec= 1.3 mm/min.

We note that the flow outside and inside the drop situated at the EP will be stationary, whether conditions (1.3) hold or not.

The pattern of the stream lines is shown in the figure, with the arrows indicating the direction of the flow. The velocity field has the following structure. Inside the drop we have two vortex filaments in the form of circles ($r = \sqrt{3/5}$, $\mu = 1/\sqrt{3}$ and $r = \sqrt{3/5}$, $\mu = -1/\sqrt{3}$) of radius $\sqrt{2/5}$, parallel to the EP and symmetrical about the centre of mass of the drop, at a distance of $2/\sqrt{5}$ from each other. Outside the drop and at large distances from its centre of mass, the liquid will flow along the rays $\mu = \mathrm{const}$. When $-1/\sqrt{3} < \mu < 1/\sqrt{3}$, it will flow towards the drop, while when $-1 \leqslant \mu < -1/\sqrt{3}$ and $1/\sqrt{3} < \mu \leqslant 1$, it will flow away from it. The rays $\mu = \pm1/\sqrt{3}$ are characterized by the fact that the radial velocity components vanish, and the maximum approach of every outer stream line to the centre of the drop occurs at the point where it intersects one of the above rays.

The case when relation (3.1) has a maximum ($\alpha < 0$), is treated in the same manner. The pattern of stream lines will be identical, but the direction of the flow will be reversed.

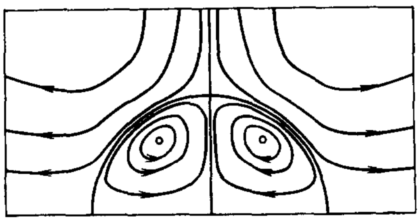
When the drop lies in the plane of stable equilibrium and relation (3.1) ($\alpha > 0$) holds, its form will be given, taking relations (2.12), (2.13), (2.17), (2.5) and (3.2) into account, by the expression

$$R(\mu) = 1 - \frac{3\alpha (aS_\infty)^2 (\beta + 4)}{20(2+\delta)^2 (\beta+1)\sigma_0} P_2(\mu) \tag{4.3}$$

The result obtained shows that the surface of the drop represents, apart from terms of the order of $o(\varepsilon)$, an ellipsoid of revolution flattened (oblate) along the direction of the outer temperature gradient, and the ratio of the lengths of its principal semi-axes is given by the relation

$$\frac{b}{c} = 1 + \frac{9\alpha (aS_\infty)^2 (\beta + 4)}{40(2+\delta)^2 (\beta+1)\sigma_0} \tag{4.4}$$

Here c is the length of the semi-axis directed along the outer temperature gradient, and b is the length of the other semi-axis.



The results (4.3) and (4.4) also hold in the case when relation (3.1) has a maximum ($\alpha < 0$). The ellipsoid of revolution will in this case be extended (prolate) along the direction of the outer temperature gradient.

We see from (4.3) and (4.4) that the degree of deviation of the surface from spherical increases as the size of the drop and the value of the outer temperature gradient increase.

For the case with numerical values given above $b/c = 1 + 4 \cdot 10^{-7}$, i.e. the deviation of the form of the bubble from spherical is infinitesimal.

In conclusion we note that an analogous analysis can be carried out when there was a gravity field parallel to the outer temperature gradient, provided that the convection due to gravity is insignificant. The velocity of motion will be found from the condition that the total force acting on the drop and equal to the sum of the force (2.7) and the mass force, is zero. When the dependence of the surface tension on temperature is non-linear, we can also have an EP (when the dependence is linear, we either have no EP, or any plane can serve as an EP). A qualitative analysis of their stability can be carried out in a manner completely analogous to that without gravity. It can also be shown that within the approximation used here the presence of the gravity force does not affect the form of the surface, since, as can be seen from (2.12), (2.13), (2.17) and (2.5), it does not depend on the velocity of motion of the drop.

REFERENCES

1. YOUNG N.O., GOLDSTEIN J.S. and BLOCK M.G., The motion of bubbles in a vertical temperature gradient, J. Fluid Mech., 6, Pt. 3, 1959.
2. BRATUKHIN YU.K., Thermocapillary drift of a drop of viscous liquid. Izv. Akad. Nauk SSSR, MZhG, 5, 1975.
3. YALAMOV YU.I. and SANASARYAN A.S., Motion of drops in a viscous liquid inhomogeneous with respect to temperature. Inzh.-Fiz. Zh. 28, 6, 1975.
4. VOCHTEN R., PETRE G. and DEFAY R., Study of the heat of Reversible adsorption at the air-solution interface. I: Thermodynamical calculation of the heat of reversible adsorption of non-ionic surfactants, J. Colloid Interface Sci, 42, 2, 1973.
5. VOCHTEN R. and PETRE G., Study of the heat of reversible adsorption at the air-solution interface, II: Experimental Determination of the heat of reversible adsorption of some alcohols, J. Colloid Interface Sci. 42, 2, 1973.
6. HANNEL G. and BRENNER H., Hydrodynamics at Low Reynolds Numbers. Mir, Moscow, 1976.

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