On the thermocapillary motion of deformable droplets

V. Berejnov

Department of Chemical Engineering, Technion, Haifa 32000, Israel

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Abstract

In studies on Marangoni type motion of particles the surface tension is often approximated as a linear function of temperature. For deformable particles in a linear external temperature gradient far from the reference point this approximation yields a negative surface tension which is physically unrealistic. It is shown that H. Zhou and R. H. Davis (J. Colloid Interface Sci., 181, 60, (1996)) presented calculation where the leading deformable drop moved into a region of negative surface tension. With respect numerical studies the restriction of the migration of two deformable drops is given in terms of the drift time.

The bulk fluid motion induced by an interface has been studied for over a century. One of the most interesting phenomena is the capillary motion of particles through a viscous fluid. Young, Goldstein and Block (1) and later Bratukhin (2) performed the first systematic study of the migration of bubbles and droplets. As noted in review (3) the capillary motion arises due to gradient of the surface tension $\gamma$ at the interface as a result of a non–uniform temperature or surfactant distribution in the surrounding media. The surface tension gradient results in a tangential stress on the interface which causes
the motion of the surrounding liquid by viscous traction. Then, the droplet or bubble will move in the direction of decreasing interfacial tension. It is necessary to note that the normal component of the capillary forces arising during the motion may deform the shape of a particle (2). Young, Goldstein and Block (1) and others have shown that in the limit of high surface tension (undeformed spherical particle) its motion is controlled by surface tension gradients only. Note that the motion of a deformable particle also depends on the surface tension itself.

If the particle moves with constant velocity the transformation of a laboratory coordinate system to a coordinate system moving with the particle frame will essentially simplify the solution (2), (3), (5). Let us denote the particle coordinate system moving with the droplet velocity \( U \) by \( \mathcal{O} \) and the laboratory coordinate system by \( \mathcal{O} \) respectively. We consider the coordinate transform from \( \mathcal{O} \) to \( \mathcal{O}' \) in the case of a drop moving in the uniform external temperature gradient \( A e_x \) (2), see Fig.1. For an arbitrary point \( F \) we obtain,

\[
R = R' + Ut, \quad V_i(R, t) = V'_i(R') + U, \quad T_i(R, t) = T'_i(R') + AUt, \tag{1}
\]

where \( i = 1, 2 \) correspond to the inner and outer liquid phase, respectively, \( V \) is the fluid velocity, \( T' \) denotes the difference between the temperature \( T \) in \( \mathcal{O} \) and a undisturbed temperature \( AUt \) at the center of \( \mathcal{O}' \), \( R \) is a radius vector which points from \( \mathcal{O} \) to \( F \) and \( t \) is the time.

In the limit of an infinitely large surface tension the normal stress boundary condition is not modified under the above transformation \( [8] \). However, in the case of finite surface tension, this boundary condition requires special attention. Usually, \( \gamma \) is assumed to be linearly dependent on temperature or on concentration is linearized \( [8] \),

\[
\gamma(R, T) = \gamma_0(T_0) + \frac{\partial \gamma}{\partial T} \bigg|_{T = T_0} (T(R) - T_0), \tag{2}
\]

where \( \partial \gamma / \partial T \) is a constant and \( T_0 \) and \( \gamma_0 \) correspond to the reference values of temperature and surface tension, respectively. Note that for many cases \( \partial \gamma / \partial T < 0 \). Due to
the transformation of $T$ the surface tension $\gamma(R, T)$ is also transformed in the moving coordinate system,

$$
\gamma^\prime(R^\prime, T^\prime) = \gamma_0(T_0) - \frac{\partial \gamma}{\partial T} A U t + \frac{\partial \gamma}{\partial T} (T^\prime(R^\prime) - T_0).
$$

[3]

The surface tension $\gamma^\prime$ is time dependent now. Recall that the surface tension must be positive [3],

$$
\gamma \geq 0, \quad \gamma^\prime \geq 0.
$$

[4]

From [3] and [4] follows an upper bound of the drift distance $Ut$ in system $O$ or an upper bound of the time of particle migration in the moving system $O'$.

Ignoring the above restrictions results in the appearance of a negative surface tension in the course of the particle migration in finite time and thus may lead to a physically unrealistic behavior of the particle. This restriction is relaxed in the case of the undeformed drop [4], [3] and [3] where the normal stress boundary condition is always satisfied. However, this is not true when the surface tension has a finite value. We noted that in the literature on thermocapillary migration of drops and bubbles no attention was paid to this point. For example, Zhou and Davis [7] first considered the problem of axisymmetric thermocapillary migration of two deformable viscous drops. The authors assumed a linear dependence of surface tension on temperature. In terms of [7] we have

$$
\gamma(x_s) = \gamma_0 + \frac{\partial \gamma}{\partial T} (T(x_s) - T_0(x_r)),
$$

[5]

where $T(x_s)$ is the temperature at a point $x_s$ on the interface and $T_0(x_r)$ is a reference temperature. In an attempt to obtain a solution which is independent of the choice of $x_r$, Zhou and Davis fix $x_r$ to be the intersection point of the axis of symmetry with the surface of the leading drop, see Fig.1 and their Fig.1 in [7]. It is important to note that this choice of $x_r$ means a coordinate transform from the laboratory frame to the coordinate system moving with the leading droplet. Hence, the normal stress balance is modified. The other boundary conditions and the governing equations remain the same due to the linearity of Stokes and Laplace equations [4]. For more details see [2] and [4].
Zhou and Davis (7) give for the dimensionless surface tension in the moving coordinate system

\[ \tilde{\gamma}(x_s) = 1 - q \tilde{T}(x_s), \]  

where \( \tilde{\gamma} = \gamma/\gamma_0 \) is the dimensionless surface tension, \( q = aA(-\partial\gamma/\partial T) \) is the dimensionless rate of change of the interfacial tension due to temperature variation, \( \tilde{T}(x_s) = (T(x_s) - T_0(x_r))/(aA) \) is the dimensionless temperature difference and \( a \) is the radius of the first drop. It can readily be seen that Eq. [6] defines surface tension which is positive for any time or migration distances. As we showed before, the correct transformation of the linear approximation [5] leads to a negative surface tension in finite time. The previous conclusion that physically acceptable solutions must be restricted by migration time contradicts Eq. [6].

Let us derive the correct form of the transformed surface tension in terms of (7). The problem of the migration of two droplets is evolutionary and it must be accomplished by a kinematic condition applied on the droplets’ surfaces. The transformation from the laboratory coordinate system to the particle coordinate system are given by (5):

\[
\begin{align*}
\mathbf{R} & = \mathbf{R}' + \int_{t_1}^{t_2} \mathbf{U}(t) \, dt, \quad \mathbf{V}(\mathbf{R}, t) = \mathbf{V}'(\mathbf{R}') + \mathbf{U}(t), \\
T_i(\mathbf{R}, t) & = T_i'(\mathbf{R}') + A \int_{t_1}^{t_2} \mathbf{U}(t) \, dt.
\end{align*}
\]

[7] [8]

The migration velocity of the droplet now depends on time and therefore the migration distance \( Ut \) on the right hand side of [3] is given as an integral term,

\[ \gamma'(\mathbf{R}', T') = \gamma_0(T_0) - \frac{\partial\gamma}{\partial T} A \int_{t_1}^{t_2} \mathbf{U}(t) \, dt + \frac{\partial\gamma}{\partial T} \left( T'(\mathbf{R}') - T_0 \right). \]

[9]

In terms of [7] we have for the dimensionless surface tension

\[ \tilde{\gamma}(x_s) = 1 + \frac{q}{a} \int \mathbf{U}(t) \, dt - q \tilde{T}(x_s). \]

[10]

The integral term in Eq. [10] changes the scenario of a numerical calculation. The surface tension changes with time and it is necessary to keep \( \tilde{\gamma} \) positive.
We shall now proceed to estimate the time when the surface tension of some point $x_r$ on the leading drop will not satisfy [1]. For simplicity let us stay in the laboratory coordinate system, for $\bar{\gamma} = 0$ we obtain the relation
\[
q \bar{T}(x_s) = 1,
\]
where $\bar{T}(x_s) = (T(x_s) - T_0(x_0))/(aA)$ and $x_0$ is a reference point in system $O$. It is readily seen that the dimensionless length of a spatial frame is given by $X = \frac{1}{\bar{\gamma}}$. Then the maximum transformation distance of the leading drop is the difference between $X$ and the initial position $x_r$. For the case of equal material parameters considered by [7] we have $a = 1$ and the surface separation distance on the axes is $\sim 1$. Hence the length of the drops’ drift is also $\sim 1$. Let us assume that the lower bound of the velocities for moving deformable drops is the velocity of non–deformable drops. For slightly unequal drops and a large separation distance between their centers the velocities are nearly the same and equal to the Young–Bratukhin value of 0.133. Following Eq. [12] in [7] we normalize this value with $2/15$ because for inner and outer liquids the viscosity and the thermal diffusivity are equal. From this normalization procedure we obtain that the migration velocities are $\sim 1$. As a result the critical value of the migration time is $\sim 1$.

We developed a numerical code for solving the problem of the motion of two deformable viscous drops in an external temperature gradient [9]. Restrictions [4] were considered in the laboratory coordinate system $O$. In Fig.2 we plotted the evolution of the minimum separation distance $d$ between the droplets’ surfaces in time. We chose $a = 1$, $\alpha = 0.5$, $q = 0.2$ in terms of [7], where $\alpha$ is the droplets radii ratio. The dotted curve confines the physical region where [4] is satisfied. The curves $1 - 10$ correspond to different initial separations. Curve 2 is in agreement with the results given by Zhou and Davis (see Fig.4 in [7]) and with the asymptotics for the non–deformable drops [5].

Our computations show that the patterns of drops deformations are similar to those described by [7] but correspond to smaller separation distances $d$. Note that our analysis

\footnote{On physical grounds this limit corresponds to phase transition.}
is restricted by \( [4] \) while the results of \( [7] \) lie in the physically unrealistic region. For initially spherical drops and an initial separation distance \( d = 0.01 \) Fig.3 depicts the series of drops’ profiles corresponding to the points \( a, b \) and \( c \) in Fig.2.

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Figure 1: Geometric sketch of a drop immersed in an external temperature gradient $\nabla T$ parallel to its axis of symmetry.
Figure 2: Evolution of the separation distances for two deformable viscous drops under a linear external temperature gradient as a function of the initial separation (9). The values of the parameters are the same as in (7): $a = 1$, $\alpha = 0.5$, $q = 0.2$. 
Figure 3: Deformation patterns for the initial separation 0.01 and $a = 1$, $\alpha = 0.5$, $q = 0.2$. Figures $a, b, c$ correspond to the respective points on curve 10 of the Fig.2.