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Drop motion with surfactant transfer in an inhomogeneous medium

ALEXEI YE. REDNIKOV,† YURI S. RYAZANTSEV† and MANUEL G. VELÁRDE‡

†E.T.S.I. Aeronauticos, Universidad Politecnica de Madrid, Ciudad Universitaria, Madrid 28 040, Spain and Instituto Pluridisciplinar, Universidad Complutense, Paseo Juan XXIII, No 1, Madrid 28 040, Spain, ‡Instituto Pluridisciplinar, Universidad Complutense, Paseo Juan XXIII, No 1, Madrid 28 040, Spain

Abstract—In the limit of low Reynolds and Peclet numbers the motion of a drop in a solution of surfactant consumed on its surface in a chemical reaction is considered when, far off the drop in the outer fluid, there is a surfactant concentration and/or temperature gradient. It is shown that the chemical reaction can induce changes in the direction of the drop motion under the external concentration and/or temperature gradient. It can also induce multiple steady states of motion. For instance, for a given set of material and flow parameters and given external gradients and buoyancy, up to *three* regimes of drop motion may be available. Also a single value of the external gradient may stop the drop motion even for multiple (up to *three*) levels of buoyancy.

1. INTRODUCTION

DUE TO capillary forces, temperature or concentration gradients created in a fluid can drastically influence the motion of a drop or a bubble. Although this effect can play an important role in many ground-based phenomena, its role is expected to be much more dramatic in processes under low/microgravity conditions as in orbital stations, where it can entirely determine the motion [1].

One of the first studies dealing with this problem dates back to Young *et al.* [2] who, theoretically and experimentally, analyzed slow stationary motion of bubbles and drops, when a constant temperature gradient was applied far off the particle. They showed that the external temperature gradient may dynamically balance buoyancy in such a way that the bubble or the drop remains motionless i.e. levitating. The analogous problem of the drop motion in a fluid with the gradient of surfactant concentration far off the drop was analyzed independently by Levich and Kuznetsov [3]. Many analytical (generally in the asymptotic limit of low Reynolds and Peclet numbers), numerical and experimental (both for ground and space conditions) investigations followed [1].

In a previous paper [4] the present authors have considered the stationary drop motion in a homogeneous surfactant solution (with constant temperature and concentration far off the drop). A number of specific effects were shown to be a consequence of a surface chemical reaction creating a radial concentration profile: (i) if there is buoyancy, whatever its value, the chemical reaction could by itself induce a change in the direction of drop motion; (ii) possible multiple steady states were identified, e.g. up to *three* velocities of the stationary drop motion for a given buoyancy could exist or a drop motion with a given value of the velocity could exist for up to *three* values of buoyancy; and (iii) instability of the motion may arise. For this reason the drop with chemical reaction is considered as an 'active' drop.

In the present paper we take up the same problem with, however, an inhomogenous medium, i.e. we consider here the effect of temperature and/or surfactant concentration gradients. Some results about the effect of an externally imposed temperature inhomogenity on *active* drops are available in the literature. For instance, ref. [5] refers to the case of a drop with uniform internal heat generation affected by a temperature gradient created far off in the continuous phase, and ref. [6] incorporates a slightly nonuniform heat generation, modelling radiation absorption. As one can anticipate, an obvious effect of the inhomogenity is just a shift of the curve $F_{hd}(U)$ found in ref. [4] (see Figs. 4 and 6) along one or the other axes, F_{hd} or U. Further, more complex effects are also possible as we shall show here in this paper.

In Section 2 we pose the problem and discuss the basic assumptions and their physical relevance. In Section 3 the equations and boundary conditions to be solved are provided. The solution is found in Section 4 and its consequences are discussed in Section 5. Section 6 deals with weakly nonlinear analyses around instability thresholds to translational motions. Finally, Section 7 provides conclusions and a summary of results.

2. STATEMENT OF THE PROBLEM

The stationary motion of a drop in an inhomogeneous surfactant solution is considered. As in ref.

NOMENCLATURE

A_n, A_n, B_n ($n = 0, 1, \ldots$) expansion coefficients, equations (2) and (3)
A'_n, B'_n ($n = 0, 1, \ldots$) expansion coefficients, equations (5) and (6)
a drop radius
a_n, a'_1, b_n, b'_0, b'_1 ($n = 0, 1, \ldots$) expansion coefficients, equations (46) and (47)
$\mathbf{b}$ $(8\text{-}\kappa)mq(\rho_2-\rho_1)a^3\mathbf{g}/(6\eta_1 D)$
C concentration field
C_∞ concentration far off the drop
c dimensionless concentration field, $C/C_\infty(0)$; $c_0+Pe\,c_1$ in the *inner* region, $c^{(0)}+Pe\,c^{(1)}$ in the *outer* region
Ca capillary number, $\eta_1 V/\sigma_0$
D bulk diffusion coefficient
D_s surface diffusion coefficient
$\mathrm{d}S$ drop surface element
$\mathbf{e}_r$ radial unit vector
$\mathbf{F}_c$ capillary force
$\mathbf{f}$ dimensionless force due to buoyancy and external temperature gradient
$\mathbf{f}'$ perturbation of $\mathbf{f}$
f_x, f_y, f_z components of vector $\mathbf{f}$ in Cartesian coordinates
$f_n(r)$, $f'_1(r)$ ($n = 0, 1, \ldots$) auxiliary functions, equation (46)
$\mathbf{g}$ gravity acceleration
h dimensionless correction to the dimensionless half mean curvature unity of the spherical surface
K $3m[2\kappa+q(4-\kappa)]/2$
$K_{n+1/2}$ ($n = 0, 1, \ldots$) modified Bessel function of third kind and order $n+1/2$
k chemical reaction rate
Ma Marangoni number, $(\mathrm{d}\sigma/\mathrm{d}\Gamma)C_\infty(0)a/(\eta_1 V)$
m modified Marangoni number, $-MaPe/[12(\alpha+\kappa)(2\delta+2\alpha+\kappa)]$
m_n, m_*, m_{**} ($n = 1, 2, \ldots$) critical values of m
P coefficient, equation (77)
Pe Peclet number, aV/D
P_i dimensionless pressure field ($i = 1, 2$; see below)
q $\kappa/(\alpha+\kappa)$
$\mathbf{r}$ radius-vector
r, θ, φ spherical coordinates
S_1 sphere of radius 1
S_a sphere of radius a
Sc Schmidt number, $\eta_1/(\rho_1 D)$
T_i temperature field ($i = 1, 2$; see below)
T_∞ temperature far off the drop
$\mathbf{U}$ drop velocity
$\mathbf{U}_\infty$ velocity far off the drop, $-\mathbf{U}$
U_{aut} autonomous motion velocity
u_{aut} dimensionless autonomous motion velocity
$\mathbf{U}$ $a\mathbf{U}_\infty/D$
$\mathbf{U}'$ perturbation of $\mathbf{u}$
$\mathbf{u}_\infty$ $\mathbf{U}_\infty/V$
$u_{ir}, u_{i\theta}, u_{i\varphi}$ dimensionless velocity field ($i = 1, 2$; see below)
u_x, u_y, u_z components of vector $\mathbf{u}$ in the Cartesian coordinates
V characteristic velocity scale
x, y, z Cartesian coordinate system.

Greek symbols

$\bar{\alpha}$ equilibrium constant between surface and bulk concentrations
α dimensionless equilibrium constant, $\bar{\alpha}a$
β η_2/η_1
Γ surfactant concentration on the drop surface
γ dimensionless surfactant concentration, $\Gamma/(aC_\infty(0))$, $\gamma_0+Pe\,\gamma_1$
δ D_s/D
$\varepsilon(\theta, v)$ departure of the drop shape from sphericity
$\Phi_n(\theta,\varphi)$, $\Theta_n(\theta,\varphi)$, $\Xi_n(\theta,\varphi)$ ($n = 0, 1, \ldots$) spherical functions of order n
κ ka^2/D
λ λ_2/λ_1
λ_i thermal conductivity ($i = 1, 2$; see below)
$\boldsymbol{\eta}$ $\rho_1 a^2\mathbf{g}/(\eta_1 V)$
η_i dynamic viscosity ($i = 1, 2$; see below)
ξ $\sigma/(\eta_1 V)$
$\xi_n(\theta,\varphi)$ spherical functions in the series $\xi(\theta,\varphi) = \Sigma_{n=1}^{\infty}\xi_n(\theta,\varphi)$
ρ ρ_2/ρ_1
ρ_i density ($i = 1, 2$; see below)
σ surface tension
σ_0 surface tension for $\gamma = \gamma_0$.

Subscripts

i 1, continuous phase; 2, drop phase
∞ value at large distance from the drop
s surface.

[4] it is assumed that the fluids are Newtonian, incompressible and immiscible. The outer fluid is infinitely extended and at rest far away from the drop. The surfactant is soluble only in the outer fluid and is consumed on the drop surface in a first order isothermal chemical reaction; the other species, if any, play no active role. The concentrations at the surface and in the adjacent bulk are in equilibrium and proportional to each other. Inertial and viscous effects in the surfactant film and Stefan flow are negligible. All the material parameters of the system do not depend on temperature or concentration except for the sur-

face tension which is assumed to vary linearly with concentration and temperature thus leading to Marangoni stresses [7]. The drop shape is assumed to be almost spherical. Reynolds and Peclet numbers are low. In the general case, buoyancy may exist.

When no drop is present, let $C_\infty(\mathbf{r})$ and $T_\infty(\mathbf{r})$ (both satisfying the Laplace equation) be the surfactant concentration and temperature profiles, respectively; $\mathbf{r}$ is the radius-vector. Then for the approximation of low Reynolds and Peclet numbers to be valid, the gradients defined by $C_\infty(\mathbf{r})$ and $T_\infty(\mathbf{r})$ must be small enough.

In the leading approximation in low Peclet number, the concentration field C around the drop satisfies the Laplace equation. We have

$$C_\infty(r,\theta,\varphi) = \sum_{n=0}^{\infty} r^n \Phi_n, \tag{1}$$

$$C(r,\theta,\varphi) = \sum_{n=0}^{\infty} \Phi_n (r^n + B_n/r^{n+1}), \tag{2}$$

where the spherical coordinate system (r, θ, φ) has the origin in the center of the drop. The radial coordinate r is measured in drop radius units, a. The values Φ_n (θ, φ) are spherical functions of first kind, of order n and of the general form. Note that here all Φ_n have the dimension of concentration. The terms with negative powers of r are absent in equation (1) since $C_\infty(r, \theta, \varphi)$ cannot be singular in the center. In equation (2) it has been already taken into account that the surfactant concentration approaches $C_\infty(r, \theta, \varphi)$ at $r \to \infty$; B_n $(n = 0, 1\ldots)$ are some constants to be determined using the boundary conditions (b.c.) at the surface.

The concentration in the surfactant film Γ can be represented as

$$\Gamma(\theta,\varphi) = a \sum_{n=0}^{\infty} A_n \Phi_n|_{r=1}, \tag{3}$$

where the drop radius a has been used to make dimensionless the unknown constants A_n $(n = 0, 1\ldots)$. The spherical functions in equation (3) are the same as in (1) and (2) since b.c.

$$r = 1, \quad C = \tilde{\alpha}\Gamma, \quad \frac{D_s}{a^2}\Delta_s\Gamma + \frac{D}{a}\frac{\partial C}{\partial r} = k\Gamma,$$

$$\Delta_s = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\varphi},$$

must be satisfied. Here $\tilde{\alpha}$ is the equilibrium constant, D and D_s are the bulk and surface diffusion coefficients, k is the chemical reaction rate, Δ_s is the surface Laplace operator. With the exception of the coordinates, all quantities have dimensions. The first condition links the concentration at the surface to that in the adjacent bulk. The second condition represents the mass balance: the left hand side (l.h.s.) is due to the diffusional flux while the right hand side (r.h.s.) comes from the chemical reaction.

Using equations (1)–(3) in the b.c. yields:

$$A_n = \frac{2n+1}{n(n+1)\delta + (n+1)\alpha + \kappa},$$

$$B_n = \frac{\alpha n - n(n+1)\delta - \kappa}{n(n+1)\delta + (n+1)\alpha + \kappa}, \tag{4}$$

with

$$\alpha = \tilde{\alpha}a, \quad \delta = D_s/D, \quad \kappa = k a^2/D.$$

Thus, the concentration field is defined by equations (2)–(4). For the temperature field we similarly obtain

$$T_\infty(r,\theta,\varphi) = \sum_{n=0}^{\infty} r^n \Phi'_n, \tag{5}$$

$$T_1(r,\theta,\varphi) = \sum_{n=0}^{\infty} \Phi_n (r^n + B'_n/r^{n+1}),$$

$$T_2(r,\theta,\varphi) = \sum_{n=0}^{\infty} A'_n r^n \Phi'_n, \tag{6}$$

where according to b.c.

$$r = 1, \quad T_1 = T_2, \quad \partial T_1/\partial r = \lambda\,\partial T_2/\partial r, \quad \lambda = \lambda_2/\lambda_1,$$

one has

$$A'_n = \frac{2n+1}{\lambda n + n + 1}, \quad B'_n = \frac{n(1-\lambda)}{\lambda n + n + 1}, \tag{7}$$

where subscripts $i = 1, 2$ correspond to the values *outside* and *inside* the drop, respectively. Symbol T_i $(i = 1, 2)$ denotes the temperature field and λ_i $(i = 1, 2)$ is the heat conductivity.

The surface tension σ is assumed to be a linear function of temperature and concentration. Thus, on the surface the surface tension gradient is

$$\nabla_s\sigma(\theta,\varphi) = \frac{d\sigma}{d\Gamma}\nabla_s\Gamma(\theta,\varphi) + \frac{d\sigma}{dT}\nabla_s T_1(r = 1, \theta, \varphi),$$

$$\frac{d\sigma}{d\Gamma} = \text{const.} \quad \frac{d\sigma}{dT} = \text{const.} \tag{8}$$

where ∇_s is the surface gradient operator.

Now to obtain the velocity field we can proceed as follows. As the gradients of temperature and/or surfactant concentration in the medium finally produce $\nabla_s\sigma$ on the drop surface, we take this quantity in the b.c. and solve the hydrodynamic problem for a drop in a *nominally* homogeneous medium. This leads to a hydrodynamic force expressed in terms of $\nabla_s\sigma$. Then in the obtained expressions we simply replace $\nabla_s\sigma$ by the relation giving it as a function of the original gradients in the *actually* inhomogeneous medium. Such an approach has been used before by Subramanian [8].

We naturally assume that the variation of the concentration field $C_\infty(r, \theta, \varphi)$ around the drop, on the length scale of the drop radius, is negligible with respect to the absolute value of the concentration. This means that the spherically symmetric component of the concentration field (2) which corresponds to the mode $n = 0$, changes faster than the remaining nonsymmetrical component $(n = 1, 2\ldots)$ on the length scale of the drop radius. Further, note that just due to the symmetry the symmetrical component does not contribute to the surface tension gradient (8), and its contribution only appears as a result of a convective disturbance.

To adequately describe the influence of the large symmetrical component in the general case a first order approximation in low Peclet number is needed. Note that here we are interested only in the leading order approximation results, while derivation of the first order approximation for the nonsymmetrical component of the concentration field will give only small corrections to the result for the surface tension gradient (8). However, for the symmetrical component this will give just the leading approximation result.

Taking into account all the above given details our problem is that of a drop moving in a homogeneous solution of a reacting surfactant, when on its surface some surface tension gradient $\nabla_s\sigma(\theta,\varphi)$ has been induced. For the constant concentration far off the drop we shall use $C_\infty(0)$, i.e. the concentration in the outer fluid if there is no drop there, in the place where the drop center is located. Finally we shall recall that the gradient $\nabla_s\sigma(\theta,\varphi)$ is due to the inhomogeneous concentration and/or temperature distributions far off the drop and employ the expression (8).

In the general case $C_\infty(0)$ changes as the drop moves. But as one can show, this change proceeds so slowly that a stationary (quasistationary) approach suffices for our study here.

The availability of a large spherically symmetrical component in the concentration field, which is due to the chemical reaction, is the essential difference between our work and that of others (for example, Subramanian's [8]). Just owing to the symmetrical component qualitatively new effects may appear. The same may be said of the situations studied in refs. [5, 6], where a large spherically symmetrical component of the temperature field exists.

3. MATHEMATICAL FORMULATION

Our first aim is to describe the stationary motion of a spherical drop in the homogeneous solution of a reacting surfactant under buoyancy and in the presence of a surface tension gradient $\nabla_s\sigma(\theta,\varphi)$ on its surface. We shall derive a relationship between $\mathbf{U}_\infty$, $\mathbf{g}$, $\nabla_s\sigma(\theta,\varphi)$ and the material parameters of the fluids. Here $\mathbf{U}_\infty$ is the velocity of the flow far off the drop in the frame of reference travelling with the drop center and $\mathbf{g}$ is the acceleration of gravity.

Clearly, it is enough to consider the leading term of the velocity field series in Reynolds number and two terms of the concentration field series in Peclet number, since the zero order term is spherically symmetrical and the major effect appears only in the first order term.

Let V be a characteristic velocity scale of the problem. Choose the other scales: a—for length, $\eta_1 V/a$—for pressure, $C_\infty(0)$—for bulk concentration and $C_\infty(0)a$—for surface concentration. Then the dimensionless equations and b.c. for the velocity, pressure and concentration fields can be written as:

$$\frac{1}{r}\Delta(r\,u_{1r}) = \frac{\partial p_1}{\partial r}, \tag{9}$$

$$\frac{1}{r}\Delta(r\,u_{2r}) = \beta^{-1}\frac{\partial p_2}{\partial r}, \tag{10}$$

$$\Delta p_i = 0 \quad (i = 1,2), \tag{11}$$

$$r\to\infty,\quad u_{1r}\to(\mathbf{u}_\infty\cdot\mathbf{e}_r),\quad p_1\to 0, \tag{12}$$

$$r\to 0,\quad u_{2r} < \infty,\quad p_2 < \infty, \tag{13}$$

$$r = 1,\quad u_{1r} = u_{2r} = 0, \tag{14}$$

$$\partial u_{1r}/\partial r = \partial u_{2r}/\partial r, \tag{15}$$

$$\left(2\frac{\partial}{\partial r} - \frac{\partial^2}{\partial r^2}\right)[r^2(u_{1r} - \beta\,u_{2r})] + \Delta_s\xi + Ma\,\Delta_s\gamma = 0, \tag{16}$$

$$-p_1 + p_2 + (\rho - 1)(\boldsymbol{\eta}\cdot\mathbf{e}_r) + 2\frac{\partial}{\partial r}(u_{1r} - \beta\,u_{2r}) = \frac{2}{Ca} + \frac{2}{Ca}h + 2\xi + 2\,Ma(\gamma - \gamma_0), \tag{17}$$

$$Pe\left(u_{1r}\frac{\partial c}{\partial r} + \frac{u_{1\theta}}{r}\frac{\partial c}{\partial\theta} + \frac{u_{1\varphi}}{r\sin\theta}\frac{\partial c}{\partial\varphi}\right) = \Delta c, \tag{18}$$

$$r\to\infty,\quad c\to 1, \tag{19}$$

$$r = 1,\quad c = \alpha\gamma, \tag{20}$$

$$\delta\Delta_s\gamma + Pe\left(\gamma\frac{\partial u_{1r}}{\partial r} - u_{1\theta}\frac{\partial\gamma}{\partial\theta} - \frac{u_{1\varphi}}{\sin\theta}\frac{\partial\gamma}{\partial\varphi}\right) + \frac{\partial c}{\partial r} - \kappa\gamma = 0, \tag{21}$$

$$\beta = \frac{\eta_2}{\eta_1},\quad \rho = \frac{\rho_2}{\rho_1},\quad Ca = \frac{\eta_1 V}{\sigma_0},$$

$$Pe = \frac{aV}{D},\quad Ma = \frac{\mathrm{d}\sigma}{\mathrm{d}\Gamma}\frac{C_\infty(0)\,a}{\eta_1 V},$$

$$\mathbf{u}_\infty = \frac{\mathbf{U}_\infty}{V},\quad \xi(\theta,\varphi) = \frac{\sigma(\theta,\varphi)}{\eta_1 V},\quad \boldsymbol{\eta} = \frac{\rho_1 a^2\mathbf{g}}{\eta_1 V},$$

where u_{ir}, $u_{i\theta}$, $u_{i\varphi}$, p_i $(i = 1, 2)$ are components of the dimensionless velocity field and dimensionless hydrodynamic pressure field, respectively; c, γ are dimensionless bulk and surface concentrations; η_i $(i = 1, 2)$ are dynamic viscosities; ρ_i $(i = 1, 2)$ are densities; γ_0 is the constant surface concentration which would exist if the fluids are at rest and the concentration at infinity is constant and equals $C_\infty(0)$; σ_0 is the surface tension for $\gamma = \gamma_0$; $\mathbf{e}_r$ is radial unit vector; and Ca, Pe, Ma are the capillary, Peclet and Marangoni numbers, respectively.

Equations (9) and (10) are the Stokes equations for the radial component of the velocity field. The angular components are eliminated using the continuity equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 u_{ir})+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\, u_{i\theta})+\frac{1}{r\sin\theta}\frac{\partial u_{i\varphi}}{\partial\varphi}=0,\quad (i=1,2). \tag{22}$$

Equation (11) follows from the Stokes equations using (22). Equation (17) is the convective diffusion equation. Boundary conditions (12), (19) and (13) show the behavior of the solution at infinity and in the center, respectively. Boundary conditions (14)–(16) account for impenetrability, slip and tangental stress balance, respectively. In principle, the latter two conditions have the form

$$r=1,\quad u_{1\theta}=u_{2\theta},$$

$$\frac{\partial u_{1r}}{\partial\theta}+\frac{\partial u_{1\theta}}{\partial r}-u_{1\theta}-\beta\times\left(\frac{\partial u_{2r}}{\partial\theta}+\frac{\partial u_{2\theta}}{\partial r}-u_{2\theta}\right)+\frac{\partial\xi}{\partial\theta}+Ma\frac{\partial\gamma}{\partial\theta}=0, \tag{23}$$

$$u_{1\varphi}=u_{1\varphi},$$

$$\frac{1}{\sin\theta}\frac{\partial u_{1r}}{\partial\varphi}+\frac{\partial u_{1\varphi}}{\partial r}-u_{1\varphi}-\beta\left(\frac{1}{\sin\theta}\frac{\partial u_{2r}}{\partial\varphi}+\frac{\partial u_{2\varphi}}{\partial r}-u_{2\varphi}\right)+\frac{1}{\sin\theta}\frac{\partial\xi}{\partial\varphi}+Ma\frac{1}{\sin\theta}\frac{\partial\gamma}{\partial\varphi}=0. \tag{24}$$

Using $(\sin\theta)^{-1}(\partial/\partial\theta)\sin\theta$ with (23) and $(\sin\theta)^{-1}\partial/\partial\varphi$ with (24), adding the two results and taking into account (22) and (14) brings us to (15) and (16).

The normal stress balance (17) deserves some comments. The first term in r.h.s. is due to the Laplace over-pressure. It is assumed to be large ($Ca \ll 1$) which is consistent with our assumption of negligible deformability. The second term is due to the deviation from sphericity, where $2h$ is the dimensionless correction to the dimensionless mean curvature 2 of the spherical surface ($h \ll 1$). This correction is neglected everywhere except for (17) where it is multiplied by a large number (Ca is in the denominator). Actually rather than $Ca \ll 1$ we shall use a stronger assumption, namely, $Ca \ll Pe^n$, where n is a positive integer. This allows us to neglect possible nonsphericity of the drop when expanding in a power series of Pe. The value ξ is defined such that its average over the surface equals zero. Equilibrium between the bulk and surface concentrations and mass balance at the surface result in b.c. (20) and (21), respectively.

4. SOLUTION

The problem (9)–(21) is solved in the asymptotic limit $Pe \ll 1$, $MaPe \cong 1$ and $Ca \ll 1$ with all other dimensionless parameters, independent from the velocity scale V and from σ_0, of order unity. Note that the number $MaPe$ does not contain the velocity scale and only contains material parameters.

The solution of equations (9)–(15) can be represented as

$$u_{1r}=(\mathbf{u}_\infty\cdot\mathbf{e}_r)\left(1-\frac{1}{r^3}\right)+\sum_{n=1}^{\infty}\left(\frac{1}{r^n}-\frac{1}{r^{n+2}}\right)\Theta_n, \tag{25}$$

$$u_{2r}=\frac{3}{2}(\mathbf{u}_\infty\cdot\mathbf{e}_r)(r^2-1)+\sum_{n=1}^{\infty}(r^{n+1}-r^{n-1})\Theta_n, \tag{26}$$

$$p_1=\sum_{n=1}^{\infty}\frac{2(2n-1)}{n+1}\frac{1}{r^{n+1}}\Theta_n, \tag{27}$$

$$p_2=p_0+15\beta(\mathbf{u}_\infty\cdot\mathbf{e}_r)r+\sum_{n=1}^{\infty}\frac{2(2n+3)\beta}{n}r^n\Theta_n, \tag{28}$$

where p_0 is some constant, $\Theta_n(\theta,\varphi)$ are spherical functions of the first kind, of order n and of the general form. They will be specified after satisfying b.c. (16) and (17).

For the concentration problem (18)–(21), taking into account equation (25), the availability of the finite velocity flow far off the drop and of the integral surfactant transfer to the drop due to the chemical reaction is characteristic. Then at $Pe \ll 1$ we shall proceed with the help of the matched asymptotic expansions method (see, e.g. refs. [9, 10]). Here we just take a two-term expansion. The solution is sought in the following form in the *outer* region ($r > O(Pe^{-1})$):

$$c=c^{(0)}+Pe\,c^{(1)}+O(Pe), \tag{29}$$

in the *inner* region ($1 < r < O(Pe^{-1})$):

$$c=c_0+Pe\,c_1+O(Pe), \tag{30}$$

on the surface ($r=1$):

$$\gamma=\gamma_0+Pe\,\gamma_1+O(Pe). \tag{31}$$

For the *outer* region the problem (18) and (19), using equation (25), can be rewritten as

$$\mathbf{u}_\infty\cdot\mathrm{grad}_R c=\Delta_R c, \tag{32}$$

$$R\to\infty,\quad c\to 1, \tag{33}$$

with $R = Pe\,r$ and grad_R and Δ_R obtained from the corresponding differential operators by replacing r by R.

Substituting (29) into (32) and (33) and putting together the terms of leading order, one can find that the problem for $c^{(0)}$ is just like (32) and (33) for c. Thus

$$c^{(0)}=1 \tag{34}$$

is a solution. In fact it is *the* solution.

The problem for the *inner* region can be easily derived by substituting (30) and (31) into (18), (20) and (21) and collecting the zero order terms:

$$\Delta c_0=0,\quad r=1,\quad c_0=\alpha\gamma_0,\quad \delta\Delta_s\gamma+\frac{\partial c}{\partial r}-\kappa\gamma=0.$$

With due regard for matching with the outer solution (34) we have

$$c_0 = 1-\frac{q}{r}, \quad (35)$$

$$\gamma_0 = \frac{q}{\kappa}, \quad (36)$$

where

$$q = \frac{\kappa}{\alpha+\kappa}.$$

Further, substituting (29) and (34) into (32) and (33) and putting together the terms of the appropriate order one gets the problem for $c^{(1)}$

$$\mathbf{u}_\infty \cdot \mathrm{grad}_R c^{(1)} = \Delta_R c^{(1)}, \quad (37)$$

$$R \to \infty, \quad c^{(1)} \to 0. \quad (38)$$

Substituting

$$c^{(1)} = \bar{c}^{(1)} \exp\left[\frac{R}{2}(\mathbf{u}_\infty \cdot \mathbf{e}_r)\right] \quad (39)$$

into (37), (38) and taking into account that $\mathrm{grad}_R [R(\mathbf{u}_\infty \cdot \mathbf{e}_r)] = \mathbf{u}_\infty$ brings us to

$$(\Delta_R - \tfrac{1}{4}|\mathbf{u}_\infty|^2)\bar{c}^{(1)} = 0, \quad (40)$$

$$R \to \infty, \quad \bar{c}^{(1)} \to 0. \quad (41)$$

The solution of (40), (41) can be easily found. Then in view of (39) one has

$$c^{(1)} = R^{-1/2} \exp\left[\frac{R}{2}(\mathbf{u}_\infty \cdot \mathbf{e}_r)\right] \times \sum_{n=0}^{\infty} K_{n+1/2}\left(|\mathbf{u}_\infty| \frac{R}{2}\right) \Xi_n(\theta, \varphi), \quad (42)$$

where $K_{n+1/2}$ are modified Bessel functions of the third kind and order $n+1/2$, Ξ_n are spherical functions of the first kind, of order n and of the general form. Using the condition of $c^{(0)} + Pe\, c^{(1)}$ matching c_0 and taking into account (34), (35), (42) brings us to $\Xi_n(\theta, \varphi) = 0$ for $n = 1, 2\ldots$ and thus to

$$c^{(1)} = -\frac{q}{R} \exp\left\{\frac{R}{2}[(\mathbf{u}_\infty \cdot \mathbf{e}_r) - |\mathbf{u}_\infty|]\right\}. \quad (43)$$

The problem for c_1 and γ_1 can be derived by substituting (30), (31), (35) and (36) into (18), (20) and (21) and collecting all the terms of first order in Pe. Finally we get

$$\Delta c_1 = \frac{q}{r^2} u_{1r}, \quad (44)$$

$$r = 1, \quad c_1 = \alpha \gamma_1,$$

$$\delta \Delta_s \gamma_1 + \frac{q}{\kappa}\frac{\partial u_{1r}}{\partial r} + \frac{\partial c_1}{\partial r} - \kappa \gamma_1 = 0. \quad (45)$$

Clearly, at this stage there is no need to know the angular components of the velocity field. The solution of the problem (44) and (45) with (25) and $c_0 + Pe\, c_1$ matching $c^{(0)} + Pe\, c^{(1)}$, where c_0, $c^{(0)}$ and $c^{(1)}$ are defined in (34), (35) and (43), is

$$c_1 = \sum_{n=0}^{\infty} f_n(r)\, \Theta_n(\theta, \varphi) + f_1'(r)\,(\mathbf{u}_\infty \cdot \mathbf{e}_r), \quad (46)$$

$$\gamma_1 = \sum_{n=0}^{\infty} a_n \Theta_n(\theta, \varphi) + a_1'\,(\mathbf{u}_\infty \cdot \mathbf{e}_r), \quad (47)$$

$$f_0(r) = b_0' + \frac{b_0}{r},$$

$$f_1'(r) = -\frac{q}{2}\left(1 + \frac{1}{2r^3}\right) + \frac{b_1'}{r^2},$$

$$f_n(r) = -\frac{q}{2}\left(\frac{1}{nr^n} + \frac{1}{(n+1)r^{n+2}}\right) + \frac{b_n}{r^{n+1}} (n = 1, 2\ldots),$$

$$a_0 = \frac{q^2}{2\kappa}|\mathbf{u}_\infty|, \quad (48)$$

$$b_0 = -\frac{q^2}{2}|\mathbf{u}_\infty|,$$

$$b_0' = \frac{q}{2}|\mathbf{u}_\infty|,$$

$$a_1' = \frac{3(4-\kappa)}{4(\alpha+\kappa)(2\delta+2\alpha+\kappa)}, \quad (49)$$

$$b_1' = \frac{3(4\alpha+\alpha\kappa+2\delta\kappa+\kappa^2)}{4(\alpha+\kappa)(2\delta+2\alpha+\kappa)},$$

$$a_n = \frac{4n(n+1)-\kappa}{2n(n+1)(\alpha+\kappa)[n(n+1)\delta+(n+1)\alpha+\kappa]}, \quad (50)$$

$$b_n = \frac{4n(n+1)\alpha + n(n+1)(2n+1)\kappa\delta + n(2n+3)\alpha\kappa + (2n+1)\kappa^2}{2n(n+1)(\alpha+\kappa)[n(n+1)\delta+(n+1)\alpha+\kappa]}$$

$$(n = 1, 2\ldots).$$

Now substituting (25)–(28), (31), (36), (47)–(50) into (16) and (17) and recalling that $MaPe \cong 1$, we obtain

$$[(8-\kappa)m + 1 + \beta](\rho - 1)(\boldsymbol{\eta} \cdot \mathbf{e}_r) + 3[3(4-\kappa)m + 1 + \tfrac{3}{2}\beta](\mathbf{u}_\infty \cdot \mathbf{e}_r) - \xi_1 = 0, \quad (51)$$

$$\Theta_1 = \tfrac{1}{3}(\rho-1)(\boldsymbol{\eta} \cdot \mathbf{e}_r), \quad (52)$$

$$\frac{m - m_{n+1}}{m_{n+1}} \Theta_n = -\frac{n(n+1)}{2(2n+1)(1+\beta)} \xi_n \quad (n = 2, 3\ldots), \quad (53)$$

$$m = -MaPe \frac{1}{12(\alpha+\kappa)(2\delta+2\alpha+\kappa)}, \quad (54)$$

$$m_n = \frac{(2n-1)(1+\beta)[n(n-1)\delta + n\alpha + \kappa]}{3[\kappa - 4n(n-1)](2\delta+2\alpha+\kappa)} \quad (n = 3, 4\ldots), \quad (55)$$

$$p_0 = \frac{2}{Ca}, \quad (56)$$

$$h = -Ca \sum_{n=2}^{\infty} \frac{n + \beta n + 2 - \beta}{n(n+1)} \Theta_n, \quad (57)$$

with the spherical functions $\xi_n(\theta, \varphi)$ defined by

$$\xi(\theta,\varphi) = \sum_{n=1}^{\infty} \xi_n(\theta,\varphi).$$

Since $\nabla_s\xi(\theta, \varphi)$ is assumed given, all functions $\xi_n(\theta, \varphi)$ $(n = 1, 2\ldots)$ are also known. The functions $\Theta_n(\theta, \varphi)$ $(n = 2, 3\ldots)$ are implicitly defined by equation (53).

Equation (51) gives in the dimensionless form the sought relationship between drop velocity, buoyancy and the imposed surface tension gradient. Multiply the l.h.s. of (51) by r and apply the gradient. Then using

$$\mathrm{grad}(\boldsymbol{\eta}\cdot\mathbf{r}) = \boldsymbol{\eta}, \quad \mathrm{grad}(\mathbf{u}_\infty\cdot\mathbf{r}) = \mathbf{u}_\infty,$$

$$\mathrm{grad}(r\,\xi_1) = \frac{3}{8\pi}\int_{S_1} \nabla_s\xi\, dS$$

one can derive

$$[(8-\kappa)m+1+\beta](\rho-1)\boldsymbol{\eta}+3[3(4-\kappa)m+1+\tfrac{3}{2}\beta]\mathbf{u}_\infty - \frac{3}{8\pi}\int_{S_1}\nabla_s\xi\, dS = 0, \quad (58)$$

where the integration is made over the entire drop surface S_1 of unit radius.

The results (52)–(56) and (58) complete the calculation of the radial velocity component and hydrodynamic pressure fields in the Stokes approximation and of the concentration field up to order Pe.

Equation (57) obtained within the assumption $Ca \ll Pe''$ permits estimation of the possible deviation of the drop shape from the spherical one. The equation of the drop surface can be written as

$$r = 1+\varepsilon(\theta,\varphi), \quad (59)$$

where $|\varepsilon(\theta, \varphi)| \ll 1$. In the limit of small departures from sphericity we obtain

$$h = -\varepsilon - \tfrac{1}{2}\Delta_s\varepsilon.$$

Then using (57) yields

$$\varepsilon = -2\,Ca\sum_{n=2}^{\infty}\frac{n+\beta n+2-\beta}{n(n-1)(n+1)(n+2)}\Theta_n, \quad (60)$$

that together with (59) describes the drop surface. Since the drop is incompressible and the center of the spherical coordinate system has been chosen to be the mass center of the drop, the zero and first modes are absent in (60).

5. DISCUSSION

Equation (55) provides the sequence of critical Marangoni values, m_n. Generally, the solution found is not valid for m lying in certain asymptotically small vicinities of m_n $(n = 3, 4,\ldots)$ due to the divergence of Θ_n as $m \to m_n$. If, however, $\xi_n = 0$, then equation (53) gives that $\Theta_n = 0$ for $m \neq m_n$, and Θ_n is an arbitrary spherical function of the order n for $m = n_n$. The correct consideration of the case $|m-m_n| \ll 1$ demands in general proceeding to a higher order approximation in (low) Reynolds and Peclet numbers. In the present paper the analysis is limited to the case $|m-m_n| \cong 1$ $(n = 3, 4,\ldots)$.

Rewrite equation (58) in dimensional form as

$$[(8-\kappa)m+1+\beta](\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1} + [3(4-\kappa)m+1+\tfrac{3}{2}\beta]\mathbf{U}_\infty - \frac{1}{8\pi a\eta_1}\int_{S_a}\nabla_s\sigma\, dS = 0, \quad (61)$$

where the integration is done over the sphere S_a of radius a.

Equation (61) permits us to express the velocity of the drop $\mathbf{U}$ $(\mathbf{U} = -\mathbf{U}_\infty)$ under buoyancy and surface tension gradient as

$$\mathbf{U} = \frac{(8-\kappa)m+1+\beta}{3(4-\kappa)m+1+\frac{3}{2}\beta}\,\frac{(\rho_2-\rho_1)a^2\mathbf{g}}{3\eta_1} - \frac{1}{8\pi a\eta_1[3(4-\kappa)m+1+\frac{3}{2}\beta]}\int_{S_a}\nabla_s\sigma\, dS. \quad (62)$$

The first contribution to the r.h.s. of equation (62) is due to buoyancy, while the second one is the strict capillary-induced velocity that, for example, governs drop motion in free fall conditions.

Equation (61) can be rewritten in the following form:

$$\frac{4\pi}{3}(\rho_2-\rho_1)a^3\mathbf{g}+4\pi\eta_1 a\frac{3(4-\kappa)m+1+\frac{3}{2}\beta}{(8-\kappa)m+1+\beta}\mathbf{U}_\infty - \frac{1}{2[(8-\kappa)m+1+\beta]}\int_{S_a}\nabla_s\sigma\, dS = 0. \quad (63)$$

Since the first term in the l.h.s. of equation (63) is the buoyancy force, one can conclude that (63) accounts for the dynamic balance of the forces acting on the drop. The second term is the hydrodynamical force in the homogeneous case obtained in ref. [4]. The third term gives the (capillary) force acting on the drop due to the induced surface tension gradient:

$$\mathbf{F}_c = -\frac{1}{2[(8-\kappa)m+1+\beta]}\int_{S_a}\nabla_s\sigma\, dS. \quad (64)$$

In the particular case $m = 0$ the second term in (63) reduces to the classical result obtained by Rybczynski and Hadamard for the drag of a drop (without surface tension gradient [1]), while (64) reduces to Subramanian's result with given albeit arbitrary surface tension gradient [8].

Let us now use (3), (6) and (8) to obtain $\nabla_s\sigma$. We have

$$\int_{S_a}\nabla_s\sigma\,\mathrm{d}S = \frac{\mathrm{d}\sigma}{\mathrm{d}\Gamma}\int_{S_a}\nabla_s\Gamma\,\mathrm{d}S + \frac{\mathrm{d}\sigma}{\mathrm{d}T}\int_{S_a}\nabla_s T\,\mathrm{d}S = \frac{\mathrm{d}\sigma}{\mathrm{d}\Gamma}\frac{8\pi}{3}a^3A_1\nabla\Phi_1 + \frac{\mathrm{d}\sigma}{\mathrm{d}T}\frac{8\pi}{3}a^2A_1'\nabla\Phi_1'.$$

In accordance with the properties of the spherical functions, only the function of the first order survives the process of integration. Then using (1) and (5) we get

$$\nabla\Phi_1 = \nabla C_\infty(0), \quad \nabla\Phi'_1 = \nabla T_\infty(0),$$

where $\nabla C_\infty(0)$ is the external concentration gradient that, when no drop is present, would appear at the expected location of the center of the drop.

Finally taking into account (4) and (7) we get

$$\int_{S_a} \nabla_s\sigma \, dS = \frac{d\sigma}{d\Gamma} \frac{8\pi a^3}{2\delta+2\alpha+\kappa} \nabla C_\infty(0) + \frac{d\sigma}{dT} \frac{8\pi a^2}{2+\lambda} \nabla T_\infty(0), \quad (65)$$

which can be used in equations (61)–(64).

In the case $|m| \gg 1+\beta$ and $|\kappa-4| \cong 1$ the results can be simplified. In particular, the expression for the drop velocity under the surfactant gradient alone is

$$\mathbf{U} = \frac{4D(\alpha+\kappa)}{4-\kappa} \frac{\nabla C_\infty(0)}{C_\infty(0)}.$$

Note that the main capillary parameter $d\sigma/d\Gamma$ does not appear. Moreover, we also see that for a given gradient an increase in the background surfactant concentration lowers the velocity.

Equations (61)–(63) give an incorrect result for the velocity if m is in some asymptotically small vicinity of m_1, where

$$m_1 = \frac{1+\frac{3}{2}\beta}{3(\kappa-4)} \quad (66)$$

(now, for simplicity, we assume $|\kappa-4| \cong 1$). Note that at $m = m_1$ the second term of (61) vanishes and as does the denominator in (62). Thus we see that if $|m-m_1| \ll 1$ the neglected higher order terms in low Reynolds and Peclet numbers, become comparable with the second term on the l.h.s. of (61). We shall come back to this case below with the help of a weakly nonlinear analysis. At this point we can only say that for given buoyancy and surface tension gradient, the velocity of the drop is, in the case $|m-m_1| \ll 1$, much larger than for $|m-m_1| \cong 1$. If one is interested in the relation between the surface tension gradient (or concentration gradient far off the drop) and buoyancy for a levitating drop, then (61) or (63) at $\mathbf{U}_\infty = 0$ give the correct leading approximation result even for $|m-m_1| \ll 1$.

In the general case if $|m-m_2| \ll 1$, equations (61)–(63) give an incorrect result for the buoyancy contribution to the velocity, where

$$m_2 = \frac{1+\beta}{\kappa-8} \quad (67)$$

($|\kappa-8| \cong 1$ is now assumed for simplicity). The reason for the incorrectness is very similar to that mentioned above for the case $|m-m_1| \ll 1$. The case $|m-m_2| \ll 1$ will also be treated below with the help of a weakly nonlinear analysis. Now one can only point out that when $|m-m_2| \ll 1$ then, to influence the drop velocity to the same extent as with $|m-m_2| \cong 1$, the buoyancy force must be much larger. If one is interested in the drop motion when buoyancy is negligible, as in free fall conditions, then equations (61) and (62) at $\mathbf{g} = 0$ give the correct result even for $|m-m_2| \ll 1$.

The critical Marangoni values m_n ($n = 1, 2, \ldots$) have been shown to be the instability thresholds for the corresponding mode of a motionless drop in a homogeneous background and no buoyancy [4]. Here m_1 and m_2 correspond to the translational mode, m_1 for a *free* drop, while m_2 is for a *fixed* drop [4]. In this paper we shall deal only with the case of a *free* drop.

Note that the analysis carried out here is in fact *linear* since the problem for the velocity field and the convective contribution to the concentration field is linear in the *inner* region. Due to this 'linearity', for given material parameters the stability status of the linear motion regimes, with $\mathbf{g} \neq 0$ and $\nabla_s\sigma \neq 0$, in the general case, coincides with that for the motionless state of the drop for vanishing $\mathbf{g}$ and $\nabla_s\sigma$.

6. WEAKLY NONLINEAR ANALYSES

Using (66) and (67), equation (61) can be rewritten as

$$3(4-\kappa)(m-m_1)\mathbf{U}_\infty + (8-\kappa)(m-m_2)(\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1} - \frac{1}{8\pi a\eta_1}\int_{S_a} \nabla_s\sigma \, dS = 0. \quad (68)$$

In each term of (68) the dimensional factors provide natural velocity *scales* of the problem. The first is associated with the drop velocity, the second with the buoyancy, while the third with the external gradients. By multiplying by a/D, equation (68) can be rewritten in terms of Peclet numbers defined by the velocity scales. Since the solution for the radial velocity field developed above contains terms proportional to each one of the velocity scales, in the general case all those Peclet numbers are of equal order and small for the solution to be valid. The higher order terms in low Reynolds and Peclet numbers have been neglected since here we just consider the leading order approximation. However, as already pointed out, if the coefficients $m-m_1$ or $m-m_2$ are small such a limitation may not be adequate as higher order terms may be of the order of the linear terms in (68).

Thus to discuss the cases $|m-m_1| \ll 1$ and $|m-m_2| \ll 1$ some (though not all) higher order contributions need to be taken into account in (68). In the case $|m-m_1| \ll 1$, $|m-m_2| \cong 1$, it is clear from equation (68) that the higher order term to be included must be independent from the velocity scales associated to buoyancy and gradients. Thus this term depends only on $\mathbf{U}_\infty$. In the case $|m-m_2| \ll 1$, a similar consideration yields that the higher order term to be retained should depend on the buoyancy velocity scale rather than on the other two scales.

To proceed we shall take advantage of the results

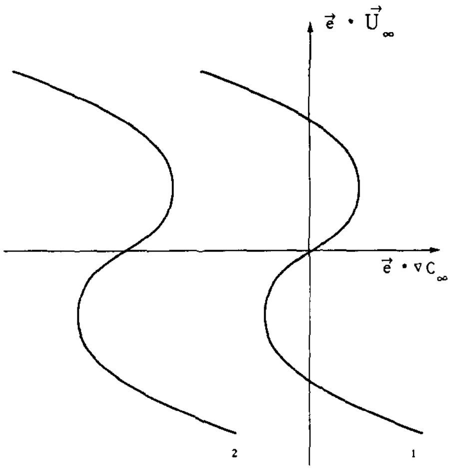

FIG. 1. Velocity vs concentration gradient, given by equations (69) and (65), in the absence of buoyancy (curve 1) and for nonzero buoyancy (curve 2), when there is no temperature gradient and the three vectors involved are collinear; **e** is a collinear unit vector.

obtained in ref. [4]. Indeed, although the analysis of ref. [4] has been carried out for a homogeneous external medium while here there are concentration and/or temperature gradients in the outer fluid, this fact does not influence the form of the higher order terms of interest.

A. *The case* $|m-m_1| \ll 1$

In the case $|m-m_1|\ll 1$, $|\kappa-4|\cong 1$, $|m-m_n|\cong 1$ ($n = 2, 3, \ldots$) instead of (68) we have

$$3(4-\kappa)(m-m_1)\mathbf{U}_\infty+\frac{3ma}{2D}[2\kappa+q(4-\kappa)]|\mathbf{U}_\infty|\mathbf{U}_\infty$$
$$+(8-\kappa)(m-m_2)(\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1}$$
$$-\frac{1}{8\pi a\eta_1}\int_{S_a}\nabla_s\sigma\,\mathrm{d}S = 0, \quad (69)$$

where the second nonlinear term in the l.h.s. has been taken from ref. [4] (equation (30)). Using (65) the last term in the l.h.s. of (69) can be written in terms of temperature and concentration gradients.

One can easily see that equation (69) can have up to *three* solutions for a given $\mathbf{U}_\infty$. This means that for given values of buoyancy and external gradient there can exist from one to three stationary regimes of drop motion.

Note that here the external concentration and/or temperature gradient enter the problem in the same way as buoyancy. The drop velocity versus the external gradient is schematically represented in Fig. 1 when multiple steady regimes may exist. Two curves corresponding to no buoyancy and to some nonzero level of buoyancy, respectively, are shown. For simplicity, Fig. 1 is drawn when there is only a concentration gradient and the vectors entering equation (69) are collinear (**e** is a unit vector). It appears that the effect of buoyancy is a mere shift of the curve along the gradient axis, as expected.

The relative stability analysis can be carried out following the scheme given in ref. [4]. When multiple steady states exist, we find that the regimes of drop motion with absolute velocity ranging from 0 to $|U_{\mathrm{aut}}|/2$ are unstable (respectively, stable), while those with velocity greater than $|U_{\mathrm{aut}}|$ are stable (respectively, unstable). Motions with velocities from $|U_{\mathrm{aut}}|/2$ to $|U_{\mathrm{aut}}|$ are stable (respectively, unstable) in the axisymmetrical problem, while unstable (respectively, stable) with respect to velocity perturbations perpendicular to the motion. Here $|U_{\mathrm{aut}}|$ is the drop velocity in the autonomous motion [4], i.e. in the absence of buoyancy and external gradients

$$|U_{\mathrm{aut}}| = \frac{2(\kappa-4)(m-m_1)D}{[2\kappa+q(4-\kappa)]ma}. \quad (70)$$

The higher order modes can also bring instability. However, if m_1 is, in absolute value, smaller than all m_n ($n = 3, 4, \ldots$) of the same sign such instability is not expected [4].

On the basis of (69) one can conclude that when the sum of the third and fourth terms on the l.h.s. is zero or small enough, the drop will move with the autonomous motion velocity in an arbitrary direction in space or at a close velocity. As for the arbitrary direction, it is clear that equation (69) gives an incorrect prediction, since the slightest nonzero buoyancy and concentration and/or temperature gradient yield a definite direction in space. Even as for the absolute value of the velocity, the prediction is not always correct. Indeed, when the sum of the third and fourth terms is much smaller than each of those terms, the higher order contributions based on the buoyancy and gradient velocity scales must in general be taken into account. Indeed, now the Peclet number based on the buoyancy velocity scale may be comparable or even larger than $m-m_1$, while this is not possible when the sum is of order of one of the terms. The next subsection is devoted to these specific asymptotics.

B. *The case of buoyancy alone stronger than the net force due to buoyancy and gradients acting together*

We continue consideration of the case $|m-m_1| \ll 1$, $|\kappa-4| \cong 1$, $|m-m_n| \cong 1$ ($n = 2, 3, \ldots$) and now the buoyancy alone is stronger than a gradient-induced force and buoyancy acting together. For simplicity, we limit consideration to the action of a temperature gradient alone taken to be constant far off the drop. The diffusional Peclet number is assumed to be much larger than the thermal Peclet number and the Reynolds number, i.e. Schmidt and Lewis numbers are extremely large which is a valid assumption if the fluid outside the drop is a liquid. Thus to find the extra appropriate nonlinear terms in (69), the expansion is only carried in diffusional Peclet number.

Clearly, the term to be taken into account of the l.h.s. of (69) necessarily depends on the buoyancy velocity scale. From the Appendix we get

$$\frac{(8-\kappa)mq(\rho_2-\rho_1)a^3\mathbf{g}}{6\eta_1 D}|\mathbf{U}_\infty|. \tag{71}$$

After developing the last term of the l.h.s. of (69) with the help of (65) (at $\nabla C_\infty = 0$) and introducing

$$\mathbf{u} = \frac{a}{D}\mathbf{U}_\infty,$$

$$\mathbf{b} = \frac{(8-\kappa)mq(\rho_2-\rho_1)a^3\mathbf{g}}{6\eta_1 D},$$

$$\mathbf{f} = \frac{a}{D}\left[\frac{\mathrm{d}\sigma}{\mathrm{d}T}\frac{a}{(2+\lambda)\eta_1}\nabla T_\infty - (8-\kappa)(m-m_2)(\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1}\right],$$

$$K = \frac{3m}{2}[2\kappa+q(4-\kappa)],$$

we obtain

$$3(4-\kappa)(m-m_1)\mathbf{u}+K|\mathbf{u}|\mathbf{u}+\mathbf{b}|\mathbf{u}| = \mathbf{f}. \tag{72}$$

In the general case all terms must have the same order. Then

$$|m-m_1| \cong |\mathbf{u}| \cong |\mathbf{b}| \ll 1, \quad |\mathbf{f}| \cong |\mathbf{u}|\,|\mathbf{b}|.$$

Equation (72) shows the possibility of multiple stationary drop motions for given buoyancy and temperature gradient. Note that, in general, the vectors **b** and **f** are not collinear and the possible velocities of the drop are different not only in magnitude, but also in direction, unlike the situation considered in Subsection A.

Let us give further consideration to the case when **b** and **f** are collinear. Instead of (72) we have now

$$3(4-\kappa)(m-m_1)u+K|u|u+b|u| = f, \tag{73}$$

where u, b, f are the only nonzero components of the corresponding vectors. Take for definiteness $\kappa > 4$ (then $m_1 > 0$ according to (66) and $K > 0$) and $b>0$. The dependence of f on u is schematically depicted in Figs. 2(a)–(d). The curve of Fig. 2(a) corresponds to $m-m_1 < 0$, $m_1-m \gg b$. As m increases, the curve looses symmetry and a discontinuity in the slope at the center appears. At $m = m_1-b/[3(\kappa-4)] \equiv m_* < m_1$ the left derivative vanishes and for $m > m_*$ the curve is shown in Fig. 2(b). We see that three regimes of drop motion exist if f is positive and small enough. Note that three regimes can already appear for $m < m_1$, unlike the situation reported in ref. [4] and in the previous subsection where three regimes can exist only for $m > m_1$. At $m = m_1+b/[3(\kappa-4)] \equiv m_{**} > m_1$ the right derivative vanishes and for $m > m_{**}$ the curve is shown in Fig. 2(c). It is still asymmetric, becoming symmetric only at $m-m_1 \gg$ b (Fig. 2(d)). Note that when $|m-m_1| \gg b$, the third term of the l.h.s. of (73) becomes negligible and the dependence $f(u)$ qualitatively coincides with that considered in the Subsection A.

For other combinations of signs of $(4-\kappa)$ and b there is no qualitative change in the transition diagram. It may only happen that instead of the curves shown in Fig.2 we may find their mirror images with respect to either of the axes.

Note that according to (72) if $3(\kappa-4)(m-m_1)/K \equiv |\mathbf{u}_{\text{aut}}| > 0$ and $\mathbf{f} = \mathbf{b}\,|\mathbf{u}_{\text{aut}}|$, where $\mathbf{u}_{\text{aut}}$ is the autonomous motion velocity (70) in the new scale, the motion at this velocity has arbitrary direction in space. Therefore, equation (72), just like the simpler equation (69), shows the possibility of the temperature gradient compensating for the action of buoyancy, i.e. that for some given buoyancy and temperature gradient, the motion can occur just like the autonomous motion in the absence of buoyancy and temperature gradient, provided $\mathbf{f} = \mathbf{b}|\mathbf{u}_{\text{aut}}|$. Nevertheless one should expect that this degeneracy, with an infinite number of stationary regimes, does not survive if the higher order contributions are taken into account.

To assess relative stability of the possible states let us linearize (72) with respect to a small stationary perturbation $\mathbf{u}'$ of the velocity $\mathbf{u}$. Then one gets

$$\mathbf{f}' = \frac{\mathrm{d}\mathbf{f}}{\mathrm{d}\mathbf{u}}\cdot\mathbf{u}',$$

where

$$\frac{\mathrm{d}\mathbf{f}}{\mathrm{d}\mathbf{u}} = \begin{vmatrix} \partial f_x/\partial u_x & \partial f_x/\partial u_y & \partial f_x/\partial u_z \\ \partial f_y/\partial u_x & \partial f_y/\partial u_y & \partial f_y/\partial u_z \\ \partial f_z/\partial u_x & \partial f_z/\partial u_y & \partial f_z/\partial u_z \end{vmatrix},$$

$$\mathbf{f} = (f_x, f_y, f_z), \quad \mathbf{u} = (u_x, u_y, u_z)$$

in a Cartesian coordinate system (x, y, z).

Since $\mathbf{f}' = 0$ (the forcing factors are not perturbed), the condition for the existence of a nontrivial solution is

$$\det\left\|\frac{\mathrm{d}\mathbf{f}}{\mathrm{d}\mathbf{u}}\right\| = 0. \tag{74}$$

For simplicity and without a loss of generality we take the coordinate system as $\mathbf{b} = (b, 0, 0)$, $b > 0$. After calculating the matrix elements with the help of (72), equation (74) can be reduced to

$$\left[3(4-\kappa)(m-m_1)+2K|\mathbf{u}|+b\frac{u_x}{|\mathbf{u}|}\right] \times\left[3(4-\kappa)(m-m_1)+K|\mathbf{u}|\right]^2 = 0$$

or

$$3(4-\kappa)(m-m_1)+2K|\mathbf{u}|+b\frac{u_x}{|\mathbf{u}|} = 0, \tag{75}$$

$$3(4-\kappa)(m-m_1)+K|\mathbf{u}| = 0. \tag{76}$$

Equations (75) and (76) define two surfaces in 3-d space (u_x, u_y, u_z) and the drop motions with velocities lying on these surfaces admit a neutral steady perturbation whose direction $\mathbf{u}'$ can be found by solving the system of three equations

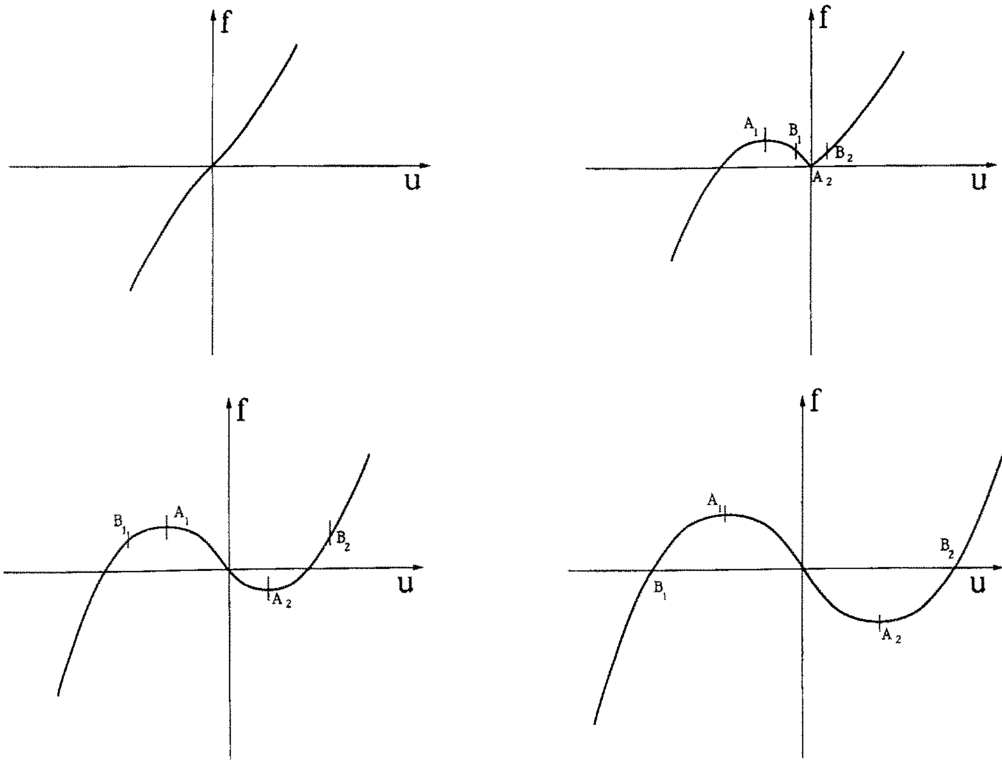

FIG. 2. The small net force due to large buoyancy and temperature gradient vs velocity in the axisymmetrical case in the absence of concentration gradient. (a)–(d) correspond to different increasing Marangoni numbers, equation (73). The points correspond to the states admitting a neutral monotonic collinear (A_1, A_2) and perpendicular (B_1, B_2) perturbation of the drop velocity.

$$\frac{d\mathbf{f}}{d\mathbf{u}}\cdot\mathbf{u}' = 0,$$

where equations (75) or (76) are taken into account. In particular, one can show that the neutral steady perturbations admitted by the basic states with velocity satisfying equation (76) can only have directions perpendicular to **u**.

As all the surfaces are symmetric with respect to the u_x-axis, we only need to consider their cross sections with, say, the (u_x, u_y) plane, as shown schematically in Figs. 3 (a)–(e). For illustration we take $\kappa > 4$ and then $m_1 > 0$ and $K > 0$. The opposite case can be considered in just the same manner. For $m < m_*$, equations (75) and (76) have no solution. Then, as m is increased above m_*, the surface (75) grows from the origin as shown in Fig. 3(a). When m passes through m_1 the acute angle at the origin changes to be obtuse and simultaneously the surface described by equation (76) appears (Fig. 3(b)). At $m = m_{**}$ the latter surface (76) encloses the surface (75) and the obtuse angle reaches its maximum value 2π (Fig. 3(c)). Then as m is increased above m_{**} the origin is no longer part of the surface (75) which becomes smooth (Fig. 3(d)) until it reaches convexity everywhere. Finally, at $m-m_1 \gg b$ both surfaces center at the origin and belong to spheres with radii $|\mathbf{u}_{\text{aut}}|$ and $|\mathbf{u}_{\text{aut}}|/2$, respectively, as illustrated in Fig. 3(e).

As one may guess, for $m_1 - m \gg b$ when equations (75) and (76) have no solution the basic drop motion is stable. Then as m is increased and the surfaces appear, one may expect that the basic motions with velocities lying in the region covered by these surfaces are unstable.

Now let us come back to the axisymmetrical case (**f**, **b** and **u** parallel). The points A_1, A_2 and B_1, B_2 marked on the curves of Fig. 2 correspond to the abscissas of the intersection with the u_x-axis of the surfaces described by equations (75) and (76), respectively. The states with velocities lying between the extreme right and extreme left A or B points are expected to be unstable and stable otherwise. If there are no such points as in Fig. 2(a), all motions are expected to be stable. Note that for $m_* < m < m_{**}$ the curve $f(u_\infty)$ qualitatively looks like the curve shown in Fig. 2(b). Nevertheless, one should keep in mind that the points B_1 and B_2 appear there only for $m > m_1$.

Note that there can exist two stable regimes of motion (for appropriate f) if $m_* < m < m_{**}$. At $m = m_{**}$ the point B_1 passes to the left of A_1 and there can exist only one stable regime.

C. *The case* $|m-m_2| \ll 1$

In the case $|m-m_2| \ll 1$, $|\kappa-8| \cong 1$, $|m-m_1| \cong 1$, $|m-m_n| \cong 1$ ($n = 3, 4\ldots$) instead of (68) we have

$$3(4-\kappa)(m-m_1)\mathbf{U}_\infty + (8-\kappa)(m-m_2)(\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1}$$

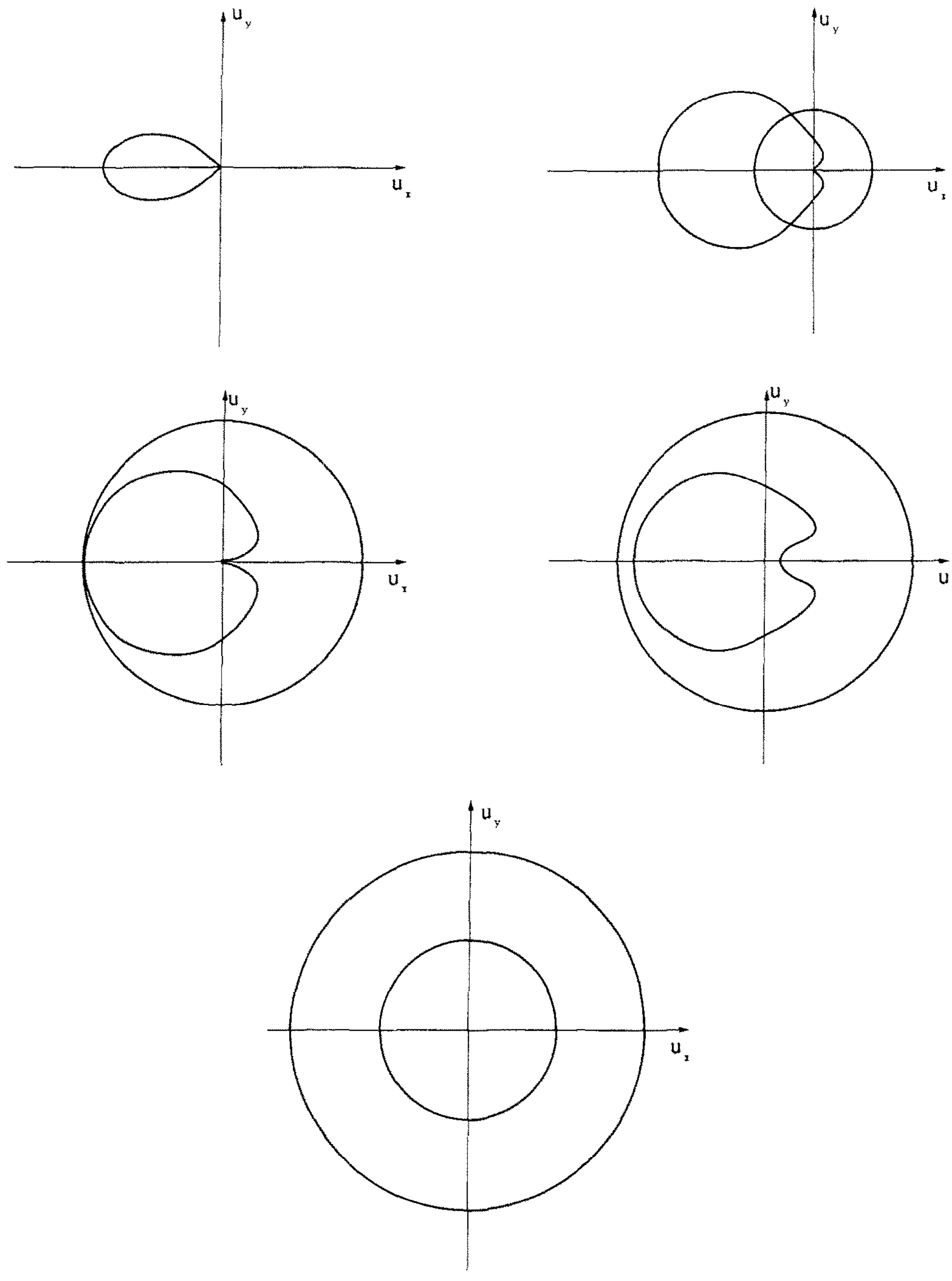

FIG. 3. The surfaces, given by equations (75) and (76), in the space of possible drop velocities, which correspond to motions admitting a neutral monotonic perturbation. The cases (a)–(e) may exist depending on the value taken by the Marangoni number m.

$$+\frac{Pa^8(\rho_2-\rho_1)^3}{27\eta_1^3D^2}|\mathbf{g}|^2\mathbf{g}-\frac{1}{8\pi a\eta_1}\int_{S_a}\nabla_s\sigma\, d\mathbf{S}=0 \quad (77)$$

with

$$P=\frac{3}{40\,Sc^2}\left(\frac{3}{5}+\frac{\beta}{2}\right)-\frac{1}{60\,Sc^2}(1+2\beta)Q$$

$$+4m\left\{\frac{\kappa}{20}-\frac{11q(\kappa-8)}{360}-\frac{3\alpha+8}{20(6\delta+3\alpha+\kappa)}\right.$$

$$\times\left[\frac{64-8\kappa+8\alpha+6\kappa\delta+5\alpha\kappa+3\kappa^2}{16(2\delta+2\alpha+\kappa)}\right.$$

$$\left.-\frac{4\kappa}{21}-\frac{\kappa}{120Sc}-\frac{\kappa}{12Sc}Q\frac{2}{Sc}Q\right]$$

$$-\frac{(6\kappa+11\alpha+40)(8\alpha+6\kappa\delta+5\alpha\kappa+3\kappa^2)}{960(\alpha+\kappa)(2\delta+2\alpha+\kappa)}$$

$$+\frac{11\kappa}{2400Sc}\frac{45-4\kappa}{600Sc^2}+\frac{57\kappa}{2800Sc}Q$$

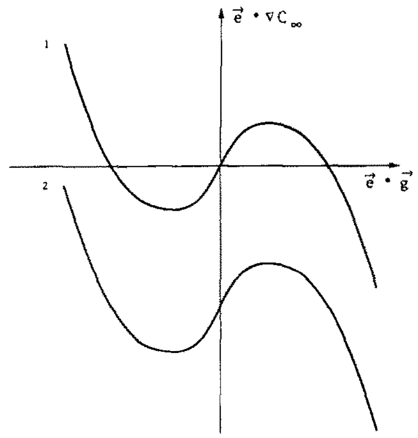

FIG. 4. Concentration gradient vs buoyancy (gravity), given by equations (77) and (65), for a levitating drop (curve 1) and for a drop moving at some *fixed* velocity (curve 2), when there is no temperature gradient and the three vectors involved are collinear; **e** is a collinear unit vector.

$$+\frac{8-\kappa}{10Sc(2\delta+2\alpha+\kappa)}Q+\frac{\kappa-8}{120Sc^2}Q\bigg\},$$

$$Q=\left\{\frac{3m(24-\kappa)(2\delta+2\alpha+\kappa)}{6\delta+3\alpha+\kappa}+5(1+\beta)\right\}^{-1}$$

$$\times\left\{\frac{1}{4}-\frac{mSc}{6\delta+3\alpha+\kappa}\left[144-18\kappa+18\alpha-\frac{3}{14}\kappa\delta\right.\right.$$

$$\left.\left.-\frac{3}{28}\kappa^2-\frac{69}{28}\alpha\kappa-\frac{3\kappa(2\delta+2\alpha+\kappa)}{10Sc}\right]\right\},$$

and

$$Sc=\eta_1/(D\rho_1),$$

where the third nonlinear term of the l.h.s. of equation (77) has been taken from [4] (equations (27)–(29) rewritten in vector form, taking into account equation (25)). The last term of the l.h.s. of (77) can be expressed using (65).

On the basis of equation (77), we can say that to drive the drop at some velocity, and in particular to keep it at rest, a single value of the external gradient may balance up to *three* different levels of buoyancy as illustrated in Fig. 4, drawn for simplicity for the case when the concentration gradient is alone and the vectors entering equation (77) are collinear (**e** is a unit vector). Curve 1 corresponds to a levitating drop, while curve 2 corresponds to a moving drop. The effect of motion appears as a mere shift of the curve along the gradient axis, as expected.

Note that while in Subsection A it has been found that qualitatively buoyancy and the external gradients act similarly on the drop motion, here this influence is different: the drop velocity changes monotonously with the gradient but nonmonotonously with buoyancy.

By analogy with the situation discussed in ref. [4], here the weakly nonlinear regimes considered for $|m-m_2|\ll 1$ are expected to be stable if, for a given set of material parameters, the motionless state of the drop is stable in the absence of buoyancy and no gradient. Then we expect stability when m_2 is, in absolute value, smaller than all m_1, m_n ($n = 3, 4, \ldots$) of the same sign.

Finally, if the sum of the first and the fourth terms of the l.h.s. of (77) is much smaller than each of them, the additional term may be incorporated as it has been done in subsection B. However, such a case does not make much sense if our interest is to calculate the drop velocity, since in this asymptotic scheme buoyancy has a weak influence.

7. CONCLUSION

Following Levich and Kuznetsov [3], Young *et al.* [2] and Subramanian [8] we have considered the possible motion of a drop under external concentration and/or temperature gradients. The novelty of our study is the consideration of an *active* drop, i.e. a drop with a chemical reaction on its surface.

We have found that the behavior of an *active* drop can be largely different from that of a reaction-free drop. In the limit, when our active drop becomes *passive*, we appropriately recover results of earlier authors and in the limit of a homogeneous medium we recover the results of our previous paper [4].

As expected, in the weakly nonlinear approximation the simplest effect of an external gradient is a mere shift of the curve representing the dependence of the buoyancy force versus drop velocity. The shift goes along the force-axis (for $m\to m_1$), when the action of buoyancy is qualitatively analogous to that of the gradients, or along the velocity-axis (for $m\to m_2$), when the gradients are equivalent to some additional drop velocity. More complex effects have been also found, particularly when the net force due to the simultaneous action of buoyancy and temperature gradient is much smaller than each of them taken separately.

We have shown that the possibility exists of multiplicity in the stationary states of the *active* drop motion. On the one hand, for a given set of material parameters, buoyancy and external temperature and/or concentration gradients, up to *three* regimes of drop motion are available, one or two of them being unstable. On the other hand, the same external gradients can be appropriate to keep the drop at rest, i.e. levitating under any of *three* different levels of buoyancy. Such multiplicity of states is clearly due to the chemical reaction and thus using *active* drops could be observed in experiments.

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APPENDIX

Here we consider the case $|m-m_n| \cong 1$ $(n = 2, 3, \ldots)$ when the temperature gradient is constant far off the drop. Then with higher order modes $\xi_n = 0$ $(n = 2, 3, \ldots)$ in (53), the formulae (25), (26), (46), (47) may be rewritten as

$$u_{1r} = (\mathbf{u}_\infty \cdot \mathbf{e}_r)\left(1-\frac{1}{r^3}\right)+\tfrac{1}{3}(\rho-1)(\boldsymbol{\eta}\cdot\mathbf{e}_r)\left(\frac{1}{r}-\frac{1}{r^3}\right), \quad (A1)$$

$$u_{2r} = \tfrac{3}{2}(\mathbf{u}_\infty \cdot \mathbf{e}_r)(r^2-1)+\tfrac{1}{3}(\rho-1)(\boldsymbol{\eta}\cdot\mathbf{e}_r)(r^2-1), \quad (A2)$$

$$c_1 = \frac{q}{2}|\mathbf{u}_\infty|\left(1-\frac{q}{r}\right)+(\mathbf{u}_\infty\cdot\mathbf{e}_r)\left[-\frac{q}{2}\left(1+\frac{1}{2r^3}\right)+\frac{b_1'}{r^2}\right]$$
$$+\tfrac{1}{3}(\rho-1)(\boldsymbol{\eta}\cdot\mathbf{e}_r)\left[-\frac{q}{2}\left(\frac{1}{r}+\frac{1}{2r^3}\right)+\frac{b_1}{r^2}\right], \quad (A3)$$

$$\gamma_1 = \frac{q^2}{2\kappa}|\mathbf{u}_\infty|+a_1'(\mathbf{u}_\infty\cdot\mathbf{e}_r)+\tfrac{1}{3}a_1(\rho-1)(\boldsymbol{\eta}\cdot\mathbf{e}_r). \quad (A4)$$

Equations (A3), (A4) together with (30), (31), (35), (36) determine the concentration field.

Consider the next order terms in the series (30), (31). Note that for our purpose, on the one hand, it is enough to look for just the first order spherical harmonics component of the additional terms, and on the other hand, we are interested only in the term depending on buoyancy, say on $\boldsymbol{\eta}$, since the term depending on $\mathbf{u}_\infty$ only has been already taken into account in (69). Then, instead of (30), (31) we have

$$c = c_0+Pe\,c_1+Pe^2 X(r)\,\Omega_1(\theta,\varphi)+\ldots, \quad (A5)$$

$$\gamma = \gamma_0+Pe\,\gamma_1+Pe^2\,Y\,\Omega_1(\theta,\varphi)+\ldots \quad (A6)$$

(here '...' replaces the omitted terms, $\Omega_1(\theta, \varphi)$ is a spherical function of first order). Substituting (A1), (A5) and (A6) into (18)–(21) and using (35), (36), (A3) and (A4) we can derive the following problem for $X(r)$ and Y:

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{2}{r}\right)X\Omega_1 = \frac{q^2}{6}|\mathbf{u}_\infty|(\rho-1)\left(\frac{1}{r^3}-\frac{1}{r^5}\right)(\boldsymbol{\eta}\cdot\mathbf{e}_r), \quad (A7)$$

$$r\to\infty, \quad X\to 0, \quad (A8)$$

$$r = 1, \quad X = \alpha Y,$$

$$-2\delta Y\Omega_1+\frac{q^2}{3\kappa}|\mathbf{u}_\infty|(\boldsymbol{\rho}-\mathbf{1})(\boldsymbol{\eta}\cdot\mathbf{e}_r)+\frac{\partial X}{\partial r}\Omega_1-\kappa Y\Omega_1 = 0. \quad (A9)$$

Note that in principle the velocity field is also to be developed in series in *Pe*. As the problem is treated in the Stokes approximation, this can only result, firstly, in the corrections to the coefficients available in (A1) and (A2), and secondly, in the appearance of higher order harmonics. Nevertheless, since the velocity at infinity and the buoyancy have been entirely taken into account already, in (A1) and (A2), there are no corrections to the coefficients. As for the higher order harmonics, they can not influence (A7)–(A9).

The solution of (A7)–(A9) is

$$\Omega_1 = (\boldsymbol{\eta}\cdot\mathbf{e}_r), \quad (A.10)$$

$$X = -\frac{q^2}{12}|\mathbf{u}_\infty|(\rho-1)\left(\frac{1}{r}+\frac{1}{2r^3}\right)+\left[\alpha Y+\frac{q^2}{8}|\mathbf{u}_\infty|(\rho-1)\right]\frac{1}{r^2}, \quad (A11)$$

$$Y = \frac{q^2(\rho-1)(8-\kappa)}{24\kappa(2\delta+2\alpha+\kappa)}|\mathbf{u}_\infty|. \quad (A12)$$

Using (A1), (A2) and (A6) with (36), (A4), (A10) and (A12) in (16), for simplicity omitting the term $\Delta_s\xi$, multiplying by r and taking gradient brings to

$$3(4-\kappa)(m-m_1)\mathbf{u}_\infty+(8-\kappa)(m-m_2)(\rho-1)\boldsymbol{\eta}/3$$
$$+Pe\frac{(8-\kappa)\,m\,q\,(\rho-1)}{6}|\mathbf{u}_\infty|\boldsymbol{\eta} = 0$$

or in dimensional form to

$$3(4-\kappa)(m-m_1)\mathbf{U}_\infty+(8-\kappa)(m-m_2)(\rho_2-\rho_1)\frac{a^2\mathbf{g}}{3\eta_1}$$
$$+\frac{(8-\kappa)mq(\rho_2-\rho_1)a^3}{6\eta_1 D}|\mathbf{U}_\infty|\mathbf{g} = 0. \quad (A13)$$

As the first terms of the l.h.s. of (69) and (A13) coincide, the third term of the l.h.s. of (A13) just gives the result (71).

To solve the problem for the complete concentration field the matching procedure is used (see Section 4 and ref. [4]). Nevertheless it is possible to prove that matching cannot affect the result of the calculation shown in this Appendix. Indeed, since the particular solution of equation (A7) does not necessarily contain terms behaving singularly at infinity, the influence of the outer region can become apparent only through the term of the form $r\Phi_1(\theta,\varphi)$ added to the r.h.s. of (A11), where $\Phi_1(\theta,\varphi)$ is a spherical function of first order to be determined by the outer solution and depends explicitly on buoyancy. Nevertheless, the appearance of such term in the Pe^2-approximation would mean that the term of order *Pe* in the outer solution depends on the buoyancy parameters. This is not the case, as one can see using equations (29), (34) and (39).