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Regular Article

On the autonomous motion of active drops or bubbles

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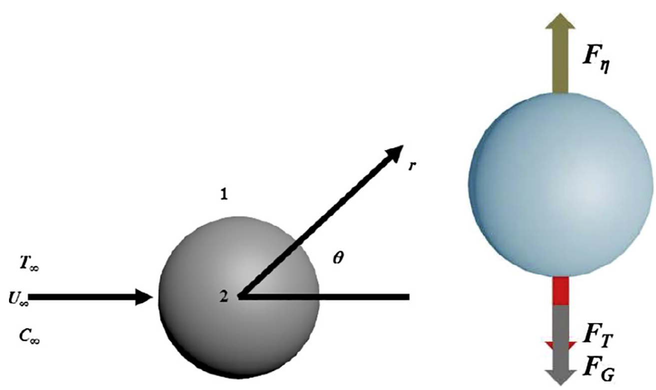
HIGHLIGHTS

- Creeping flows of active drops of radii in the millimeter range.
- Viscous diffusion transport compatible with fluid itself being of small viscosity.
- Low thermal Peclet number flows thus disregarding convected heat.
- Very high solute Peclet numbers highlighting both diffusion and convected solute.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermo-capillary stresses on the surface of a drop can be the result of a non-isothermal surface chemical conversion of a reactant dissolved in the host fluid. The strength of heat production (with e.g. absorption) on the surface is ruled by the diffusion of the reactant and depends on the state of motion of the drop. Such thermo-capillary stresses can provoke the motion of the drop or its motionless state in the presence of an external body force. If in the balance of forces, including indeed viscous drag, the net resultant force vanishes there is the possibility of autonomous motion with constant velocity of the drop. Focusing on drops with radii in the millimeter range provided here is a quantitative study of the possibility of such autonomous motion when the drop, considered as active unit, is seat of endo- or exo-thermic reactive processes that dominate its motion. The framework is restricted to Stokes flows in the hydrodynamics, negligible heat Peclet number while the solute Peclet number is considered very high. A boundary layer approximation is used in the description of reactant diffusion. Those processes eventually end up in the action being expressed by surface tension gradients and the Marangoni effect. Explicit expressions of the force acting on the drop and the velocity fields inside and outside the drop are provided. Some significant particular cases are discussed to illustrate the usefulness of the theory.

1. Introduction

Decades ago the study of the autonomous motion of drops and bubbles was a problem of mere academic interest or at most of

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interest to space scientists. The latter (from NASA, ESA and the former Soviet Space Agency) were interested due to its relevance for technological processing in platforms where the effective gravity was significantly reduced down to microgravity conditions [1–11]. Recently, however, there has been a renovated interest due to possibilities offered by autonomous motion, with or without a prescribed direction including drop levitation, like in cases where use is done of the spontaneous conversion of chemical energy into mechanical activity or there is an underlying laser-guiding process or there is an omnidirectional thermal gradient or a Leidenfrost-like effect comes into play. Drops have been shown to be natural candidates for use as micro-fluidic carriers, micro-swimmers or even as micro-fluidic reactors, when appropriate control of their formation and transport can be achieved. Drops containing smaller drops or bubbles (compound agents) are of practical interest in engineering (heat exchangers) or biology (mimicking eukaryotic cells). During the motion of compound drops heat and/or mass transport from one to the other may occur as the surface of the encapsulated drop may be active, e.g. a surfactant may be secreted from it. Aqueous drops in the range from a few pico-liters to sub-femto-liters can serve as reaction vessels for the chemical manipulation of single cells, individual sub-cellular organelles, and single molecules. Encapsulating, e.g., a cell into pico-liter drops permits not only to confine the cell but also reagents secreting molecules of desired reactivity. For instance, *Escherichia coli* (*E. coli*) can be encapsulated and manipulated inside a water-in-oil drop in microfluidic chips. On the other hand, it is possible for a micro-swimmer encaged in a drop to propel its viscous cage and co-swim with it. This set-up can be of interest for drug delivery under appropriate circumstances [12–29]; for a review accounting for some old and recent results see [30].

Worth highlighting are several recent publications that illustrate the timeliness of the interest and diversity of approaches in the study of self-propelled drop migration processes [25–28]. Dai et al. [27] have studied the ringlike migration of a drop of a rather viscous fluid immersed in a host liquid in which an omnidirectional radial temperature gradient (3C/cm) is set. This a typical case of a passive drop moving under the influence of thermo-capillary sresses. In another work [28] thermo-capillary migration is related to differential contact angle and its hysteresis. Zhang et al. [26] have performed a detailed study of the self-fueled behavior of drops of alloys of liquid-metals inside channels. The underlying chemo-capillary problem is the reaction of the drop with an aluminum piece that is not part of the container, which –as the authors emphasize- is a motor working just like a biomimetic mollusk since it closely resembles the nature by "eating" aluminum as "food". The work of Bormashenko et al. [25] serves as another example of the high research activity in self-propelling of drops and bubbles. They have studied the motion of aqueous etanol solution marbles. The drops were placed onto a water surface, and, though heat comes into play, the driving force for the motion is chemo-capillarity due to the evaporation of etanol and its condensation on the water surface. The latter process leads to cooling of the surface of the drop and slight heating of the water surface near the drop. Since the ethanol concentration decreases as times increases, the evaporation rate decreases, and therefore the Marangoni stress appears sustaining drop migration.

The geometry and some defining quantities of the problem are indicated in Fig. 1. Our aim is to obtain analytical explicit expressions of both the velocity field and the corresponding force acting on a drop. When, in the presence of various agents like thermo- and/or soluto-capillarity or other agent added to viscous drag, the total force is zero, provided the velocity does not vanish, we shall have the possibility of self-propulsion or autonomous motion. In view of the great difficulties of a general approach to the problem, as a first step we shall consider here only Stokes flows corresponding to the so-called creeping flow approximation. If the Reynolds number is low enough, fluid transport tends to be dominated by viscous diffusion, inertia plays no role and viscous drag is paramount. Note that highly viscous behavior is compatible with the fluid itself being of small viscosity. The consideration of creeping flows also leads us to restrict consideration to drops of radii in the millimeter range thus leaving for a future report the study of drops with radii down in the submillimeter range with velocities that could be large yet compatible with flows at a low Reynolds number as then the lowering in the space scale is the dominant feature. We also leave for a future report the case of flows with non-vanishing Reynolds numbers hence beyond Stokes flow approximation [30]. On the other hand, though further limitations are outlined in Section 2, where we also make explicit the

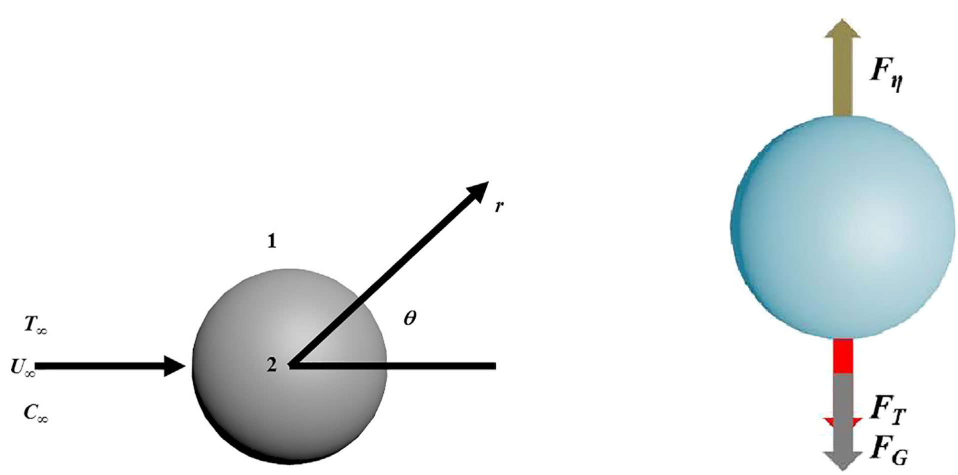

Fig. 1. Geometry and some defining quantities of the problem. Left panel: 1 and 2 refer to host and drop fluids, respectively. The values of quantities at infinity refer to background fluid and flow for a drop at rest. Thermo-capillary stresses would be considered along the surface of the drop leading to relative motion of the drop in such background. Alternatively, one can consider the background fluid at rest while the drop moves with opposite value of U_∞. Right panel: if we include forces like gravity (grey, F_G) or other body force, thermo-capillary force (red, F_T). and, indeed, viscous drag (brown, F_η) if the outcome of the balance of forces is such that the velocity vector is aligned antiparallel (opposite sign) with the net resultant force we shall have thrust, otherwise we have augmented resistance. The former is expected to be consequence of, say, the thermo-capillarity (red, F_T). The balance $F_G + F_T = F_\eta$ (size of arrows is arbitrary) is what provides the condition of drop motion with constant velocity along the vertical aligned with F_G. If the latter does not enter then thermo-capillary stresses F_T compete only with viscous drag F_η. In the reference frame attached to the drop the flow velocity (vector) is directed aligned with the latter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

evolution equations, let us note that here we are mostly interested in the role of transport processes in the limits of low thermal Peclet numbers and very high solutal Peclet numbers. This is done in view of highlighting the role of both molecular diffusion and convective transport of solute/surfactant around the surface of a drop.

As in [26] $Pe_T \neq 0$ and $Pe_D = 0$ and, moreover, the shape of the drop changes from spherical to annular along the experiment we cannot relate it to our present work as here a constant spherical shape is assumed. In [28] the thermocapillary migration is related to contact angle hysteresis which is a process not considerd in the present work. In Zhang et al work [26] despite that the size of the drops is relatively large, 60 μL, the width of the channels is small relative to the drop's diameter, and hence the drops are ellipsoids with high aspect ratios, a situation also not considered in the present work. Two major ingredients make the work of Bormashenko et al. [25] not amenable to comparison with the theory developed in the present work. On the one hand, the volume of the drop decreases as time increases due to ethanol evaporation (notice that drops with up to 85% ethanol volumen fraction have been studied!), and, on the other hand, the drops do not remain spherical due to the Leidenfrost-like effect levitation driven Marangoni effect. The above mentioned disparities with the present work suggest directions of extension of our theory here to appropriately account for the various specific features of each of the experiments described in the just mentioned works.

Section 3 is devoted to the study of the velocity field and a recall of the universal expression of the force acting on the drop. In Sections 4 and 5 we analyze the mass and heat transfer problems, respectively. Using the results of the previous sections, Section 6 deals with the explicit expression of the velocity of the autonomous motion. In Section 7 we provide details of a particular albeit significant case to illustrate the possibilities offered by the more general results obtained in the previous sections. Finally, in Section 8 some concluding remarks illustrate the range of validity of our results hence outlining its limitations.

2. Approximate evolution equations and boundary conditions

Let V, P, T and C denote velocity, pressure, temperature and solute concentration, respectively. Let i = 1 correspond to the ambient, surrounding or otherwise denoted host liquid and i = 2 to the liquid forming the drop (alternatively, the gas in the bubble; for simplicity, however, in what follows we shall be referring only to drops). Let a, U, ν, χ and D denote radius of the drop, an appropriate velocity scale (like U_∞ in Fig. 1), kinematic viscosity, thermal diffusivity and mass diffusion coefficients, respectively. Then the groups $Re = aU/\nu$, $Pe_T = aU/\chi$, $Pe_D = aU/D$ define the Reynolds, thermal Peclet and solute Peclet numbers, respectively.

Let us consider the limit case $Re \ll 1$ (in fact we shall take $Re = 0$ corresponding to the Stokes flow which is a useful approximation for creeping motions in highly viscous surroundings or flows with quite small drops), $Pe_T \ll 1$ and $Pe_D \gg 1$ (that with $\chi > D$ permits taking $Pe_T = 0$ with Pe_D finite). Hence we shall be disregarding the role of convected heat while emphasizing the major role played by both molecular diffusion and convective transport of solute/surfactant around the surface of the drop. Then the following equations define the problem to be considered [8,9,22–25]

$$div\,\vec{V}_i = 0 \tag{1}$$

$$0 = -\frac{1}{\rho_1}\nabla p_i + \nu_i \Delta \vec{V}_i \tag{2}$$

$$0 = \Delta T_i \tag{3}$$

and

$$\left(\vec{V_1}\nabla\right)C = D\Delta C \tag{4}$$

with $divV = \frac{1}{r^2}\frac{\partial(r^2 V_r)}{\partial r} + \frac{1}{r sin\theta}\frac{\partial}{\partial\theta}(V_\theta sin\theta)$, $\nabla \equiv \vec{i}_r \frac{\partial}{\partial r} + \vec{i}_\theta \frac{\partial}{\partial\theta}$, and $\Delta \equiv \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}(sin\theta)\frac{\partial}{\partial\theta}$; $\vec{V}_i$ denotes a velocity vector for both i = 1, 2 with corresponding components V_r and V_θ.

These differential Eqs (1)–(4) obey the following boundary conditions:

in the center of the drop:

$$r = 0 : \vec{V}_2 < \infty,\ T_2 < \infty \tag{5}$$

far away from it:

$$r \to \infty : \vec{V}_1 \to \vec{U}_\infty, T_1 \to T_\infty,\ C \to C_\infty \tag{6}$$

and on the surface of the drop:

$$r = a : V_{r1} = V_{r2}, V_{\theta 1} = V_{\theta 2}, C = 0,\ T_1 = T_2 \tag{7}$$

$$\frac{p_2 - p_1}{2} = \eta_2\frac{\partial V_{r2}}{\partial r} - \eta_1\frac{\partial V_{r1}}{\partial r} + \frac{\sigma}{a} \tag{8}$$

$$\eta_1\left(\frac{\partial V_{\theta 1}}{\partial r} - \frac{V_{\theta 1}}{r}\right) - \eta_2\left(\frac{\partial V_{\theta 2}}{\partial r} - \frac{V_{\theta 2}}{r}\right) + \frac{1}{a}\frac{\partial\sigma}{\partial T}\frac{\partial T_1}{\partial\theta} = 0 \tag{9}$$

$$QD\frac{\partial C}{\partial r} + \lambda_1\frac{\partial T_1}{\partial r} - \lambda_2\frac{\partial T_2}{\partial r} = 0 \tag{10}$$

where ρ denotes density, $\eta = \rho\nu$ is the shear viscosity, σ denotes surface or interfacial tension and Q accounts for the strength of involved (released or otherwise) heat per unit mass of reactant.

3. Velocity field and universal expression of the force acting on the drop

In view of the above, having in mind the symmetry of the problem (Fig. 1), we can take

$$V_{ir} = \frac{1}{r^2 sin\theta}\frac{\partial\psi_i}{\partial\theta},\ V_{i\theta} = -\frac{1}{r sin\theta}\frac{\partial\psi_i}{\partial r} \tag{11}$$

thus defining the stream function ψ. Accordingly, the Eqs. (1) and (2) combine to

$$E^4\psi_i = 0, \tag{12}$$

with $E^2 = \frac{\partial^2}{\partial r^2} + \frac{1-\mu^2}{r^2}\frac{\partial^2}{\partial\mu^2}$ and $\mu = cos\theta$. Then at the surface of the drop we have $r = a$: $\psi_1 = \psi_2 = 0, \frac{\partial\psi_1}{\partial r} = \frac{\partial\psi_2}{\partial r}$ whereas at the center of the drop $r = 0$: $\psi_2/r^2 < \infty$

and far away from the drop $r \to \infty$, $\psi_1 \to r^2(1-\mu^2)/2$.

The solution of the problem given by Eq. (12) is

$$\psi_1 = \left(r^2 + Ar - \frac{A+1}{r}\right)\frac{1-\mu^2}{2},$$
$$\psi_2 = \left(A + \frac{3}{2}\right)(r^4 - r^2)\frac{1-\mu^2}{2} \tag{13}$$

Clearly, the free constant is to be determined using boundary condition defined by Eq. (9).

It is known [30–34] that in Stokes approximation the explicit expression of the force acting on the drop has the universal form

$$F = -4\pi\eta_1 aAU_\infty \tag{14}$$

The quantity A embraces the essence of the dynamics of the problem. Note that when F and U_∞ are parallel (same sign; note that U_∞ is equivalent to U) we have drag whereas if antiparallel (opposite sign) the expression (14) corresponds to thrust. This shows the significance of the sign of the quantity A. Let us now proceed to determine its value.

Making use of the boundary condition for tangential stresses on the drop surface (9) we have:

$$(2A+2+3\beta+2\beta A)sin\theta+\frac{2}{3}\frac{\sigma_T QC_\infty D}{\eta_1\lambda_1 U_\infty}\frac{\partial\varphi_1(a,\theta)}{\partial\theta}=0 \quad (15)$$

where $\beta\equiv\eta_2/\eta_1$, $\sigma_T\equiv(\partial\sigma/\partial T)$ and

$$\varphi_1(r,\theta)\equiv\frac{\lambda_1}{QDC_\infty}(T_1-T_\infty) \quad (16)$$

To complete the calculation, we need the temperature distribution on the drop. Hence to proceed further we must consider the overall energy balance at the surface of the drop. We have

$$\frac{\partial\varphi_1(a,\theta)}{\partial r}+\frac{\partial\Gamma(a,\theta)}{\partial r}=\delta\frac{\partial\varphi_2(a,\theta)}{\partial r} \quad (17)$$

where $\delta\equiv\lambda_2/\lambda_1$, T_∞, and C_∞ are as indicated in Fig. 1, and

$$\Gamma(r,\theta)\equiv\frac{C(r,\theta)}{C_\infty} \quad (18)$$

It remains to analyze the mass transfer problem.

4. Mass transfer problem

For universality in the argument we shall use now appropriate dimensionless quantities. Length is scaled with the radius of the drop, a. The velocity is scaled with U_∞ and time with a/U_∞. For temperature and solute concentration, we use as units T_∞ and C_∞, respectively. The stream functions are also made dimensionless using the above given scales. Thus, in view of Eq. (4) we can write for the rescaled dimensionless solute concentration Γ,

$$V_{1r}\frac{\partial\Gamma}{\partial r}+\frac{V_{1\theta}}{r}\frac{\partial\Gamma}{\partial\theta}=\frac{1}{Pe_D}\Delta\Gamma \quad (19)$$

Thus using the expressions of the velocity components in Eq. (11), it follows

$$Pe_D\left(\frac{1}{sin\theta}\frac{\partial\psi_1}{\partial\theta}\frac{\partial\Gamma}{\partial r}-\frac{1}{sin\theta}\frac{\partial\psi_1}{\partial r}\frac{\partial\Gamma}{\partial\theta}\right)=\frac{\partial}{\partial r}\left(r^2\frac{\partial\Gamma}{\partial r}\right)+\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\Gamma}{\partial\theta}\right) \quad (20)$$

Now recalling the assumption $Pe_D\gg 1$, the quantity $\varepsilon = 1/Pe_D^{1/2}\ll 1$ can be taken to advantage as a smallness parameter. In the vicinity of the surface of the drop we have $r=1+\varepsilon$, $\varepsilon=r-1<<1$, $r-1<<r$, and hence as i = 1 corresponds to the surrounding fluid we have the following useful approximation:

$$\psi_1=\left(r^2+Ar-\frac{A+1}{r}\right)\frac{1-\mu^2}{2}\rightarrow\psi_1\approx\frac{1}{2}(2A+3)\varepsilon sin^2\theta+O(\varepsilon^2) \quad (21)$$

In a thin layer near the surface of drop, appropriate boundary layer quantities can be introduced as follows

$$Y=\sqrt{Pe_T}(r-1)\approx 1,\ \psi=\frac{2A+3}{2}Ysin^2\theta,\ 1/\sqrt{Pe_T}<<1 \quad (22)$$

With such new variables we can write the equation of mass transfer in the boundary layer in the following approximate form

$$\left(\frac{\partial\psi}{\partial\theta}\right)_Y\left(\frac{\partial\Gamma}{\partial Y}\right)_\theta-\left(\frac{\partial\psi}{\partial Y}\right)_\theta\left(\frac{\partial\Gamma}{\partial\theta}\right)_Y=sin\theta\frac{\partial^2\Gamma}{\partial Y^2} \quad (23)$$

where now one has Y, θ, Ψ and Γ, as variables. It seems useful to make appeal to a boundary layer coordinate transformation $(Y,\theta)\rightarrow(\Psi,\theta)$ first introduced by von Mises [35,36]. Then Eq. (23) becomes

$$-\frac{\partial\Gamma}{\partial\theta}=\frac{(2A+3)sin^3\theta}{2}\frac{\partial^2\Gamma}{\partial\Psi^2} \quad (24)$$

Eq. (24) can be further simplified by yet another change of variables

$$\Psi\rightarrow\Psi,\theta\rightarrow\tau=\frac{1}{2(1+\beta)}\int_\theta^\pi sin^3xdx=\frac{(2A+3)}{2}\left[\frac{2}{3}+cos\theta-\frac{cos^3\theta}{3}\right] \quad (25)$$

Then Eq. (24) finally reduces to

$$\frac{\partial\Gamma}{\partial\tau}=\frac{\partial^2\Gamma}{\partial\Psi^2} \quad (26)$$

which is analogue to the unsteady Fourier heat (or Fick mass) diffusion equation. Taking into account the relation of new and old variables $\tau=0\rightarrow(\theta=\pi),\Psi=0\rightarrow(Y=0,r=1)$, $\Psi\rightarrow\infty\rightarrow(Y\rightarrow\infty,r\rightarrow\infty)$, the boundary conditions for Γ become $\Gamma(0,\Psi)=1$, $\Gamma(\tau,0)=0$ and $\Gamma(\tau,\infty)=1$.

The solution of Eq. (26) for the concentration Γ is:

$$\Gamma(\tau,\Psi)=erf\left(\frac{\Psi}{2\sqrt{\tau}}\right)\ with\ erf(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-z^2}dz \quad (28)$$

$$\Psi=\frac{2A+3}{2}Ysin^2\theta \quad (29)$$

$$\tau=\frac{(2A+3)}{2}\left[\frac{2}{3}+cos\theta-\frac{cos^3\theta}{3}\right] \quad (30)$$

and

$$\Gamma(r,\theta)=erf\left(\frac{3Pe_D(2A+3)}{8}\right)^{1/2}\frac{(r-1)(1-cos\theta)}{\sqrt{2-cos\theta}} \quad (31)$$

Then the gradient of concentration which determines the flux of reagent on the surface of the drop is

$$\left(\frac{\partial\Gamma}{\partial r}\right)_{r=1}=\left(\frac{3Pe_D(2A+3)}{2\pi}\right)^{1/2}\frac{(1-cos\theta)}{\sqrt{2-cos\theta}} \quad (32)$$

Now note that the difference between $Z(\theta)=\frac{(1-cos\theta)}{\sqrt{2-cos\theta}}$ and its approximation given by $F(\theta)=0.58(1-cos\theta)$, plotted in Fig. 2, shows that the difference between these two functions is quite small. Hence, replacing $Z(\theta)$ with $F(\theta)$ the relationship (32) becomes

$$\left(\frac{\partial\Gamma}{\partial r}\right)_{r=1}=0.4\sqrt{Pe_D(2A+3)}(1-cos\theta) \quad (33)$$

which is going to permit us a significant simplification in what follows.

In view of the above it seems clear that the function $\varphi_1(r,\theta)$ appearing in the Eq. (15) for A can be fixed.

5. Dimensionless temperature fields

When Pe_T vanishes, Eq. (3) reduce to

$$0=\Delta\varphi_1,\ 0=\Delta\varphi_2 \quad (34)$$

Then the axially symmetric solution for the dimensionless temperature fields using a two-term expansion approximation is

$$\varphi_1(r,\theta)=a_0+\frac{b_0}{r}+\left(a_1r+\frac{b_1}{r^2}\right)cos\theta \quad (35a)$$

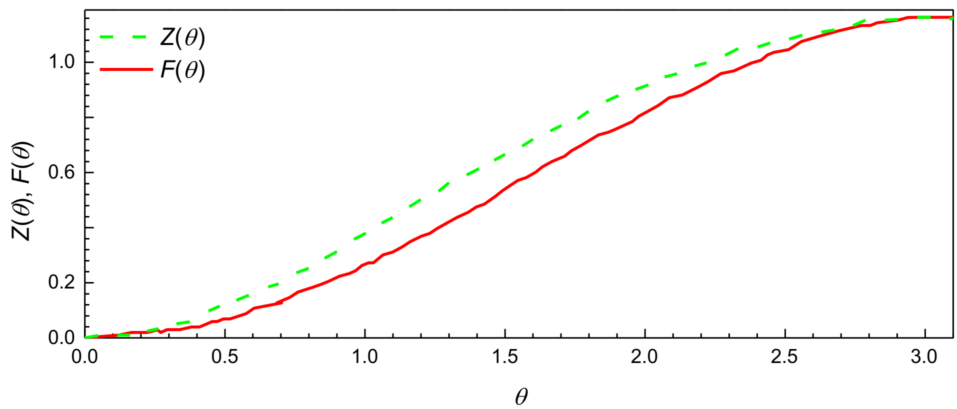

Fig. 2. $Z(\theta) = \frac{(1-cos\theta)}{\sqrt{2-cos\theta}}$ (green line) and $F(\theta) = 0.58(1 - cos\theta)$ (red line) against θ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and

$$\varphi_2(r,\theta) = c_0 + \frac{d_0}{r} + \left(c_1 r + \frac{d_1}{r^2}\right)cos\theta \tag{35b}$$

The boundary conditions at infinity and at the center of drop give $\varphi_1(\infty,\theta) = 0$, $\varphi_2(0,\theta) \neq 0$, $a_0 = 0$, $a_1 = 0$, $d_0 = 0$ and $d_1 = 0$. Therefore,

$$\varphi_1(r,\theta) = \frac{b_0}{r} + \frac{b_1}{r^2}cos\theta \tag{36a}$$

and

$$\varphi_2(r,\theta) = c_0 + c_1 r cos\theta \tag{36b}$$

Using the boundary condition for the temperature on the drop surface we find $r = 1 : \varphi_1(1,\theta) = \varphi_2(1,\theta) \Rightarrow c_0 = b_0, c_1 = b_1$. Then the dimensionless temperatures outside and inside of the drop are (36a) and

$$\varphi_2(r,\theta) = b_0 + b_1 r cos\theta \tag{36c}$$

After using the tangential boundary condition (9) we find

$$\varphi_1(r,\theta) = 0.4\sqrt{Pe_D(2A+3)}\left(\frac{1}{r} - \frac{1}{(2+\delta)r^2}cos\theta\right) \tag{37a}$$

and

$$\varphi_2(r,\theta) = 0.4\sqrt{Pe_D(2A+3)}\left(1 - \frac{r}{(2+\delta)}cos\theta\right) \tag{37b}$$

Thus the angle dependence of the temperature on the drop surface ($r = 1$) is given by the expression

$$\varphi_1(r,\theta) = 0.4\sqrt{Pe_D(2A+3)}\left(1 - \frac{1}{2+\delta}cos\theta\right) \tag{38}$$

6. Autonomous velocity.

The results so far obtained permit, using now the original dimensional quantities, to rewrite the Eq. (15) for the force factor A as

$$2A + 2 + 3\beta + 2\beta A + \frac{K}{\sqrt{U_\infty}}\sqrt{2A+3} = 0 \tag{39}$$

with $K = \frac{0.8}{3}\frac{\sigma_T Q C_\infty \sqrt{aD}}{(2+\delta)\eta_1\lambda_1}$.

Then the expression (14) for the force acting on the drop can finally be obtained in explicit form. As expected, in the absence of thermo-capillary forces $K = 0$ and $A = -(1 + 3\beta/2)/(1+\beta)$. Accordingly, in such a case the relationship (14) is the Rybczynski-Hadamard expression for the viscous resistance experienced by a passive drop (i = 2) in a surrounding fluid (i = 1). Thus for a passive drop, A is in the interval $-3/2 < A < -1$. The former limit value corresponds to $\beta \to \infty$ which is the case of a solid sphere with $F = -6\pi\eta_1 aU$, which is Stokes law, whereas for $\beta = 0$ we have the case of an empty bubble with $F = -4\pi\eta_1 aU$. For an active drop the range of values of A may, in principle, extend beyond the above given extreme limits for a passive drop. When $-1 < A$, the resistance force is lower than the corresponding Rybczynski-Hadamard expression. At $A = 0$, the resistance force is totally compensated by the force arising from the source of activity of the drop. Hence, the drop can move autonomously in the absence of any external force. The case $A < -3/2$ deserves a particular comment. While for $A > -3/2$ in the above mentioned range the Stokes flow only changes in the actual value of the velocity for a given value of A, there is no qualitative change in its structure. However, when $A < -3/2$, the flow around the drop experiences a drastic change. A closed axially symmetrical zone of finite thickness with a closed circulation flow appears near the surface of the drop. This creates a velocity field quite complex. For instance, along the axis of the flow two critical points appear ahead and behind the drop. Accordingly, the structure of the streamlines does not permit the use of the above introduced boundary layer approximation.

As earlier said, the autonomous motion is the free motion of a drop when thermo-capillary and viscous forces compensate each other. Therefore, one has $F = 0$ albeit with constant velocity. With $A = 0$ we find that the expression of the autonomous velocity is

$$U_\infty = \frac{3K^2}{(2+3\beta)^2},\ U_\infty = 0.21\frac{\sigma_T^2 D a Q^2 C_\infty^2}{3(2+\delta)^2\lambda_1^2\eta_1^2(9\beta^2+12\beta+4)} \tag{40}$$

which shows its explicit dependence on the parameters of the problem.

As an illustration here follows values for a particular case ($U \equiv U_\infty$). With ε the smallness parameter characterizing diffusion and $\eta_1 = \eta_2 = 10^{-1}$ g/cm s, $C_\infty = 0.1$ g/cm^3, $D = 10^{-5}$cm^2/s, $Q = 0.5$ cal/g, $\sigma_T = 2.2\ 10^{-1}$ g/Ks^2, $\lambda_1 = 1.4\ 10^{-3}$ cal/cm s K, $\lambda_2 = 10^{-4}$ cal/cm s K, $\delta = 0.0714$, and $\beta = 1$, we obtain $U = 0.0122$ a/s (otherwise $U =$ 0.7 a/min). Hence for $a = 0.2$ cm, with $Re = 0.049 = 4.9\ 10^{-2}$, $Pe_T =$ 0.35 = 3.5 10^{-1}, and $Pe_D = 49$ (hence $Pe_D \gg Pe_T > Re$) and the smallness $\varepsilon = 1/{Pe_D}^{1/2} = 0.14$, the result is $U = 0.0024$ cm/s (otherwise, $U = 0.147$ cm/min).

Clearly, setting $A = 0$ in Eq. (39) is a direct way to find the autonomous velocity. Formally, we can consider A as a function of K in order to write the force as $F = -4\pi\lambda_1 a A(K) U$ (recall the equivalence of U and U_∞) from Eq. (39) we get

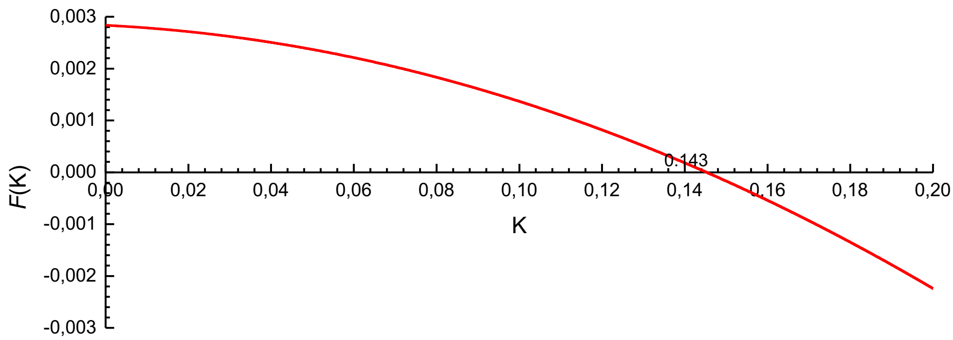

Fig. 3. Force $F(K) = A(K,U)$ against controllable parameters of the activity of the drop (σ_T and Q) embodied in K, for a given constant value of the velocity U of the drop. The value at $K = 0$ corresponds to the (Stokes)-Rybczynski-Hadamard law. The point $K = 0.143$ (hence $F = 0$) provides the velocity of the autonomous motion which here is $U = 0.002$. From this value of K down to $K = 0$ an active drop experiences a lower drag lower than the (Stokes)-Rybczynski-Hadamard law for a similar albeit passive drop. In the region of negative values of F there is thrust, self-propulsion due to the activity of the drop hence due to the Marangoni effect, as the sign of F is opposite to the sign of U in the universal relationship provided by Eq. (14) Noteworthy is that an active drop, with thermo-capillary forces, must always be in motion to be stable. As expected, in the case of free fall in the gravity field, in the range $0 < K < 0.143$, an active drop will have a velocity greater than an equivalent passive drop.

$$A = -\frac{2+3\beta}{2(1+\beta)} - \frac{K\left(\frac{-K}{\sqrt{U}} + \sqrt{\frac{K^2}{U} + 4 + 4\beta}\right)}{4\sqrt{U}(1+\beta)^2} \tag{41}$$

As $A = A(K,U)$ then when $A(K,U) = 0$ we, indeed, recover the autonomous velocity (40). Finally, as K is related to the values of both σ_T and Q we have the possibility of autonomous motion with velocity depending on these two parameters.

7. Example of dependence of the force on the characteristic parameters of the dynamics (σ_T and Q).

Take now the value of the velocity of the drop to be constant and (approximately) equal to $U = 0.002$ cm/s which corresponds to the case discussed in the preceding section for $K = 0.143$, β=1 and hence $F = 0$. Fig. 3 depicts the behavior of $F = \left(-\frac{2+3\beta}{2(1+\beta)} - \frac{K\left(\frac{-K}{\sqrt{U}} + \sqrt{\frac{K^2}{U}+4+4\beta}\right)}{4\sqrt{U}(1+\beta)^2}\right)U$ as a function of K for a given constant value of U. Thus the crossing point of the curve $F(K)$ with the abscissa corresponds to the autonomous motion of the drop, which is the free motion in the absence of external forces with, indeed, the value $U = 0.002$ for $K = 0.143$ and $F = 0$.

In the interval $K = 0$–0.143 the force acting to the drop is a resistance force. Going down in the value of K it increases from the zero value at $K = 0.143$, that corresponds to autonomous motion with total compensation of viscous and thermo-capillary stresses, up to the pure viscous Rybczynski-Hadamard value at $K = 0$, hence always lower than the classical value for a passive drop. For $K >$ 0.143 we have thrust as the activity and hence the Marangoni effect supports the constancy of translatory stationary motion of the drop as it is directed opposite (antiparallel) to the velocity. The force of thermo-capillary traction becomes bigger than the viscous drag and can only be compensated by some other external force opposite to the thermo-capillary one.

Finally, note that in case of non-zero Reynolds number the range where $K > 0.143$ would correspond to a greater value of the autonomous velocity. Nonlinearity would be replacing the need of an external force to sustain steady motion. Then the motion would be autonomous with a constant velocity different from the value corresponding to $K = 0.143$.

8. Concluding remarks

In this report we have considered the possibility of autonomous motion of active drops seat of endo- or exo-thermic reactive processes. The latter eventually end up in the action being expressed by surface tension gradients, hence thermo-capillary stresses and the Marangoni effect. Explicit expressions of the force acting on the drop and the velocity fields, inside and outside drops, have been provided with illustration of some significant particular cases. We have been mostly interested in the role of transport processes in the limits of low thermal Peclet numbers and very high solutal Peclet numbers with drops. This was done in view of highlighting the role of both molecular diffusion and convective transport of solute/surfactant around the surface of a drop. Accordingly, in the analysis presented here using a boundary layer approximation, the solute, mass diffusion, Peclet number, $Pe_D = aU/D$, has played a key role. The radius of the drop is the length scale and, as our approximation uses $Pe_D \gg 1$, it seems pertinent to recall realistic values of the parameters involved. One element that goes in the direction of the validity of the approximation of very high Peclet number is the smallness of the diffusion coefficient $D \sim 10^{-5}$ cm^2/s (say in the range $10^{-6} < D < 1\ 0^{-4}$). If the minimal velocity of an active drop is not less than one radius-space distance in hundred seconds and if $D = 10^{-5}$ cm^2/s then $Pe_D \gg 1$ implies $a > 1$ mm. Further, if the velocity of the drop, V, is expressed in units a/s then we have $Pe_D = a^2V/D$. Accordingly, for values of V in the range $10^{-4} < V < 10^{-3}$ a/s, this means that a drop traverses a distance equal to its radius in 10^2–10^3 s for, say, $D = 10^{-6}$ cm^2/s. Accordingly, the approximation $Pe_D \gg 1$ can be satisfied only for drops with radii $10^{-2} < a < 10^{-1}$ cm thus ruling out our boundary layer approximation. In subsequent work we shall try to overcome this limitation by proceeding to a higher-order approximation in the analysis of the autonomous motion of active drops with radii down into the submillimeter range. Noteworthy is that an active drop, with thermo-and/or soluto-capillary forces, must always be in motion to be stable. Similar phenomena, though not directly related to the present work, have been discussed in quite a number of recent theories and experiments [30] and details of several of them have been recalled in the introduction [25–29].

To conclude, let us remark that there are several mechanisms that can underly a driving force permitting conversion of energy into mechanical motion. The use of thermo-capillary forces is only one of them. Thus the specificity of such mechanisms in the realm of thermo- and chemo-capillarity offers approaches and results that are worth considering when dealing with an extensión of the theory here presented. Indeed, This is to be done elsewhere.

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