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Self-propulsion on liquid surfaces

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ABSTRACT

Surface tension gradients are at the origin of the self-motion and deformation of millimeter-sized floating objects. For (quasi-)non-deformable systems, like solids and gels, the motion-mode is mainly controlled by the shape of the object and by the way the surface active propellant is released on the surrounding surface. Two situations are reviewed. In the first one, the propellant container is the propelled object itself, while in the second case the propellant is placed in a reservoir embarked on a manufactured float. The properties and efficiency of these solid systems are examined and compared for different geometries. They are also compared with the intriguing properties of self-motile liquid lenses/drops which present several additional abilities (spontaneous deformation to adapt their shape to the selected motion-mode, presence of complex fluid flows outside and inside the drops, partial break-ups…). Three mechanisms leading to spontaneous motility have been identified in the literature. Among them two are more largely exemplified in the following as they involve a contribution of the "Marangoni driven spreading" effect, leading to velocities on the cm/s scale. The main theoretical tools usually used for describing the motion and deformation of such self-propelled systems are also reviewed.

1. Introduction

Far-from-equilibrium systems exhibit a wide variety of spatial and temporal patterns known as dissipative structures. The interplay between physico-chemical processes and mass or heat transfer may give rise to spatio-temporal structures induced by convective flows [1]. The conversion from chemical to mechanical energy is at the origin of a wide variety of dissipative structures such as regular convective cells, interfacial deformation or interfacial turbulences [2]. These flows, triggered by density or surface tension gradients [3] are crucial to many natural and man-made situations as for instance, in extraction processes, spreading of spills in aquifers, oil recovery, ocean and atmospheric flows and of course in chemical reactors at all scales.

When the size of the phases in contact is very different, this energy transduction may set the smaller phase into spontaneous motion [4]. The increased interest observed in the last ten years is also related to new kinds of possible applications in miniaturization techniques. In microfluidics, these phenomena recently appeared as a possible answer to problems related to fluid circulation and homogenization of microreactors [5]. The induced motility is also a key motivation in the domain of artificial cell design. Motion is one of the vital functions of microorganisms in search of new resources. The aim is to reproduce different propulsion modes observed in biological systems [6] in order to identify the possible energy sources and observe the shapes and trajectories spontaneously chosen to adapt to motility [7,8]. A crucial point of living systems however is autonomy. The object itself is at the origin of the modifications inducing motility or deformation.

In number of artificial systems, external constraints are at the origin of the movement [9]. It is the case, for instance, for the directional motion of liquid drops on solid surfaces. Motility can be induced by preprinting wettability gradients on the substrate, the difference in surface tension induced at the front and rear of the drop giving rise to translation motion. The drop submitted to such non-compensated Young forces can even overcome gravity forces and climb on an inclined surface [10]. However to reach autonomy the drop must be at the origin of the surface dissymmetry. Dos Santos and Ondarcuhu [11] obtained such behavior by dissolving a silanization precursor in the droplet. When deposited on a glass substrate and pushed in one direction, the heterogeneous reaction forms dense grafted monolayers that render the surface hydrophobic. However this surface modification is irreversible and a droplet cannot cross the hydrophobic trail left by itself or another drop.

Such behavior is in fact much more prevalent on liquid substrates. The modification of its surroundings by an object deposited on liquid can occur not only by a chemical reaction, but also by diffusion, spreading and solute mass transfer. Another advantage of the liquid substrate to sustain motion is the enhanced possibility of fast regeneration of the surface after the object has passed. Surface modifications are labile, and evaporation and solubilization can exert at the time scale of the movement allowing motion on a circular trail or periodical deformation.

In this article, we will focus on millimeter-sized systems showing self-induced motion or deformation, due to surface tension modification of their surroundings. The first systems we consider are solids

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and gels, which are (quasi-)non-deformable, but offer the possibility to be manufactured. The second part of this work is devoted to floating drops. Drops can deform and spontaneously adapt their shape, minimizing the free energy variation for a given motion regime. Two different mechanisms are at play for these systems. They both involve spreading of a surface active compound in the surrounding of the floating object (Fig. 1.a and b). In Section 4, we have gathered several very recent examples whose specificity lies on the fact that the object move toward lower surface tension zones. One of these systems gives us the opportunity to introduce a third mechanism (Fig. 1.c) which does not involve spreading of a surfactant on the surrounding surface. Although not completely relevant in regard to the topic of the present issue, we believe that it is important to mention this mechanism to provide a more complete picture of Marangoni driven self-motility. Before concluding this review, we recall also, in Section 5, the main theoretical tools needed for an analytical description of these self-propelled systems.

2. Self-motion of (quasi)-non-deformable systems: solids and gels

Self-motion under isothermal conditions induced by surface tension modification of a liquid surface requires three successive steps. The first one is the formation of concentration gradients of a surface active compound emitted by the object. Then, to observe motion, a symmetry breaking mechanism is required. It can be induced either by a local fluctuation, by gently pushing the float in the desired direction, by a fluctuation or by an anisotropy of the shape of the object itself. Once motion is initiated, the dissymmetry is maintained by the movement. Finally, motion is sustained only if out of equilibrium conditions are maintained, i.e. if there is a physico-chemical process restoring the free surface after the passage of the object.

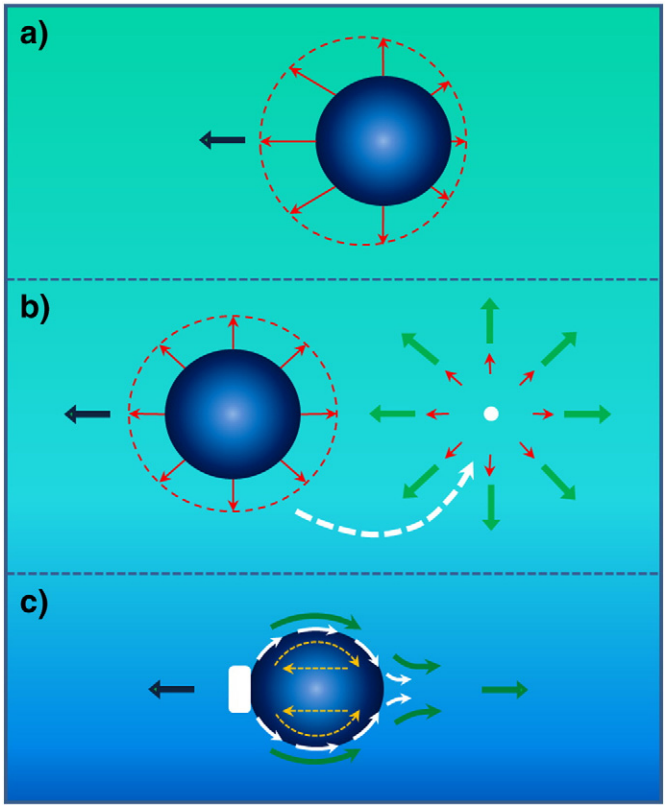

Fig. 1. Top-view schemes of three identified mechanisms of surface tension driven motility: a) surface tension imbalance around the floating system; b) distant surface liquid mixing pushing the object; c) inhomogeneous water/oil surface tension creating an outside flow which drives the drop forward. The red arrows represent surface tension forces. The green and yellow arrows indicate the fluid flows in the liquid substrate and inside the drop, respectively, while white arrows show the trajectory of surfactant molecules expulsed from the floating object.

A famous example of such behavior is undoubtedly the dance performed by a camphor grain on a water surface. Deposited on water a camphor grain dissolves and forms an hydrophobic layer in its surroundings. The extent of this layer is limited by sublimation creating surface tension gradients and a subsequent surface tension imbalance that drives the solid grain (Fig. 1.a and Eqs. (12) and (13) in Section 5). The extended investigations performed in Nakata's group have established the dependence of motion on several parameters as chemical structure of the camphor derivative, surface tension of the supporting liquid, shape of the cell and shape of the camphor scraping. The last parameter was shown to be determinant to control the dynamics of the moving object [12]. For instance a U-shaped fragment exhibits unidirectional motion (4 cm/s) while fragments with a shape of a comma show self-rotation (up to 360 rpm) on an orbital trajectory (Fig. 2.I.a). Clockwise or counterclockwise rotation is in this case determined by the chirality of the shaped solid. A higher concentration of the camphor layer at the concave area (rear) than at the convex one (front) explains this deterministic behavior. The resulting force induces linear motion of the axisymmetric U while, shifted from the center of gravity, it induces rotation of the comma (Eqs. (3) and (7) in Section 5).

The possibility to use a camphor disk as a motor to propel a small boat made of a polyester sheet has also been operated. Stuck at the stern of the boat, directional motion is observed for a few tens of minutes in a circular canal [13], while intermittent motion is obtained by simply changing the position of the camphor motor [14]. Placed at an extremity of the boat, it leads to continuous motion with a mean constant velocity of 0.5 cm/s, while placed at the center of a relatively long plastic plate, mode-switching, alternating between rest and fast translation (13 cm/s), is observed.

The contribution of the “Marangoni effect” to the displacement of camphor is still not clearly established. Although intensive convective cells are clearly observed below a camphor disk maintained at a fixed position [15], their magnitude decreases with an increase in the velocity of the camphor disk [14]. It is however interesting to point out that asymmetric convective cells, due to an irregular height of the water level, can accelerate or decelerate the disk, a larger depth resulting in an increased magnitude of convection.

In the following examples, the surface active propellants are water-soluble organic solvents. We will first consider systems for which the propellant container is the propelled object itself. The shape of the container is here decisive to determine the desired motion. In the second part, the propellant reservoir is embarked on manufactured floats from which the directional release of the spreading liquid is the motion-determining parameter. The shape, size and maximum velocity reached by the following examples are gathered in Fig. 2.

2.1. Self-propulsion of polymeric systems

Polymeric gels offer the advantage to be malleable, light, non-soluble and able to absorb high quantities of liquid. The gel swells, modifying the interaction between molecular chains. The idea to take advantage of these properties to design self-propelled objects appeared in the late nineties with the work of Osada's group [16]. They have used amphiphilic polymers resulting from the copolymerization of an acrylic monomer with a long chain alkyl side group. If a piece of the gel is swelled with tetrahydrofuran (THF) and then placed on water, it quickly forms a crystalline skin layer. The organic solvent is released from the gel by osmotic and hydrostatic pressure. Once ejected from the gel, it rises up onto the water surface because of its lower density and rapidly spreads on it because of the large difference in surface activity. The rapid and turbulent expansion of the organic solvent on the aqueous surface, also known as “liquid mixing”, imparts the reaction force to the gel that enters into motion (Fig. 1.b). The mode of motion is determined by whether or not the net reaction force passes through the mass center