Surface Tension Gradients as a Mechanism for Self-Propulsion

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Abstract: This TFG explores the physical mechanisms that enable certain insects to walk and move across the water surface. It focuses on *Microvelia*, an aquatic insect known for its propulsion method. *Microvelia*, secretes surfactants from its rear that generate a localized gradient in the water's surface tension pulling the insect forward and allowing it to move rapidly without active movements. This study analyses the fundamental thermodynamic and mechanical principles governing surface tension and the the role of surfactants in modifying it. Via dimensional analysis and the deduction of the equations of motion, this study demonstrates that the Marangoni force is the dominant propulsive mechanism for the *Microvelia* enabling the insect to reach peak speeds within milliseconds, highlighting the remarkable efficiency of the Marangoni Propulsion.
Keywords: Surface Tension, Stress Boundary Conditions, Surfactants, Dimensional Analysis, Marangoni Efect
SDGs: High-quality Education and Land Life

I. INTRODUCTION

Several animal species can move across the water's surface, employing various locomotion mechanisms. Considering the animal forces involved on an animal moving across the water, we can classify water-walking animals as [1]:

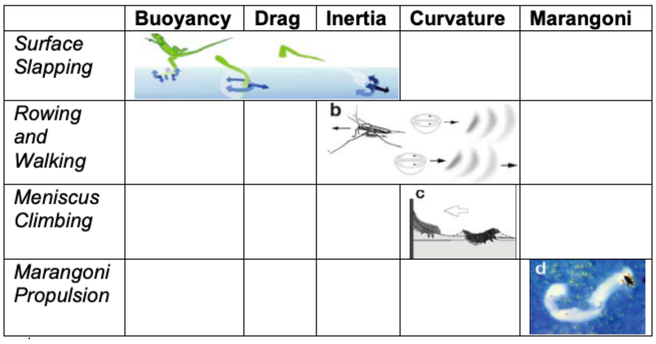

Figure 1: Dynamic classification of water walkers representing the forces involved as rows in each locomotion mechanism as columns. Adapted from [1].

- **Surface Slapping**
  The dominant propulsion forces in this case can be seen in the first row of Figure 1,
  - Buoyancy Force: It depends on the density of water, ρ, the gravitational acceleration, g, the immersion depth, h, and the contact area, A. It is an upward-acting force.
  - Inertia: It arises from the need to accelerate the water around the moving body. Inertia is determined by ρ, the volume of the animal, V, and the acceleration of the animal's foot during locomotion on the water surface, $\frac{dU}{dt}$, where U is the speed of the feet.
  - Pressure Drag Force: It is a force that opposes the motion of an object through a fluid and originates from the pressure difference created between the front and rear of the moving object. It is influenced by ρ, U and A.
- **Rowing and Walking**
  Consider the second row of Figure 1. The dominant propulsion forces are:
  - Pressure Drag Force.
  - Curvature Force: the meniscus's curvature around the legs plays a crucial role in propulsion. It is a function of A, the characteristic leg width, a, and the surface tension, γ.
- **Meniscus Climbing**
  See in the third row of figure 1. In this case, the relevant force is:
  - Curvature Force.
- **Marangoni Propulsion**
  Finally, as considered in the last row of Figure 1, the dominant propulsion force in this mechanism is:
  - Marangoni Force: It is determined by surface tension gradients, $\vec{\nabla}\gamma$.

The purpose of this TFG is to examine one of the propulsion mechanisms stated before: **Marangoni propulsion**. The TFG will specifically focus on the *Microvelia*, which is is a very small insect, whose dimensions can be estimated from the shape shown in Figure 2. It has the ability to self-propel by secreting a substance from its rear that generates surface tension gradients in the water. *Microvelia* typically inhabits stagnant water in Argentine and Uruguay [2]. It is an arthropod, which means it is an invertebrate characterized by a rigid exoskeleton and a segmented body.

Figure 2: Microvelia dorsal view with dimensions of 1,5mm in length and 0,8mm in width. The scale bar indicates 1mm. Taken form [2].

To understand the physics behind the propulsion mechanism of this insect, we will first establish definitions for surface tension and briefly talk about surfactants. Following this, we will perform a dimensional analysis of the problem to then derive the insect's equations of motion.

II. SURFACE TENSION

All insects, like *Microvelia*, that stand and move on the surface water do so thanks to surface tension.

Surface tension is the result of the attractive forces between the molecules of a fluid. These forces, which include Van der Waals forces and hydrogen bonding, cause the molecules to be drawn inward, bringing about cohesion in the liquid. Since at the surface around a given a fluid volume, there are no molecules outside, attractive forces are not balanced. As a reset, the molecules are pulled more strongly towards each other, resulting in a tendency to minimize their surface area. The extent of this energy minimization is determined by the nature of the intermolecular forces. [3]

From a thermodynamic point of view, increasing the area of an interface with surface tension γ by an infinitesimal area element $dA = Ld\vec{l}$ requires doing work.

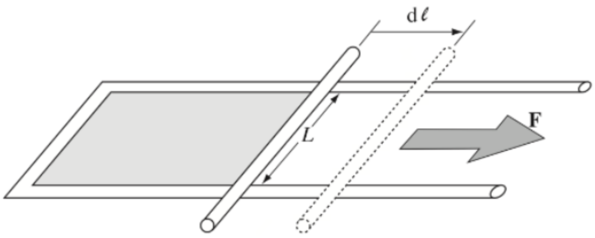

Figure 3: Representation of a surface area expansion dA due to a displacement $d\vec{l}$ aligned with the extended force $\vec{F}$. Image taken from [3].

$$dW_{rev} = \vec{F} \cdot d\vec{l} = \frac{F}{L} Ldl = \gamma dA \qquad (1)$$

where $\gamma = \frac{F}{L}$ is the surface tension between the fluid and air. It is the force per unit length required to increase the area. Note that increasing the area then requires doing work.

Once reversible work is obtained, we can identify the relevant intensive/extensive pair as (γ, A). Surfaces then are (γ, A, T, N) systems. Since there is an equation of state, three of the four variables are independent. If additionally $N = cte$, we only need two independent macroscopic degrees of freedom to finally characterize the thermodynamic state of the surface. Choosing them as (S, A), where S is the entropy, allows writing a Gibbs equation in terms of the energy:

$$dE = TdS + \gamma dA \quad (cte\ N) \qquad (2)$$

from where we find that

$$\left(\frac{\partial E}{\partial A}\right)_{S,N} = \gamma \qquad (3)$$

Equation (3) reveals that γ is the energy cost for increasing surface area at $S = cte$.

To connect to mechanics, we recall that stress is the contact force per unit of surface area. For a fluid at rest, the stress it exerts is known as hydrostatic pressure, being isotropic and normal to the fluid surface. When a fluid is in motion, an extra stress component emerges that is tangential to the fluid surface. Therefore, we must know the orientation of the surface element, $d\vec{A}$, determined by the normal vector $\hat{n}$, and the values of the three components of force per unit area, which together define a 3x3 tensor, *the stress tensor*, $[\sigma]$ [3]. The components of this tensor are defined by:

$$\sigma_{ij} = \frac{dF_i}{dA_j}; \qquad dF_i = \sum_j \sigma_{ij} dA_j \qquad (4)$$

The stress vector is defined by

$$\frac{d\vec{F}}{dA} = [\sigma] \cdot \hat{n}$$

In continuum mechanics, γ appears in the boundary conditions associated to the stress tensor. Force balance on a volume V enclosed by surface S with boundary C [4] results in:

$$\int_V \rho \frac{\partial \vec{u}}{\partial t} dV' = \int_V \vec{f} dV' + \int_S \left[[\sigma]^{(1)} \cdot \hat{n} - [\sigma]^{(2)} \cdot \hat{n}\right] dS' + \oint_C \gamma d\vec{l} \qquad (5)$$

where, $\frac{d}{dt}\int_V \rho\, \vec{u}\, dV' = \int_V \rho \frac{\partial \vec{u}}{\partial t} dV'$ is the inertial force associated with acceleration of the fluid. $\int_V \vec{f} dV'$ is the body force, $\int_S \left[[\sigma]^{(1)} \cdot \hat{n} - [\sigma]^{(2)} \cdot \hat{n}\right] dS'$ is the contact force exerted by both fluids to both sides of surface S, and $\oint_C \gamma d\vec{l}$ is the surface tension force.

To focus on the interface, we consider a very small volume. Then:

$$\int_S \left[[\sigma]^{(1)} \cdot \hat{n} - [\sigma]^{(2)} \cdot \hat{n}\right] dS' + \oint_C \gamma d\vec{l} = 0 \qquad (6)$$

Applying Stokes Theorem and vector identities, see Appendix A [4], allows expressing (6) as:

$$\oint_C \gamma d\overrightarrow{l} = \int_S \left[\overrightarrow{\nabla_S}\gamma - \gamma\hat{n}\left(\overrightarrow{\nabla_S}\cdot\hat{n}\right)\right] dS' \qquad (7)$$

where $\overrightarrow{\nabla_S} = \overrightarrow{\nabla} - \hat{n}\frac{\partial}{\partial n}$ is the tangential gradient operator and it appears because γ and $\hat{n}$ are only defined on the surface S. With this understanding, we use $\nabla_S \equiv \overrightarrow{\nabla}$ from now on. The surface force balance becomes:

$$\int_S \left[\left[\sigma^{(1)}\right]\cdot\hat{n} - \left[\sigma^{(2)}\right]\cdot\hat{n}\right] d\overrightarrow{S} = \int_S \left[\gamma\hat{n}\left(\overrightarrow{\nabla}\cdot\hat{n}\right) - \overrightarrow{\nabla}\gamma\right] dS' \qquad (8)$$

For arbitrary S, we then have the **Stress Balance**:

$$\left[\left[\sigma^{(1)}\right]\cdot\hat{n} - \left[\sigma^{(2)}\right]\cdot\hat{n}\right] = \gamma\hat{n}\left(\overrightarrow{\nabla}\cdot\hat{n}\right) - \overrightarrow{\nabla}\gamma \qquad (9)$$

The term $\gamma\hat{n}\left(\overrightarrow{\nabla}\cdot\hat{n}\right)$ is the normal curvature force per unit area, while $\overrightarrow{\nabla}\gamma$ is the tangential stress associated with gradients in γ [4].

The **Normal** component then is:

$$\left([\sigma]^{(2)}\cdot\hat{n}\right)\cdot\hat{n} - \left([\sigma]^{(1)}\cdot\hat{n}\right)\cdot\hat{n} = \gamma\hat{n}\left(\overrightarrow{\nabla}\cdot\hat{n}\right) = \gamma\left(\frac{1}{R} + \frac{1}{R'}\right) \qquad (10)$$

The **Tangential** component is:

$$\left[\left[\sigma^{(1)}\right]\cdot\hat{n} - \left[\sigma^{(2)}\right]\cdot\hat{n}\right]\cdot\hat{t} = -\overrightarrow{\nabla}\gamma \qquad (11)$$

In the case of the *Microvelia*, one of the two fluids involved is a gas, air. In this instance, we have $\left[\sigma^{(1)}\right]\cdot\hat{n} = 0$. Hence, equation (9) becomes:

$$\left(\left[\sigma^{(water)}\right]\cdot\hat{n}\right)\cdot\hat{t} = \overrightarrow{\nabla}\gamma \qquad (12)$$

If $\gamma = 0$, the Normal Stress Balance reduces to:

$$\left([\sigma]^{(2)}\cdot\hat{n}\right)\cdot\hat{n} = \left([\sigma]^{(1)}\cdot\hat{n}\right)\cdot\hat{n}, \qquad (13)$$

reflecting continuity of the normal stresses at the interface.

If $\overrightarrow{\nabla}\gamma = 0$, the Tangential Stress Balance becomes:

$$\left[\left[\sigma^{(1)}\right]\cdot\hat{n}\right]\cdot\hat{t} = \left[\left[\sigma^{(2)}\right]\cdot\hat{n}\right]\cdot\hat{t} \qquad (14)$$

showing continuity of the tangential stresses at the interface.

III. SURFACTANTS

Surfactants are amphiphilic molecules with a hydrophilic head that likes being in contact with water, and with a hydrophobic tail that dislikes being in contact with water. In bulk, surfactants for liquid crystal phase generally, liquid crystals, unlike isotropic liquids and gases, exhibit long-range order usually associated to solids. This order can be due to the orientation of the molecules, their positional arrangement or both. An example of these phases in the smetic, characterized by positional order in one direction, resulting in layers, and orientational order, such that the molecules align parallel to each other. In surfactant solution, the equivalent phase is the lamellar phase, characterized by bi-layers with polar heads exposed to the water [6]; see the right side of Figure 4. At lower concentration, the micelles form. These are aggregates of surfactants that organize to minimize energy, shielding their hydrophobic parts from water while keeping their hydrophilic parts in contact with it, as shown in the right side of Figure 4. Micelles form above a minimum concentration of amphiphilic molecules, known as the critical micelle concentration.

The presence of interfaces provides a natural place for surfactants to locate, with their polar part exposed to the polar liquid and the hydrophobic part exposed to the less polar liquid. This reduces the attractive forces between the fluid molecules that cause surface tension, thereby decreasing the surface tension and the energy cost to increase surface area [4]. Increasing surfactant concentration, decreases γ. Introducing concentration gradients thus induce gradients in surface tension, $\overrightarrow{\nabla}\gamma$.

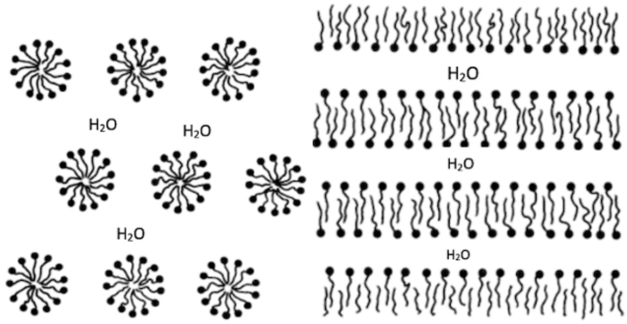

Figure 4: Structures formed by amphiphilic surfactant molecules in an aqueous solution. Right side shows the lamellar phase forming bi-layers separated by aqueous domains, where hydrophilic heads shield hydrophobic tails from water. Left side shows micelles, formed to isolate hydrophobic tails in their core. Image taken from [5].

IV. ANALYSIS OF HYDRODYNAMIC FORCES ENABLING MICROVELIA LOCOMOTION

A. Dimensional Analysis

Dimensional analysis allows grouping variables intervary in a given problem into dimensionless groups. Dimensional analysis is based on the Buckingham π theorem, which states that a physical relationship between a dimensional variable and n dimensional governing parameters can be rewritten as a relationship between a dimensionless parameter and m dimensionless products of the governing parameters so that $m = n - r$, with r being

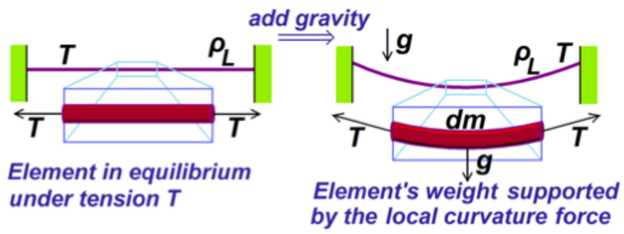

Figure 5: Magnitudes acting on element dm on a fluid surface, with ρ_L the fluid density. Surface tension force is represented as T and the gravitational force g [4].

the number of governing parameters with independent dimensions. Applying the Buckingham π theorem is useful to simplify the problem, as these dimensionless groups of parameters show us which combination of variables truly control the behavior of a system [7]. To perform a dimensional analysis in our problem, we need to identify the relevant physical variables and simplify the problem by obtaining dimensionless parameters. Therefore, in our case, considering the forces acting on the arthropod, the relevant physical variables we can in principle consider are the density of arthropod ρ_a, ρ, g, A, V, U, h, a, water viscosity μ, and γ.

As we consider our system as mechanical, our base magnitudes are mass (M), length (L) and time (T). Using the the Buckingham π Theorem we can rewrite the relationship between physical variables to obtain $m = 10 - 3 = 7$ dimensionless parameters combining all these variables in such a way that their units cancel out.

We naturally obtain the following groups:

- Reynolds: $Re = \frac{Ua}{\mu} \equiv \frac{intertia}{viscous}$
- Weber: $We = \frac{\rho U^2 a}{\gamma} \equiv \frac{intertia}{curvature}$
- Bound: $B_o = \frac{\rho g h}{\gamma / a} \equiv \frac{bouyancy}{curvature} \equiv \frac{weight}{curvature}$
- Froude: $Fr = \frac{U^2}{ga} \equiv \frac{intertia}{gravity}$
- Capillary: $Ca = \frac{\mu U}{\gamma} \equiv \frac{viscous}{curvature}$
- Marangoni: $Ma = \frac{\nabla \gamma}{\gamma / a} \equiv \frac{marangoni}{curvature}$
- Dimensionless length: $\lambda = \frac{a}{h} \equiv \frac{leg\ width}{immersion\ depth}$

We are going to study the case of *Microvelia*, an insect that moves without displacing its legs. Therefore, the velocity of its feet, $U \approx 0$, and

$$Re \approx 0; \quad We \approx 0; \quad Fr \approx 0; \quad Ca \approx 0$$

This reveals that the potentially relevant forces are the Curvature Force, the Buoyancy Force, the Weight and the Marangoni Force.

B. Equation of Motion

1. **Microvelia at Rest**
With the arthropod at rest, the only forces at play act normal to the surface and are the Arthropod Weight, mg, the Bouyancy force, and the Curvature force. Their sum needs to be zero:

$$\sum \vec{F} = 0 \tag{15}$$

Figure 5 illustrates that the curvature force, which is proportional to surface tension, acts tangentially to the surface and due to surface curvature it has an horizontal and vertical components. As seen in Figure 5, the horizontal component cancels out because it acts in both directions. The vertical component acts in the same direction as the weight but opposite to it. The buoyancy force is also an upward force. Therefore,

$$F_{bouyancy} + F_{curvature} - F_{weight} = 0 \tag{16}$$

$$0 = \rho g h A + \frac{\gamma A}{a} - \rho_a V g \tag{17}$$

Dividing by the weight, we obtain a dimensionless equation:

$$0 = \frac{\rho h A}{\rho_a V} + \frac{\gamma A}{a \rho_a V g} - 1 \tag{18}$$

Using some dimensionless parameters defined above,

$$0 = \frac{\rho h A}{\rho_a V} + \frac{1}{B_o} - 1 \tag{19}$$

Assuming the volume of immersion, hA, is significantly less than the Microvelia's volume, V, and given that their densities are expected to be of the same order of magnitude, we obtain:

$$B_o = 1 \tag{20}$$

Since the Bond number is a dimensionless quantity that represents the ratio of gravitational body forces to surface tension forces. For $B_o \approx 1$, both forces balance each other. Therefore, in our problem this means that the gravitational forces acting on *Microvelia's* body are perfectly balanced by the surface tension forces supporting it. As a result, γ supports the weight of the insect.

2. **Moving Microvelia**
Dimensional analysis reveled that the forces governing the case of *Microvelia* on water are the Curvature force, the Buoyancy force, the Weight and the Marangoni force. In the tangent plane, we have:

$$m \frac{\partial \vec{v}}{\partial t} = \vec{F}_{Marangoni} = \vec{\nabla} \gamma A \tag{21}$$

with $\vec{v}$ the velocity of **Microvelia**. Dividing by the curvature force, $\frac{\gamma A}{a}$, we obtain a dimensionless equation:

$$\frac{a}{\gamma A} m \frac{\partial v}{\partial t} = \frac{\left|\vec{\nabla}\gamma\right|}{\gamma / a} = Ma; \qquad \frac{\partial \vec{v}}{\partial t} = \frac{\gamma A}{am} Ma \tag{22}$$

We conclude that acceleration is governed by the Marangoni number, and given the Marangoni number's dependence on surface tension gradients, $\vec{\nabla}\gamma$, the insect acceleration is consequently also determined by these gradients.

In reference [1], the authors present several examples of insects that use this type of propulsion. Among them is Microvelia which is discussed in studies by Schildknecht regarding the surfactant secreted by the insect [1]. The type of surfactants secreted can reduce the surface tension from 72 to 49 dynes/cm. *Microvelia's* length is $d = 1,5mm$, see Figure 2. Since surface tension gradients are generated along the length of the insect, we estimate:

$$|\vec{\nabla}\gamma| \sim \left|\frac{\Delta\gamma}{d}\right| = \left|\frac{4,9\cdot 10^{-2} - 7,2\cdot 10^{-2}\ N/m}{1,5\cdot 10^{-3} m}\right| \approx 15\ N/m^2 \tag{23}$$

To obtain *Microvelia's* acceleration, we calculate the contact as from $A \approx 1,5\ mm \cdot 0,8\ mm = 1,2\ mm^2$, using the information given in Figure 2. Assuming $\rho_a \approx \rho = 10^6\ g/m^3$ and that the insect height visually estimated from Figure 2 is $\zeta \approx 0,4mm$, we obtain *Microvelia's* mass:

$$m \approx \rho A \zeta \approx 10^6 g/m^3 \cdot 1,2 \cdot 10^{-6} m^2 \cdot 4 \cdot 10^{-4} m = 4,8 \cdot 10^{-4} g$$

Therefore,

$$\left|\frac{\partial \vec{v}}{\partial t}\right| = \frac{|\vec{\nabla}\gamma| A}{m} = \frac{15 N/m^2\ \cdot 1,2\cdot 10^{-6} m^2}{4,8\cdot 10^{-7} kg} \approx 40\ m/s^2 \tag{24}$$

From here, knowing that *Microvelia's* peak speed during Marangoni propulsion is $v_{max} \approx 17cm/s$, we can estimate the time required for *Microvelia* to reach its maximum speed:

$$t = \frac{v_{max}}{|\partial v / \partial t|} = \frac{0,17\ m/s}{40\ m/s^2} \approx 4,5\cdot 10^{-3} s \tag{25}$$

This gradient generates a powerful propulsive force propelling the arthropod forward very quickly. This impressive acceleration is used by the insect, primarily, for rapid escape from predators.

V. CONCLUSIONS

Dimensional analysis allows concluding that the *Microvelia's* dominant propulsion force is the Marangoni force. *Microvelia's* self-propulsion is given by the strategic secretion of a surfactant from its rear. This surfactant locally reduces the surface tension of water, creating a surface tension gradient. This gradient generates the propulsive Marangoni force allowing the insect to move across the water's surface from lower gradients to higher gradients.

Our findings indicate that the surface tension gradient created by the surfactant secretion by a *Microvelia* is $|\vec{\nabla}\gamma| \approx 15 N/m^2$ resulting in an acceleration of $40 m/s^2$ that accelerates the insect from rest to $v_{max} = 0,17 m/s$ in $4,5\cdot 10^{-3} s$. The calculated values attest to the highly effective nature of the Marangoni propulsion to escape predators.

In addition, the finding that Bond number is 1 indicates that surface tension enables the insect to remain afloat.

Acknowledgments

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[1] John W. M. Bush, David L. Hu, "Walking on Water: Biolocomotion at the interface" (38, p.339-369, 2006).
[2] Melo, M. C., Dellapé, P. M. Gerromorpha, Nepomorpha and Leptopodomorpha, "(Hemiptera: Heteroptera) species from Argentina and Uruguay" [https://biodar.unlp.edu.ar/gerro-nepo-lepto/].
[3] Etienne Guyon, Jean-Pierre Hulin, Luc Petit, Catalin D. Mitescu, "Physical Hydrodynamics" (Oxford Academic, Oxford, 2015).
[4] John W. M. Bush, "18.357 Interfacial Phenomena", (MIT Mathematics, Massachusetts, 2010).
[5] J. F. Nagle, and H. Scott, "Biomembrane phase transitions" (31, p. 38–47, 1978).
[6] Alberto Fernandez-Nieves, Antonio Manuel Puertas, "Fluids, colloids and soft materials: an introduction to soft matter physics", (Wiley, New Jersey, 2016).
[7] G. Pardo Sanchez, F. Gonzalez Caballero, J.M. Bruque, "Mecanica" (Paraninfo, Madrid, 1974).

Surface Tension Gradients as a Mechanism for Self-Propulsion

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Resum: En aquest TFG s'han estudiat els mecanismes físics que permeten a determinats animals caminar sobre la superfície de l'aigua. L'estudi es centra, principalment, en l'autopropulsió de la Microvelia, que es tracta d'un insecte de dimensions molt petites i es desplaça sobre l'aigua gràcies a l'efecte Marangoni. Per fer-ho, secreta una substància, des del seu darrere, generant un gradient en la tensió superfícial de l'aigua que li permet desplaçar-se ràpidament sense moure les potes.
Per estudiar aquest fenòmen, s'han desenvolupat fonaments termodinàmics i mecànics de la tensió superficial i el paper dels surfactants en la modificació d'aquesta. Mitjançant un anàlisi dimensional y la deducció de les equacions de moviment de la Microvelia s'ha demostrat que la força principal que permet aquest mecanisme és la Forca Marangoni, que permet a l'insecte assolir velocitats màximes en pocs milisegons cosa que li permet escapar ràpidament dels seus predadors.
Paraules clau: Tensió superficial, Condicions de Contorn d'esforços, Surfactants, Anàlisi Dimensional, Efecte Marangoni.
ODSs: Aquest TFG està relacionat amb els Objectius de Desenvolupament Sostenible (SDGs) d'Educació de qualitat i Vida terrestre.

Objectius de Desenvolupament Sostenible (ODSs o SDGs)

1. Fi de la es desigualtats		10. Reducció de les desigualtats	
2. Fam zero		11. Ciutats i comunitats sostenibles	
3. Salut i benestar		12. Consum i producció responsables	
4. Educació de qualitat	X	13. Acció climàtica	
5. Igualtat de gènere		14. Vida submarina	
6. Aigua neta i sanejament		15. Vida terrestre	X
7. Energia neta i sostenible		16. Pau, justícia i institucions sòlides	
8. Treball digne i creixement econòmic		17. Aliança pels objectius	
9. Indústria, innovació, infraestructures			

A. Stokes' Theorem for Scalar Fields

[4] According to Stokes' Theorem,

$$\oint_C \vec{F} \cdot d\vec{l} = \int_S \hat{n} \cdot (\vec{\nabla} \times \vec{F})\, dS' \tag{A1}$$

for the closed contour C, the line element is defined as $d\vec{l} = \hat{m}\, d\ell$, with $\hat{m}$ being tangential to the surface. Then:

$$\oint_C \vec{F} \cdot \hat{m}\, d\ell = \int_S \hat{n} \cdot (\vec{\nabla} \times \vec{F})\, dS' \tag{A2}$$

Let's set $\vec{F} = \vec{f} \times \vec{b}$, for an arbitrary constant vector $\vec{b}$. The expression becomes:

$$\oint_C (\vec{f} \times \vec{b}) \cdot \hat{m}\, dl = \int_S \hat{n} \cdot (\vec{\nabla} \times (\vec{f} \times \vec{b}))\, dS' \tag{A3}$$

By applying standard vector identities, we that $(\vec{f} \times \vec{b}) \cdot \hat{m} = -\vec{b} \cdot (\vec{f} \times \hat{m})$ and also that:

$$\vec{\nabla} \times (\vec{f} \times \vec{b}) = \vec{f}(\vec{\nabla} \cdot \vec{b}) - \vec{b}(\vec{\nabla} \cdot \vec{f}) + \vec{b} \cdot \vec{\nabla} \vec{f} - \vec{f} \cdot \vec{\nabla} \vec{b} = \tag{A4}$$

$$= -\vec{b}(\vec{\nabla} \cdot \vec{f}) + \vec{b} \cdot \vec{\nabla} \vec{f}$$

given that $\vec{b}$ is a constant vector. This simplifies equation (A3) to:

$$\vec{b} \cdot \oint_C (\vec{f} \times \hat{m})\, d\ell = \vec{b} \cdot \int_S [\hat{n}(\vec{\nabla} \cdot \vec{f}) - (\vec{\nabla} \vec{f}) \cdot \hat{n}]\, dS \tag{A5}$$

Because $\vec{b}$ is arbitrary, this equality implies that

$$\oint_C (\vec{f} \times \hat{m})\, d\ell = \int_S [\hat{n}(\vec{\nabla} \cdot \vec{f}) - (\vec{\nabla} \vec{f}) \cdot \hat{n}]\, dS' \tag{A6}$$

By making the choice $\vec{f} = \gamma \hat{n}$ and using the relation $(\hat{n} \times \hat{m})dl = -\vec{dl}$, we get the following:

$$-\oint_C \gamma \vec{dl} = \int_S [\hat{n} \vec{\nabla} \cdot (\gamma \hat{n}) - \vec{\nabla}(\gamma \hat{n}) \cdot \hat{n}]\, dS' =$$

$$= \int_S [\hat{n} \vec{\nabla} \gamma \cdot \hat{n} + \gamma \hat{n}(\vec{\nabla} \cdot \hat{n}) - \vec{\nabla} \gamma \cdot \hat{n} - \gamma(\vec{\nabla} \hat{n}) \cdot \hat{n}]\, dS'$$

Finally, we observe that $\vec{\nabla}\gamma \cdot \hat{n} = 0$, as $\vec{\nabla}\gamma$ must be tangent to the surface S. We also see that $(\vec{\nabla}\hat{n}) \cdot \hat{n} = \frac{1}{2}\vec{\nabla}(\hat{n} \cdot \hat{n}) = \frac{1}{2}\vec{\nabla}(1) = 0$. These conditions lead to our desired result:

$$\oint_C \gamma d\vec{l} = \int_S \left[\vec{\nabla}\gamma - \gamma n \left(\vec{\nabla} \cdot n\right)\right] dS' \tag{A7}$$