18.357: Lecture 10

Marangoni Flows III:

Surfactants

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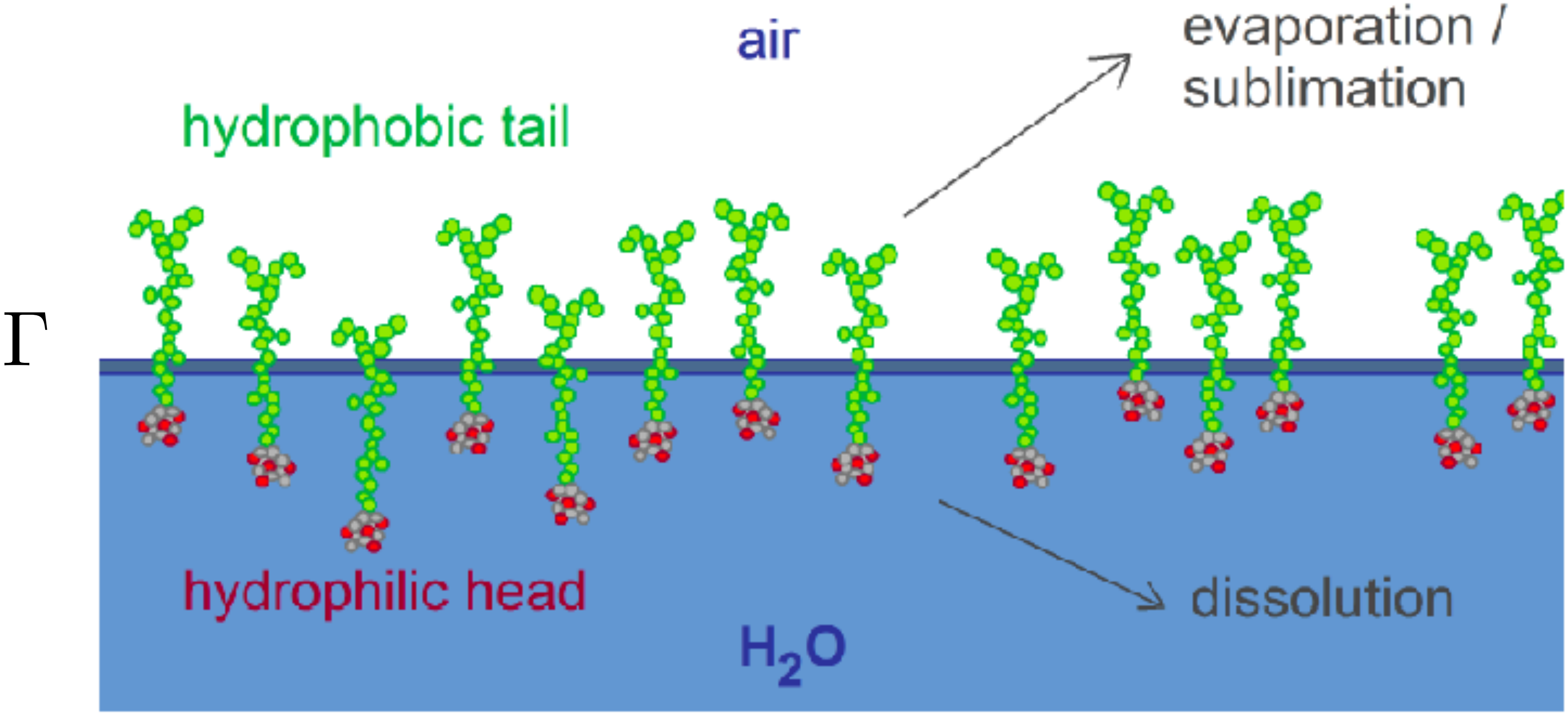
Surfactants: surface-active reagents

- molecules that find it energetically favourable to reside at an interface

  e.g. commercial detergents



- generally act to reduce σ locally, $\frac{d\sigma}{d\Gamma} < 0$: may induce Marangoni flows

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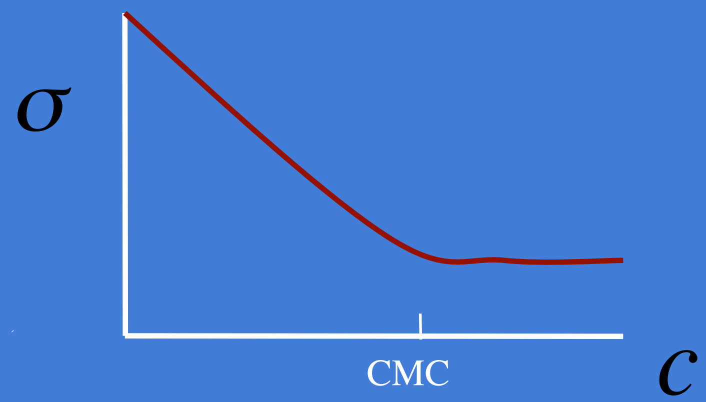
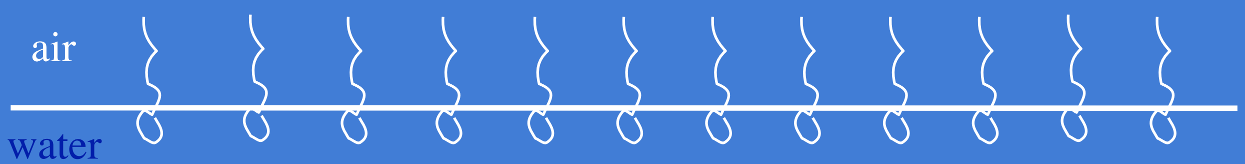
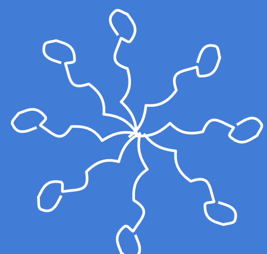


e.g. Soap boat

- beyond the CMC (critical micell concentration), there is no further dependence of σ on c

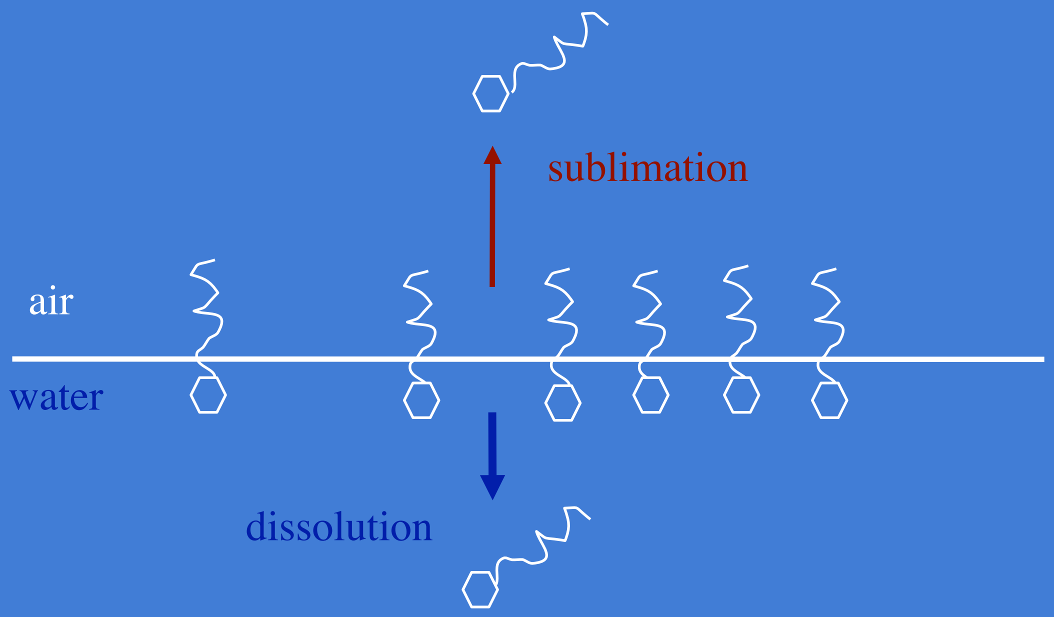




MICELL

micells shed by saturated interface, desorbed into bulk

Surfactant properties



Diffusivity

- prescribes the rate of diffusion, D_s , of a surfactant along an interface
- prescribes the rate of diffusion, D_b , of a surfactant within the bulk

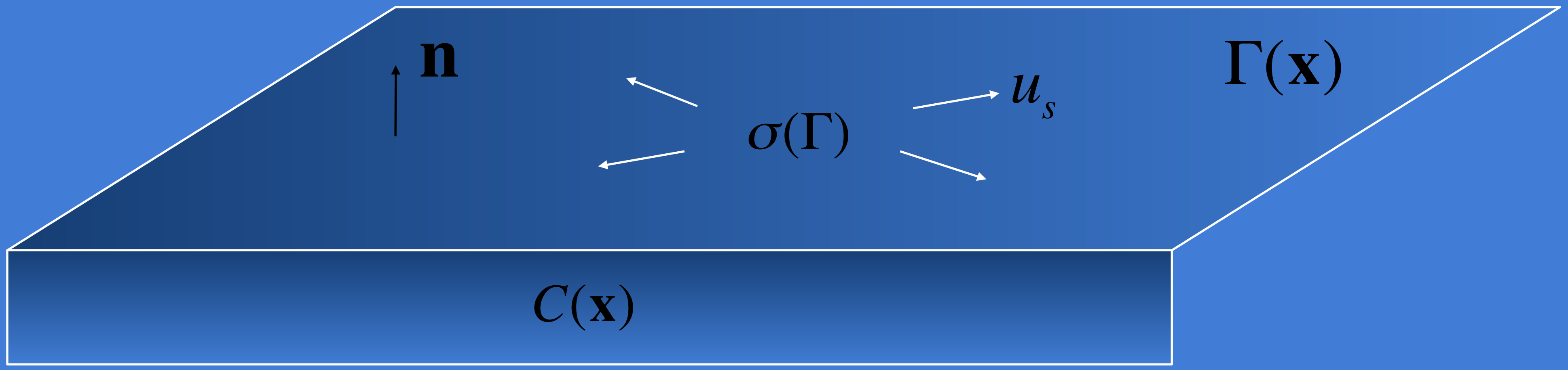
Solubility

- prescribes the ease with which surfactant passes from the surface to the bulk
- an insoluble surfactant cannot dissolve into the bulk, must remain on surface

Volatility

- prescribes the ease with which surfactant sublimates/evaporates from surface

The evolution of a surfactant-laden interface



Since $\sigma(\Gamma)$, N-S equations and BCs must be augmented by

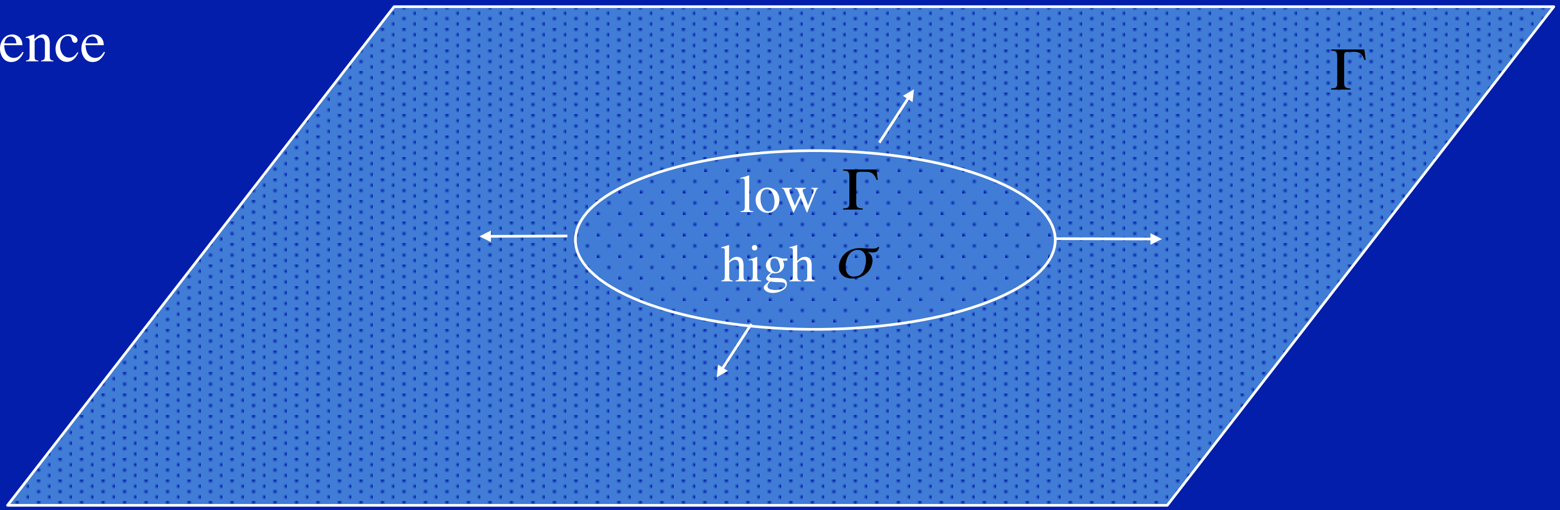
Surfactant evolution equation:

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot \left(\Gamma u_s\right) + \Gamma \left(\nabla_s \cdot n\right)\left(u \cdot n\right) = J(\Gamma, C) + D_s \nabla_s^2 \Gamma$$

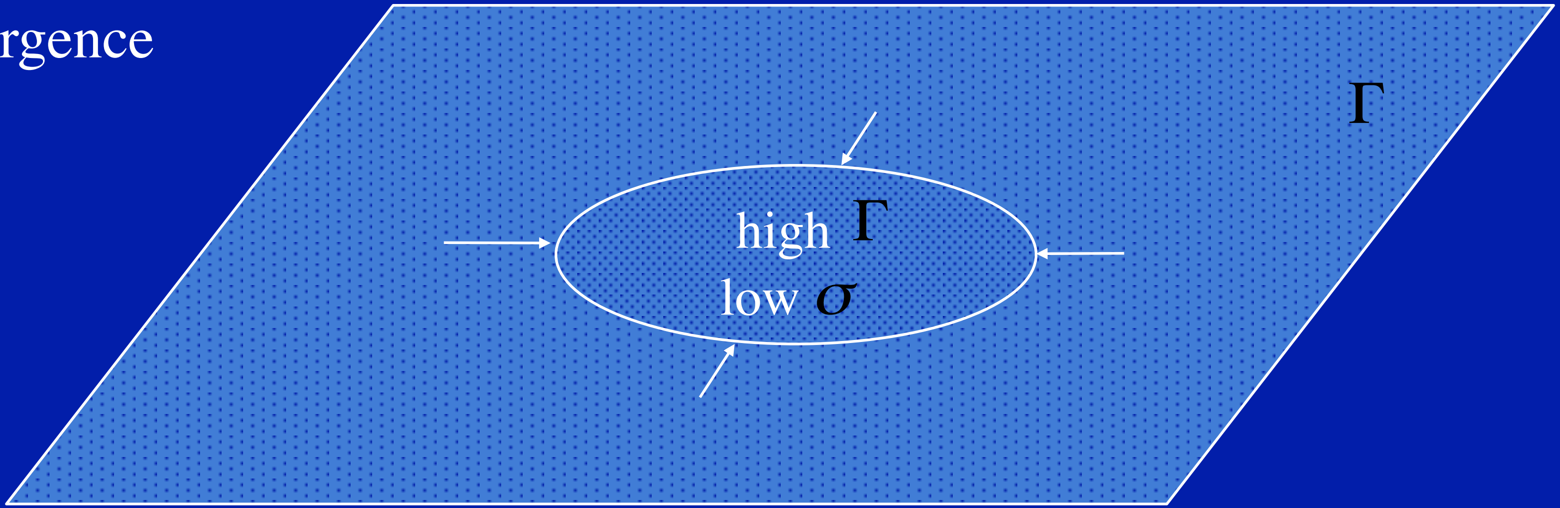
advection — surface expansion — exchange with bulk — surface diffusion

Surfactants: impart effective elasticity to contaminated interfaces through resisting flows with non-zero surface divergence

Surface divergence



Surface convergence



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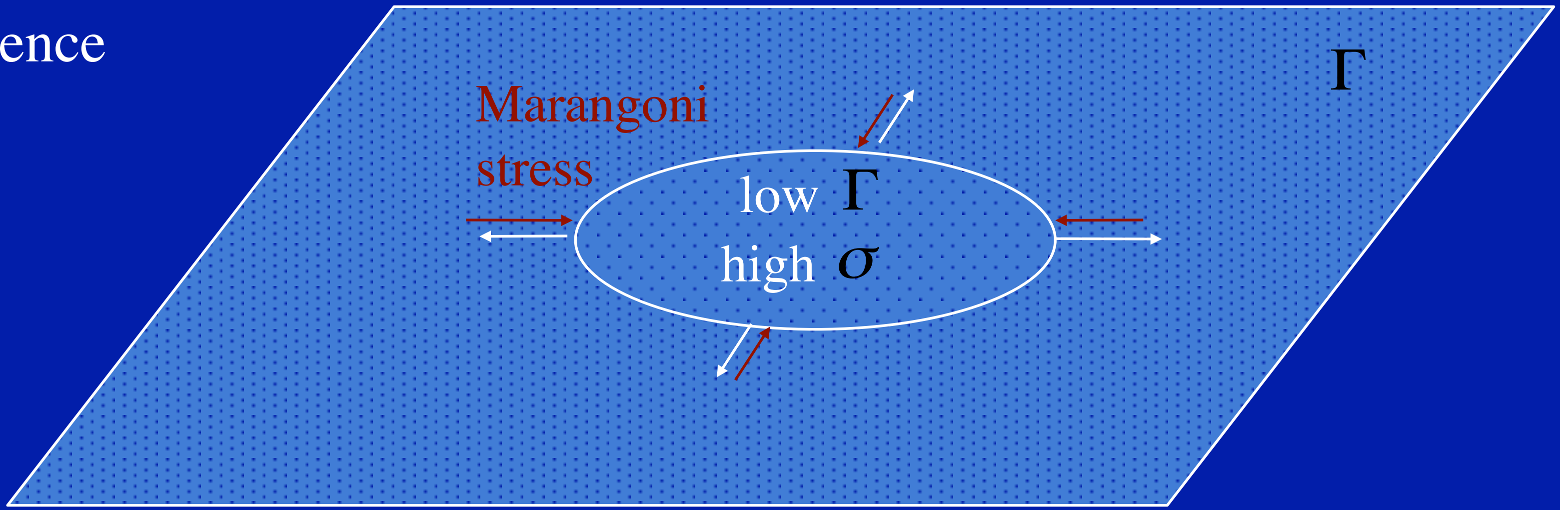
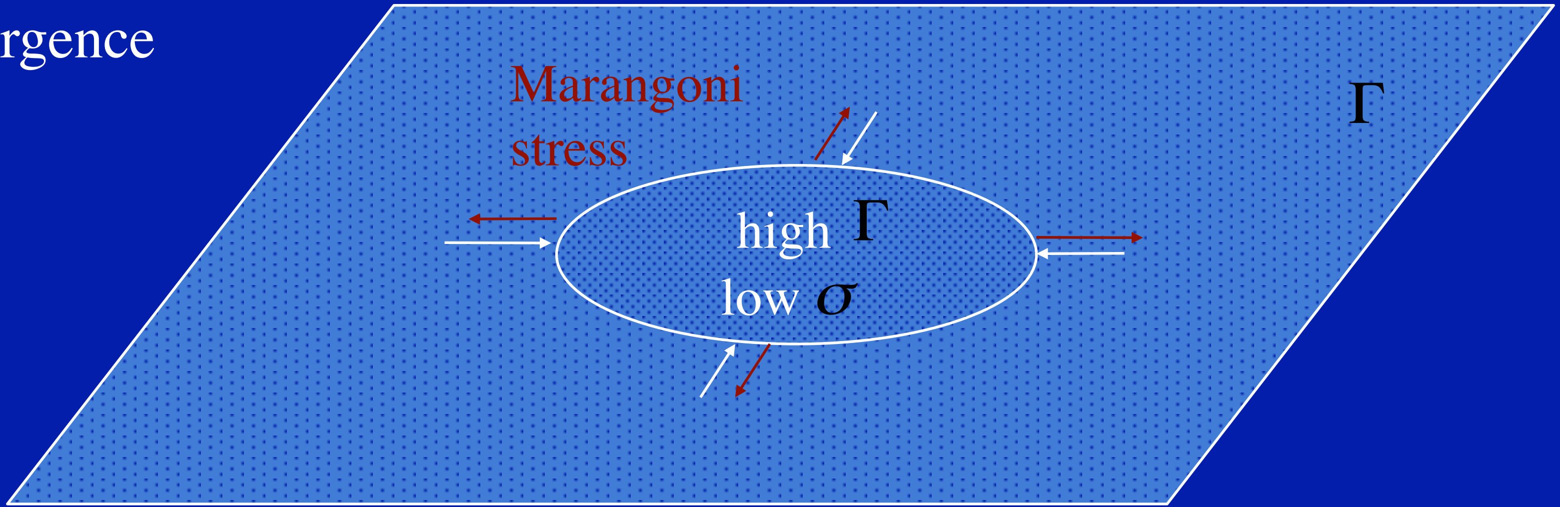
Surface divergence

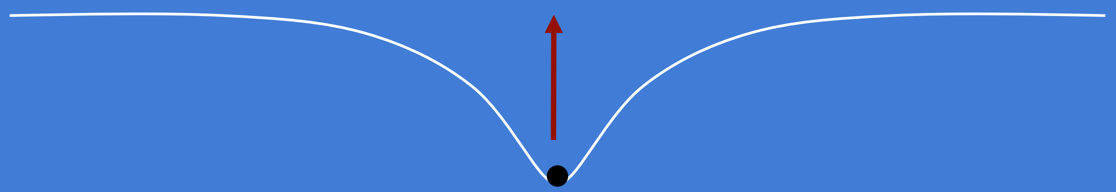


Surface convergence



Clean interface = `slippery trampoline’

- resists deformation through generation of normal curvature pressures
- cannot generate traction on the interface



Surfactant-laden interface = trampoline

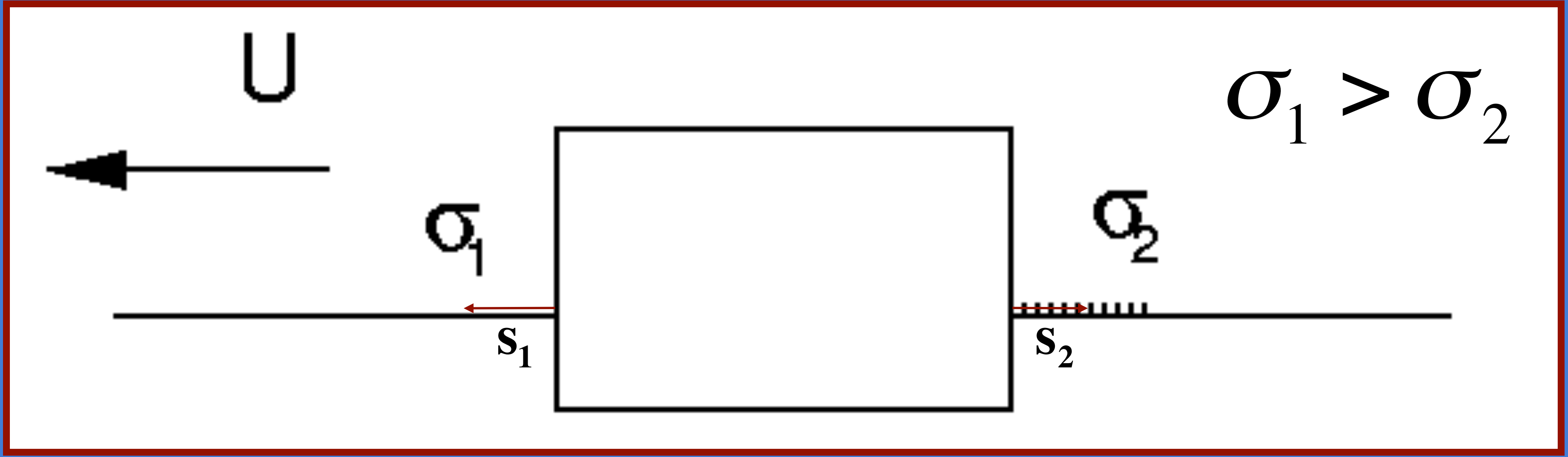
- resists surface deformation as does a clean interface
- can support tangential stresses via Marangoni elasticity

Surfactant-driven Marangoni propulsion

- lateral force may be generated by surface tension gradient

$$F = \int_C \sigma \, \mathbf{s} \, d\ell$$

integrate around contact line



e.g. water-walking insects, dispersal of pine needles

- motion driven by soap cannot be sustained in a closed contained
- motion may be sustained if driven by a volatile component (e.g. camphor)

Camphor boats

Nakata (2005)

Camphor boat races

Nakata (2006)

The cocktail boat: fueled by alcohol

Video: Lisa Burton

IOP Publishing Bioinspiration & Biomimetics
Bioinspir. Biomim. 8 (2013) 044003 (6pp) doi:10.1088/1748-3182/8/4/044003

COMMUNICATION

Biomimicry and the culinary arts

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Received 30 May 2013
Accepted for publication 5 September 2013
Published 4 October 2013
Online at stacks.iop.org/BB/8/044003

Abstract
We present the results of a recent collaboration between scientists, engineers and chefs. Two particular devices are developed, both inspired by natural phenomena reliant on surface tension. The cocktail boat is a drink accessory, a self-propelled edible boat powered by alcohol-induced surface tension gradients, whose propulsion mechanism is analogous to that employed by a class of water-walking insects. The floral pipette is a novel means of serving small volumes of fluid in an elegant fashion, an example of capillary origami modeled after a class of floating flowers. The biological inspiration and mechanics of these two devices are detailed, along with the process that led to their development and deployment.

(Some figures may appear in colour only in the online journal)

1. Introduction

"El gran llibre, sempre obert I que cal esforçar se a llegir, és el de la Naturalesa."[5]

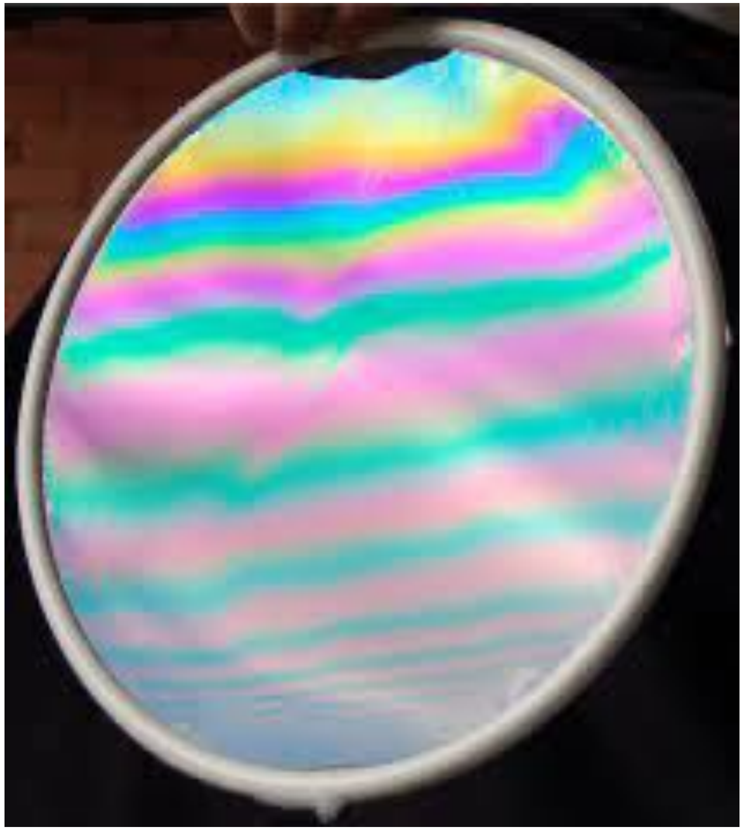
– Antoni Gaudi

dominate those of gravity for fluid systems small relative to the capillary length $\ell_c = \sqrt{\sigma/\rho g}$, where ρ represents the fluid density and g gravity. For air–water systems, the capillary length corresponds roughly to the size of a raindrop. Surface tension is thus an important player in the lives of

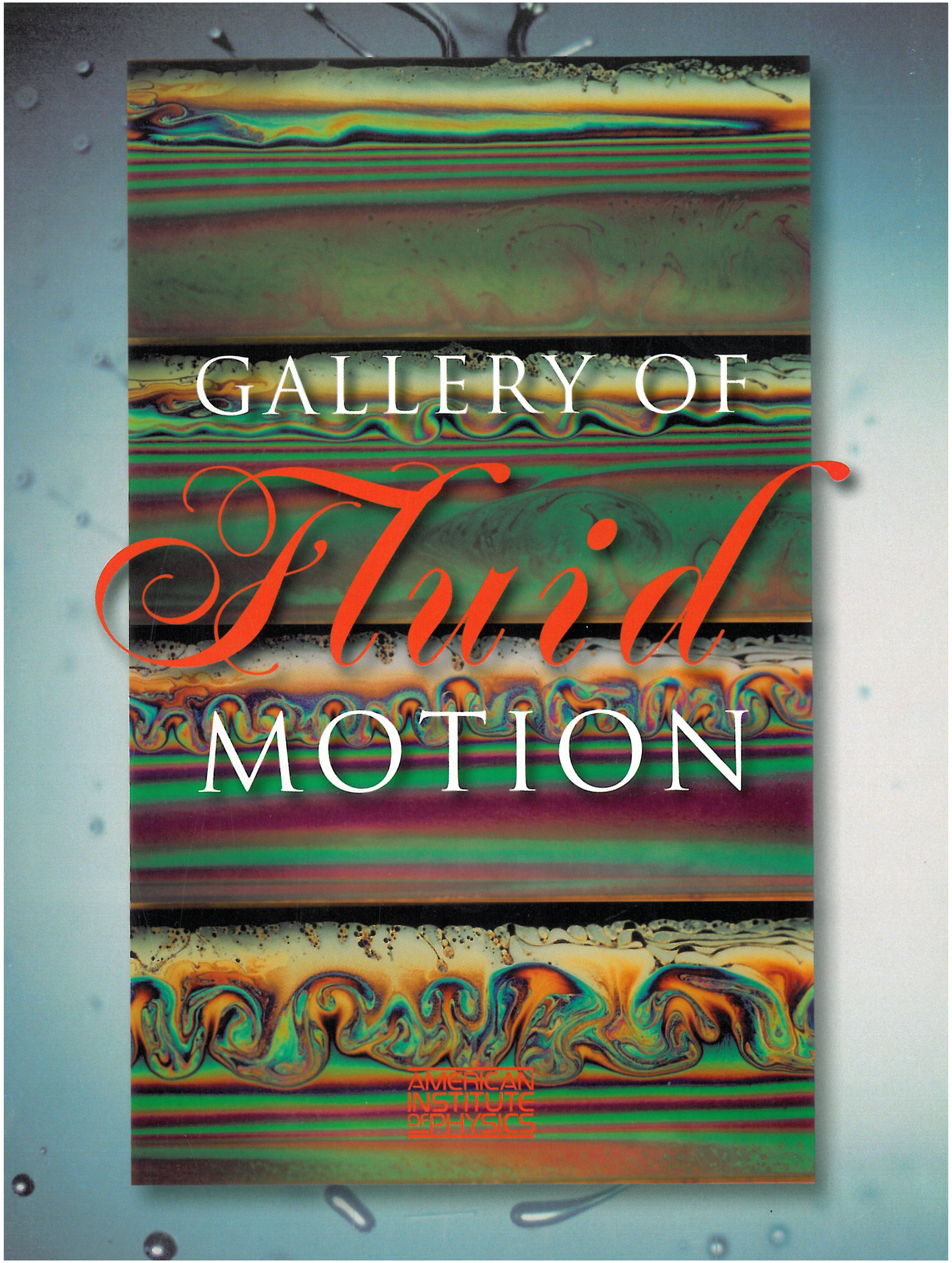
Soap films

- prevalent in art owing to their aesthetic appeal

Soap films



- color due to interference of light reflected from both sides of film
- film thickness comparable to wavelength of light

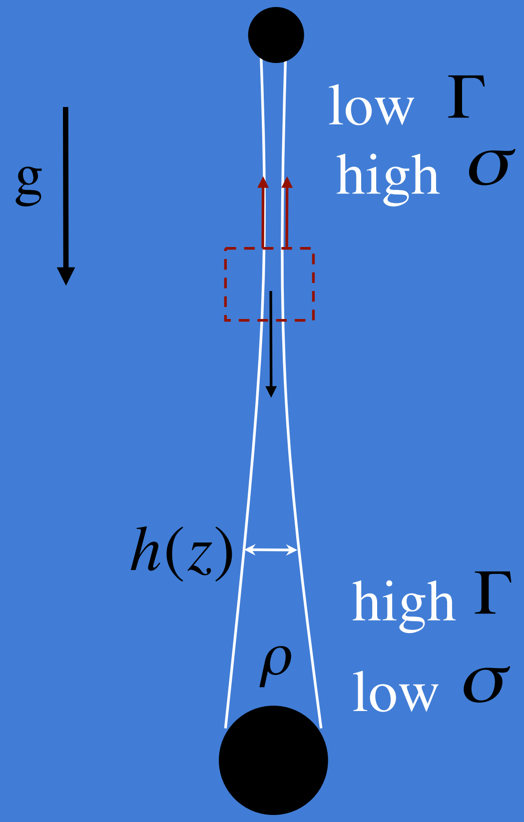


Soap films

- stabilized against rupture by presence of surfactants

Draining soap film

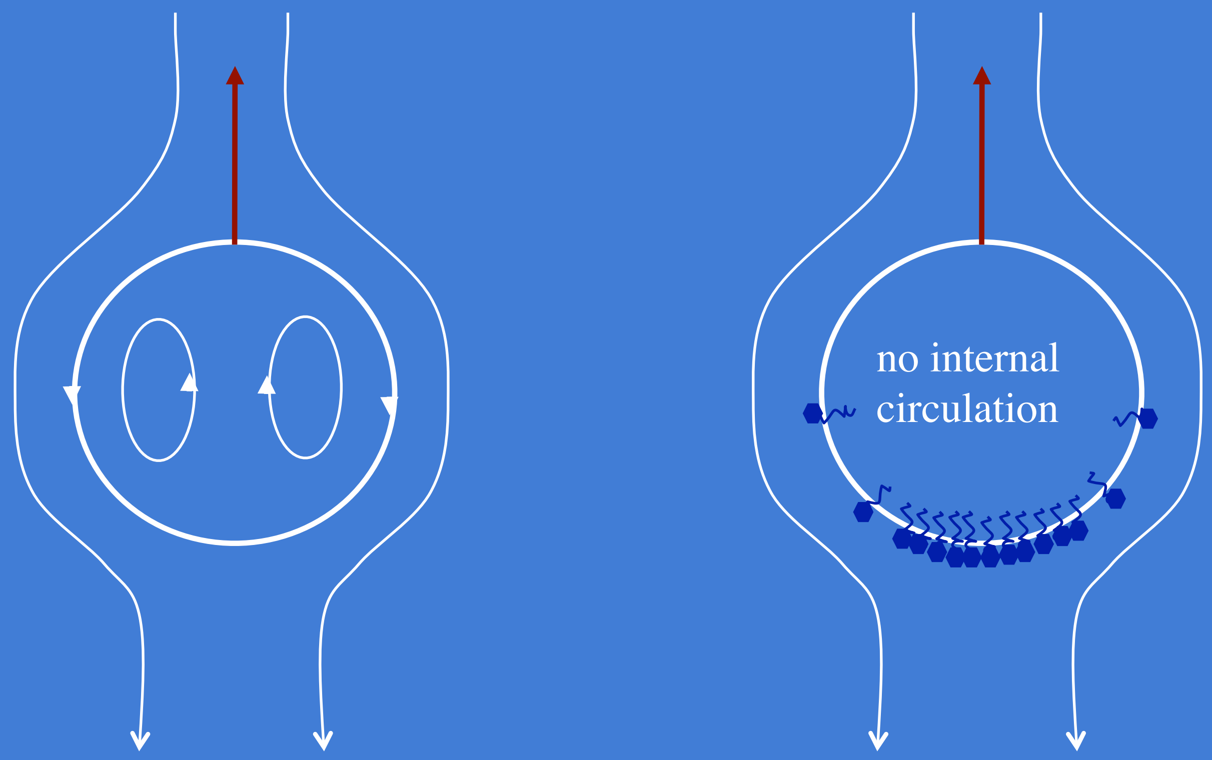
- weight of film supported by Marangoni stress



$$\rho\, g\, h(z) = 2\,\frac{d\sigma}{dz} = 2\,\frac{d\sigma}{d\Gamma}\,\frac{d\Gamma}{dz}$$

The influence of surfactant on bubbles and drops

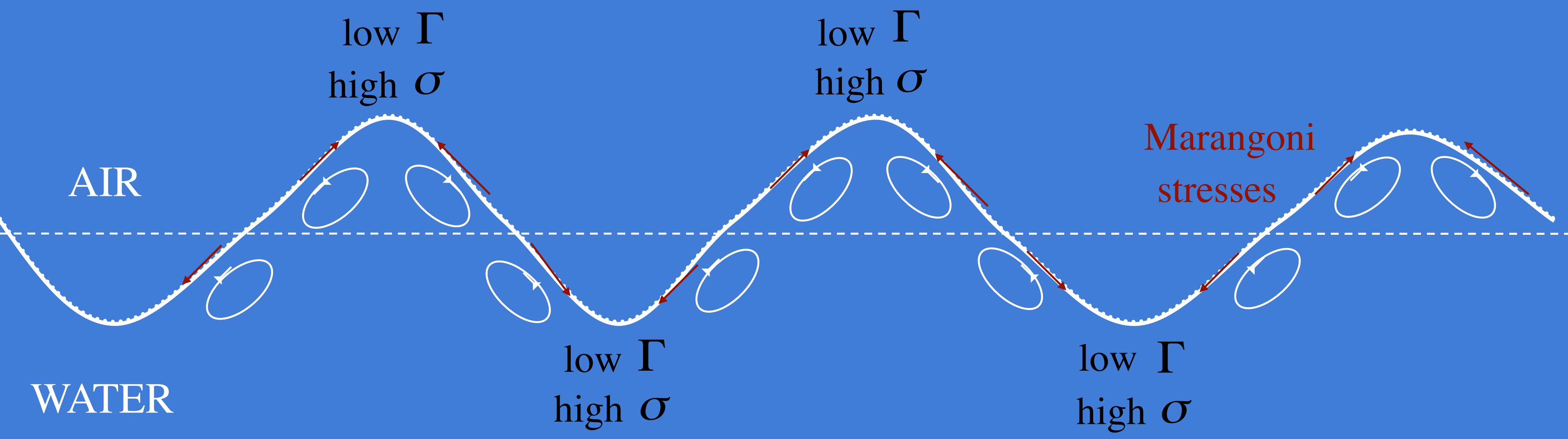
Observation: small bubbles, drops rise at speeds anticipated for RIGID particles



- rearrangement of surfactant → Marangoni, viscous stresses balance on surface
- surfactant rigidifies drop surface: internal circulation suppressed
- effect most pronounced for small drops, bubbles since $\nabla\sigma \sim \frac{\Delta\sigma}{a}$

The suppression of capillary waves by surfactant

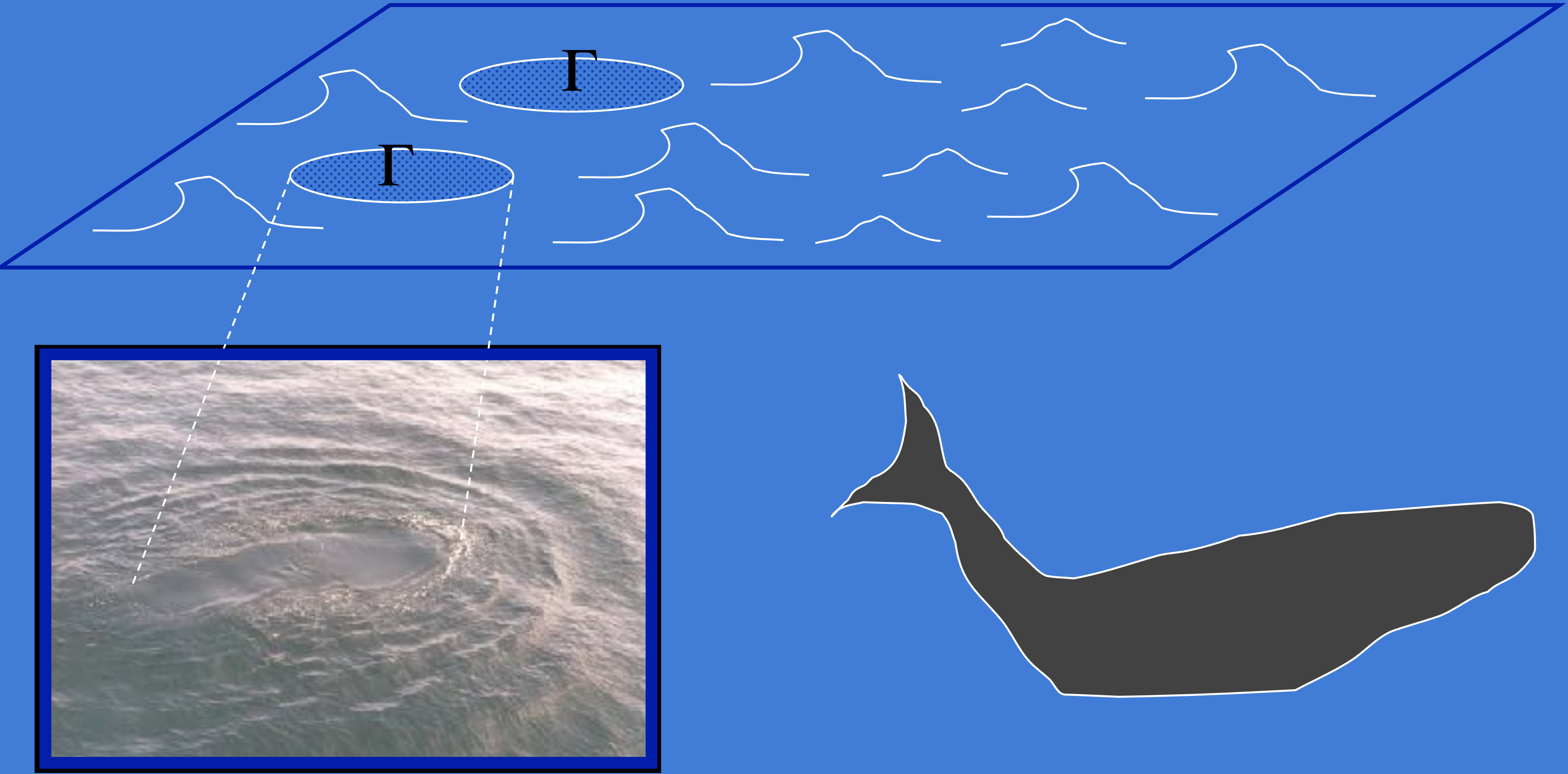
- wave motion generates regions of surface divergence
- concomitant surfactant gradients generate Marangoni stresses $\frac{d\sigma}{d\Gamma} < 0$
- resulting small scale flows extremely dissipative



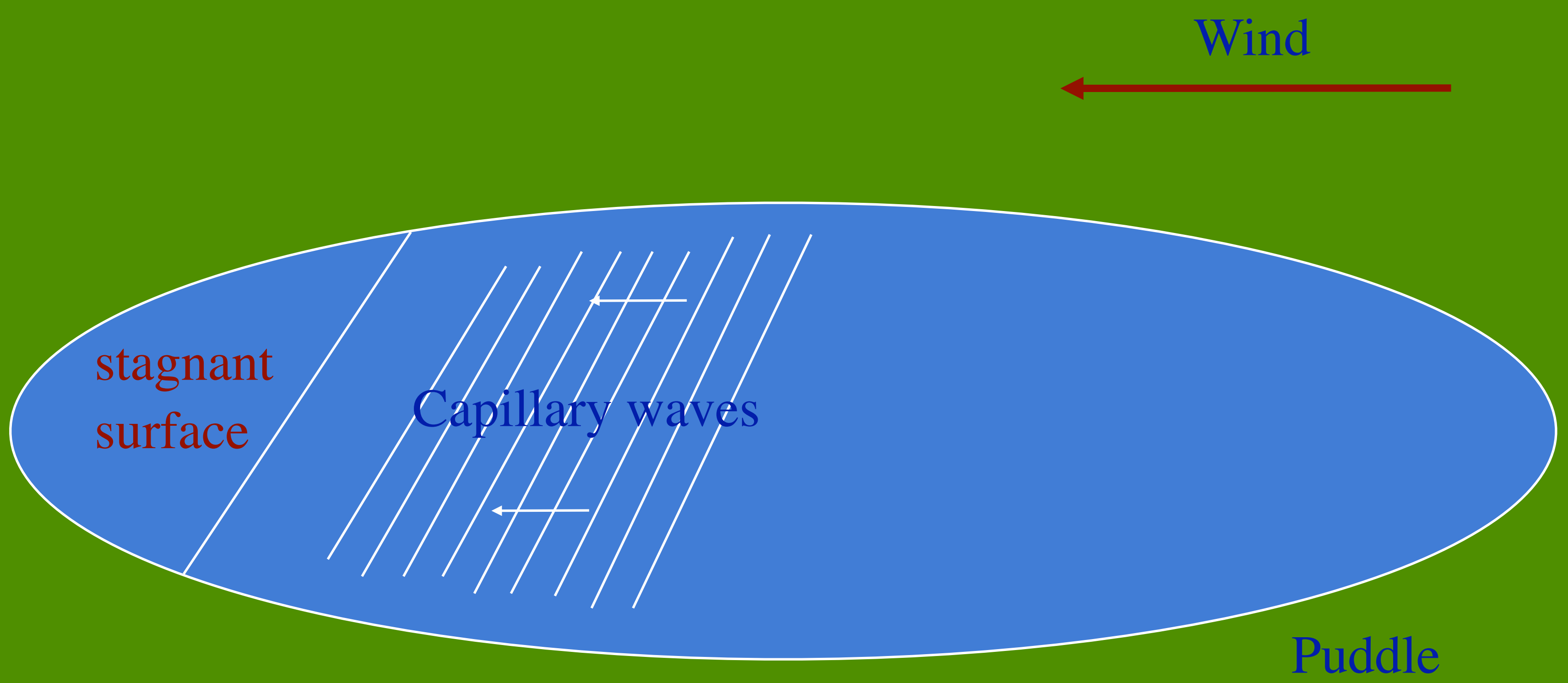
- flat ship wakes first remarked upon by Pliney the Elder
- examined by Benjamin Franklin, motivated by Bermudan spear fishermen
- now used to track submarines: flat wakes visible on satellite images

The footprints of whales

- surfactants (biomaterial in water column) swept to surface by diving whales
- suppress capillary waves and cascade to larger scale waves
- similar rationale for the glassy wake of ships

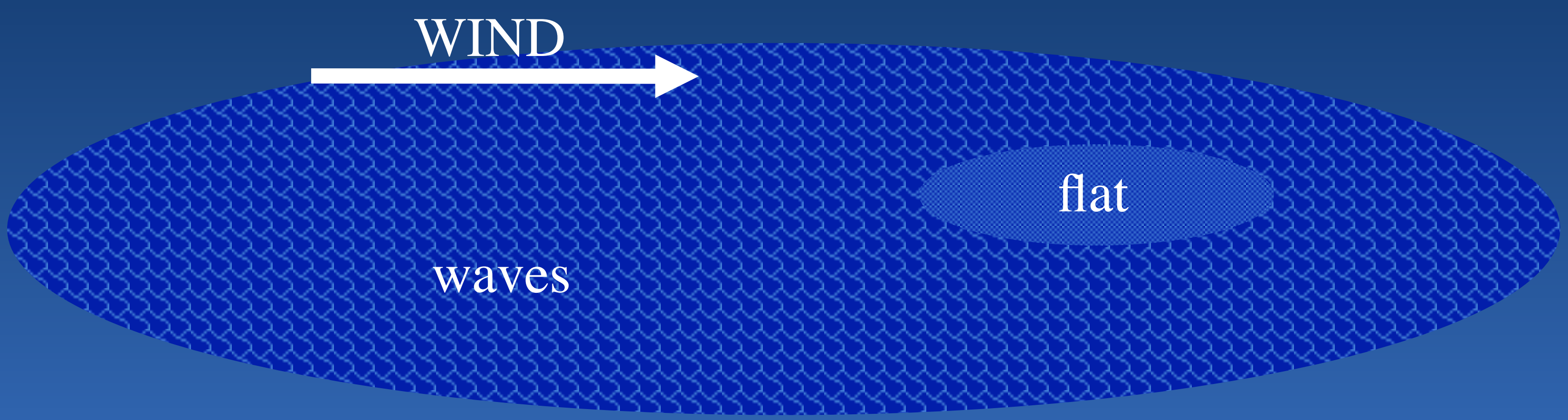


The dynamics of puddles



- surfactants swept to lee of puddle by wind stress
- Marangoni stress balances wind stress $\Longrightarrow$ stagnant surface
- capillary waves suppressed by surfactant in lee of puddle

Surfactants and a murder mystery



Who dunnit?

"In the autumn of 1878 a man committed a terrible crime in Somerset, which was for some time involved in deep mystery. His wife, a handsome and decent mulatto woman, disappeared suddenly and entirely from sight, after going home from church on Sunday, October 20. Suspicion immediately fell upon the husband, a clever young fellow of about thirty, but no trace of the missing woman was left behind, and there seemed a strong probability that the crime would remain undetected. On Sunday, however, October 27, a week after the woman had disappeared, some Somerville boatmen looking out towards the sea, as is their custom, were struck by observing in the Long Bay Channel, the surface of which was ruffled by a slight breeze, a long streak of calm such as, to use their own illustration, a cask of oil usually diffuses around it when in the water. The feverish anxiety about the missing woman suggested some strange connection between this singular calm and the mode of her disappearance. Two or three days after – why not sooner I cannot tell you – her brother and three other men went out to the spot where it was observed, and from which it had not disappeared since Sunday, and with a series of fish-hooks ranged along a long line dragged the bottom of the channel, but at first without success. Shifting the position of the boat, they dragged a little further to windward, and presently the line was caught. With water glasses the men discovered that it had caught in a skeleton which was held down by some heavy weight. They pulled on the line; something suddenly gave way, and up came the skeleton of the trunk, pelvis, and legs of a human body, from which almost every vestige of flesh had disappeared, but which, from the minute fragments remaining, and the terrible stench, had evidently not lain long in the water. The husband was a fisherman, and Long Bay Channel was a favourite fishing-ground, and he calculated, truly enough, that the fish would very soon destroy all means of identification; but it never entered into his head that as they did so their ravages, combined with the process of decomposition, would set free the matter which was to write the traces of his crime on the surface of the water. The case seems to be an exceedingly interesting one; the calm is not mentioned in any book on medical jurisprudence that I have, and the doctors seem not to have had experience of such an occurrence. A diver went down and found a stone with a rope attached, by which the body had been held down, and also portions of the scalp and of the skin of the sole of the foot, and of clothing, by means of which the body was identified. The husband was found guilty and executed."

Nature, 22, 1880

The Thoreau-Reynolds Ridge

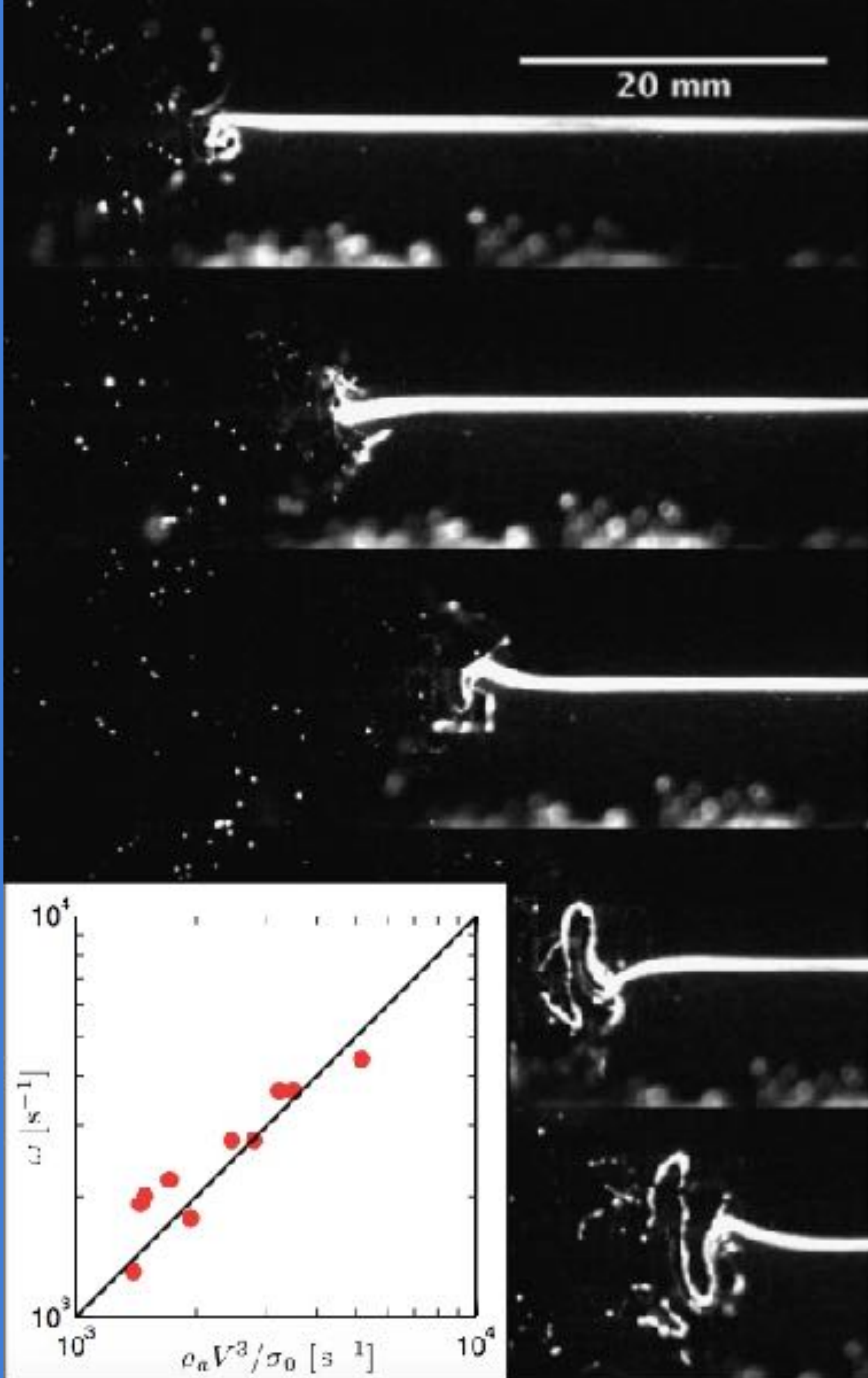
The Thoreau-Reynolds Ridge

- arise upstream of blocked flow regions; *e.g.* floating log, canoe paddles
- surfactants adjoining the blocker suppress waves, impede surface flow

Flapping retracting soap films

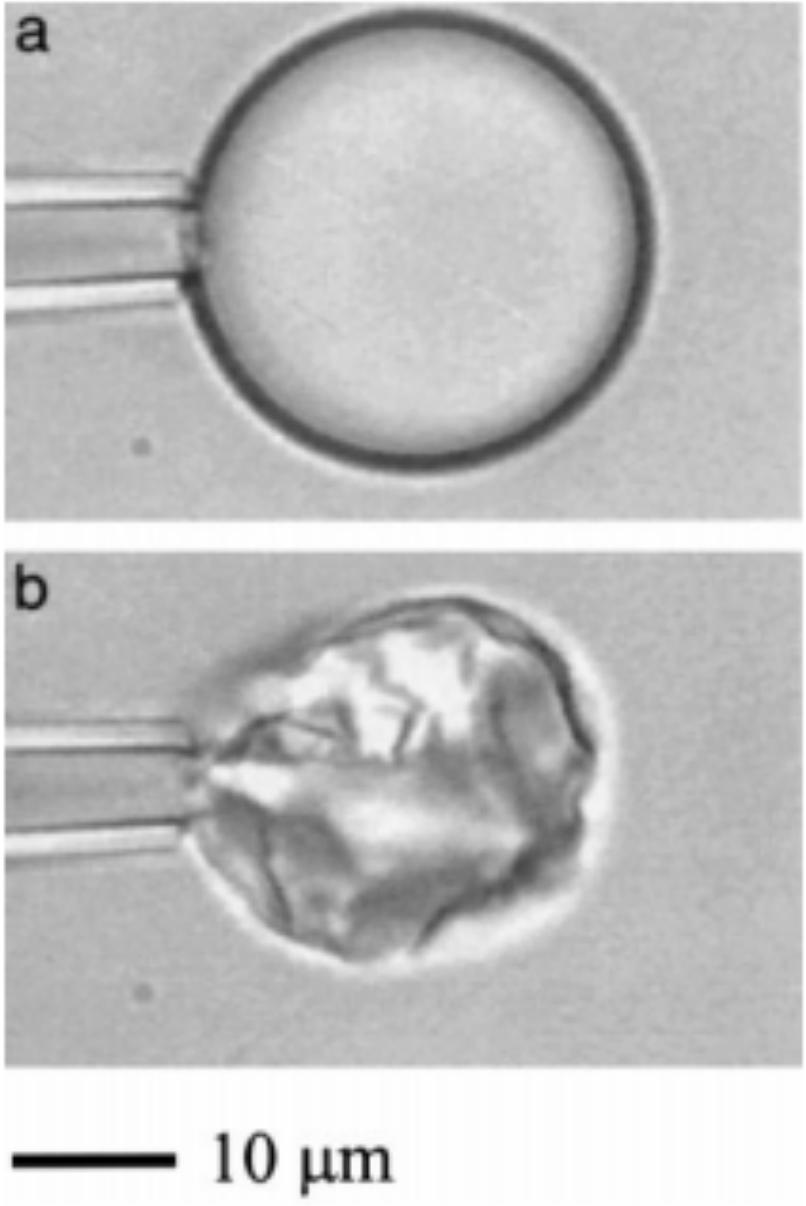
(Lhuissier & Villermaux, 2009)

- rationalized in terms of Marangoni elasticity of the film



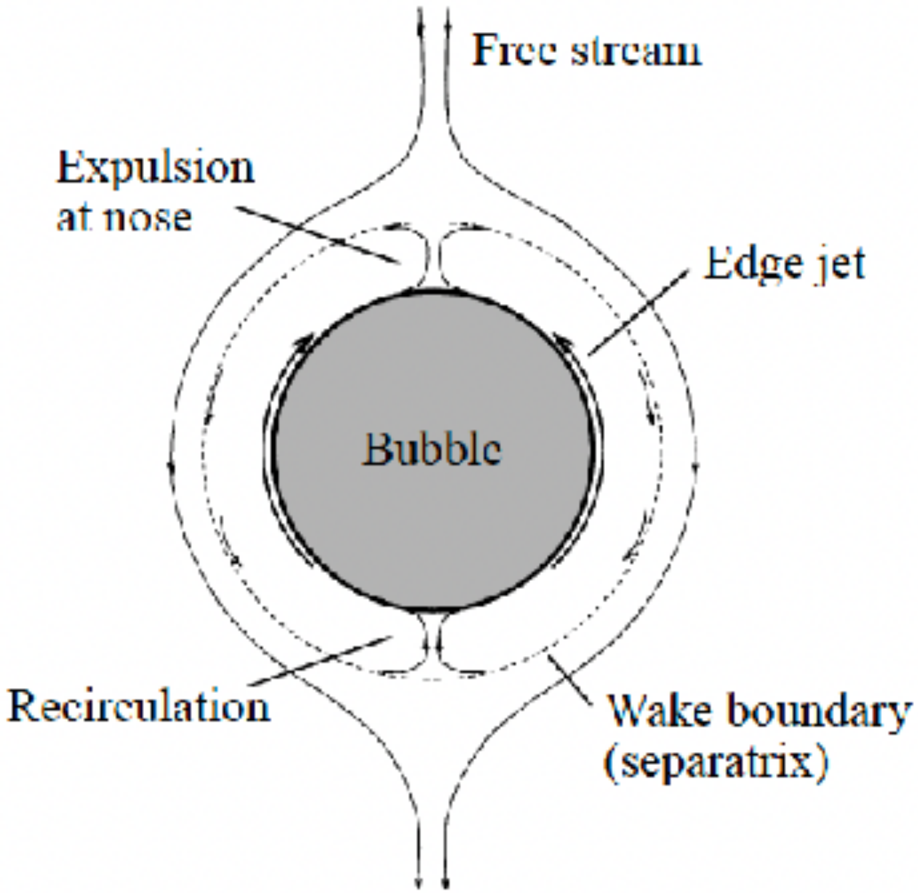
Marangoni buckling

The collapse of a water drop in a surfactant-laden oil

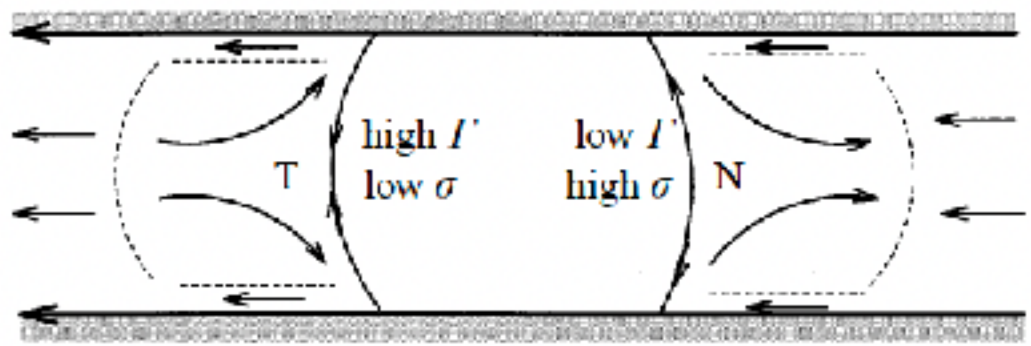


Emulsification through Area Contraction
T.Dabros A.Yeung J.Masliyah J.Czarnecki

Bubbles in a thin gap



Bush (JFM, 1997)



- surface divergence at leading edge, convergence on trailing edge
- resulting surface tension gradients induce Marangoni jets towards bubble nose
- rationalized in terms of surfactant-induced Marangoni elasticity

Marangoni Doomsday

The storage of radioactive liquid waste.