NOTTINGHAM TRENT UNIVERSITY

Surfactants, Biosurfactants And Adhesion To Superhydrophobic Surfaces

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School of Science & Technology

34th Meeting US Adhesion Society, Savannah, USA

www.naturesraincoats.org

15th February 2011

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Neil's Obsession with Snails

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Overview

1. Land Snails

- Hostile surfaces
- Adhesive locomotion
- What defeats a snail?

2. Superhydrophobic Surfaces and Snails

- Experiment 1: Snail Snack Time
- Experiment 2: Snail Maze
- Experiment 3: Snail Roundabout (Centrifuge)

3. Superhydrophobicity and Surfactants

- Contact angles on superhydrophobic surfaces
- SDS type behavior and adhesion
- Weak bio-surfactant hypothesis

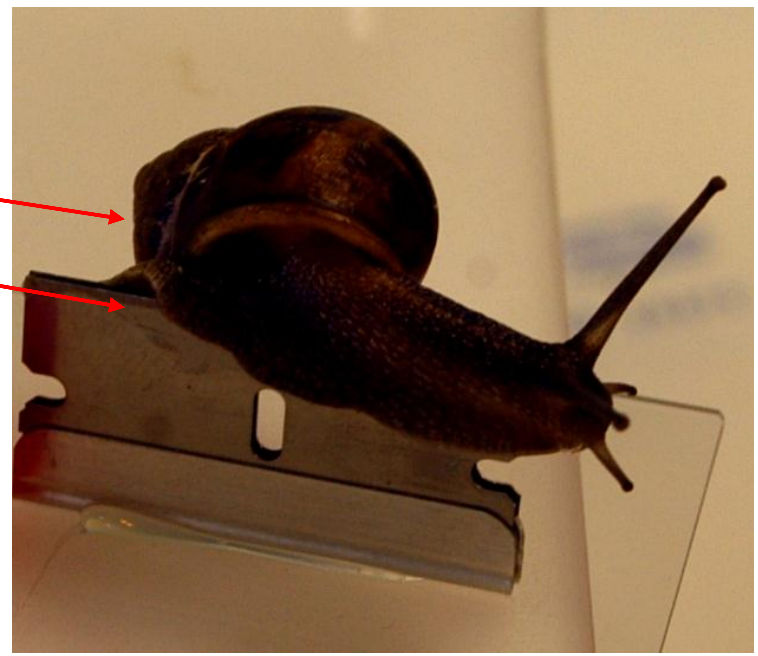
Land Snails

Snails and Hostile Surfaces

- Crawl over porous and non-porous surfaces
- Not deterred by rocks, soil or fences
- Climb up any angle surface – inclined or vertical
- Strong temporary attachment
- Adhesive works statically and dynamically
- Can crawl across surfaces with sharp edges

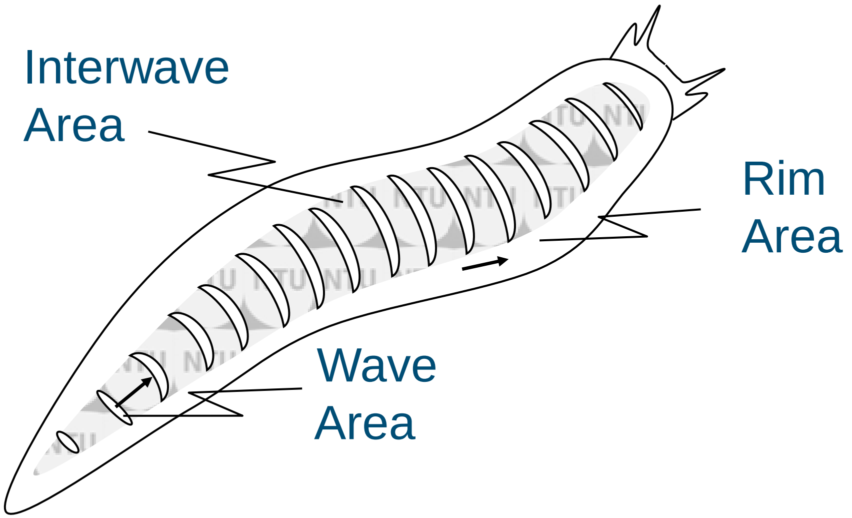
Snail

crawling across
a razor blade



Adhesive Locomotion

- Snails create a layer of adhesive slime/mucus – energetically expensive
- "Pull" themselves across using non-linear properties of the slime (solid-like at low stress and viscous liquid-like at high stress)
- Snail foot is attached at all times



- Outer rim moves at the same constant speed as the snail as a whole
- Wave of muscle contraction occurs cross inner undulating area
- Yield stresses in interwave region remain below the critical yield stress
- Interwave regions are almost stationary to the ground and provide adhesion
- Stresses in the wave region drive a flow

What Defeats Snails?

Not ….

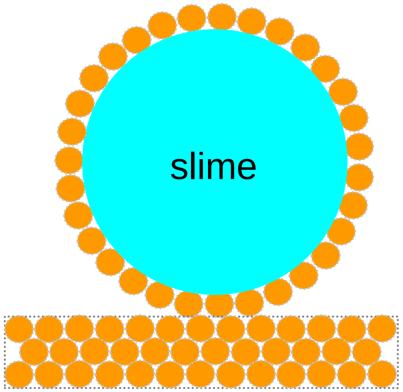
- PTFE/Teflon with low water droplet contact angle hysteresis
- Superslippery hydrogels

Successful snail repellent materials include ….

- Soot, sawdust, ash, crushed eggshells and sand

Because ….

- Draws water from the slime, or
- Coats slime with particles to create a liquid marble with a solid-on-solid contact



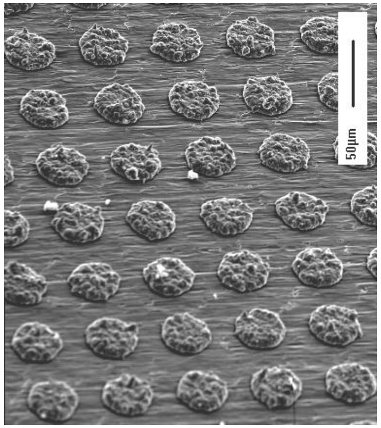
Some plants are snail resistant

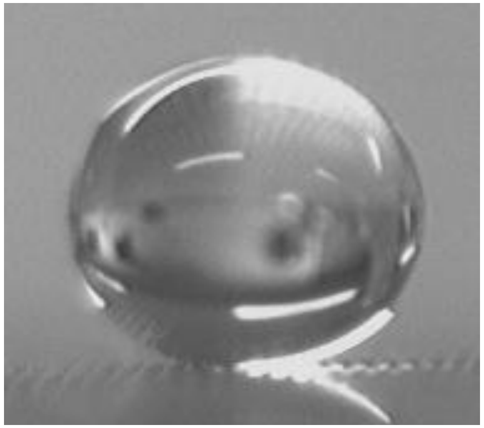
- Unclear why

Superhydrophobic Surfaces and Snails

Superhydrophobic Surfaces

- Water/oil repellent surface chemistry
- Sharp or high aspect ratio topography
- Topography can be on different length scales (nm to μm)
- Large contact angles with low contact angle hysteresis
- Super slippy surfaces





The question is "who wins"?

Super-adhesive snail

or

super-slippy superhydrophobic surface?

Experiment 1 – Snail Snack Time

- Common garden snails (*Helix aspersa*) and a few banded snails (*Cepaea nemoralis*)
- Coat sides of upturned plant pots in superhydrophobic coatings
- Place lettuce leaf on top and leave in a box of snails overnight

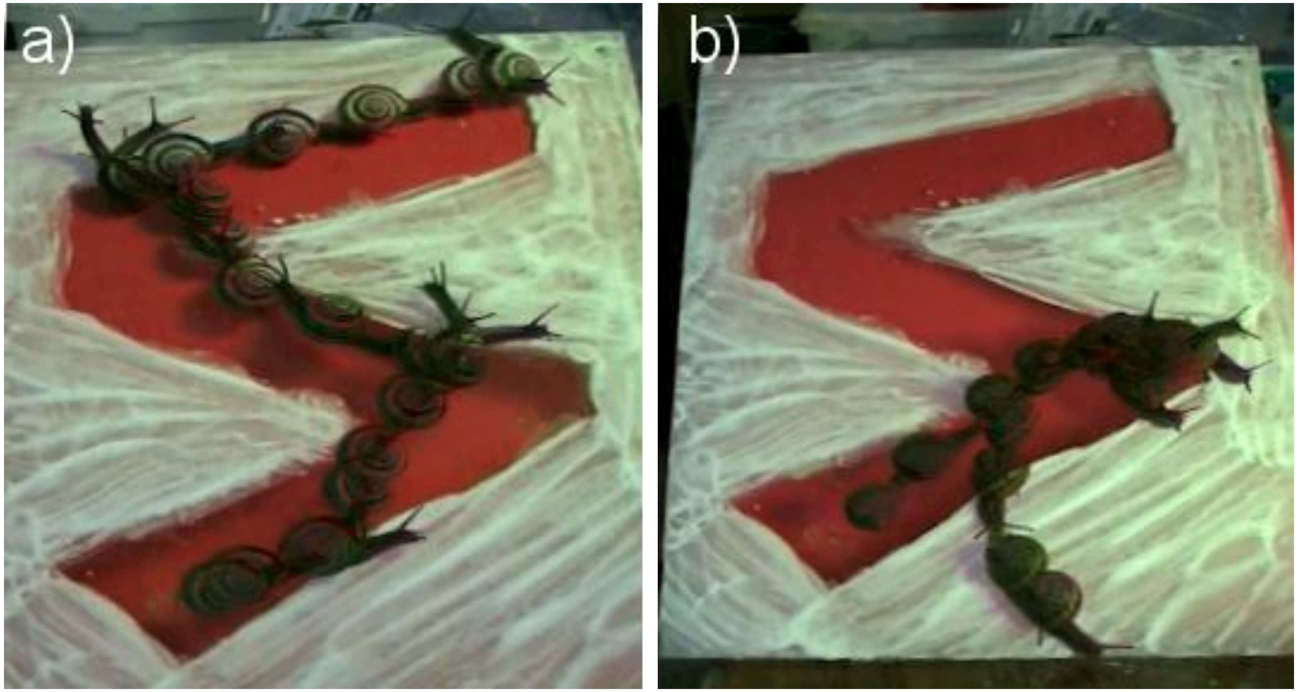
Mostly, snails win, but one superhydrophobic coating we tested works …

Not ……

- Toxicity
- Dislike of chemical
- Liquid marble effect
- Drawing out water

Experiment 2 – Snail Maze

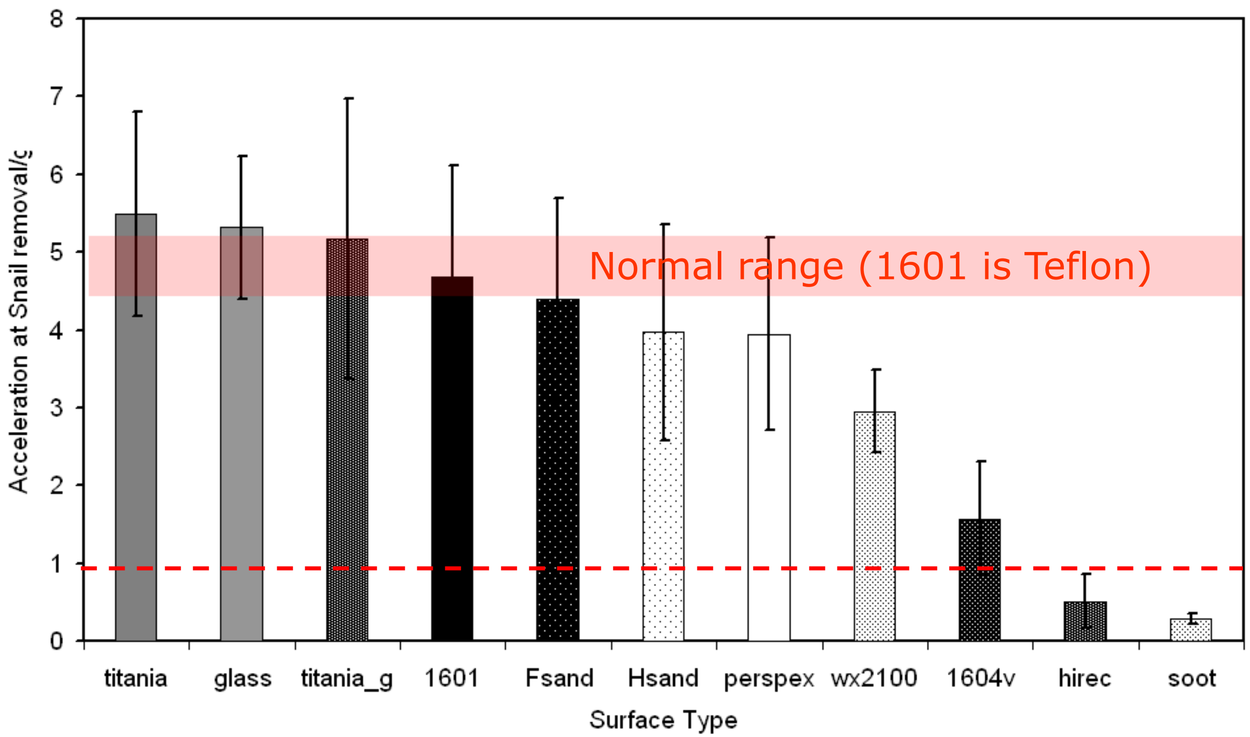
- Z-shaped path painted onto acrylic
- Snails followed maze on vertically mounted sheet (fig. a)
- Snails escaped when maze was horizontally mounted or at slight incline (fig. b)



- Snails detached when a fully painted sheet was tilted towards vertical

Experiment 3 – Snail Roundabout/Centrifuge

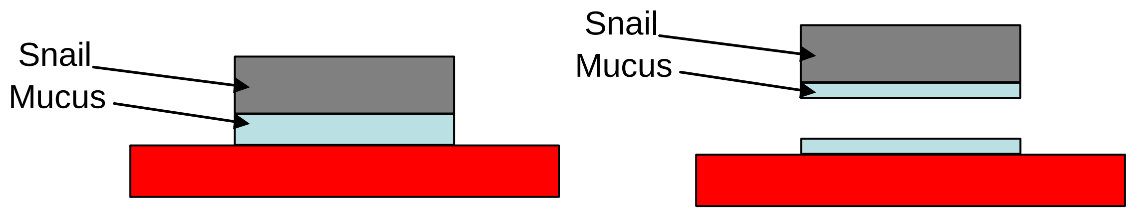
- Horizontal disk rotated at increasing speeds until snail detached
- Disk with different coatings – some superhydrophobic, some not
- Data is average over many snails



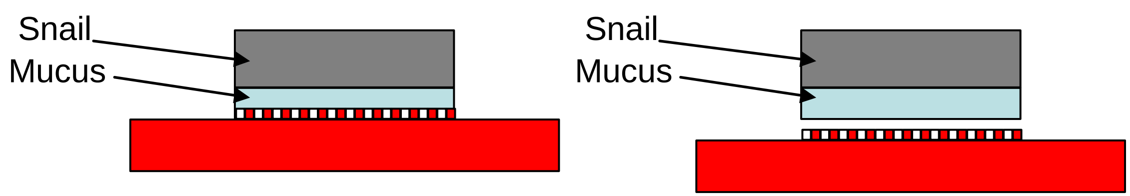
- Only the two surfaces with acceleration < 1*g* are snail resistant surfaces when mounted vertically

Snail Adhesion Modes of Failure

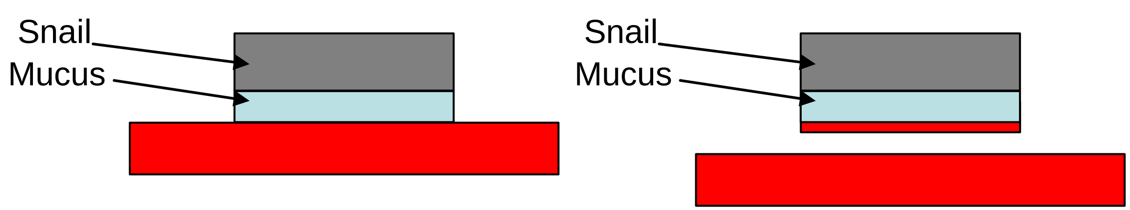
1. Within mucus layer



2. At mucus to solid interface



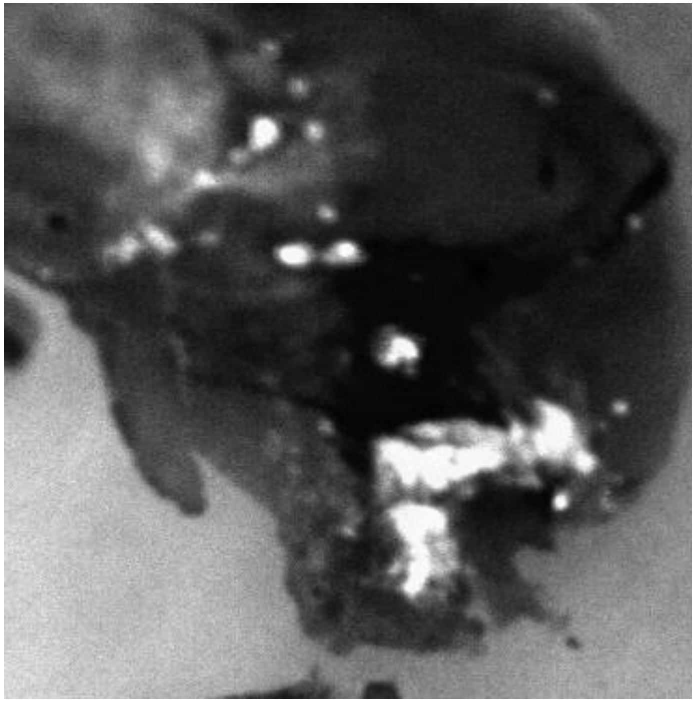
3. Within solid



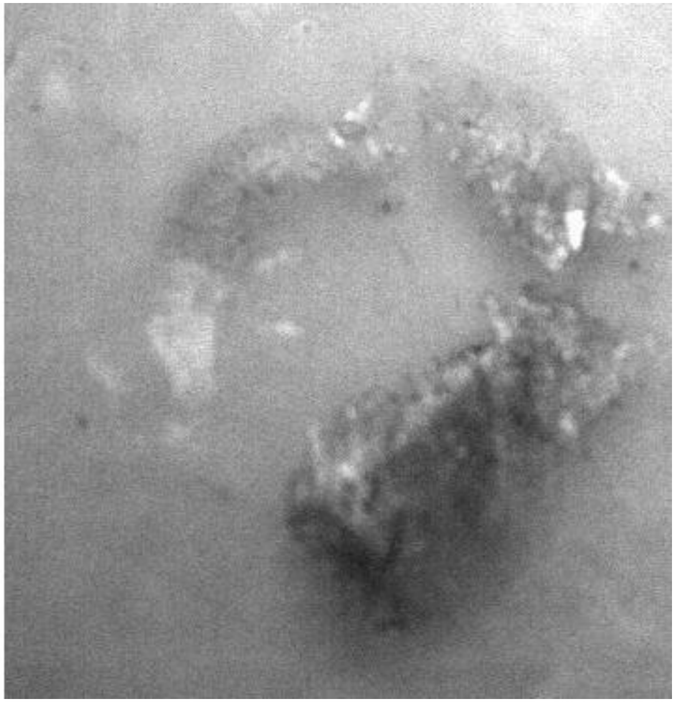
Failure on Superhydrophobic Surface

- Snail marks on surface after removal (made visible with 1% w/w silver nitrate solution)

Normal Surface



Superhydrophobic Surface

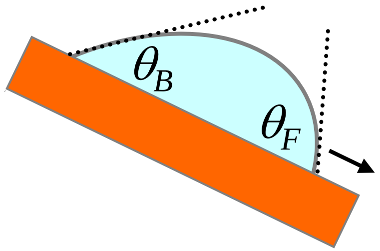


- Poor adhesion in centre of foot on snail resistant superhydrophobic surface
- On snail resistant superhydrophobic surface failure was between mucus and solid

Superhydrophobicity and Surfactants

Contact Angles and Sliding Adhesion

- Not as simple as just a high static contact
- Force resisting sliding is related to contact angle hysteresis
- Imagine a droplet on a substrate
- Tilting substrate causes a front, θ_F, and back, θ_B, contact angle
- At the instant before motion (assume) these give advancing, θ_A, and receding angles, θ_R.

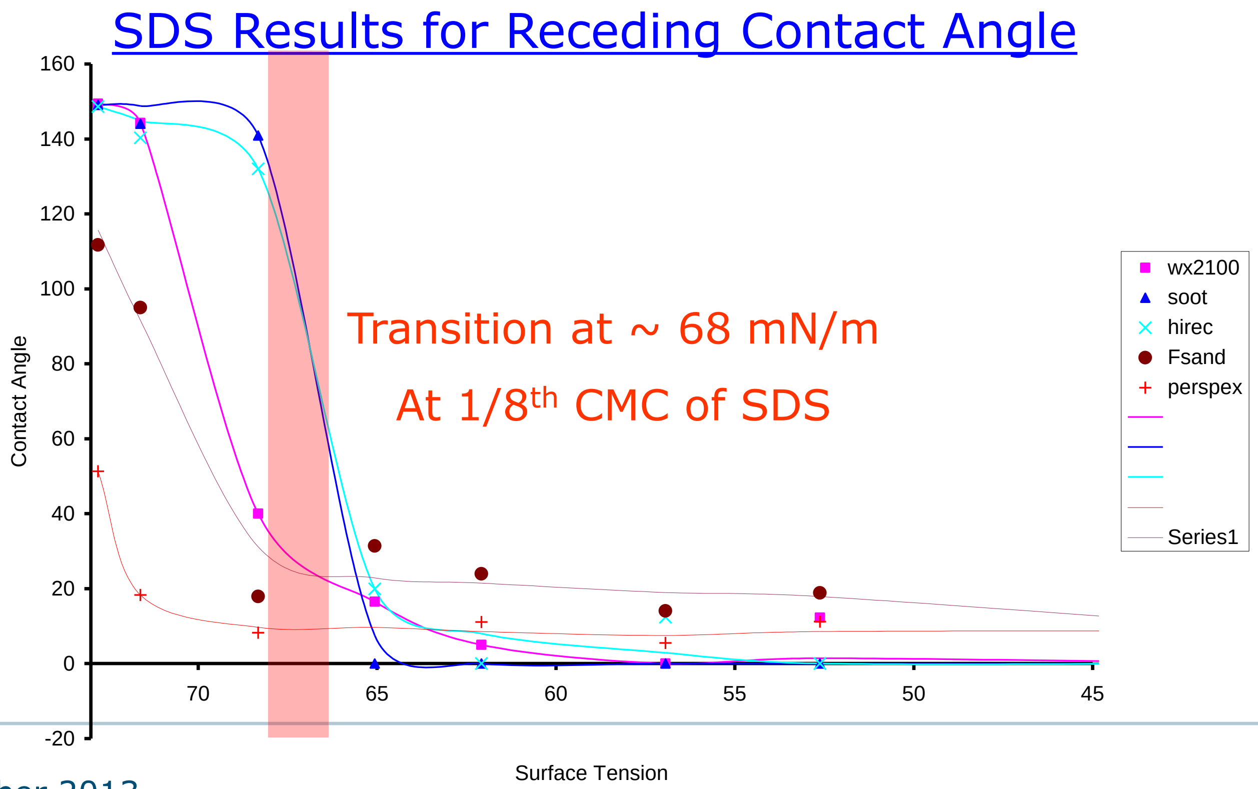


$$\text{Force} = \gamma_{LV}(\cos\theta_R - \cos\theta_A)$$

High advancing angle with low receding angle gives high adhesion/resistance to sliding

Surfactants on Superhydrophobic Surface

- Measured contact angles of water, oil and the anionic surfactant SDS (sodium dodecylsulfate) on superhydrophobic surfaces
- Advancing contact angle only decreases slightly on all surfaces
- Receding contact angle has a transition to a much lower value with concentration – creation of soap film bridges between peaks of roughness
- Surfactant aided penetration is only of substrate surface layer



Surfactant Response of a S/H Foam

- White superhydrophobic sol-gel (MTEOS) foam immersed in water and SDS solutions each with pink dye

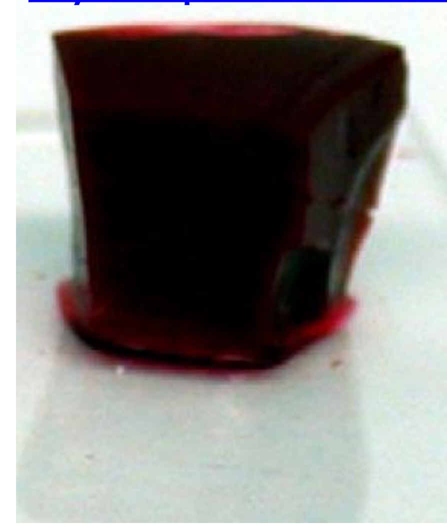
Superhydrophobic Foams

Pink water on foam with high θ_R pearls off

Pink 0.08M SDS on foam with intermediate θ_R leaves pink patches

Pink 0.08M SDS on foam with zero θ_R leaves pink surface layer

Hydrophilic Foam



Fully penetrated non-superhydrophobic foam

Reference Shirtcliffe, N.J., *et al.*, Maters. Chem. Phys., 103 (2007) 112–117.

Bio-Surfactant Hypothesis

- Snails defeat almost all superhydrophobic surfaces we tested
- Snail slime is a complex mixture of water together with dissolved salts, and a high molecular weight glycoprotein which, in solution, forms a cross-linked gel network
- Snail slime is amphiphilic allowing attachment to both hydrophilic and hydrophobic surfaces
- Existence of snail slime trail suggests low receding contact angle
- Good wetting and penetration needed to prevent adhesive failure
- But must not lose slime into the surface
- Slime achieves a Cassie-Baxter to partial penetration/Wenzel switching
- Surfactant response of superhydrophobic surfaces mirrored snail performance

Hypothesis

"Land snails use a weak bio-surfactant to achieve high advancing contact angles with low receding contact angles and hence a high adhesion/resistance to sliding"

Summary

1. Snails defeat most superhydrophobic surfaces we tested
2. One superhydrophobic surface shows an ability to resist slime wetting
3. Correlation of surfaces with snail repellency seems to be *via* the response of the receding contact angle to surfactants
4. Poor wetting allows adhesive failure
5. Snail slime appears to use a weak bio-surfactant effect enabling surface restricted penetration into pores/spaces between surface features

The End

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