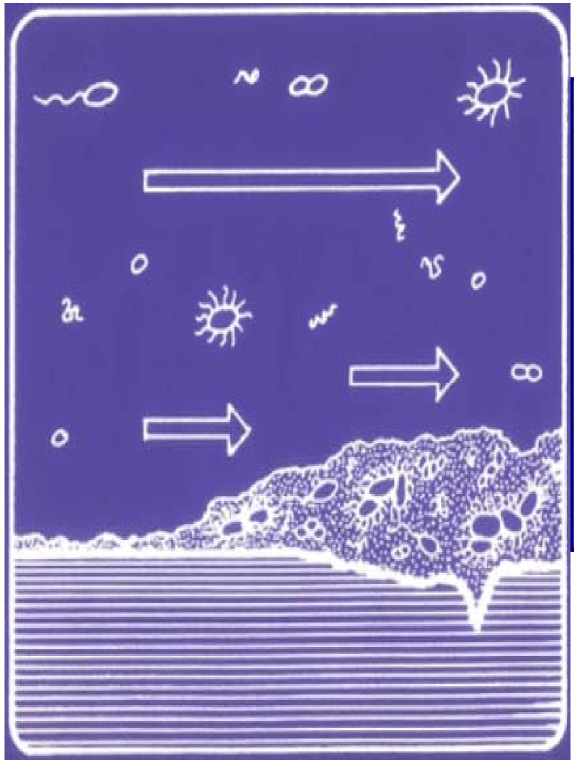
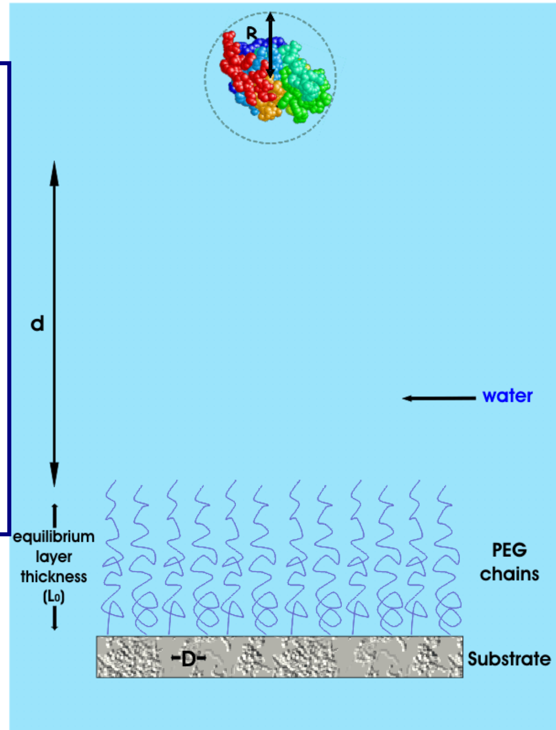
Biofouling and Anti-Biofouling Interface

Fajun Zhang



Outline

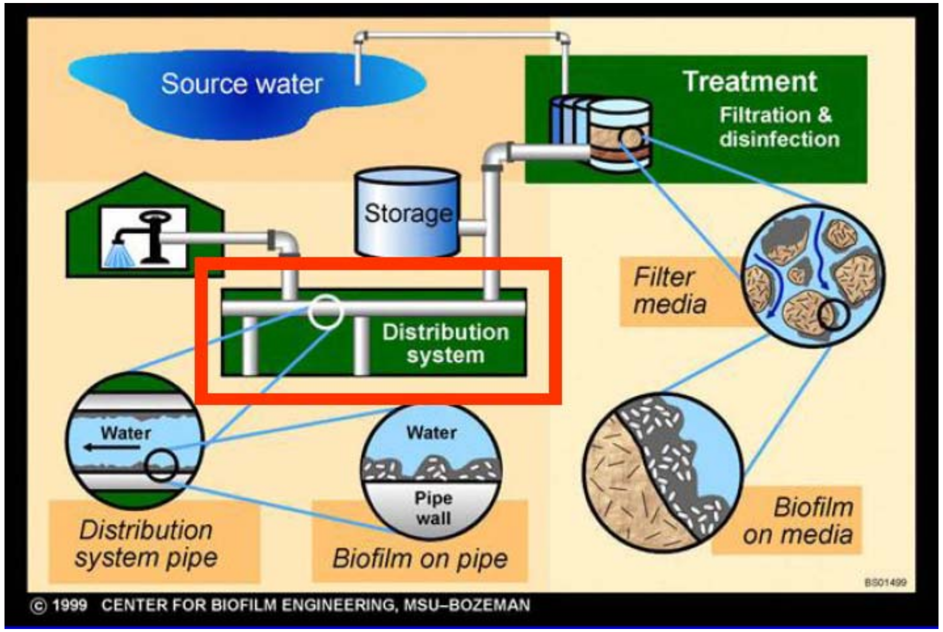
- Biofouling/Protein adsorption
- Procedure of biofouling
- Surface energy, adhesion
- Strategy of anti-biofouling



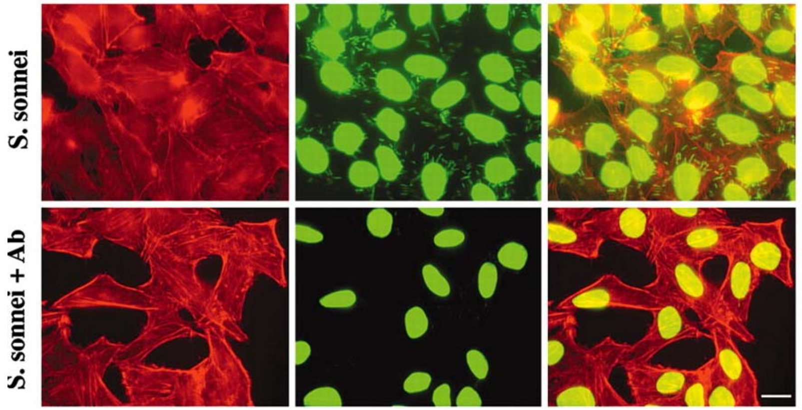
Biofouling

- Biofouling is non-desirable accumulation and growth of living matter (micro-organisms) on material surface;
- World wide problem with
  - Pulp and paper manufacturing
  - Food industry
  - Cooling tower
  - Ship hulls, fishing farms
  - Heat exchangers
  - Water desalination systems

Air Apparent 12 months



Marine organisms and bacteria



Bacteria, proteins, etc.

Marine biofouling systems Algae, barnacle, mussel,

Procedure of Biofouling

Extracellular Polymeric Substrances (EPS)

Steps in biofilm formation

a) **Formation of conditioning film**

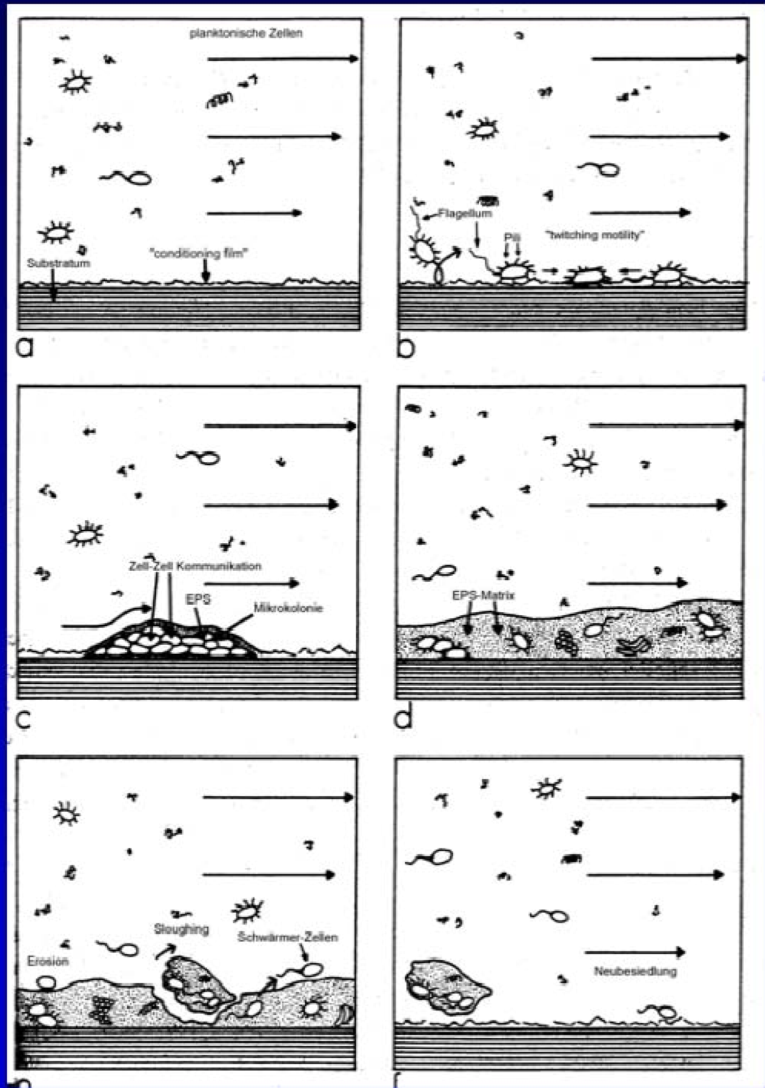
b) **Primary adhesion, reversible and irreversible**

c) **Formation of microcolonies, surrounded by EPS**

d) **Development of a continuous biofilm**

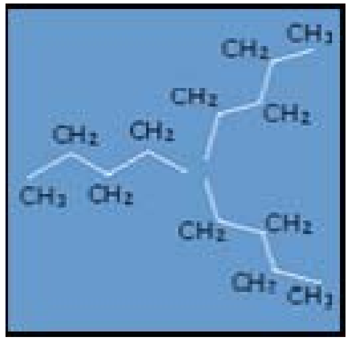
e) **Sloughing off of biofilm parts**

f) **Transport of biofilm particles (flocs) throughout the system, initiation of further biofilm formation**



Strategy for anti-biofouling

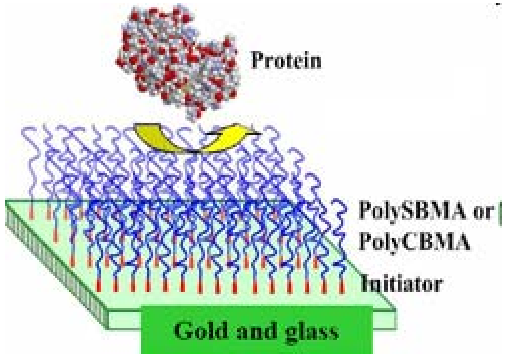
- Mechanical detachment of biofoulers if possible;
- Killing biofoulers using antibiotics, biocides, cleaning chemicals, etc.;
  - TBT-Silver Bullet: get rid of biofouling once and forever!
  - Toxic, banned by the year 2008

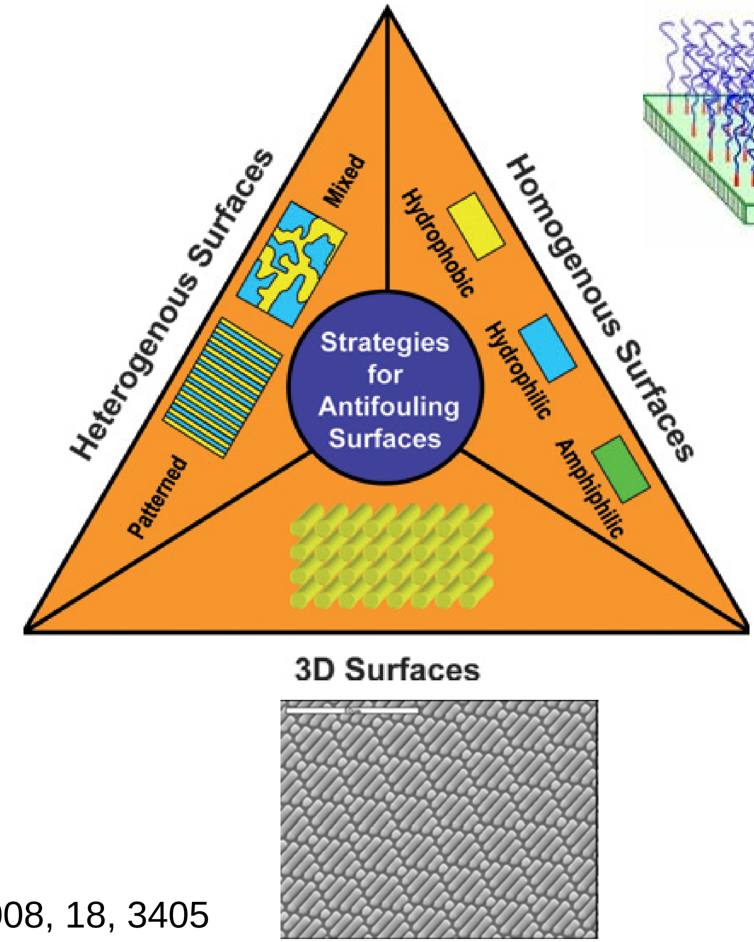


tributyltin

Strategy for anti-biofouling

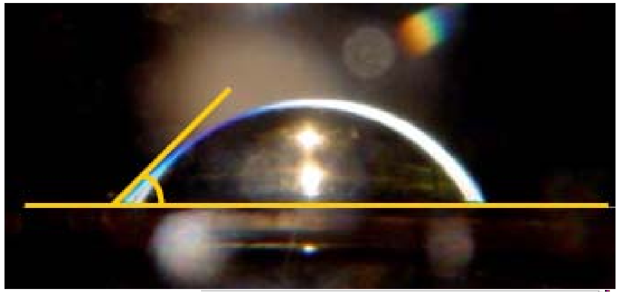
- Surface engineering:
  - Low energy
  - Low adhesive
  - Non-sticking





S. Krishnan et al. J. Mater. Chem. 2008, 18, 3405

Surface Energy, the Work of Adhesion

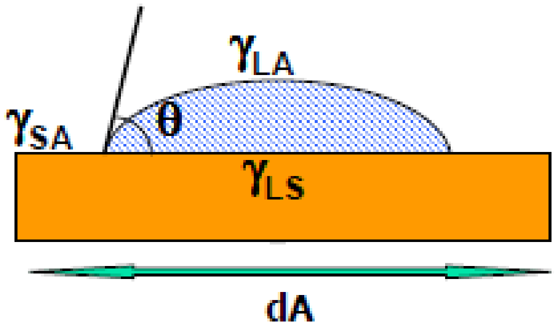


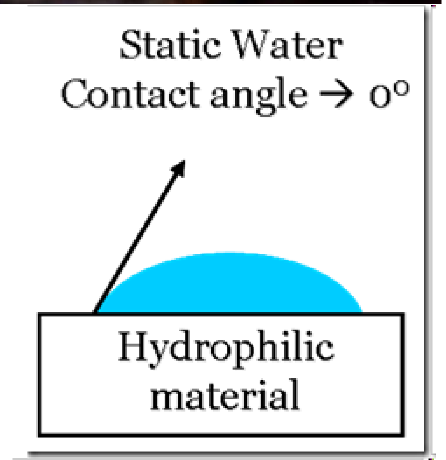
- Work can be expressed in terms of surface energies and interfacial energies

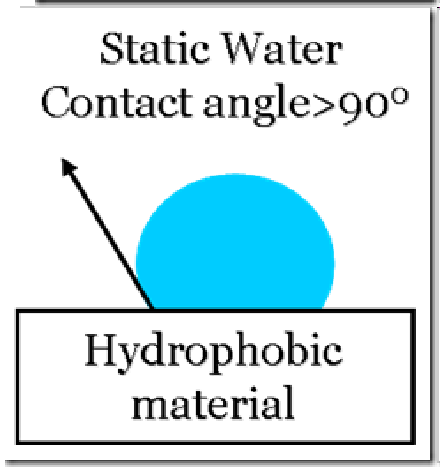
$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$$

- Contact angle θ
- $\gamma_{sa} = \gamma_{ls} + \gamma_{la} \cos\theta$
- Young-Dupre equation

$$W_{sl} = \gamma_l (1 + \cos\theta)$$

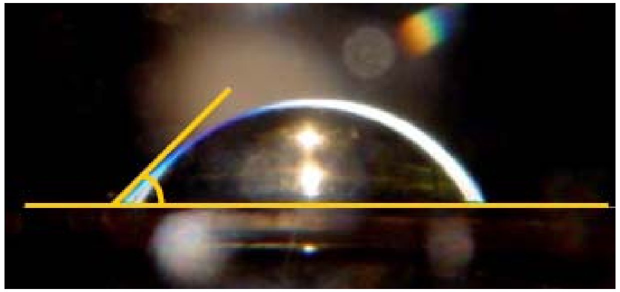






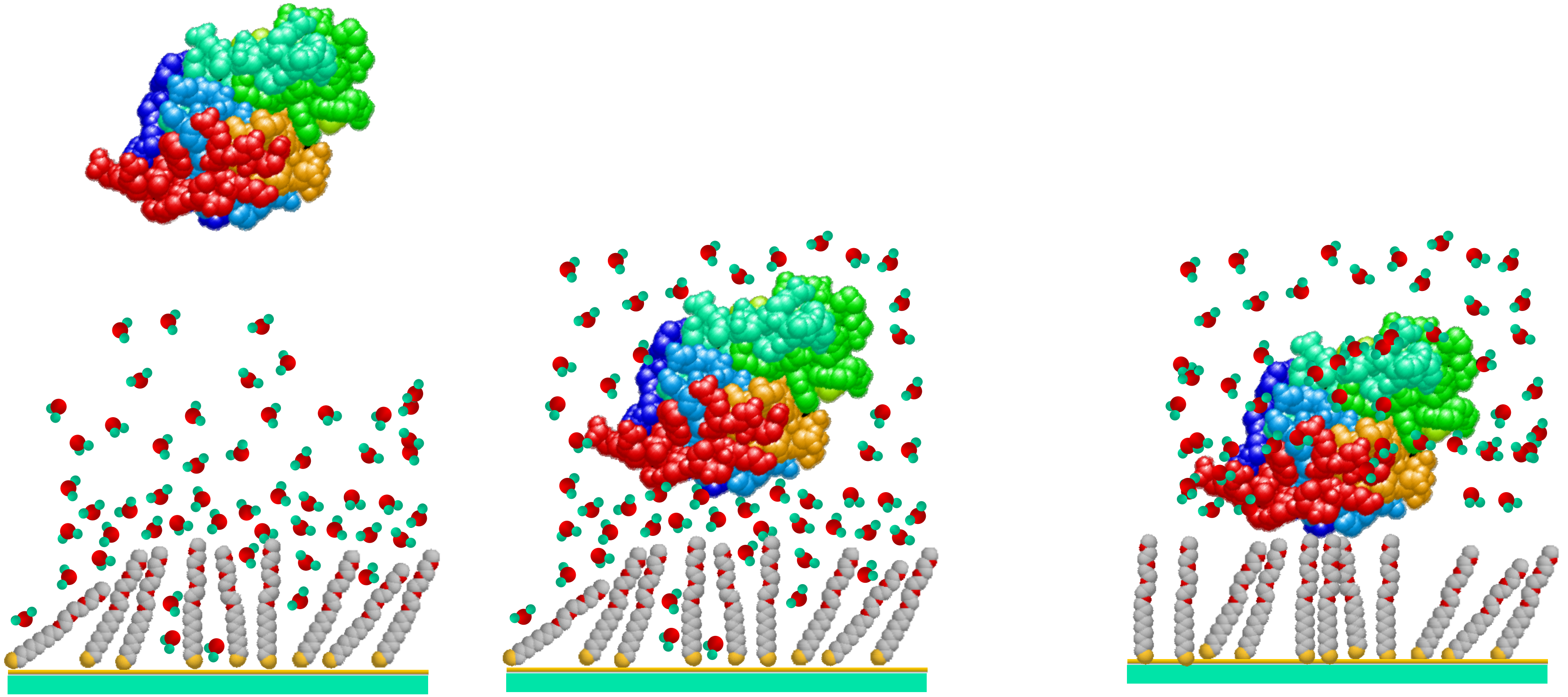
Surface Energy, the Work of Adhesion

- For an organism (O) in aqueous medium (w) in the presence of a surface (S)
- $W_{sow} = -\gamma_{so} + \gamma_{sw} + \gamma_{ow}$
- For dispersion forces $W_{AB} = \sqrt{W_{AA} W_{BB}}$
- The work of adhesion can be expressed using contact angle as
- $W_{sow} = 1/2\gamma_w(1-\cos\theta o)(1-\cos\theta s)$



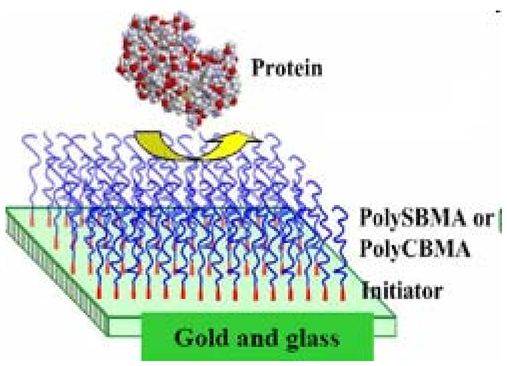
Strategy I: low Energy hydrophilic surface

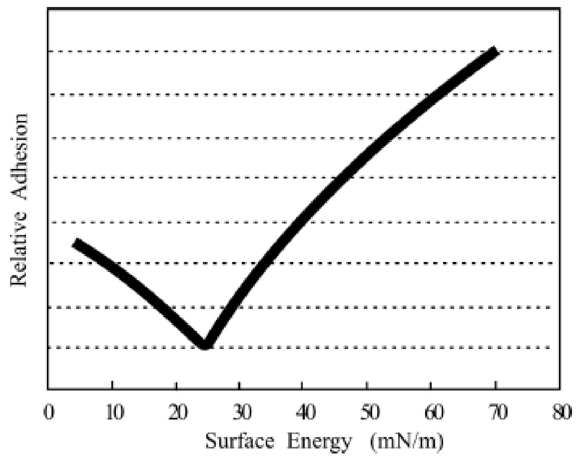
- $W_{sow} = 1/2\gamma_w(1-\cos\theta o)(1-\cos\theta s)$
- According to the equation, as θs approaches zero (hydrophilic surface) the work of adhesion does too;

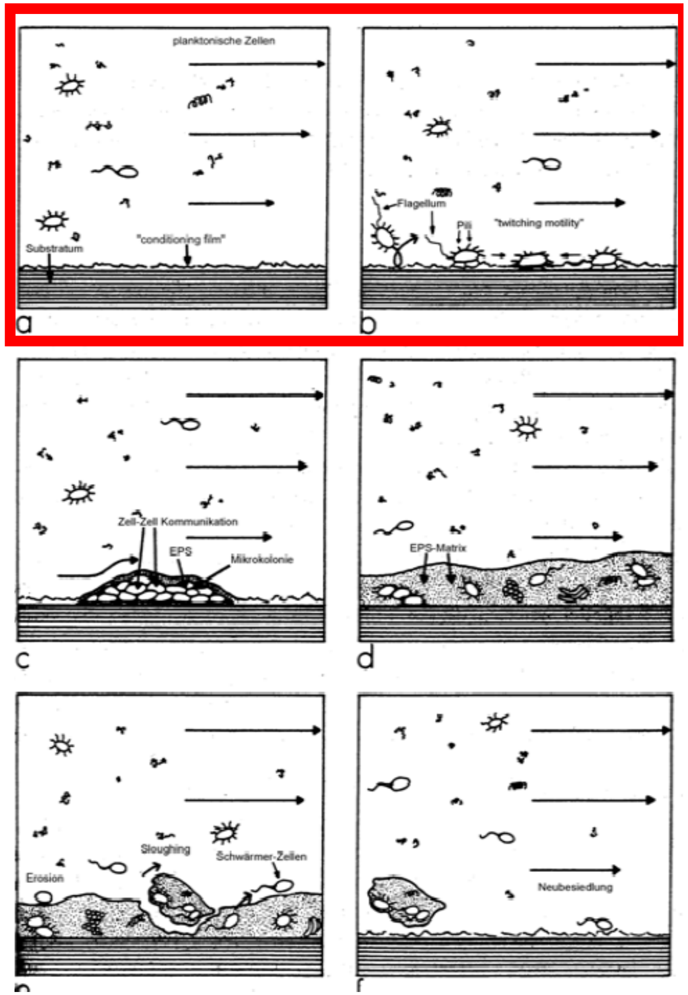


Strategy I: low Energy hydrophilic surface

- Interficial energy (work of adhesion) – Strong hydrophilic interface
  - Poly(ethlyene glycol) (PEG) self-assembled monolayer (SAM)
  - OEG SAM
  - Very low surface energy about 5 mJ/m^2



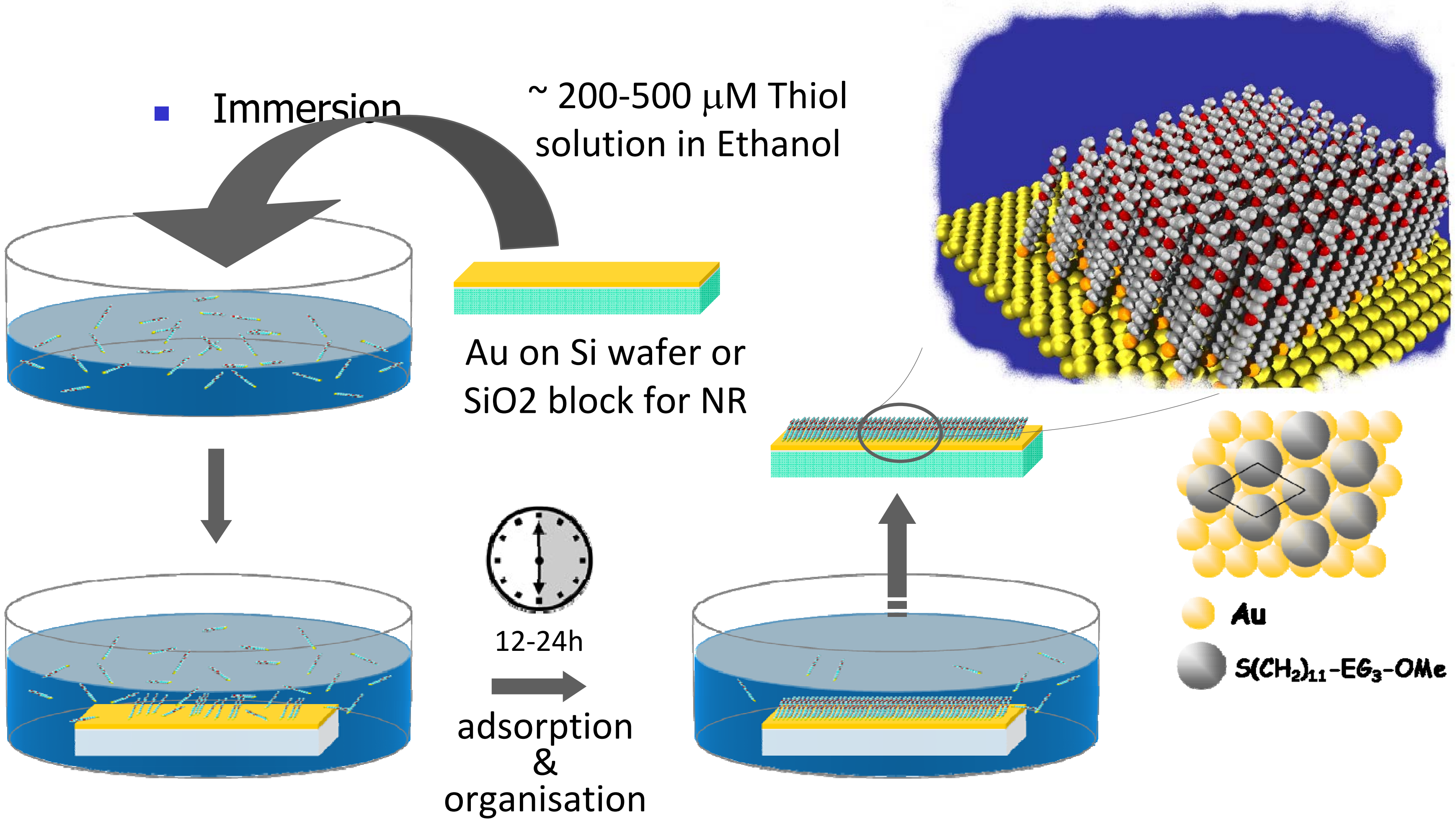




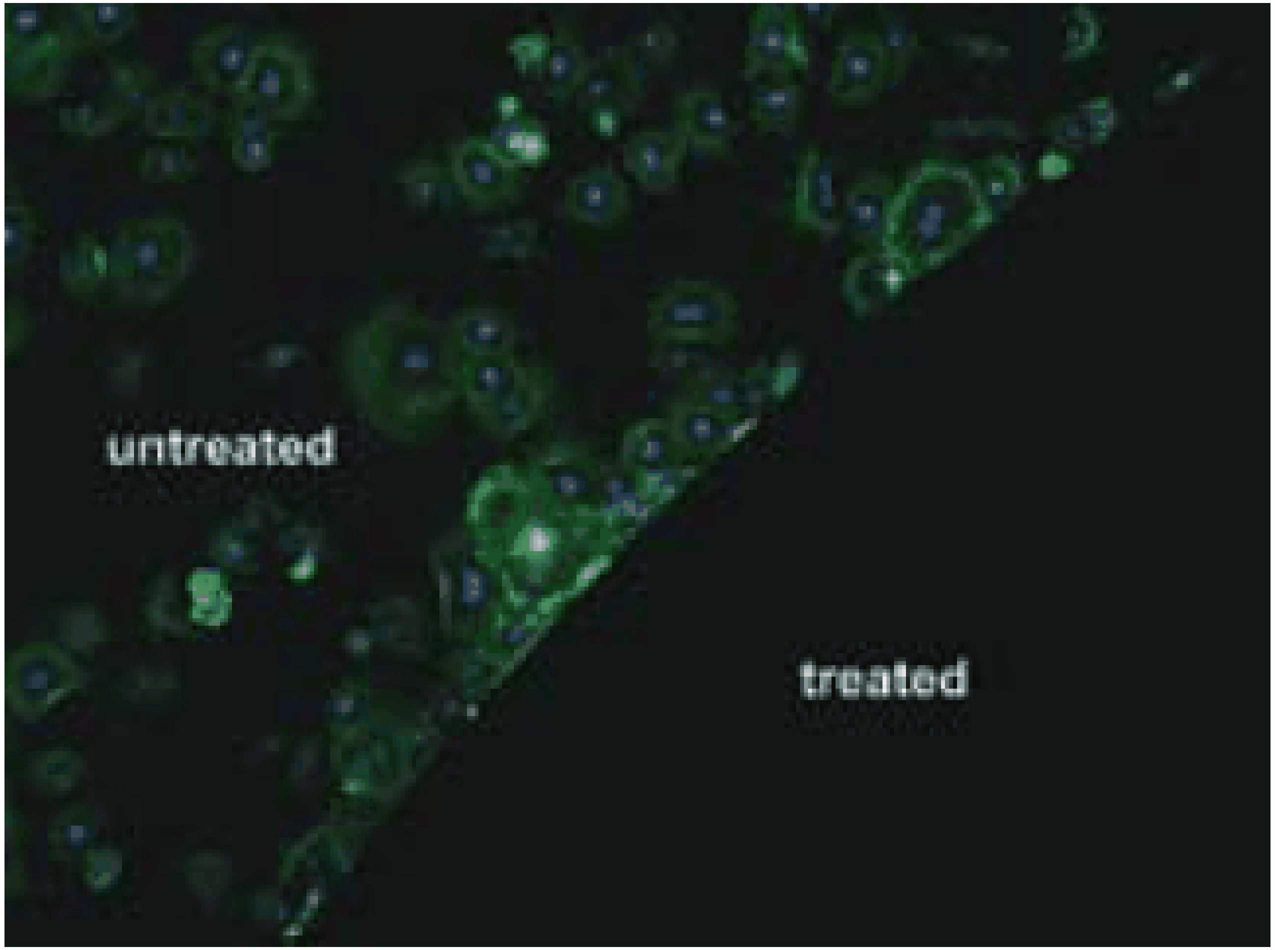
The Baier curve, Andersson, et al., *J. Marine Design,* B84, 2003, 11

OEG and PEG SAM: Preparation of SAM

- Immersion

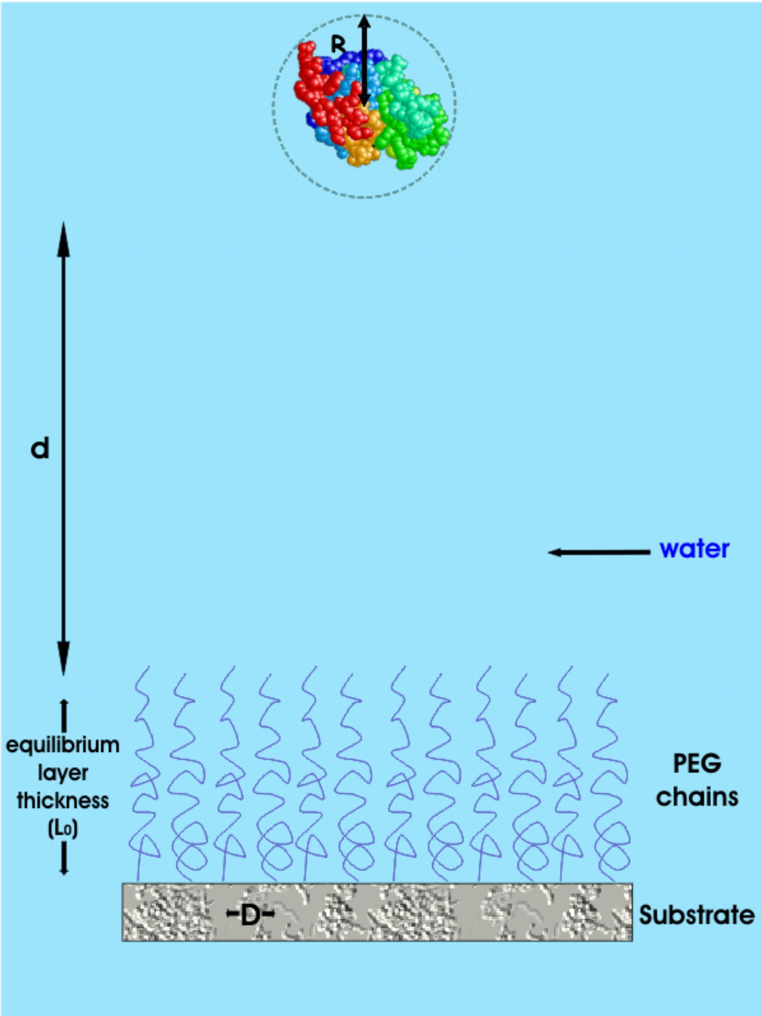


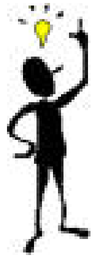
Cell Adhesion



- S. Schilp et al Langmuir 2009, 25, 10077

Steric Repulsion of *Poly*-EG





competing interactions:

- **attractive:**
  - van der Waals:

$$\frac{\Delta F_s}{kT} = -\frac{A}{6kT}\left(\frac{R}{d} + \frac{R}{d+2R} + \ln\frac{d}{d+2R}\right)$$

  - hydrophobic attraction
  - entropic (excluded volume)

- **repulsive (steric, entropic):**

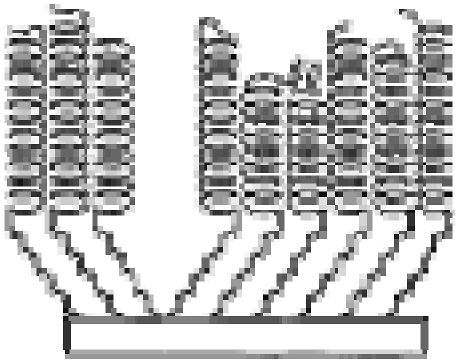
$$\frac{\Delta F_s}{kT} = \frac{k_1}{a^2}\left(\frac{7}{5}\frac{k_2}{k_1}\right)^{5/12} N\sigma^{11/6}\left\{\left[\left(\frac{L_0}{L}\right)^{5/4} - 1\right] + \frac{5}{7}\left[\left(\frac{L_0}{L}\right)^{7/4} - 1\right]\right\}$$

  - osmotic & elastic
  - de/compression of PEG chains
  - solvation energy

  - long chains, high density

Jeon, S.I.; Andrade J.D.; de Gennes, P.G., *J.Colloid Interface Sci.* **1991**, 142, 159

PEG

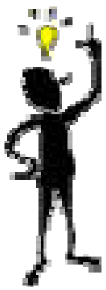


long chains

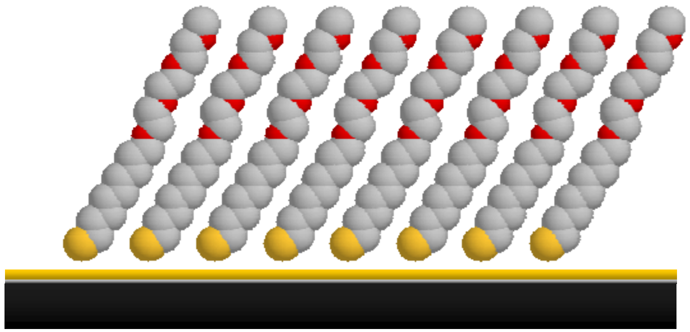
hydration

conformational changes

Additional 'steric' repulsion



e.g. $HS-(CH_2)_{11}-(EG)_3$

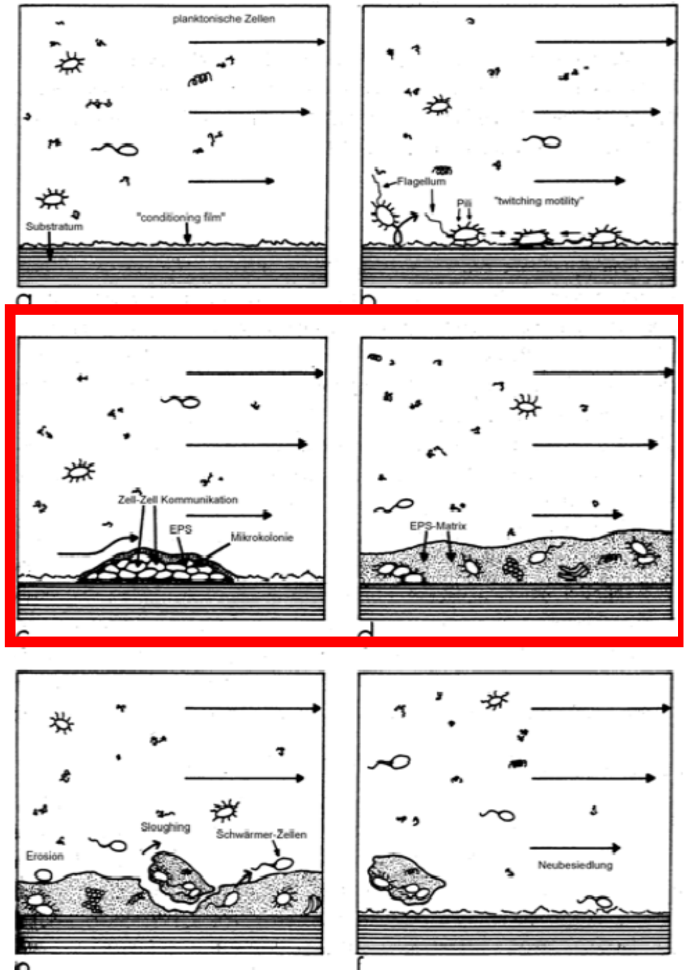


short chains

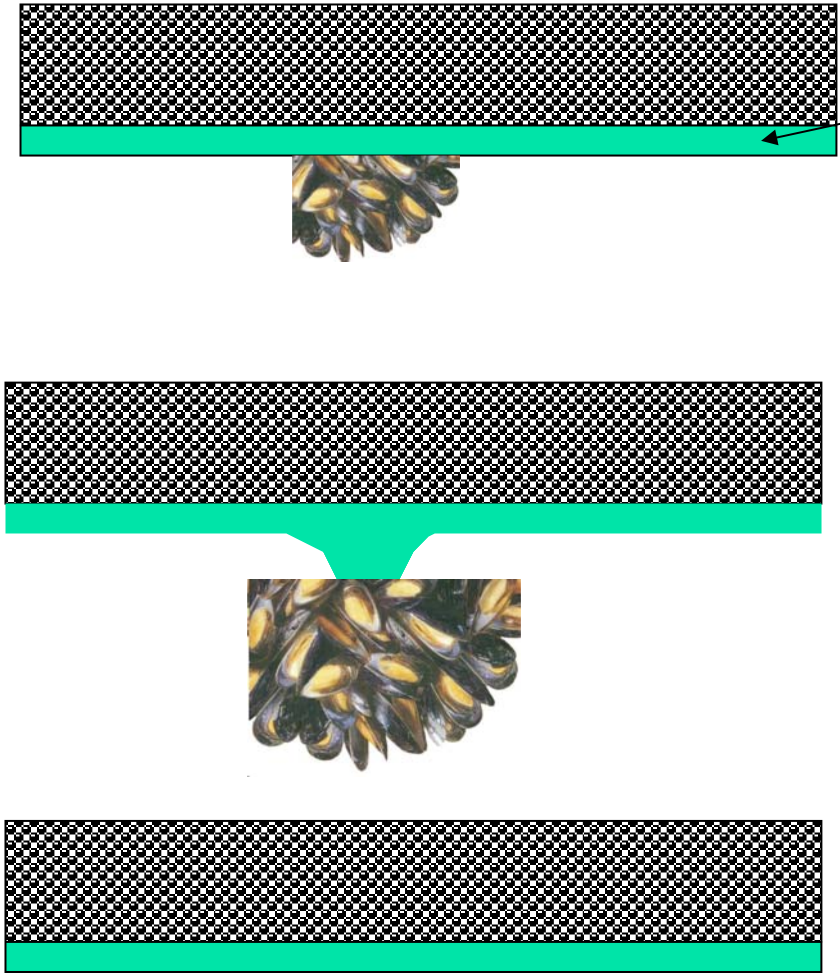
Pure low interfacial energy

Strategy II: low Modulus x Energy

- Only consider the interfacial energy, we have:
- $W_{sow} = 1/2\gamma_w(1-\cos\theta_o)(1-\cos\theta_s)$
- An organism cannot distinguish a hydrophilic surface from a watery environment and attaches preferentially to a hydrophobic surface
- Now we consider also the mechanical property of the coating materials:



Strategy II: low Modulus x Energy



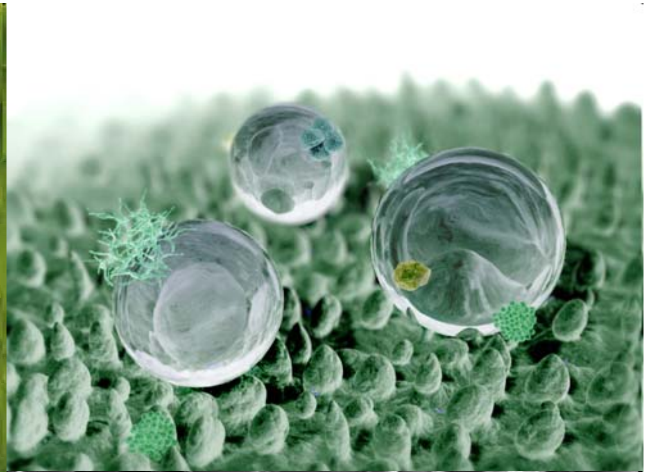
Siloxane elastomer coating

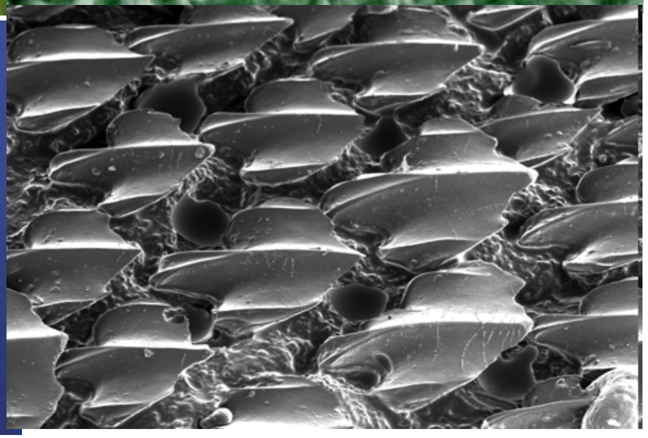
hydrophobic

Surface energy ~50 mJ/m^2

- $W_{sow} = 1/2\gamma_w(1-\cos\theta o)(1-\cos\theta s)$
- Peeling force: $P \sim (E\gamma)^{1/2}$
- Detaching by the weight of fouling materials
- Detaching by shearing/weight
- PDMS (polydimethylsiloxane)

Strategy III: Non-sticking structured interface
surface roughness, 3D patterning, energy and modulus





- Surface roughness leads to superhydrophobic
- Low hysterisis of contact angle
- Low friction, reduction of drag in fluid flow
  - Lotus leaf
  - Shark skin

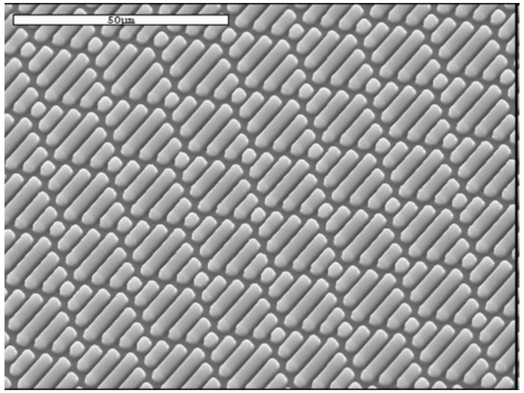
dermal denticles ribbed with longitudinal grooves.

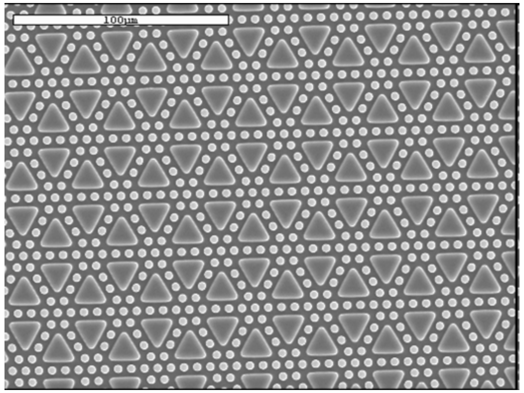
Reduce vortices formation,

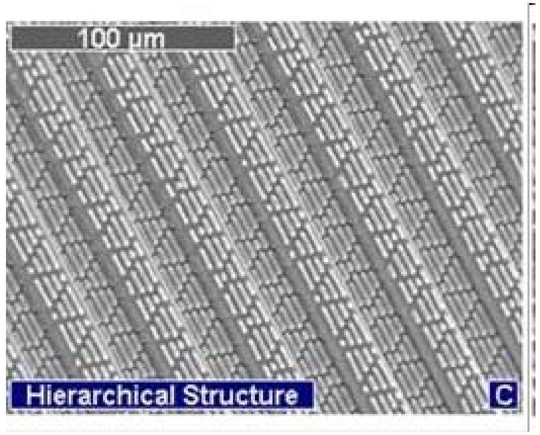
Water flow more efficiently

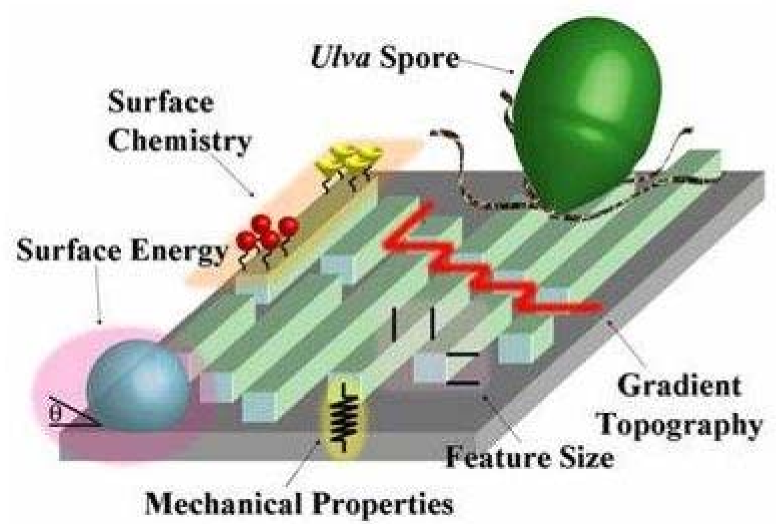
Protection from marine fouling: against adhesion and growth of organisms

Strategy III: Non-sticking structured interface
surface roughness, 3D patterning, energy and modulus









Summary

- Biofouling is a complex procedure involving chemical, physical and biological processes.
- Current strategy focus on surface engineering:
  - Low interfacial energy: strong hydrophilic (water like)
  - Low modulus and energy (elastomers): weak peeling force
  - 3D structure: disturbing the settlement of marine organisms