Lecture One

Bogota

May 2016

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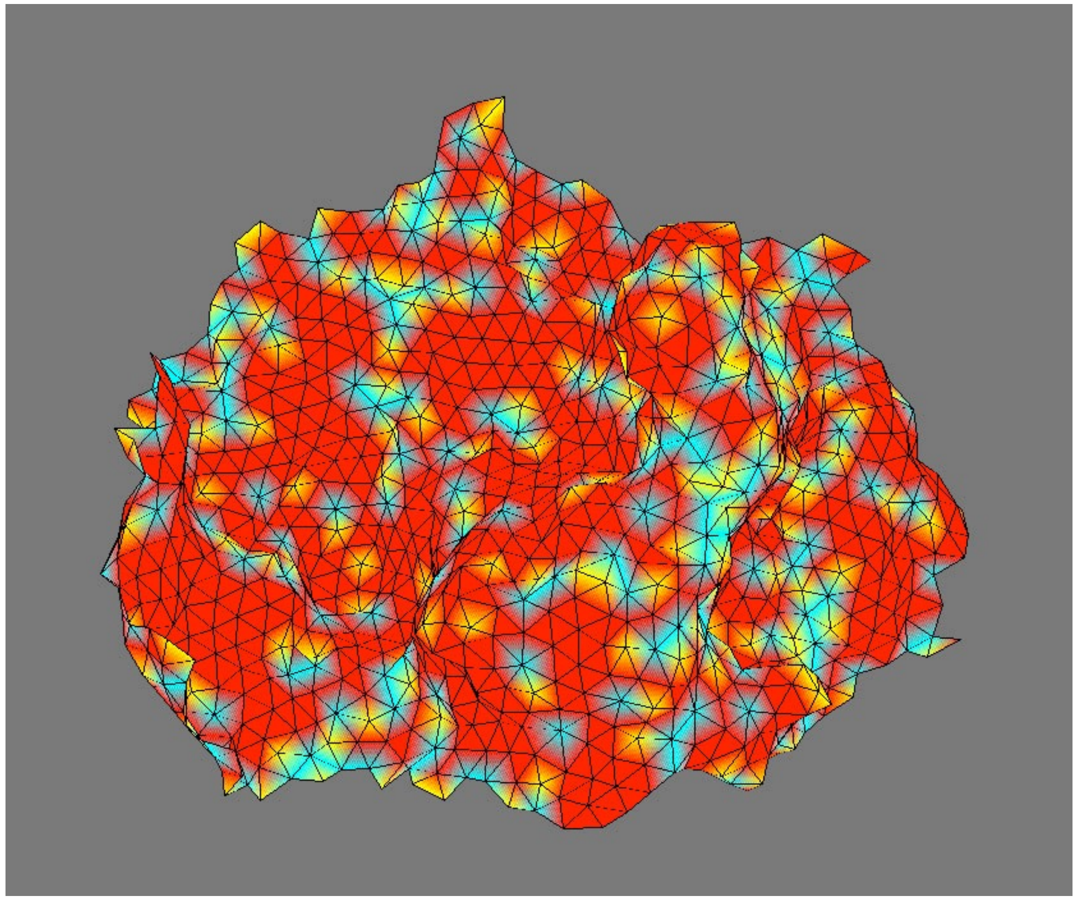
Soft Matter Program Syracuse



Central features of soft matter

- Easy deformability (soft) leads to complex geometries.

  Although the large scale structure of the universe is flat the mesoscopic geometry of matter is spatially very rich

- Multiple phases as a function of length and time scales

  Enormous expansion in the richness of emergent phases of matter

- Extreme responses to small changes in conditions

  Configurable matter

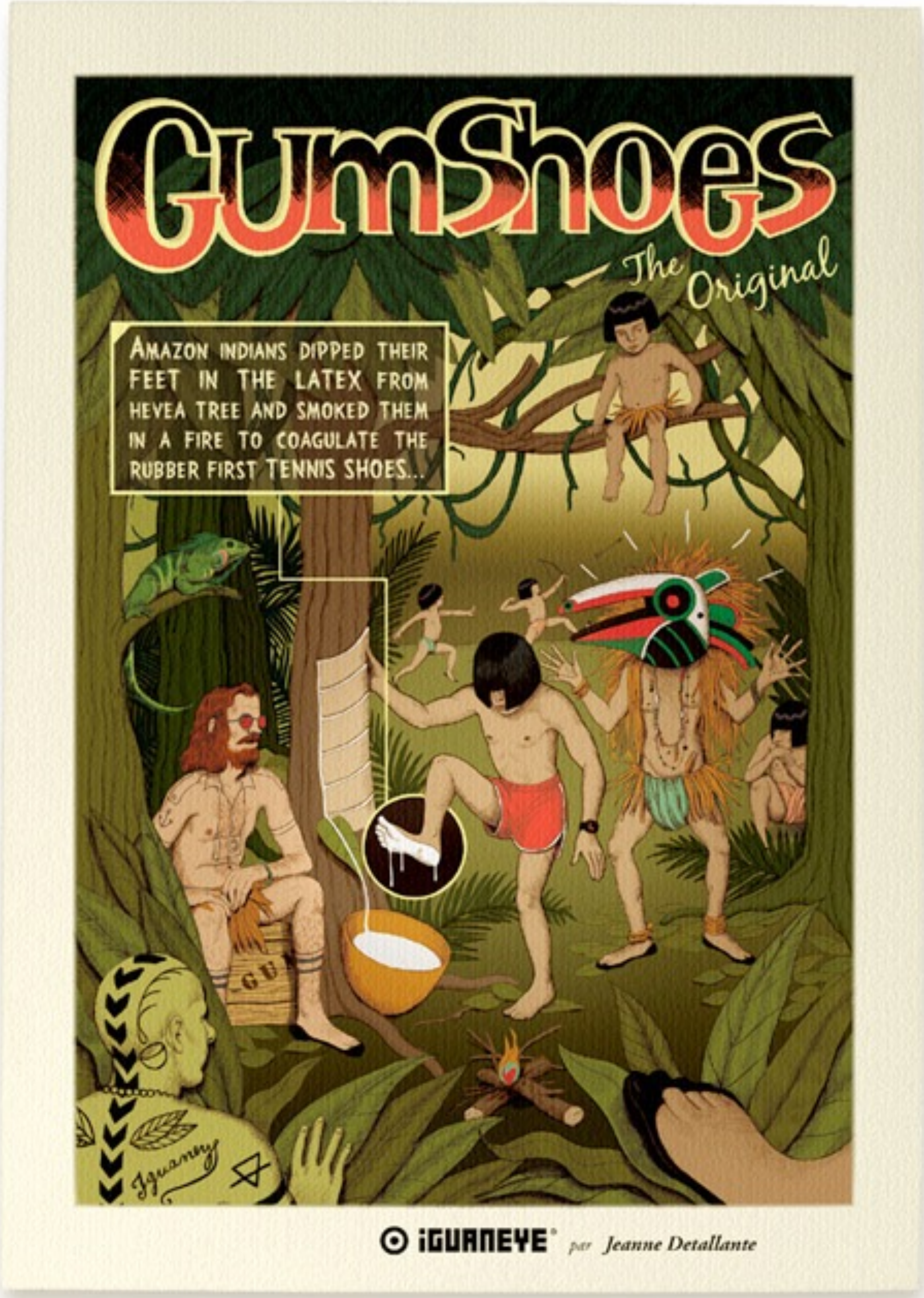
- Entropic Dominance
- Unusual Ground States (T=0)

Five Vignettes

- The Amazon boot and Mr Goodyear
- Heated Polymers
- Fluid Membranes
- Elastic Membranes
- Faceted Liquids

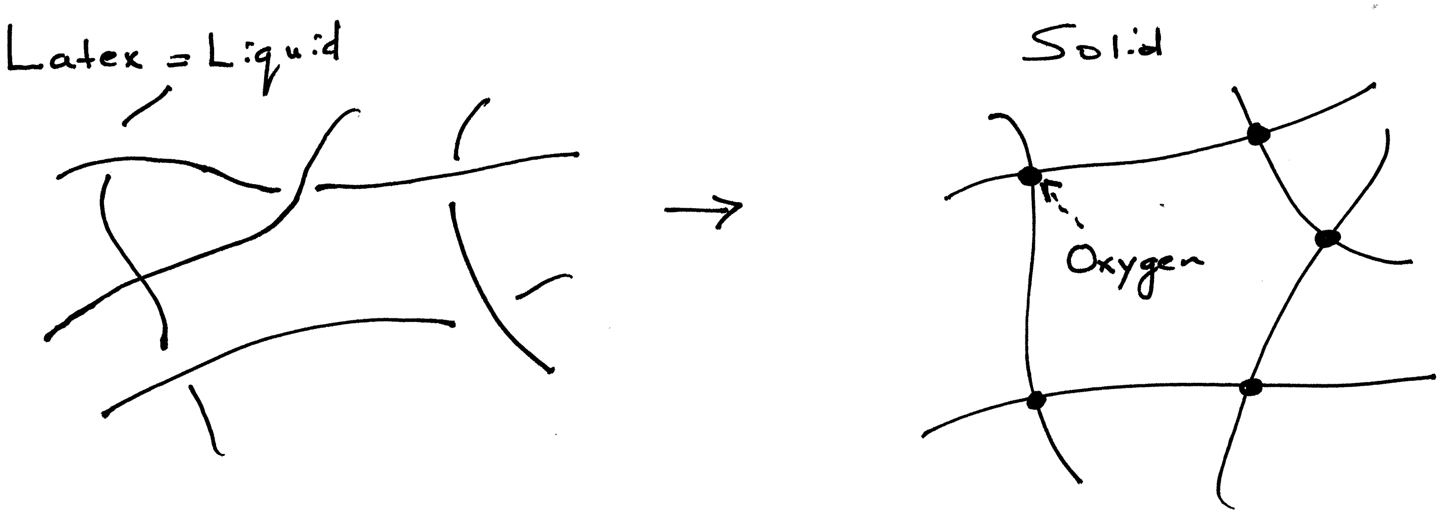
The Amazon Boot & Mr Goodyear

configurable matter



How do we understand this trick today 2500 years later?

The initial liquid, or *latex*, contains long-chained molecules, like spaghetti, quite soft and quite flexible.
The noodles are 100,000 smaller than ramen noodles.
After exposure to air, oxygen crosslinks the chains.



The solid is very unusual

It is solid at the macroscopic scale, but a fluid at the microscopic scale. This is rubber.

But: the amazon boot disintegrates after a day. The oxygen is too reactive and eventually cuts the chains so the rubber net falls apart.

How can this prevented?

Goodyear (1839) boiled hevea latex with sulphur. Sulphur cross-links like oxygen but doesn't cut the chains. This yields **natural rubber**.

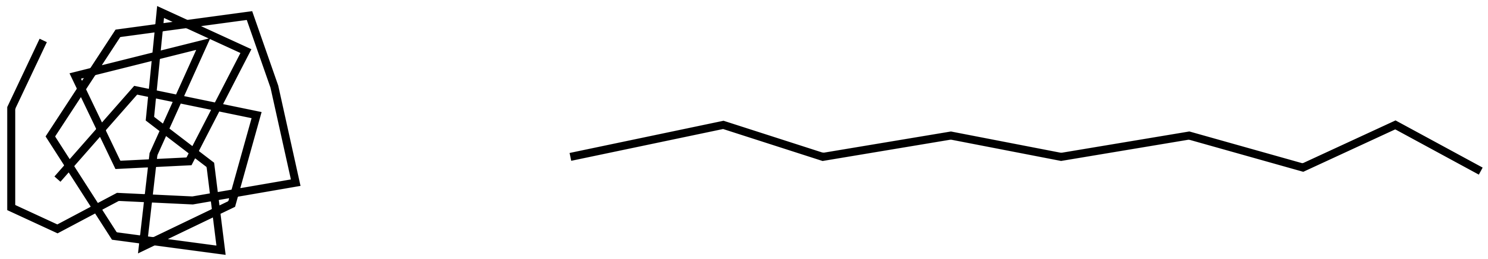
Only one in 200 Carbon atoms reacts with sulphur - a tiny effect can trigger a phase transformation!

Heated polymers:
entropic dominance

Thermodynamic equilibrium determined by minimizing a free energy

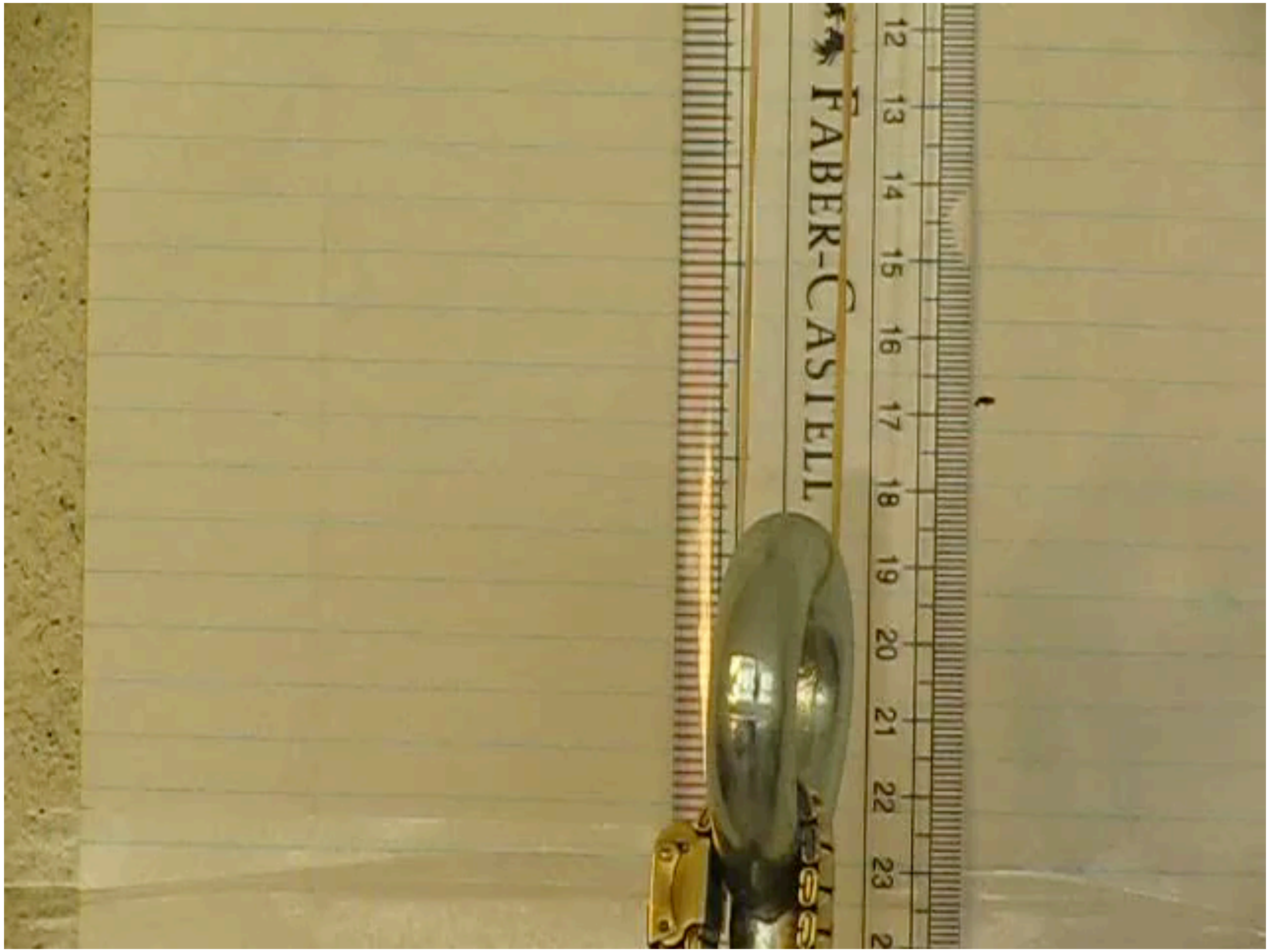
$$F = U - TS$$

Many more configurations are crumpled vs straight



The entropy for crumpled configurations is higher than for straight configurations and entropy is dominant as T increases

Thus polymers contract when heated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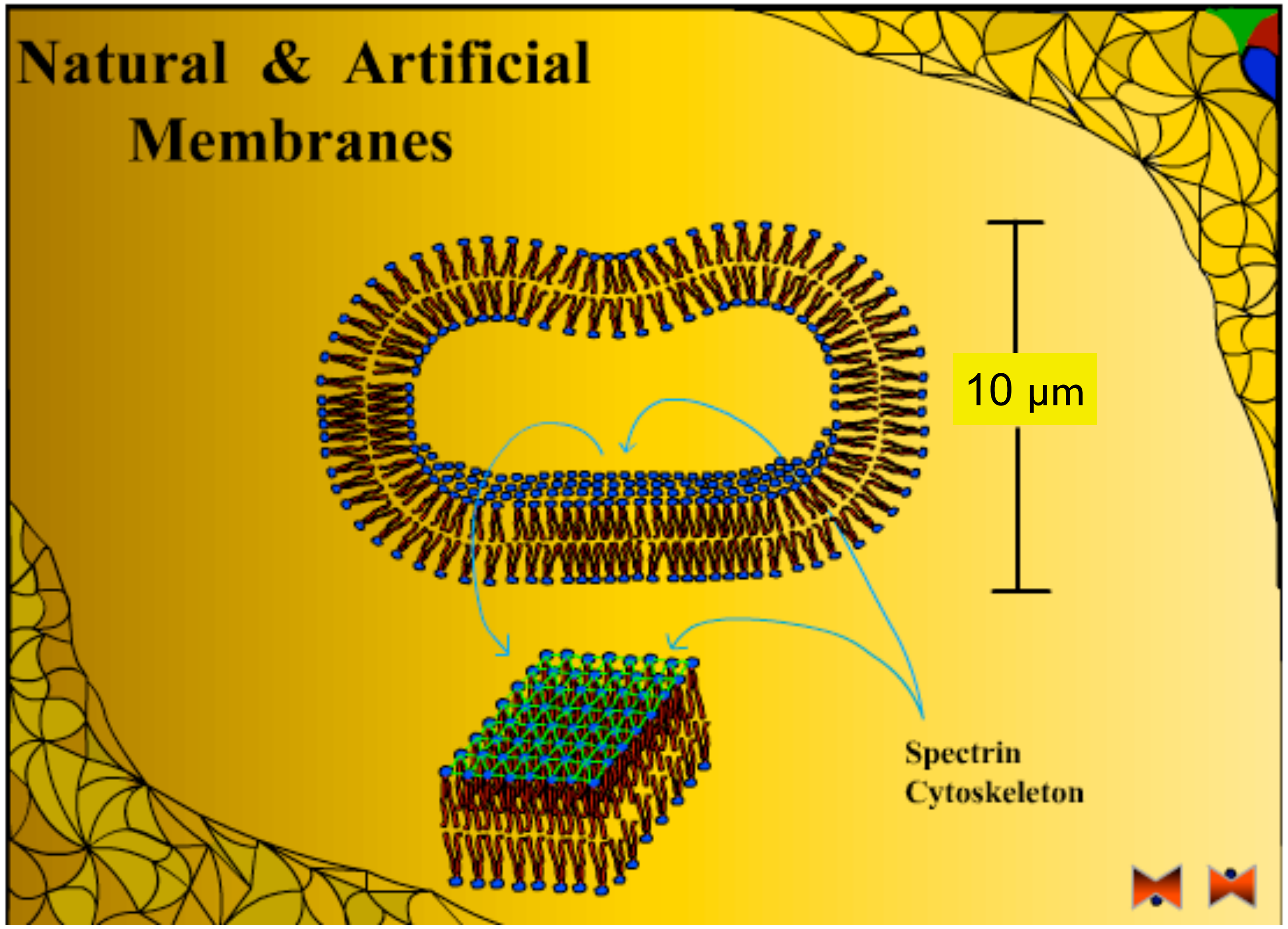
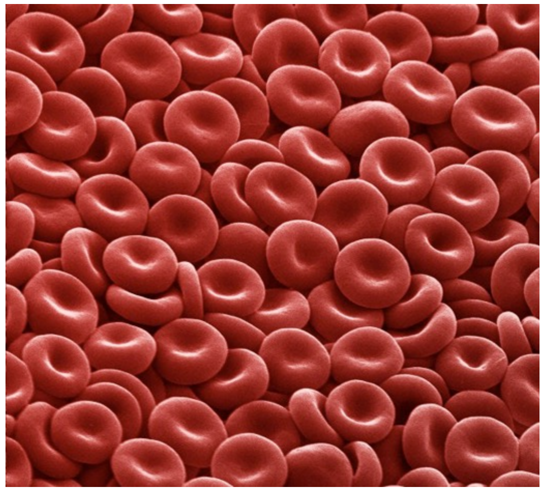
Fluid Membranes

Ultimate softness





Red blood cells flicker when viewed in a microscope.

The flickering was considered by some naturalists at the beginning of the 20th C to be some kind of manifestation of life.

But red blood cells are highly flexible even though fragile.

$$E = \kappa \int d^2x\, H^2$$

$$\kappa_R(q) = \kappa - \frac{3kT}{4\pi} \ln(1/qa)$$

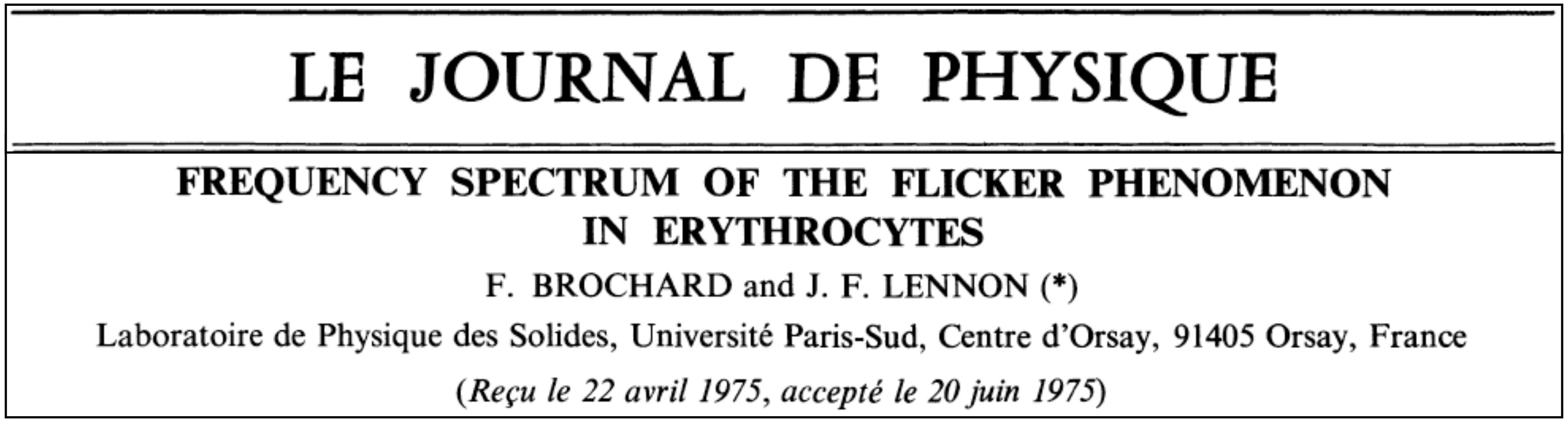
Thermal fluctuations reduce the bending rigidity at large length scales so that large thermal shape fluctuations are possible

$$\beta(\alpha_R = \kappa_R^{-1}) = -\frac{3kT}{4\pi}\alpha_R^2$$

Asymptotic freedom!

At the IPC (Paris, 1975) J.F. Lennon studied the correlations of the membrane. He observed the cell:

- at a particular point and at a given time, and
- at another point some time later



LE JOURNAL DE PHYSIQUE

FREQUENCY SPECTRUM OF THE FLICKER PHENOMENON IN ERYTHROCYTES

F. BROCHARD and J. F. LENNON (*)
Laboratoire de Physique des Solides, Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France

(*Reçu le 22 avril 1975, accepté le 20 juin 1975*)

Francoise Brochard (1975) calculated these correlations from pure shape fluctuations and they matched!

Physics not mysticism!

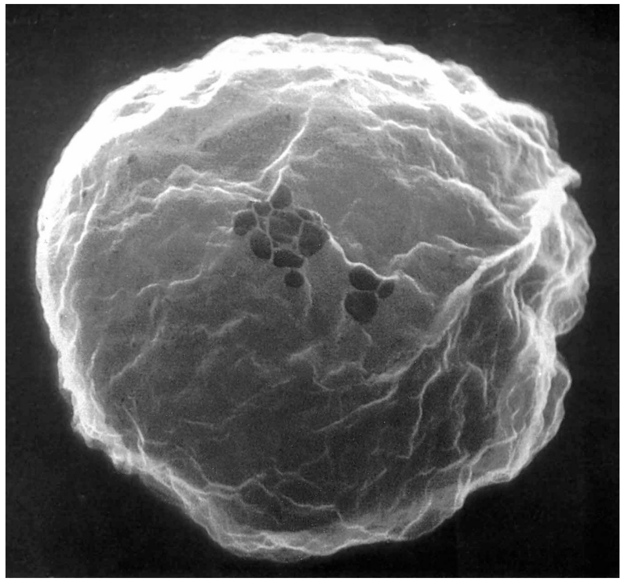
Elastic (polymerized) membranes

Entropically-stabilized phases

$$\mathrm{E} = \mathrm{E}_{el} + E_{bend}$$

$\uparrow$

shear (μ) + compression (K)



$$\mathrm{E}_{el} = \frac{1}{2}\int d^2x[2\mu u_{ij}^2 + \lambda u_{kk}^2]$$

where $\mathrm{u}_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i h \partial_j h)$ (strain tensor)

$$\mathrm{E}_{bend} = \frac{\kappa}{2}\int d^2x(\nabla^2 h)^2$$

In this case thermal fluctuations stiffen the membrane at large wavelengths and soften the shear modulus

$$\kappa_R(q) \to \infty \;\; (q \to 0)$$

$$\mu_R(q) \to 0 \;\; (q \to 0)$$

$$K_R(q) \to 0 \;\; (q \to 0)$$

Poisson ratio

$$\sigma = \frac{K - \mu}{K + \mu} \to -1/3$$

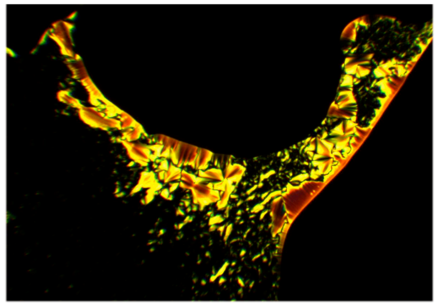
Universal entropic-driven anti-rubber

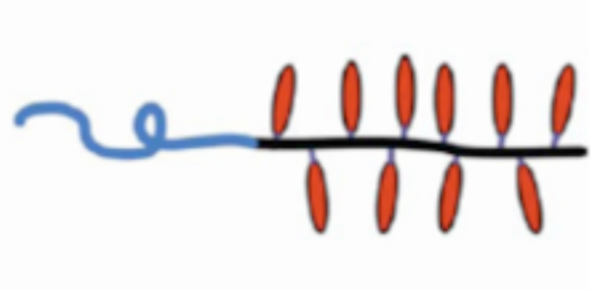
Faceted Liquids: How to build a liquid with the shape of a gem stone

Unusual ground states

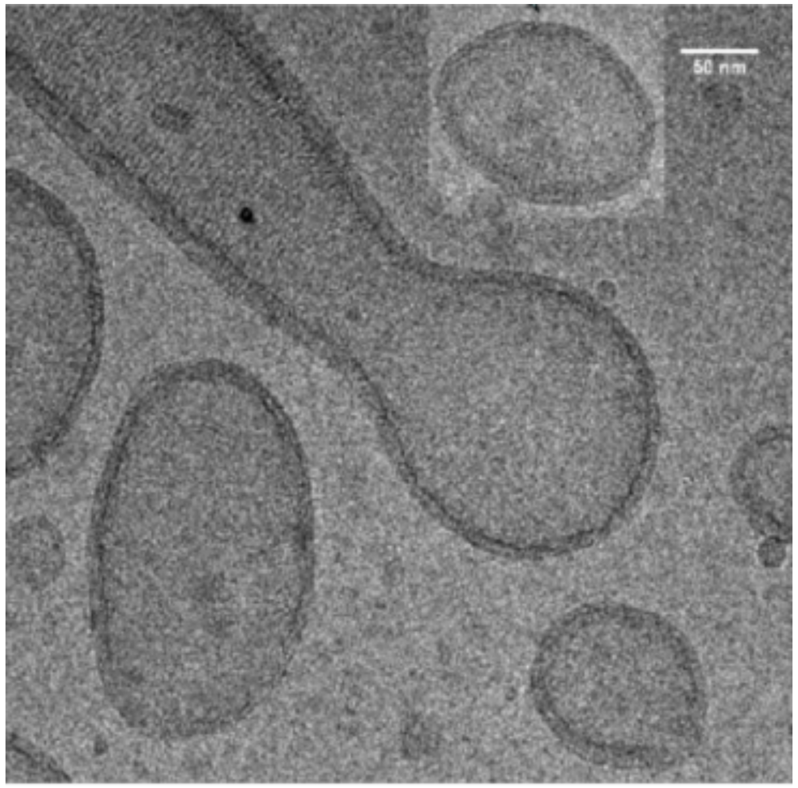
Ingredients

A rod-coil A-B block copolymer
+ side-chain liquid-crystal formers





These synthetic amphiphiles self-assemble to form bilayers and giant unilamellar vesicles called **polymersomes**



PEG2000-*b*-PAChol (28/72)

Vesicle: microscopic sac that encloses a volume with a molecularly thin membrane

With clever chemistry the vesicle acquires 2D layered or **smectic** order

What determines the shape of this LC-vesicle?

The energy is a sum of the 2d LC energy and the bending energy (shape)

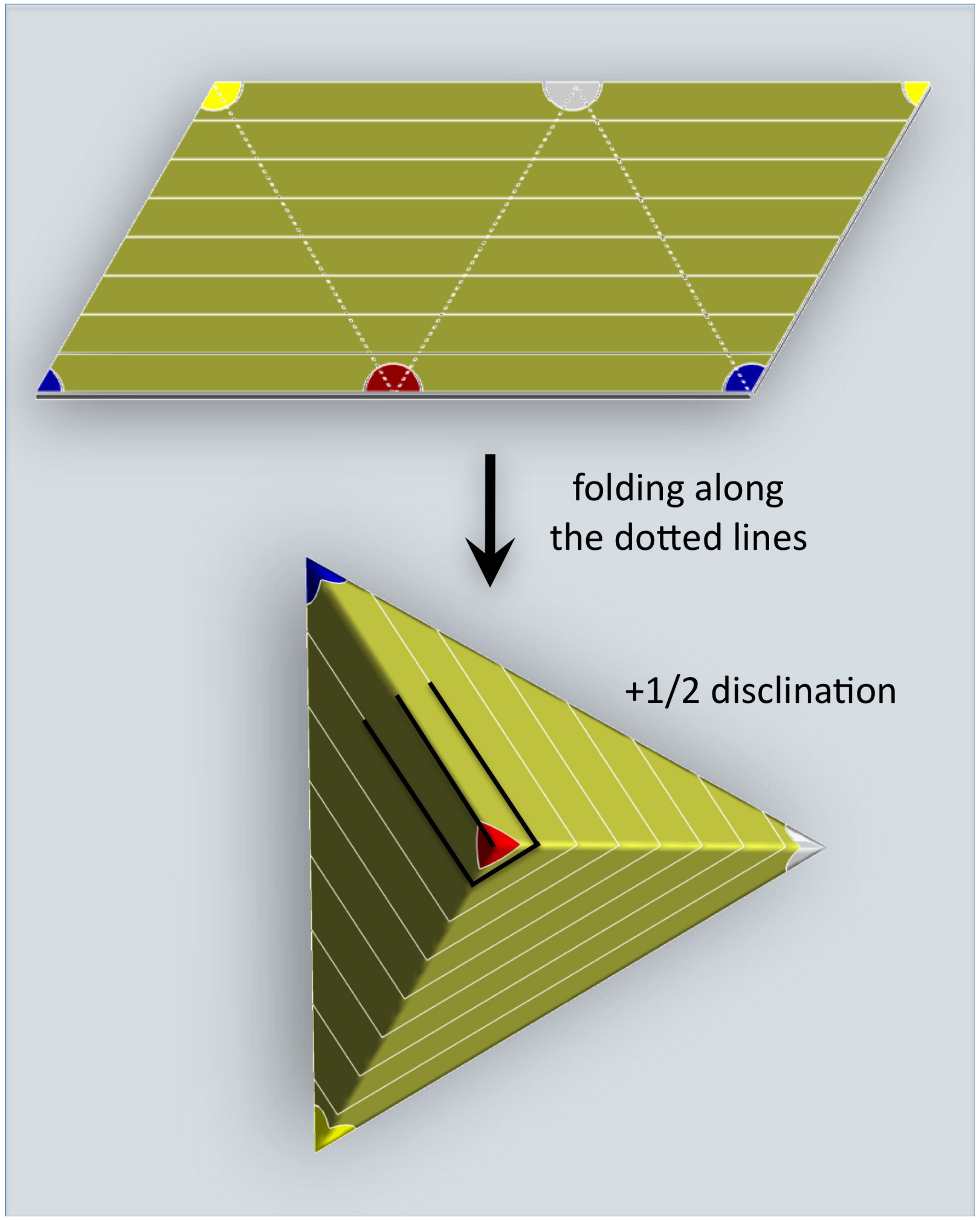
$$E = K E_{LC} + \kappa E_{\rm bend}$$

For large bending rigidity κ you get round vesicles

For small bending rigidity you parallel layers on a flat surface which has to be topologically round

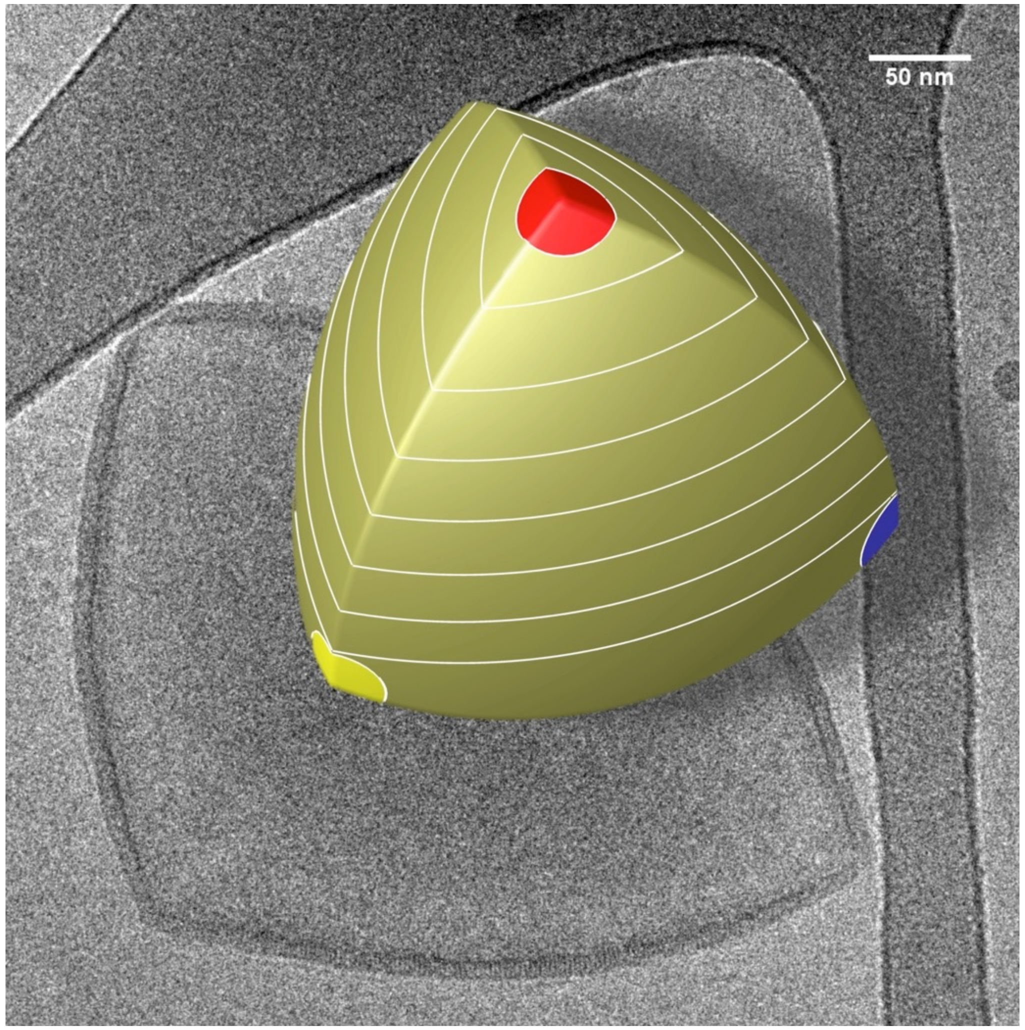
The solution?

Go polyhedral!



folding along
the dotted lines

+1/2 disclination



Smectic Trojan Horse: Barcelona

Conclusions

- Easy deformability (soft) leads to complex geometries.
  - Polymer walks, crumpled membranes, polyhedral liquids
- Multiple phases as a function of length and time scales
  - Microscopic fluid to macroscopic solid (Amazon boot)
- Extreme responses to small changes in conditions
  - 0.5% cross-linking radically changes phase
- Entropic Dominance
  - Negative coefficient of thermal expansivity for polymers
  - Thermal stiffening of elastic membranes
- Unusual Ground States (T=0)
  - Faceted liquids