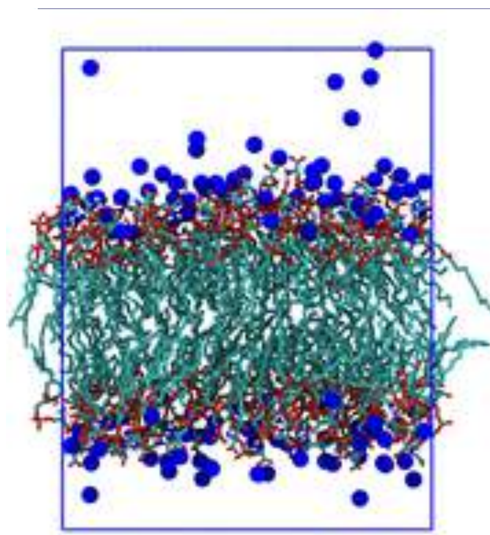
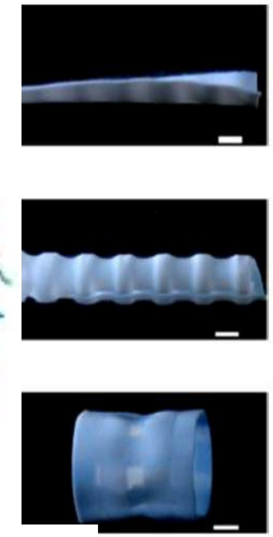
“Soft Materials Design by Computer Simulations”

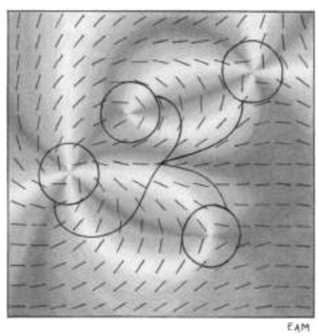
Monica Olvera de la Cruz

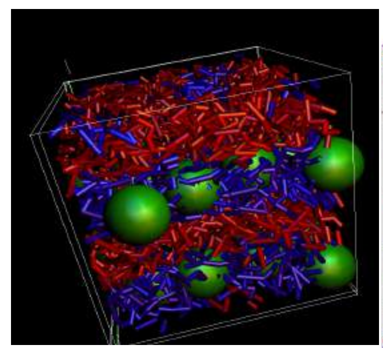
NORTHWESTERN UNIVERSITY

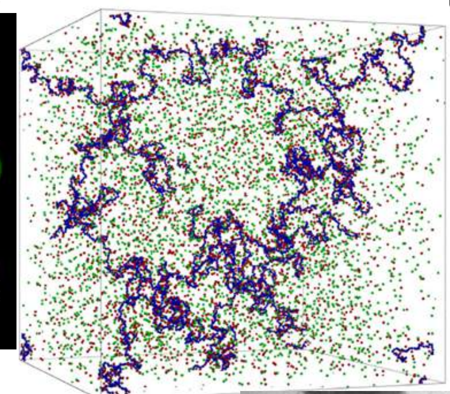
Soft materials constitute the basic component of living systems, are integrated into the fabric of modern society, and will play a key role in futuristic devices.





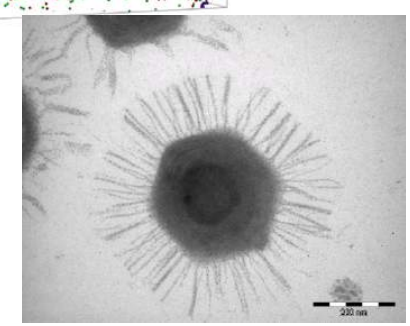






Examples:

Liquid crystals, colloids,
polymers, surfactants,
membranes (liquid or elastic),
gels, viruses,…



Soft Materials are Hard

- Polymers and soft materials are for the most part *amorphous* fluids or solids with embedded structures spanning nanometers to microns and even millimeters or more.

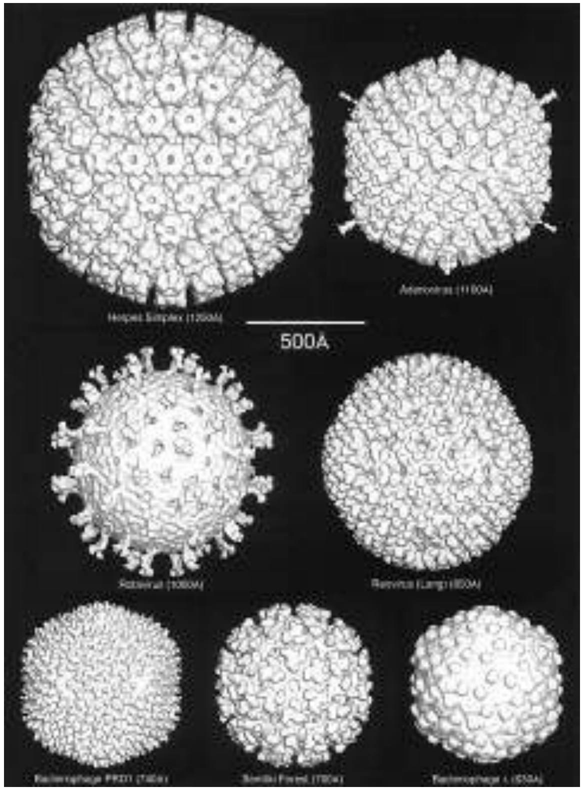
- Soft materials can possess an extraordinarily broad spectrum of *timescales* often covering more than ten orders of magnitude.

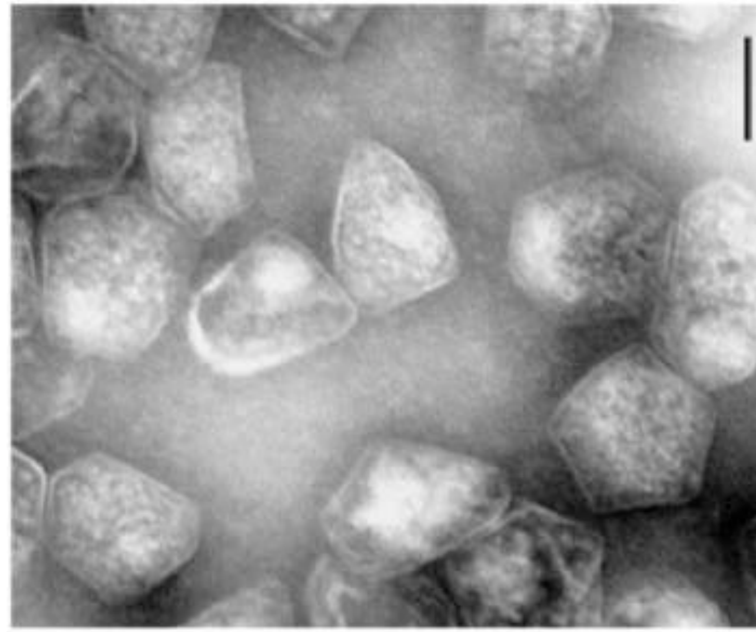
- In many cases the relaxation processes contributing to this broad spectrum involve nonequilibrium phenomena such as vitrification, jamming, or constrained crystallization

Motivation

- Because of the combination of chemical versatility and the ability to create structures with unique tailored features at different length scales, soft matter entities are attractive materials from which to construct novel materials
- Soft matter is fascinating and there are many open problems
- Advances rely on physics, chemistry, biology and engineering

Shells in the Living World

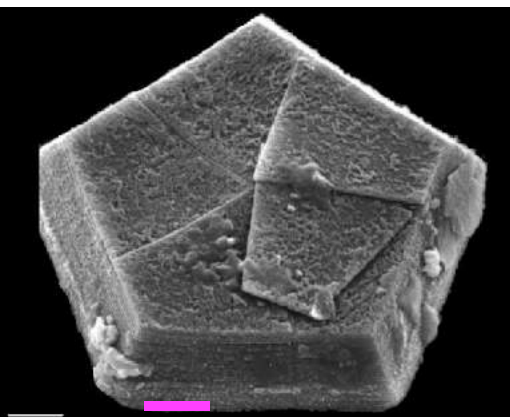




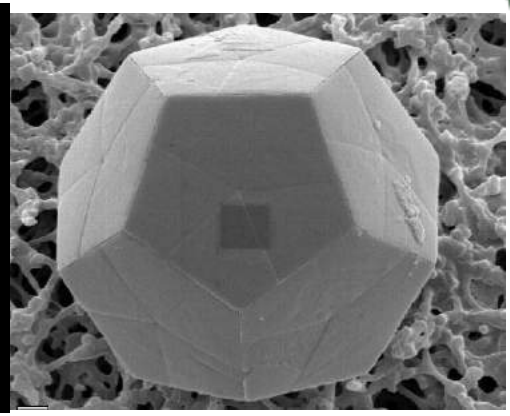
Viral capsids are the shells of viruses that contain DNA or RNA) are icosahedra when they are large

Organels are cellular nano-compartments (nano-reactors that synthesize energy) that take many polyhedral geometries (Bacterial microcompartments Fan CG, et al. PNAS (2010))

Dodecahedral Coccolithophorids

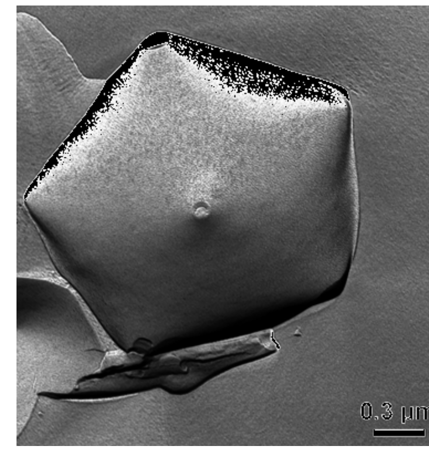


1 µm

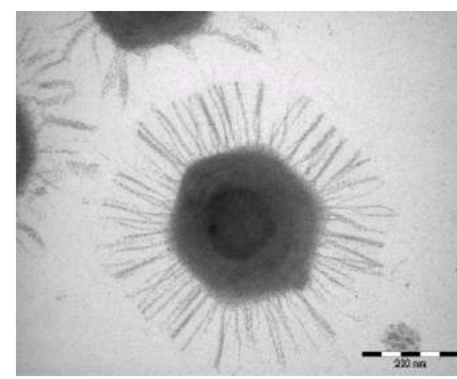


Braarudosphaera bigelowii *Braarudosphaera bigelowii*

images from Jeremy Young's web page
National History Museum, London, UK
images courtesy of Pupa Gilbert, UW-Madison



Glinel,K. et al.

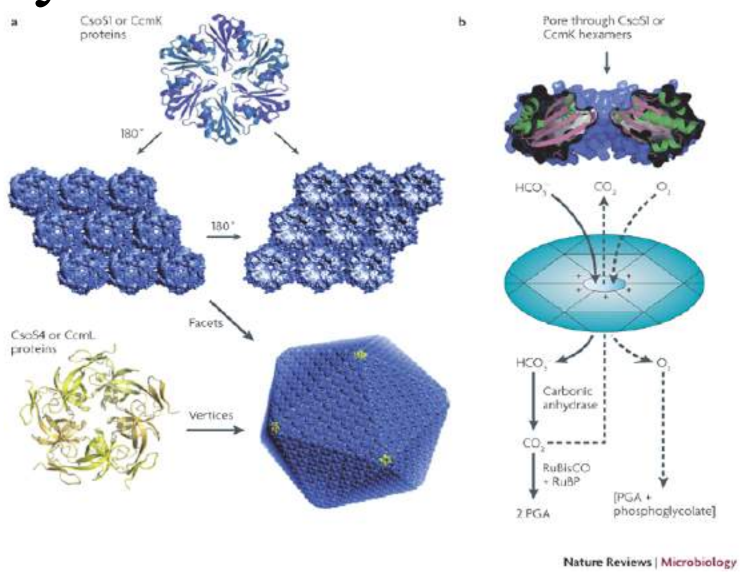


Viruses (ex: Mimivirus)

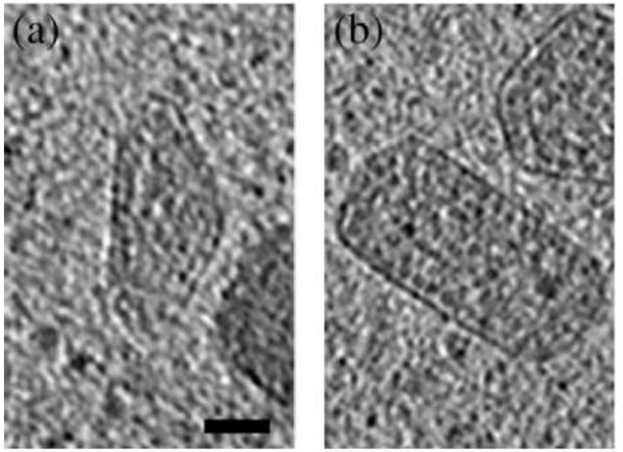
Biological examples include viruses, organelles and archaea organisms

Carboxysomes

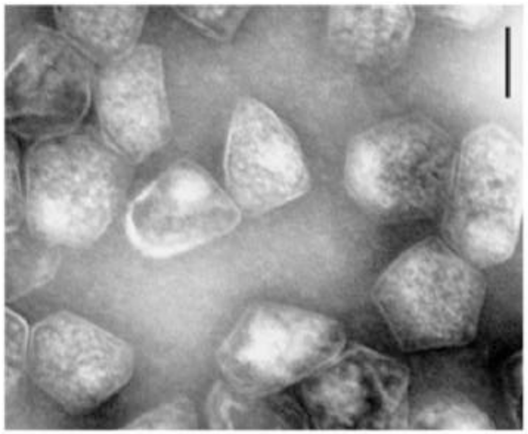
(Iancu, *et al.*, J. Mol. Biol. (2010))



(T.O. Yeates et al Nature Rev. 2008)



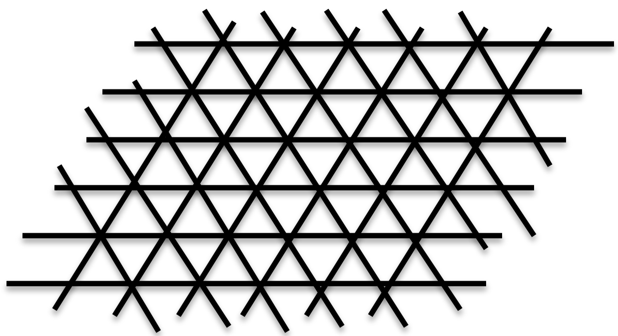
Carboxysomes are bacterial microcompartments (~80 to 140 nm) that contain enzymes (like RuBisCO) involved in carbon fixation.
These organelles are found in all bacteria that fix carbon dioxide.

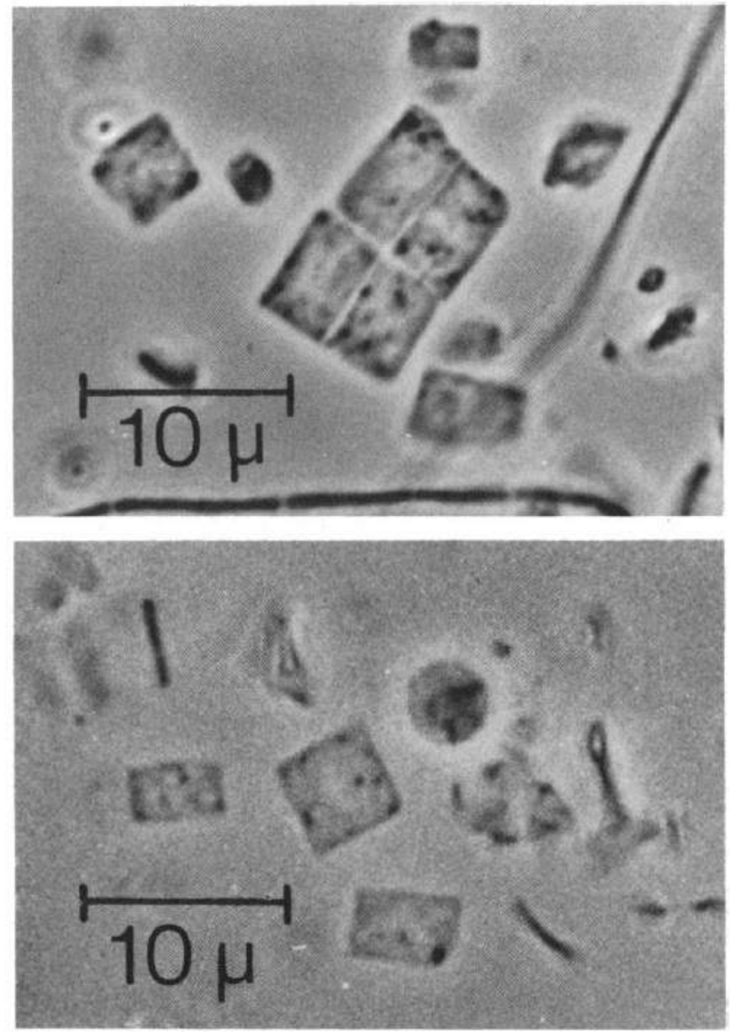


Bacterial microcompartments
Fan CG, et al. PNAS (2010)

Halophilic organisms live at very high salt concentrations

ARCHAE organisms envelops take polyhedral shapes. They have hexagonal packing crystalline surfaces



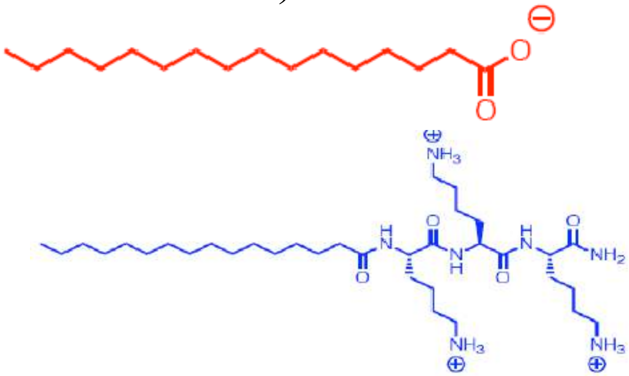


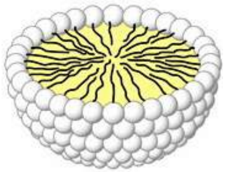
Walby’s Square Baterium (W. Stoeckenius J. BACTERIOLOGY, (1981), 148, 352-360 . Has a hexagonal lattice (W. Stoeckenius *J. BACTERIOL.* (1981))

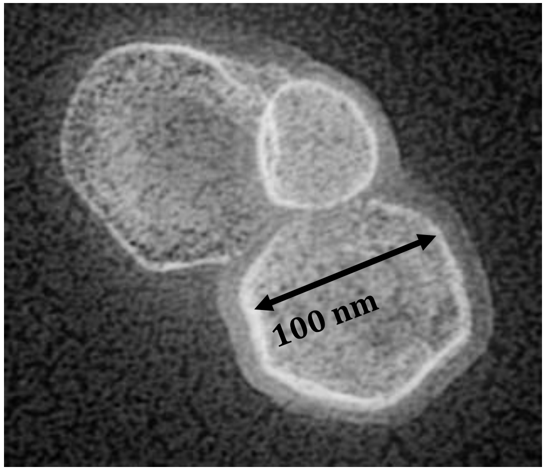
Ionic Membranes

What is the shape of crystalline ionic shells?

palmitic (water insoulble) acid trilysine
(micelle in water)



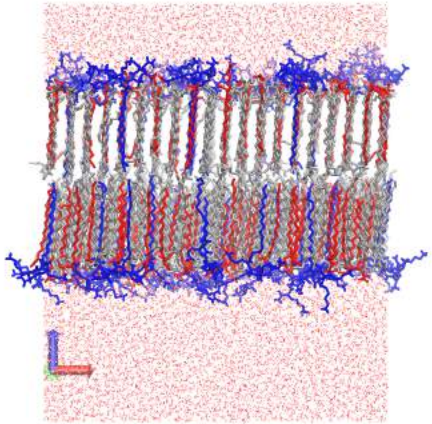




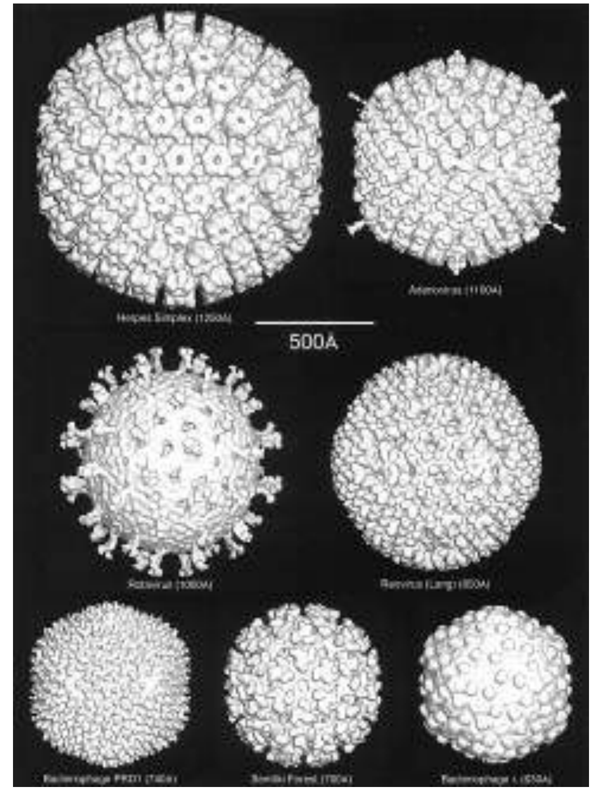
3;1 cationic-anionic amphiphiles (Greenfield, et al., *JACS 2009; Leung et al ACS Nano, 2012)*

X-ray scattering and TEM show a hexagonal lattice that buckled into low symmetry shapes: WHY?

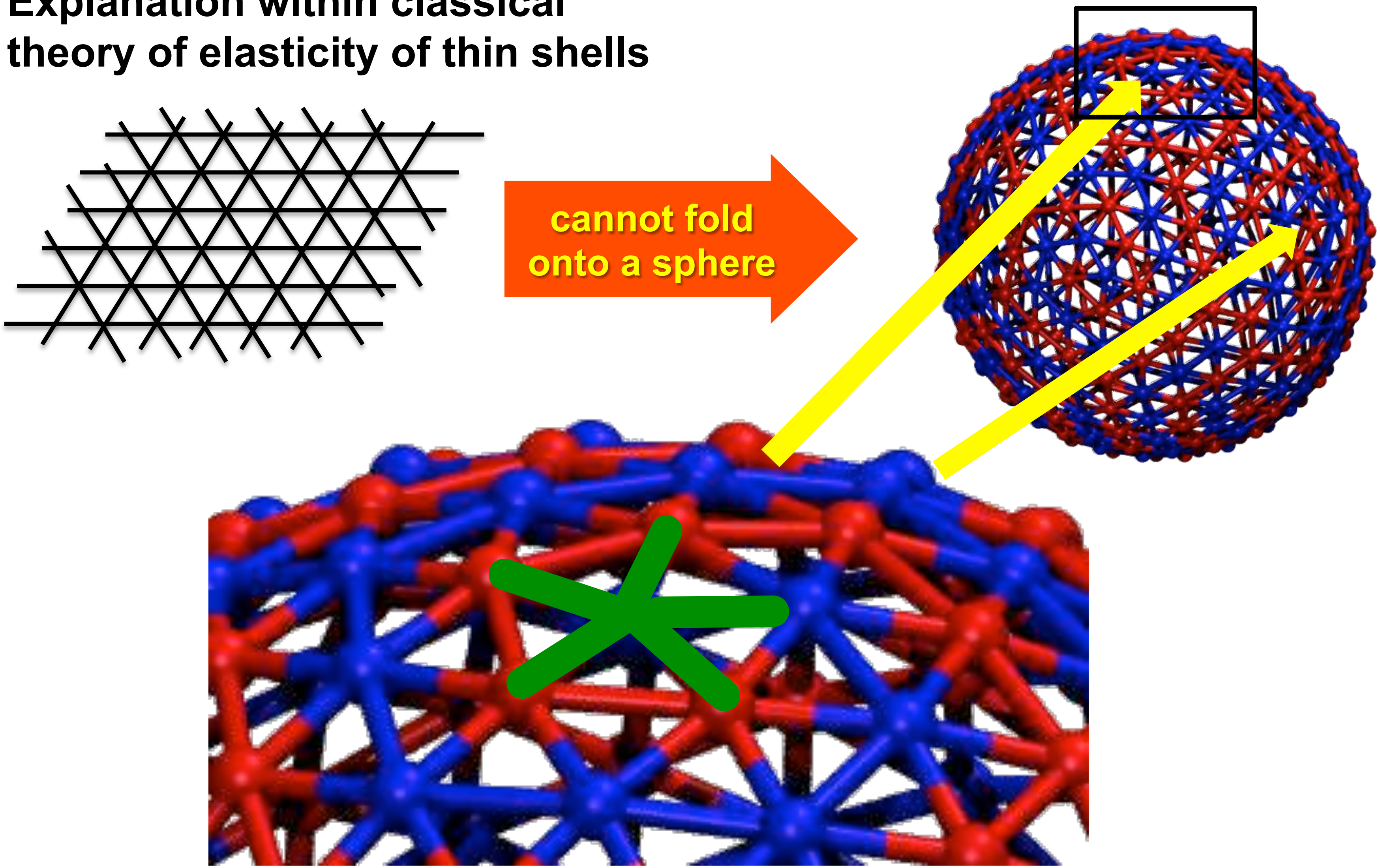
These crystalline shells, are stable even at high salt concentrations. Good for biomedical applications.



Why the icosahedron is ubiquitous?



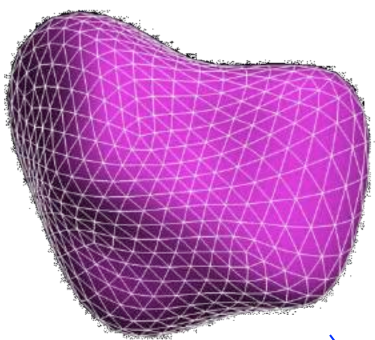
Explanation within classical theory of elasticity of thin shells

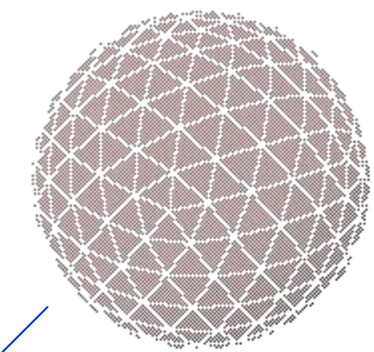


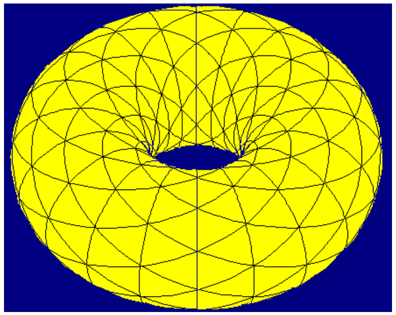
Defects on curved surfaces

$$N_5 - N_7 = 12(1-g)$$

g=1





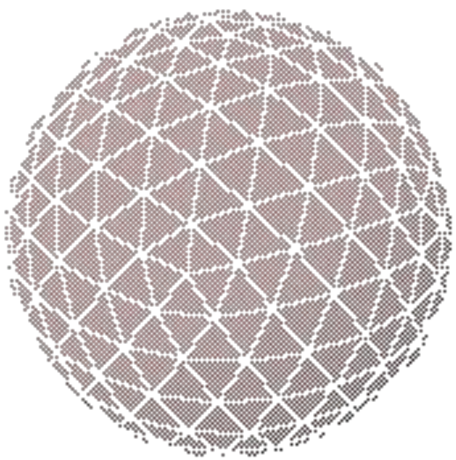


g=0

$$N_5 = N_7 = 0$$

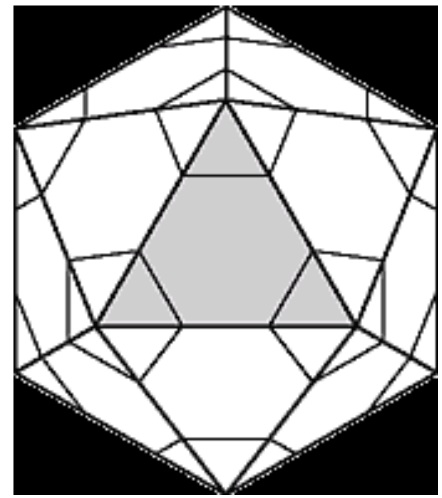
$$N_5 = 12, \;\; N_7 = 0$$

Defects (disclinations) on curved crystalline closed spherical surfaces



$g=0$

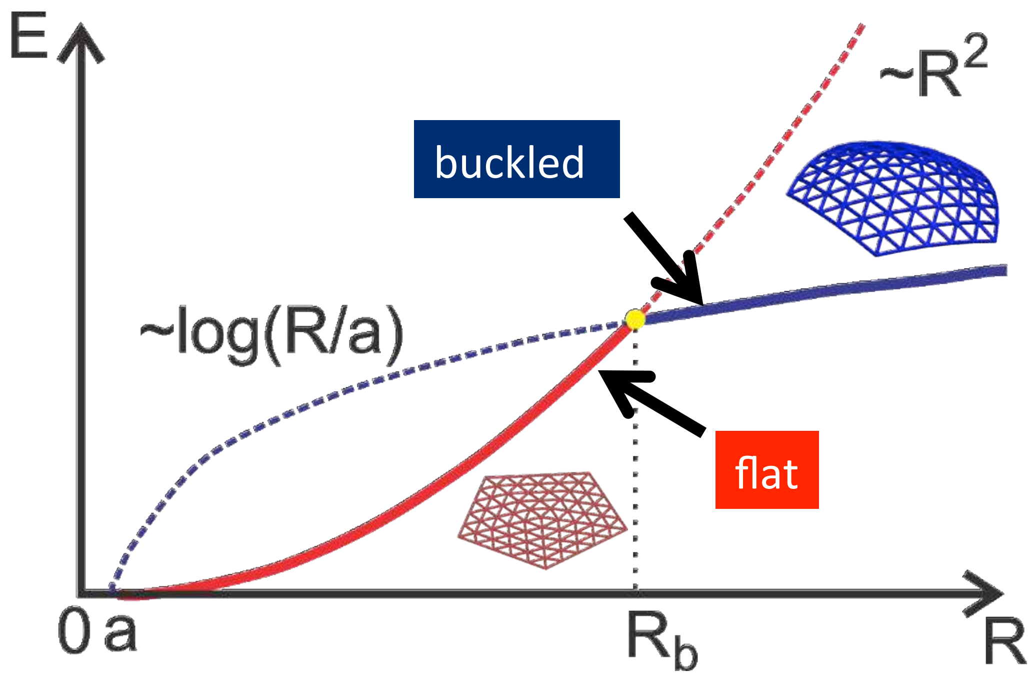
$$N_5 = 12$$

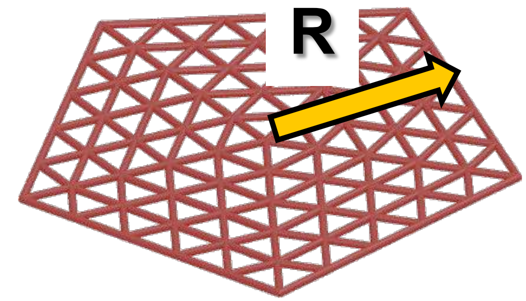


Defects are in icosahedral positions (Bowick, Nelson, Travesset Phys. Rev. B (2000))

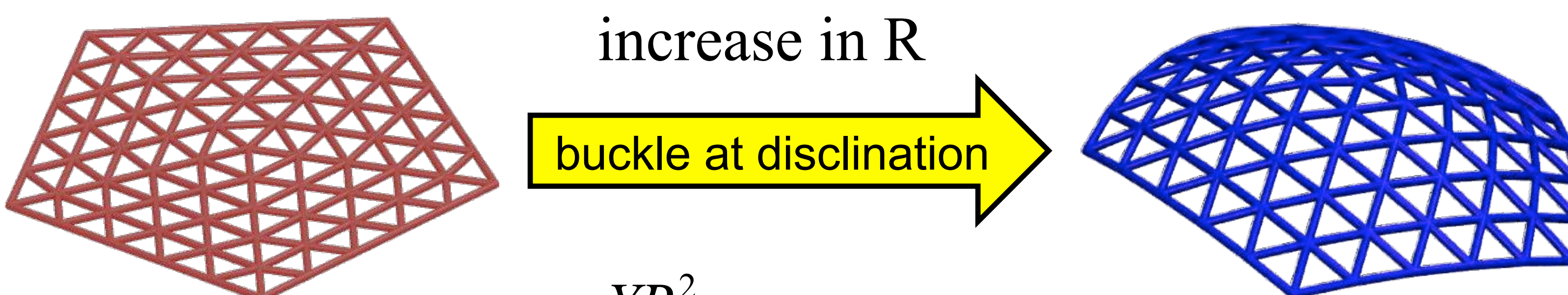
Icosahedral symmetry is not icosahedral buckling (Lidmar, et al, Phys. Rev. E (2003))

Buckling





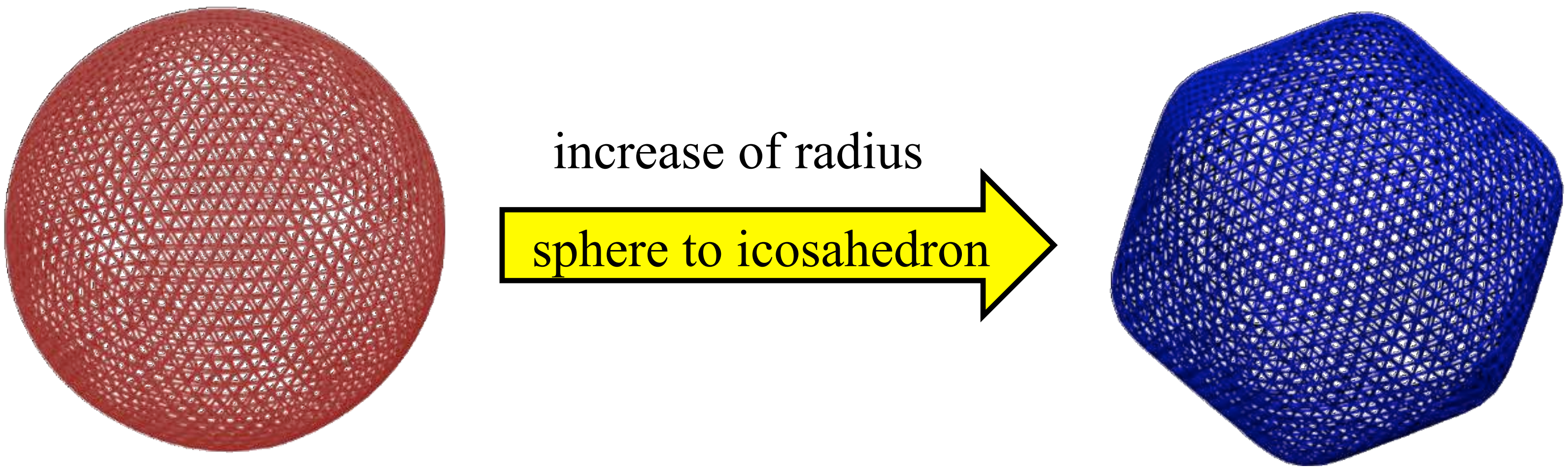
Seung & Nelson, PRA (1988)



$$\gamma = \frac{YR^2}{\kappa} \geq 154$$

Y – Young’s modulus,κ– bending rigidity

On a sphere all 12 defects simultaneously act as seeds for buckling.

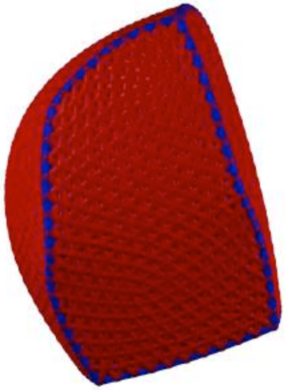


Lidmar, et al, PRE (2003)

How about heterogeneities?

* of elastic parameters

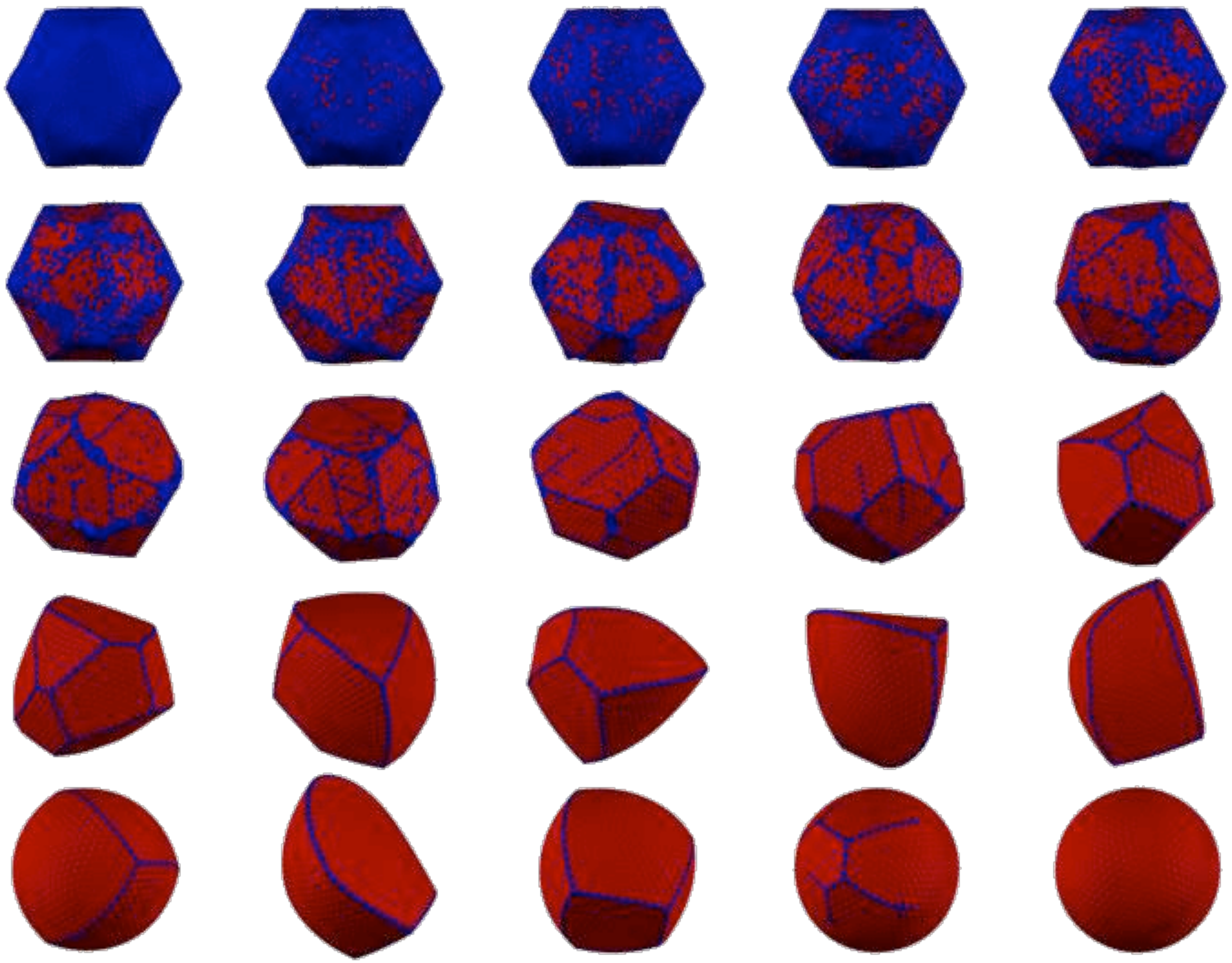
Elastically heterogeneous shells



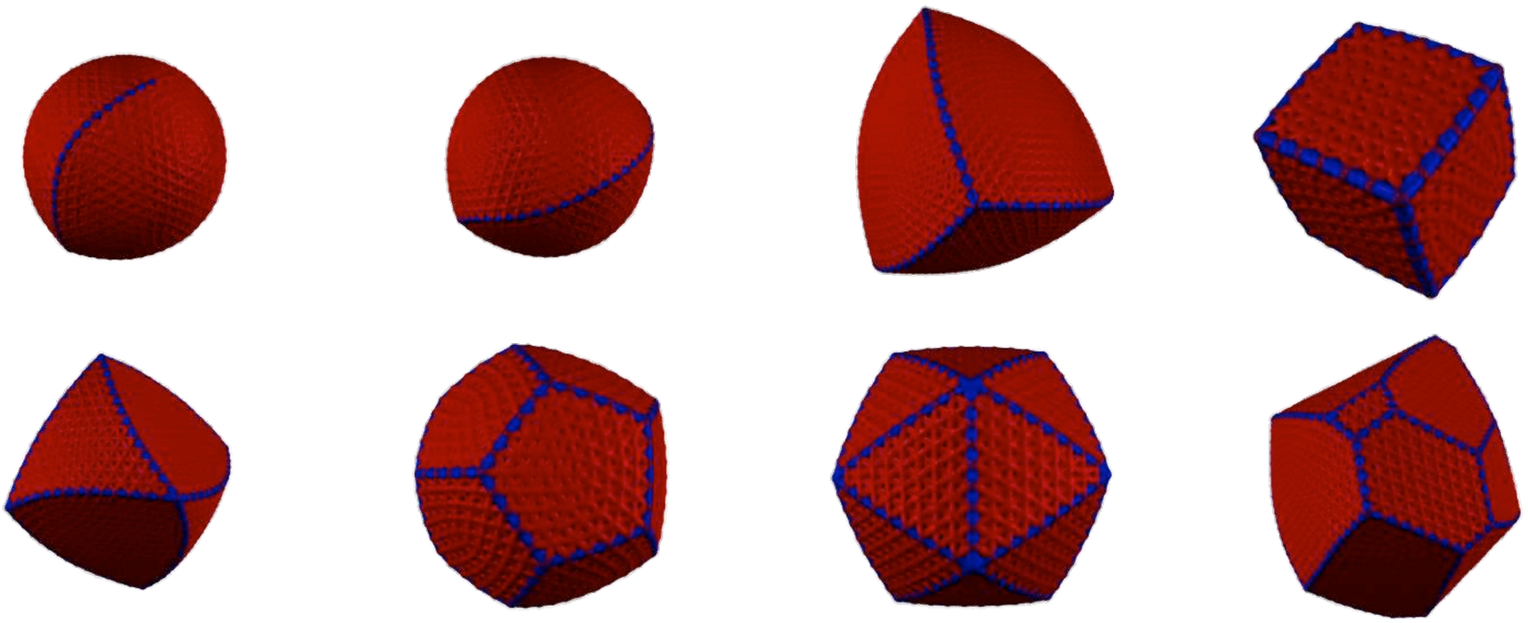
- Shells made by more than one protein or components
- They for many polyhedral geometries with patterns even without chemical incompatibility.
- That is, even compatible components are segregated due to their different mechanical properties which leads to specific buckled shapes.
- The patterns are coupled to the shape of the shell.

Structures of shells

$\kappa_{hard}/\kappa_{soft}=50,\ Y_{hard}/Y_{soft}=1$



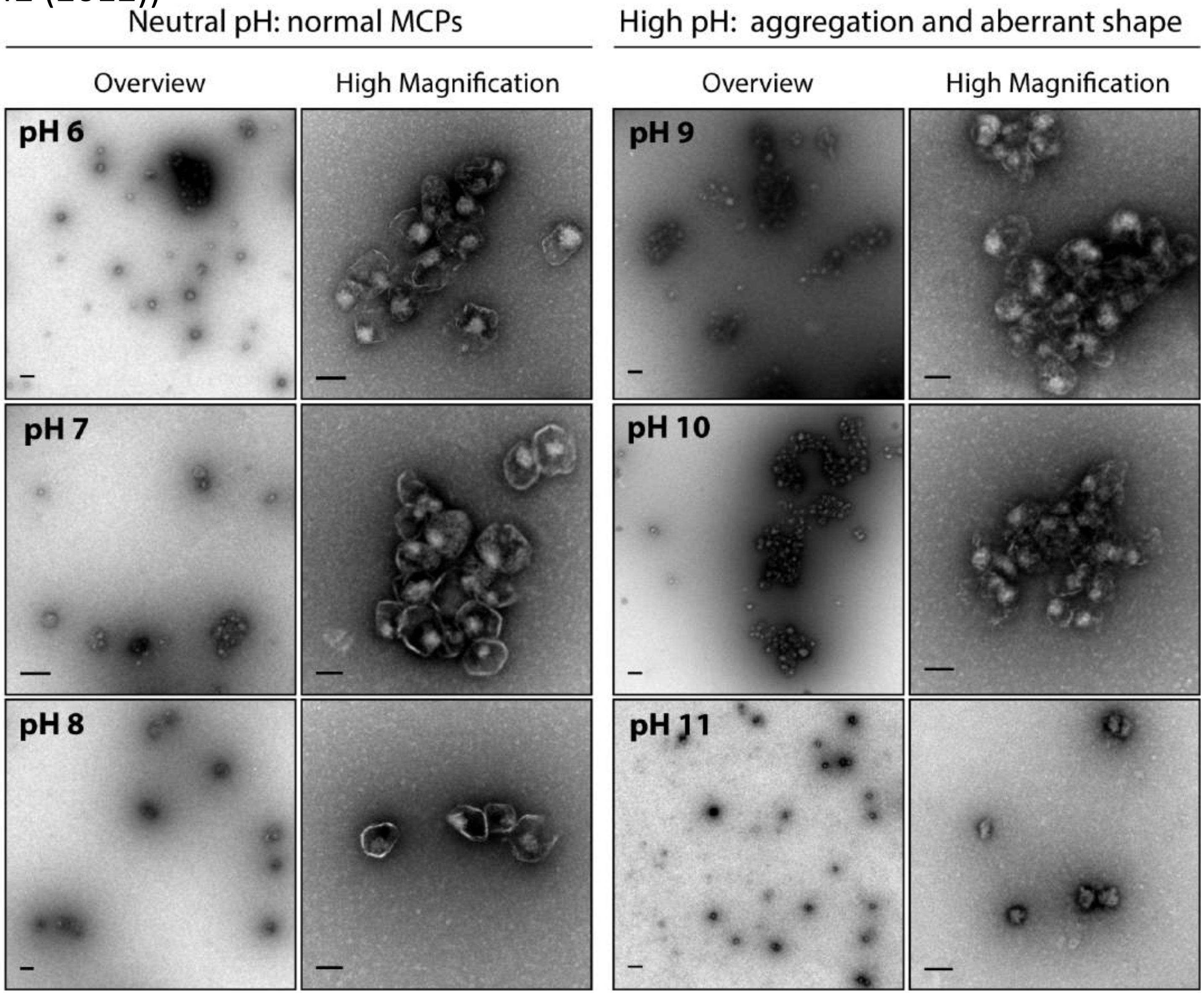
(G. Vernizzi, R. Sknepnek, M. Olvera de la Cruz – PNAS 108, 4292 (2011))



1-hosohedron and 2-hosohedron (top row, on the left), regular platonic solids (tetrahedron, cube, octahedron, dodecahedron and icosahedron) and the truncated polyhedra.

Fragmentation!!

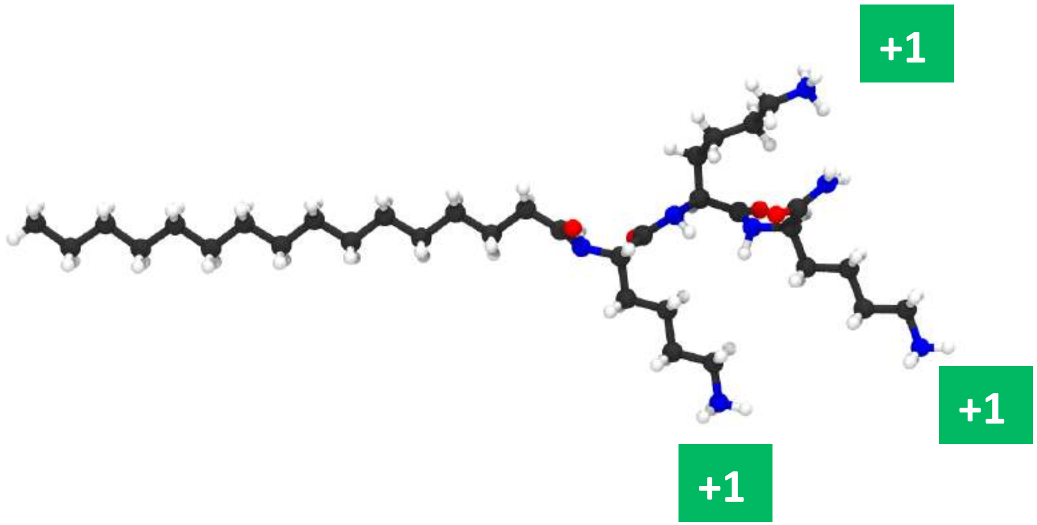
Salmonella Pdu Microcompartments, courtesy of Danielle Tullman-Ercek, UCB (note, when only one protein is present shape is spherical: Schmidt-Dannert Plos One 7, e33342 (2012))



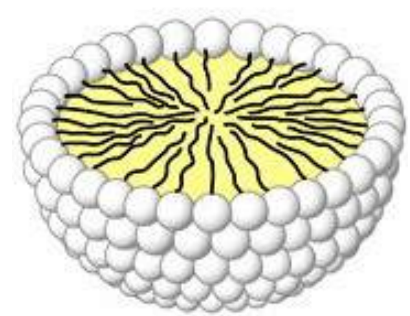
Experiments

palmitic acid trilysine

+3 cation from three lysine amino acid residues



form micelles in water

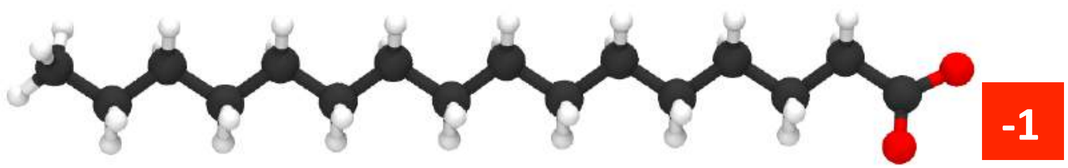


Israelachvili, 1992

---

palmitic acid

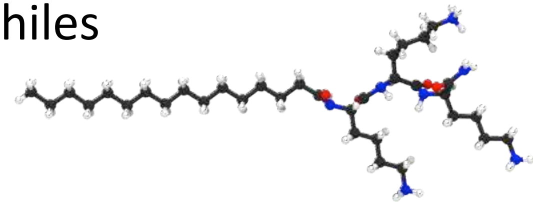
-1 anion from carboxylic acid



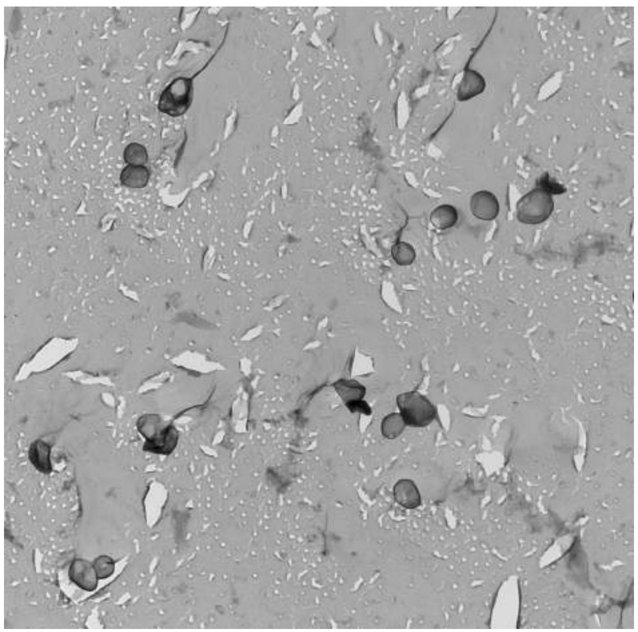
water insolvable

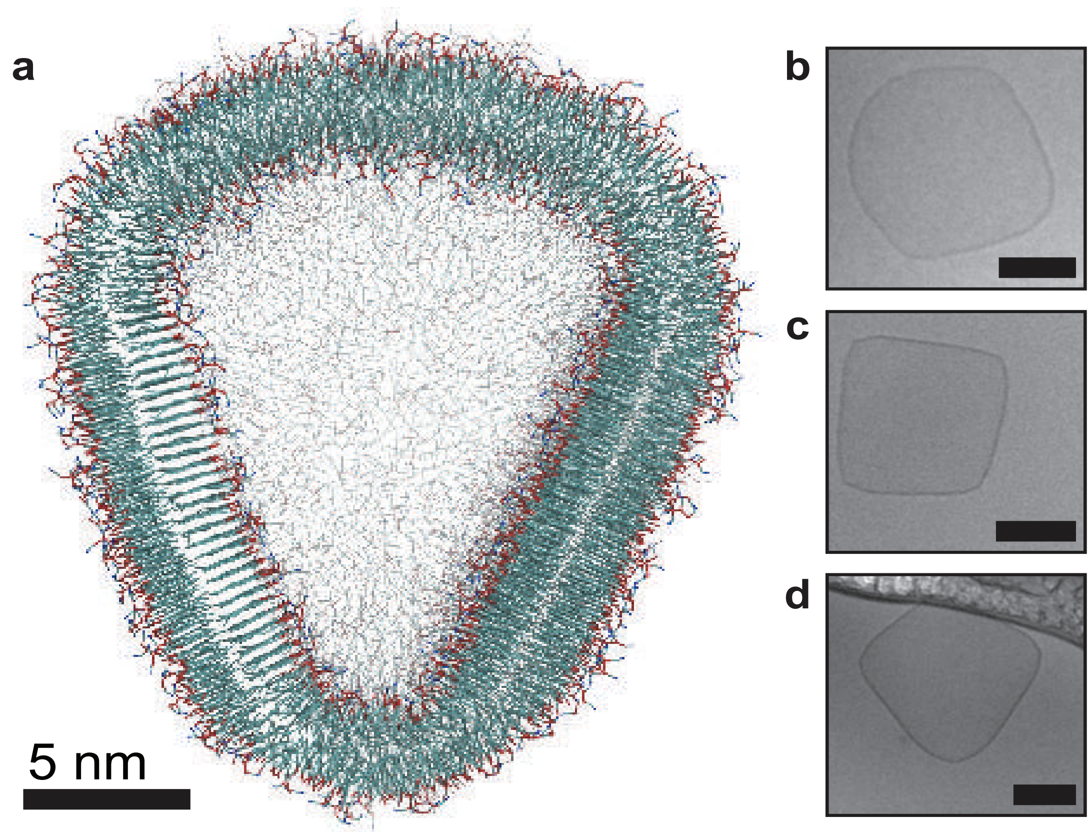
Mixtures of 3+ and -1 amphiphiles

-1

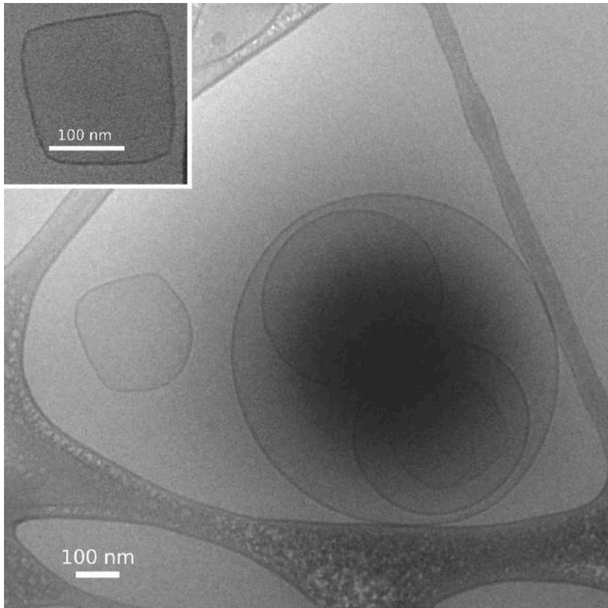


+3

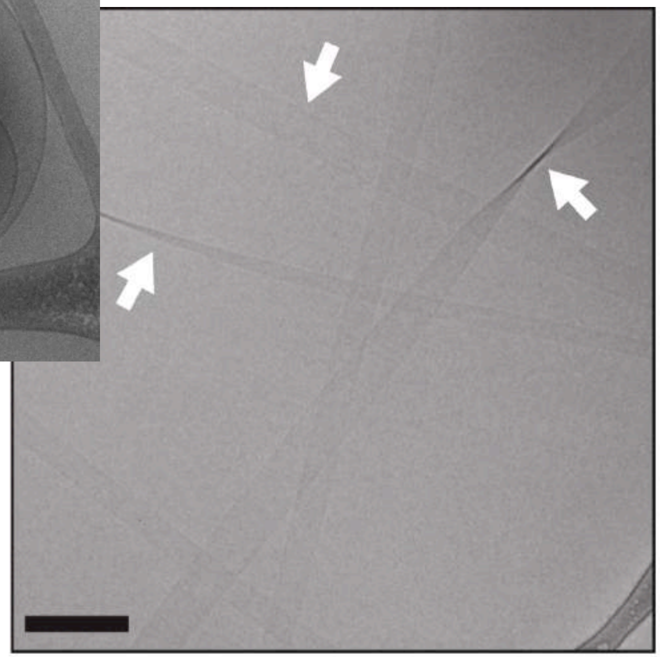




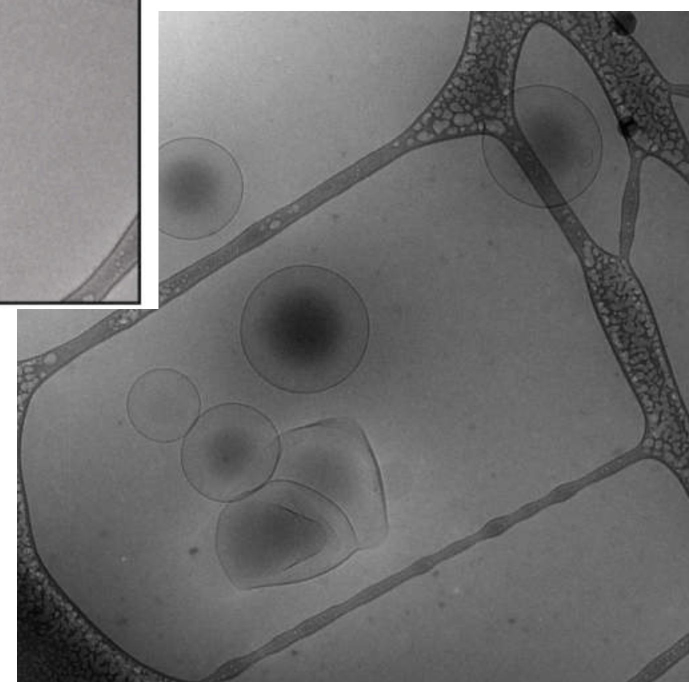
pH 3 to 7 vesicles



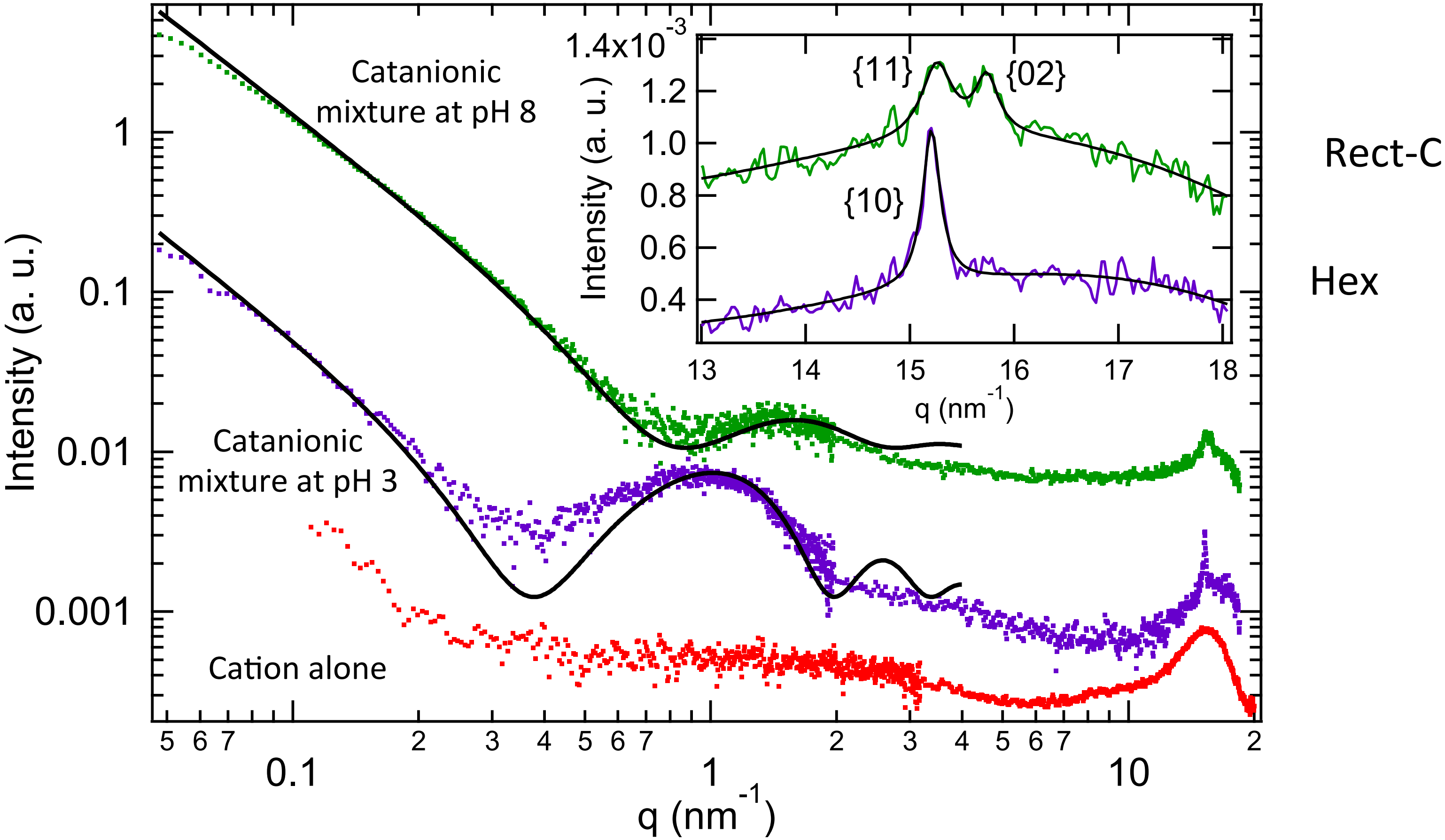
ph 7 to 9 ribbons



ph 10 vesicles



WAXS region

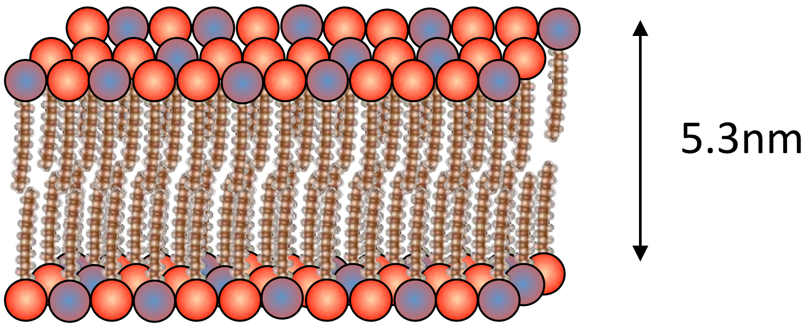


- Lattice was formed only with cation + anion mixture
- The scan with cation micelles alone do not have sharp peaks
- Electrostatic attraction induce crystallization of tails

(Leung et al ACS Nano, 2012)

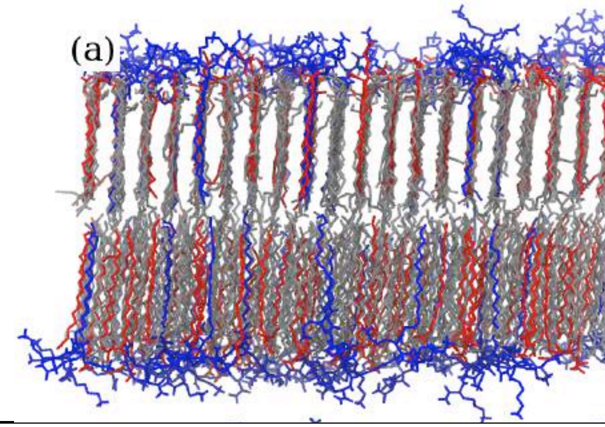
SAXS region

Catanionic bilayer at pH~3
(only some anion ionized)

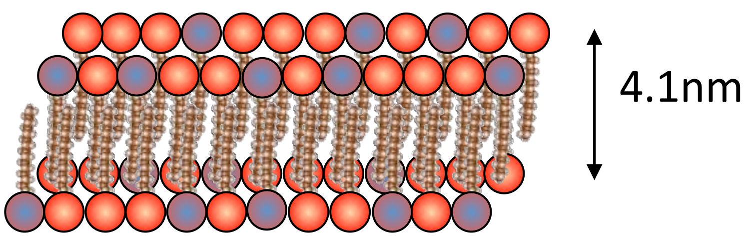


3.9 nm (hydrophobic layer)

Analog to
30% ionization of palmitic acid in atomistic simulation

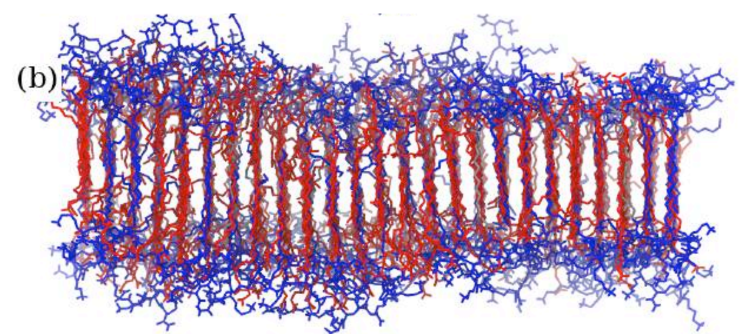


Catanionic bilayer at pH~8
(anion fully ionized)



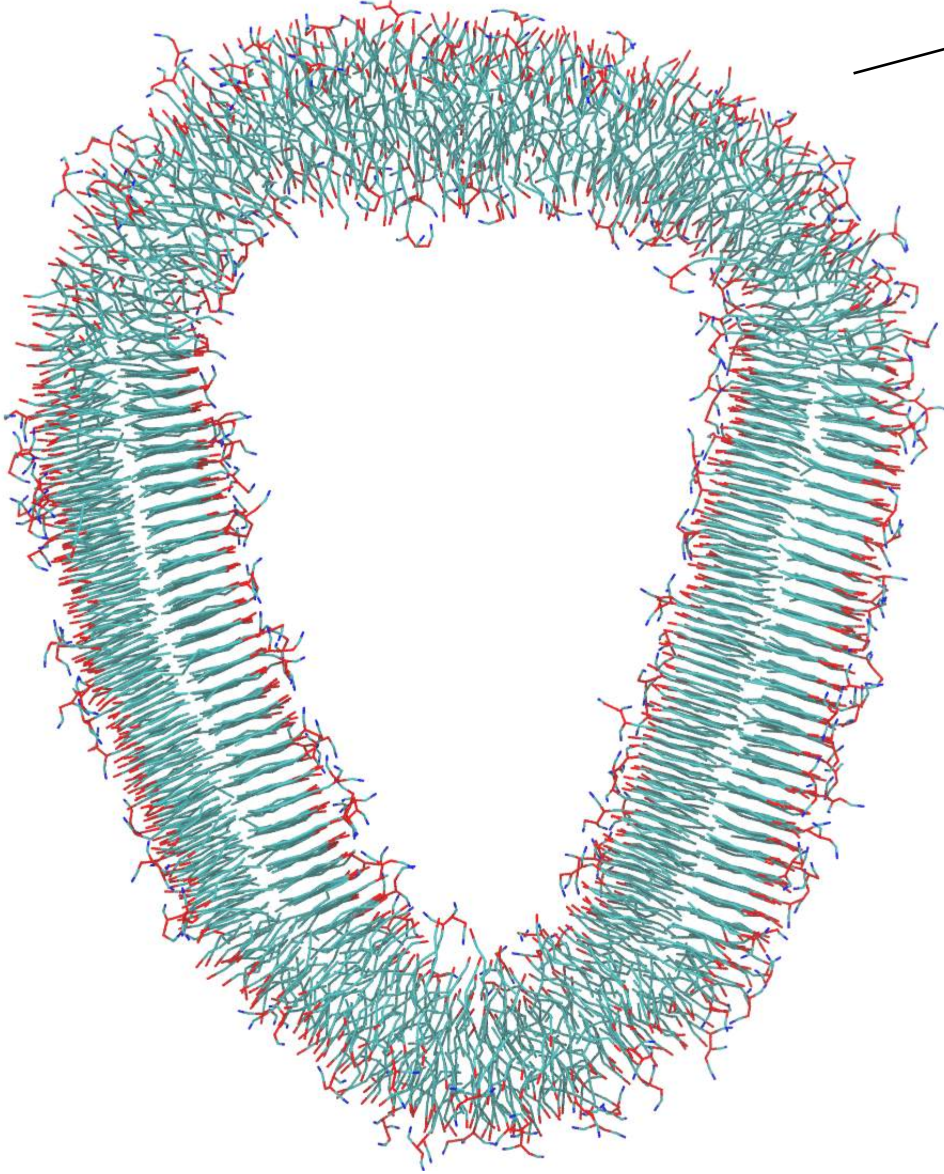
2.5 nm (hydrophobic layer)

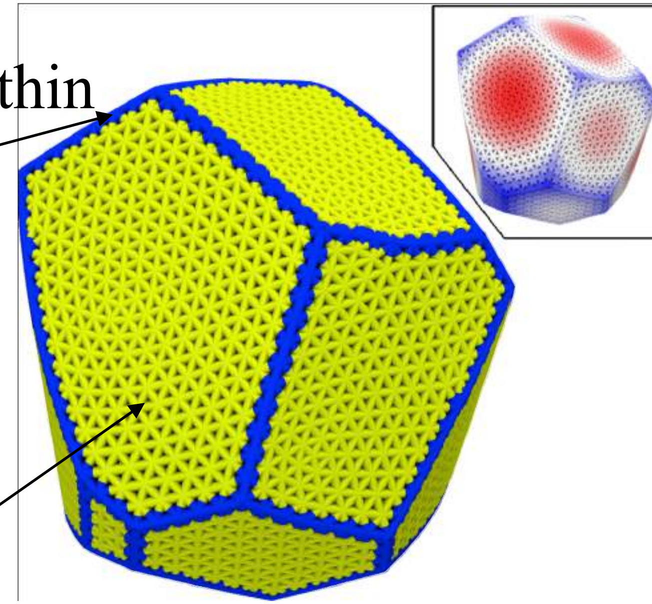
Analog to
95% ionization of palmitic acid



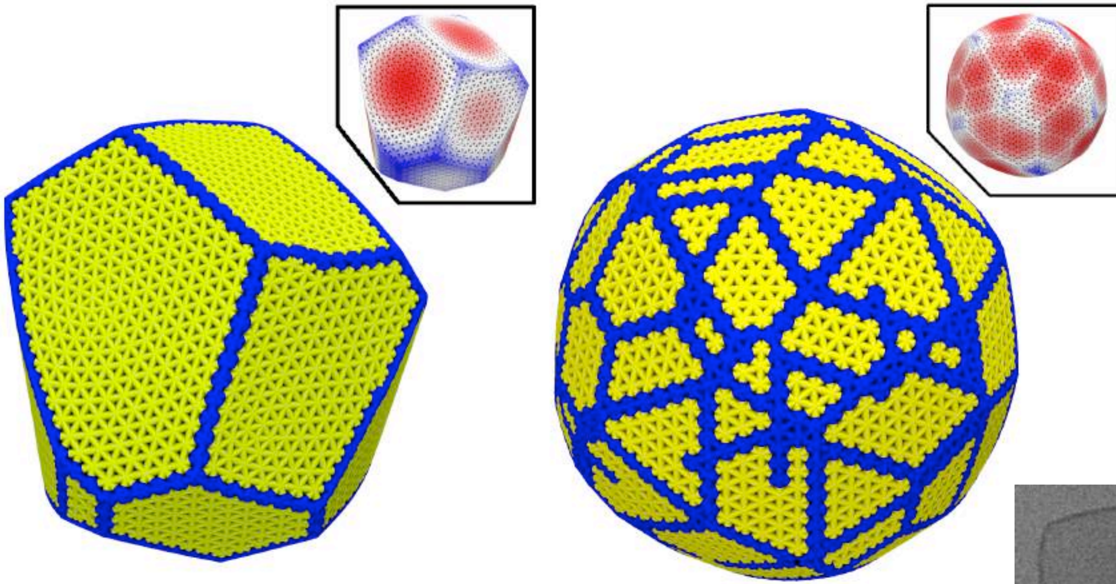
(Leung et al ACS Nano, 2012)

Water or molecule permeations?



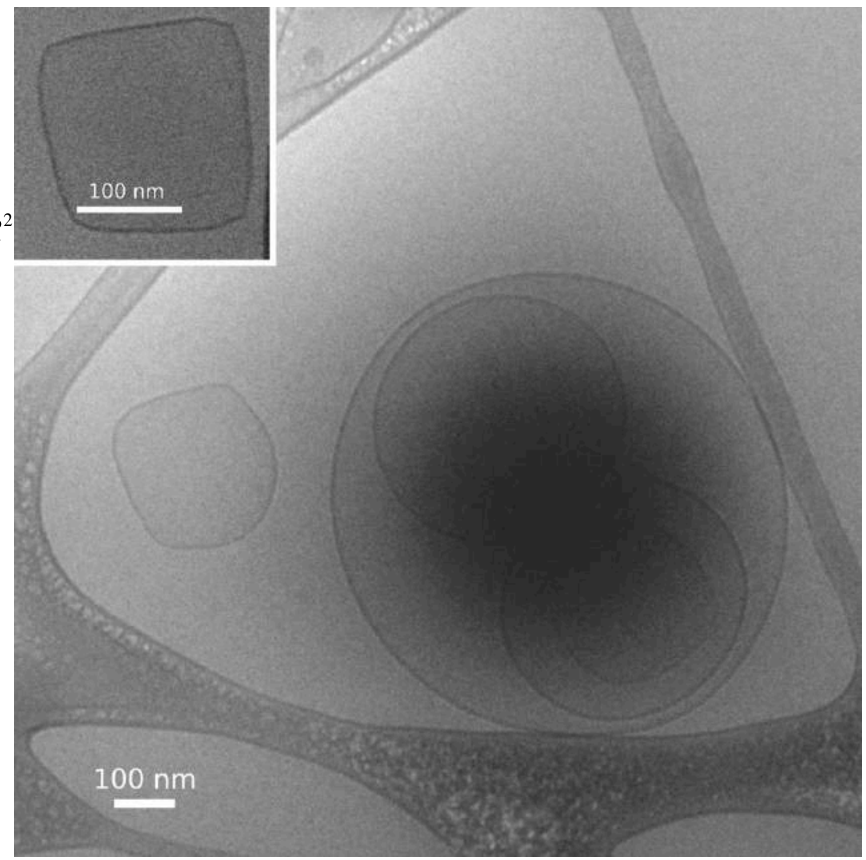


Thinner membrane (h_s) and more disorder along the highly bended areas than along the flat areas (h_h). Mechanics of thin solids suggests that the bending rigidity goes as h^3 (so is very less sensitive to thickness)



pH=5, hexagonal lattice

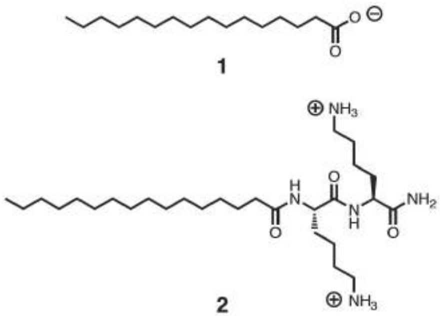
$E_s \sim \alpha(f) R^2$



For R=50nm vesicle with 25x25(=625)nm^2 crystalline domains (from WAXS broadening of peaks), there are ~ 50 platelets. Small R gives less symmetric vesicles than
large R (more spherical).

STABLE AT HIGH SALT

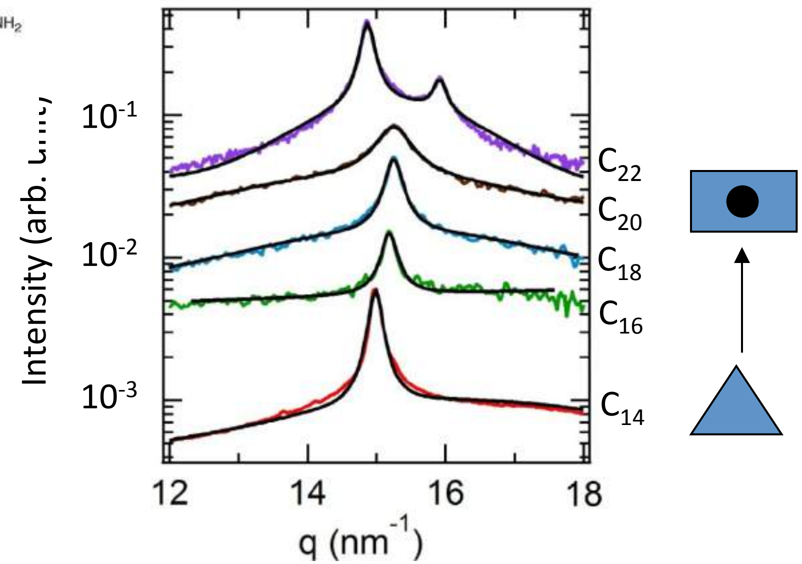
2+/-1 Ampjhipiles at Fixed pH = 3
Varying tail length

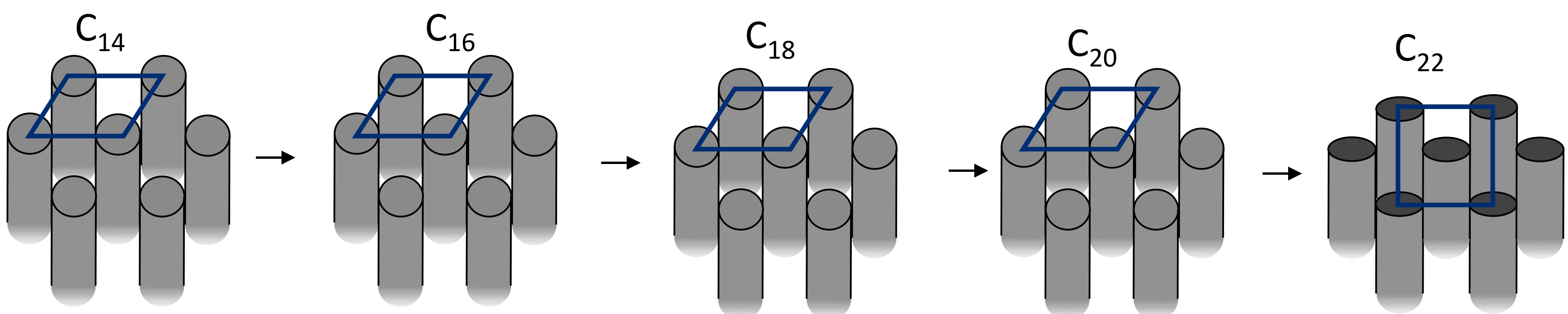


1

2

WAXS results

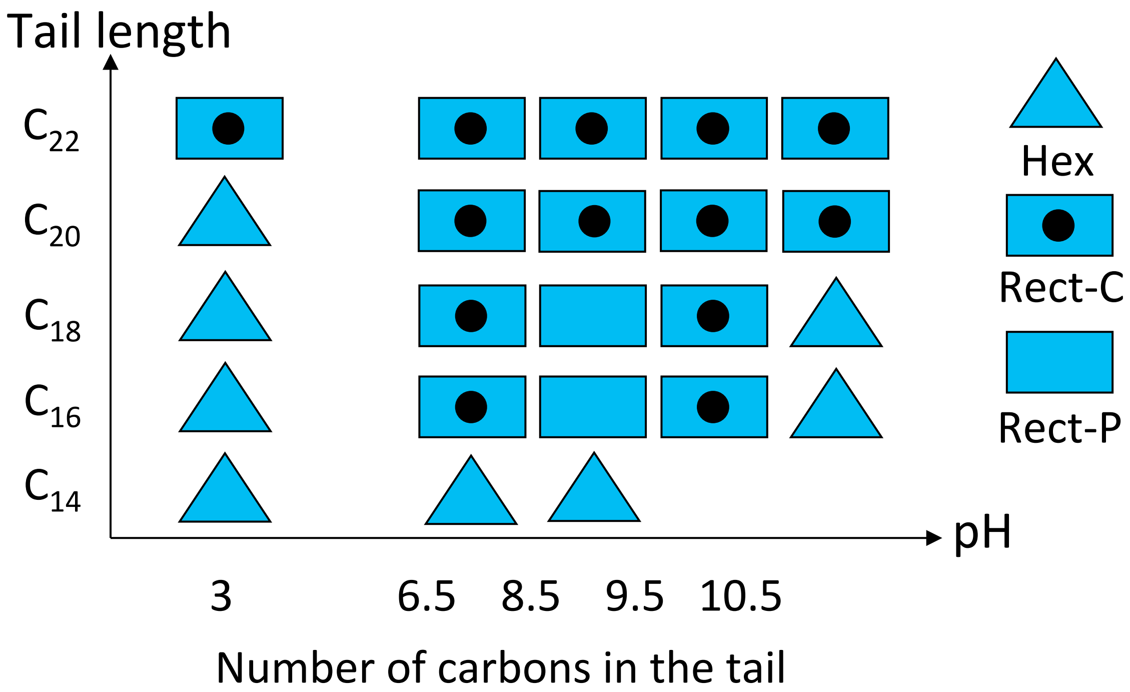


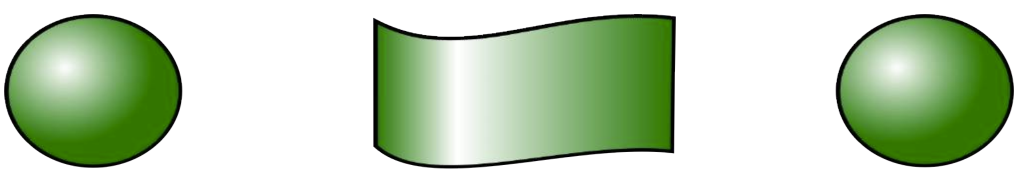


C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Area/ molecule = 0.205 nm^2	Area/ molecule = 0.197 nm^2	Area/ molecule = 0.197 nm^2	Area/ molecule = 0.197 nm^2	Area/ molecule = 0.197 nm^2

Phase diagram for 2D crystal lattice 2+/-1 amphiphiles (tail length versus pH)

(Leung *et al*, PNAS 2013)



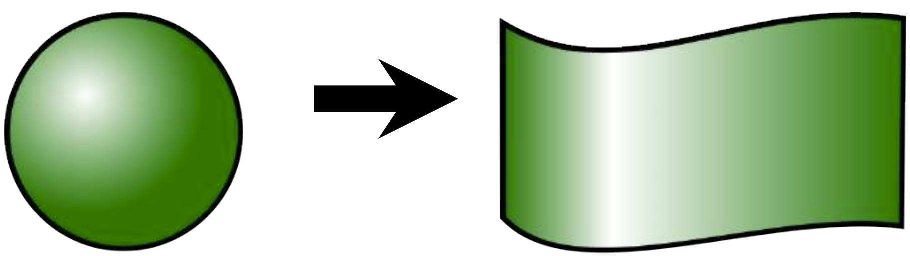


Small window on chain length where all interactions are of the same order of magnitude
KT give pH re-entrant transitions

Analogy to ceramics

Ceramics are typically 3D crystals with ionic bonds.

Ionic square crystals break up due to curvature.



Ceramics are strong until they shatter under shear.

from wikipedia

Summary

- Regular and irregular polyhedral geometries, arise spontaneously in shells formed by more than one component such as cellular containers.

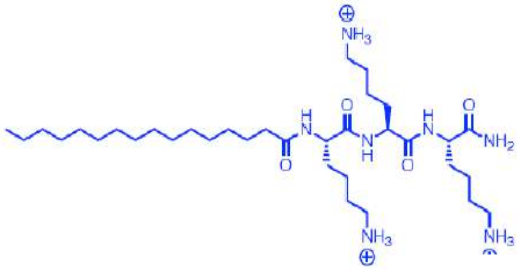
- While spherical and icosahedral shells are abundant in nature, the less symmetric polyhedral shells are potentially more functional and appear at the nanometer length scales where their functionality can be fully exploited.

- Ionic closed crystalline membranes have hexagonal lattices (important for design).

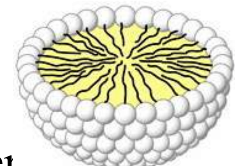
- A subtle balance of interactions allows transitions by external parameters (pH in this case).

Ionic nanocontainers experiments and modeling over various length scales

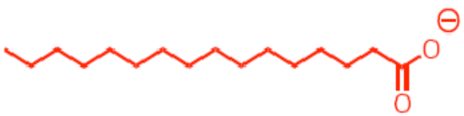
Leung*, Palmer*, Qiao*, et al., *ACS Nano*, **2012**, *6*, 10901.

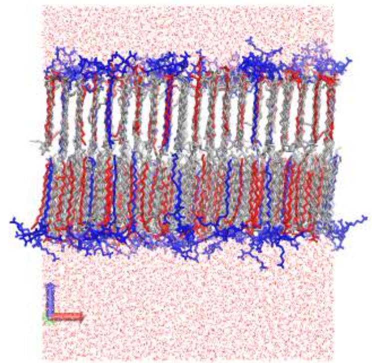


+3*e* (micelle in water)

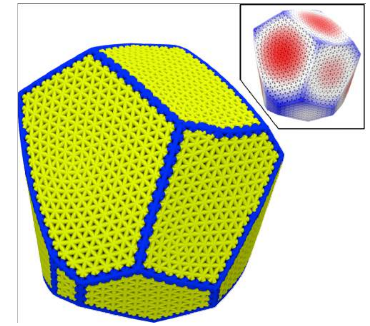


-1*e* (insolvable in water)

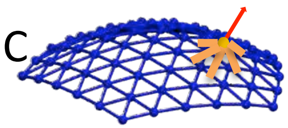


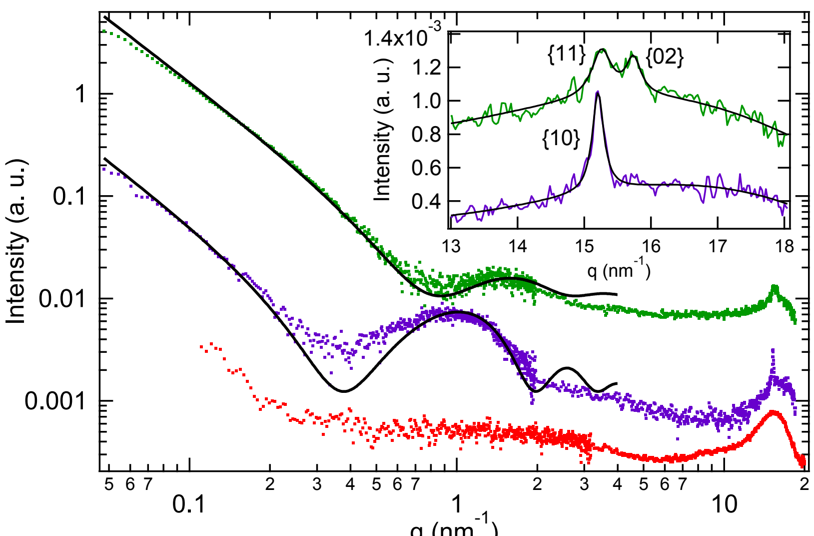


Full atom MD

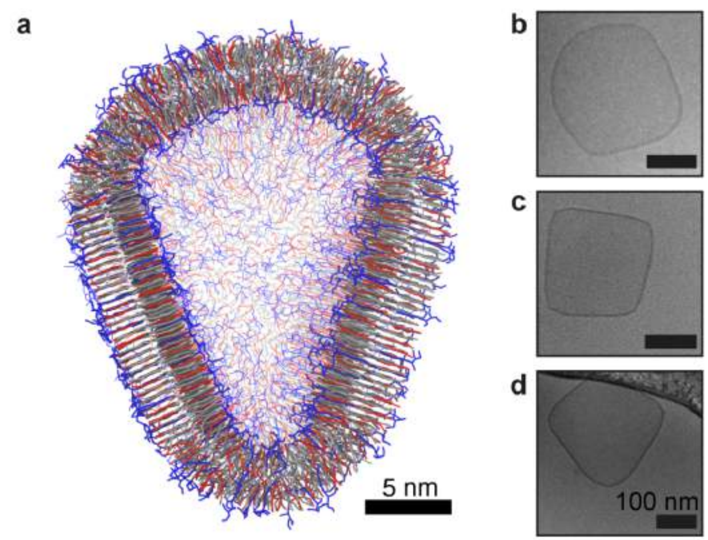


Continuum via MC



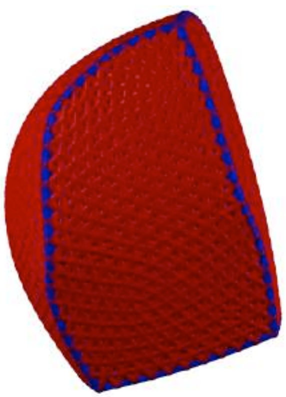


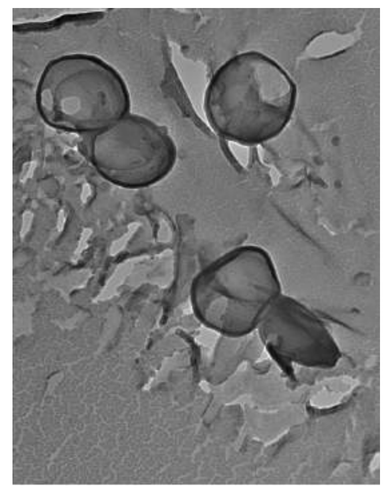
X-Ray gives tails symmetry packing but with by neutron (deuterion label) superlattices! !



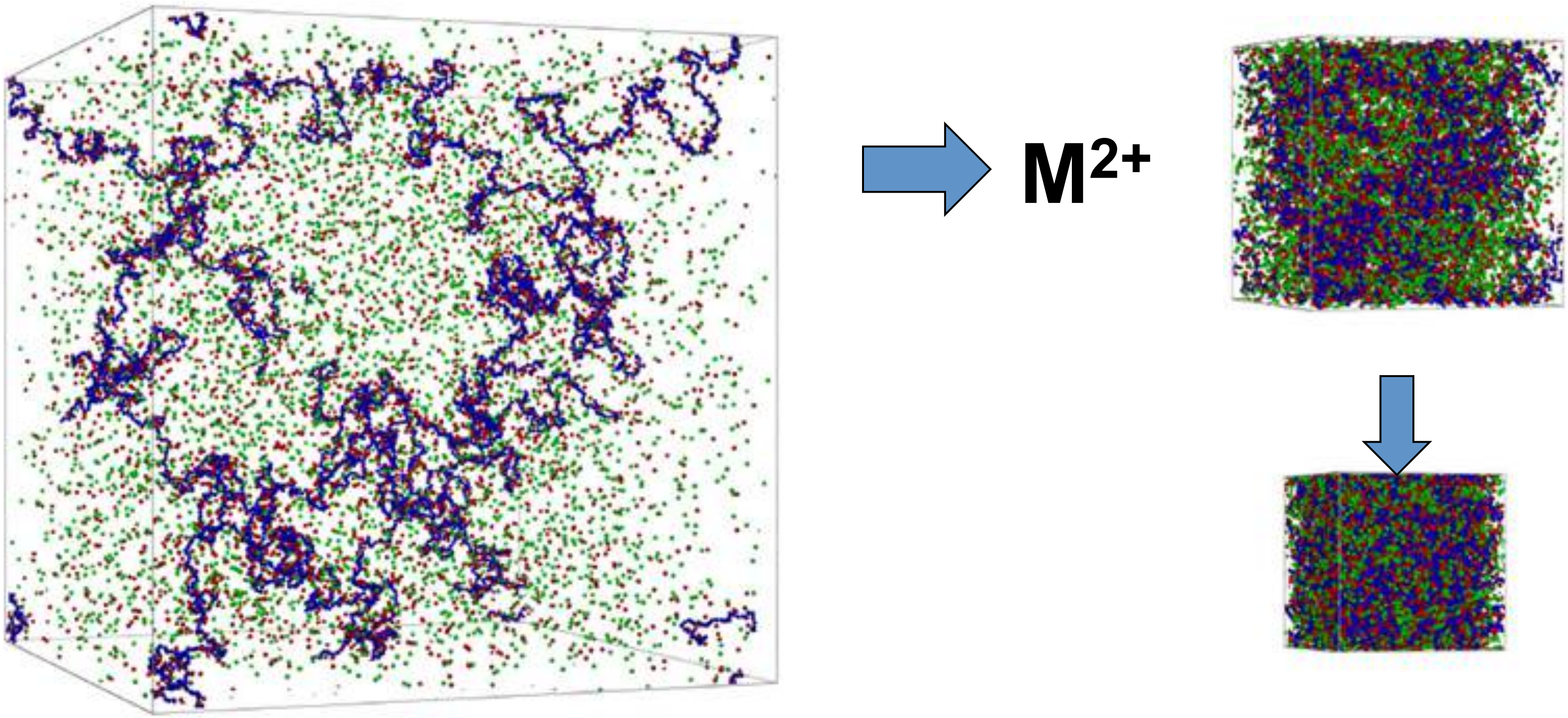
(a) CG simulation (Martini), & (b-d) TEM

Our model predicts faceting into many possible polyhedra with decorated surfaces that offer higher functionality





Strongly charged polyelectrolyte gels expand in monovalent salts and adsorb water (dipper) but collapse in divalent salts (chromosomes)



Monovalent swollen gel

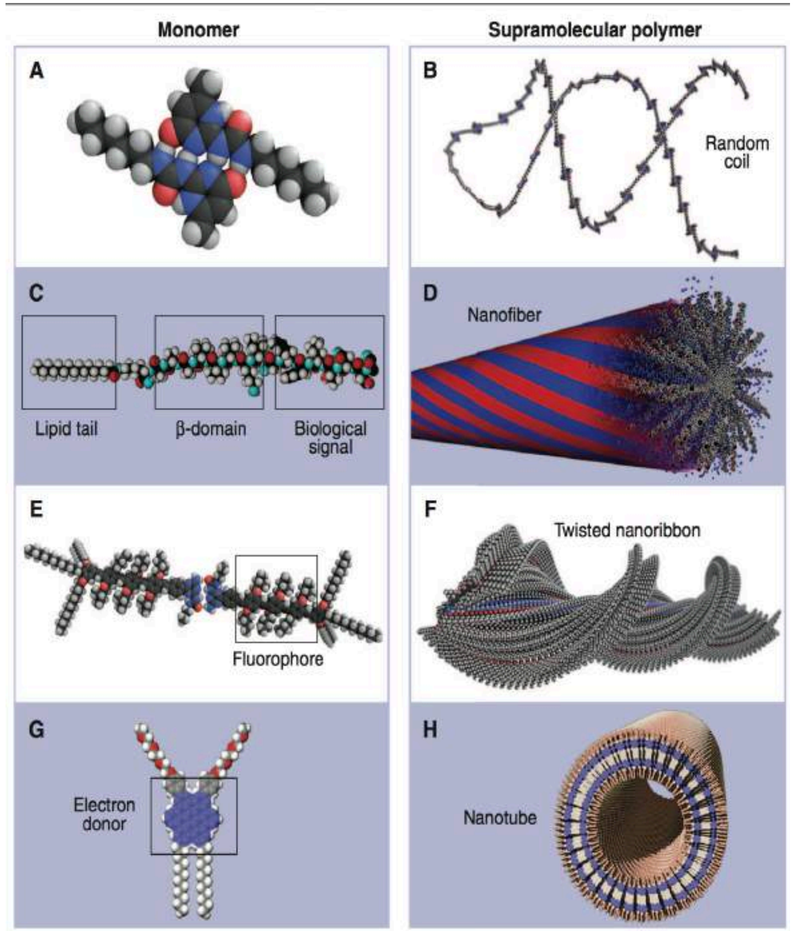
Divalent compacted gel

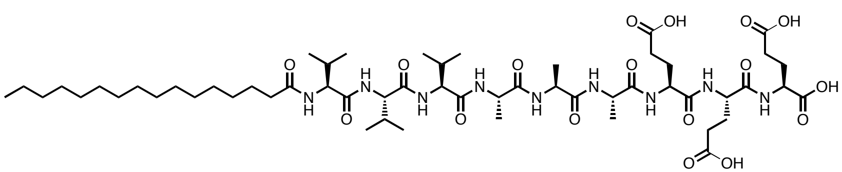
Soft Matter; JCP; PRE; Macromolecules

Physics: Swell to increase osmotic pressure of the ions and collapse due toionic correlations

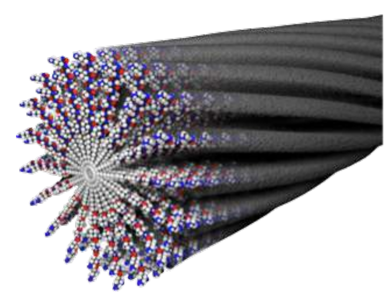
Challenge: Structures are not periodic like molten salts!

Supramolecular materials mimic biological fibers or cytoskeleton of cells including microtubules, actin filaments, and intermediate filaments and tissues offering the possibility to fabricate materials with the properties of living systems.

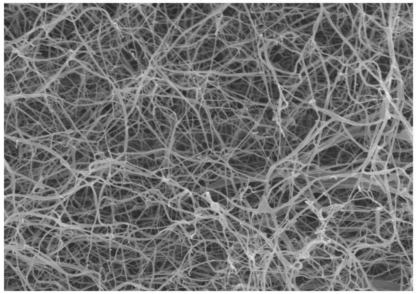


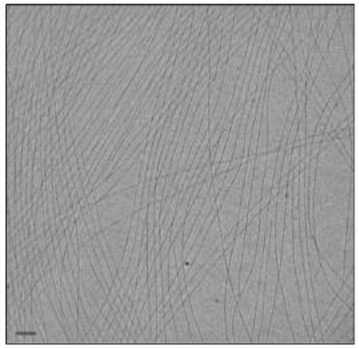


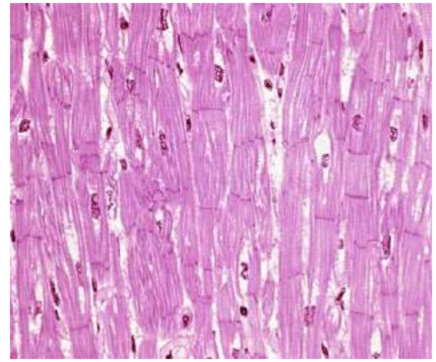
Peptide amphiphiles (PA)



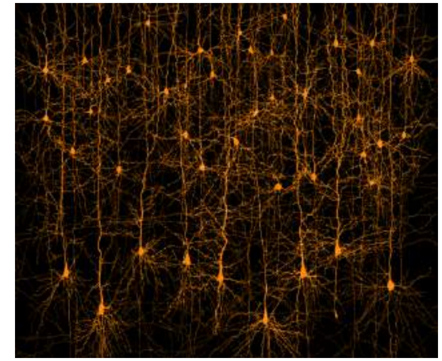
Hydrogels as synthetic cell scaffolds







Cardiac muscle in the heart[1]



Neurons in the brain[2]

Substrate stiffness influences cellular

- adhesion
- movement
- proliferation
- differentiation

Highly aligned cellular environments:

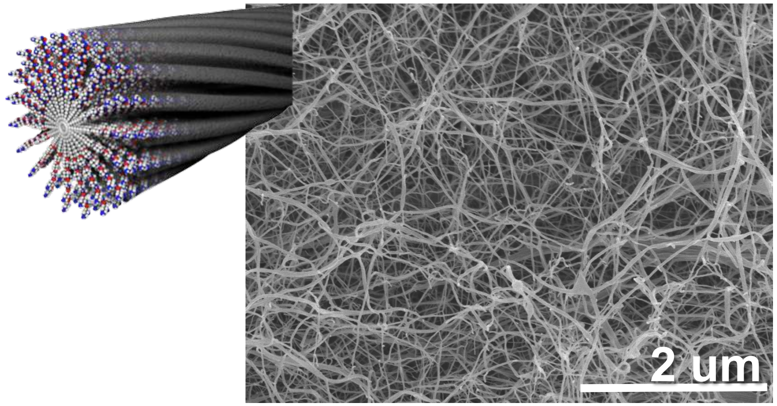
- smooth muscle
- cardiac muscle
- brain
- spinal cord

GOAL: Develop methods to align peptide amphiphile (PA) nanofibers.

Challenge: Alling micron size fibers that are soft and small to be manipulated directly

[1] "Muscle," Microsoft® Encarta® Online Encyclopedia, 2009.
[2] IBM/EPFL Blue Brain Project

micrometers long with diameter ~10 nm



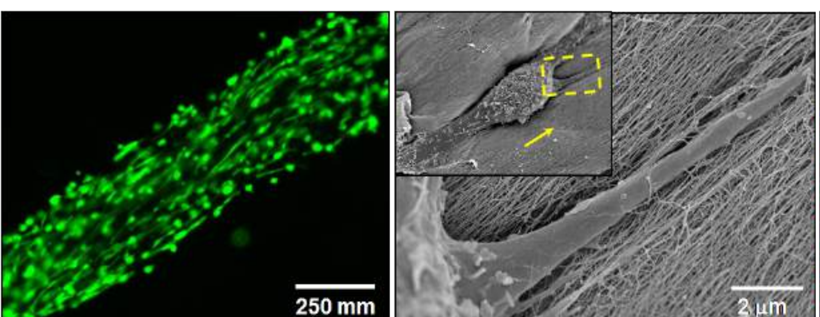
Milimmeter thread

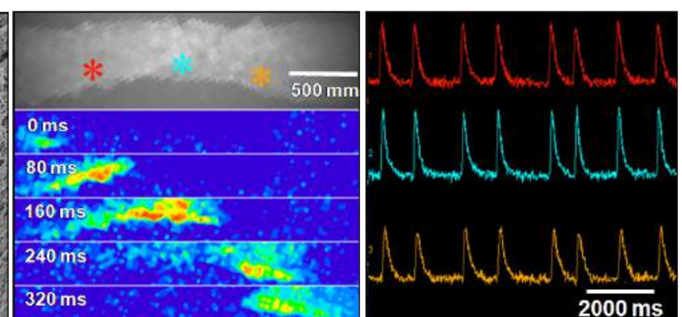
Nature Materials 9, 594 (2010)

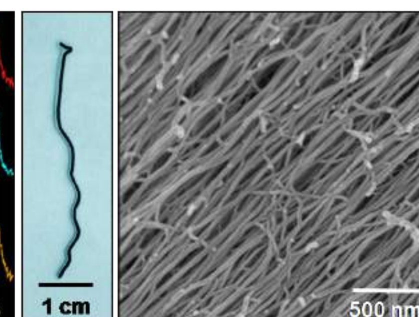
Preferential alignment of human mesenchymal stem cells along the axis of a noodle

Action potential propagation in a noodle seeded with cardiomyocytes

Conductive noodle with carbon nanotubes



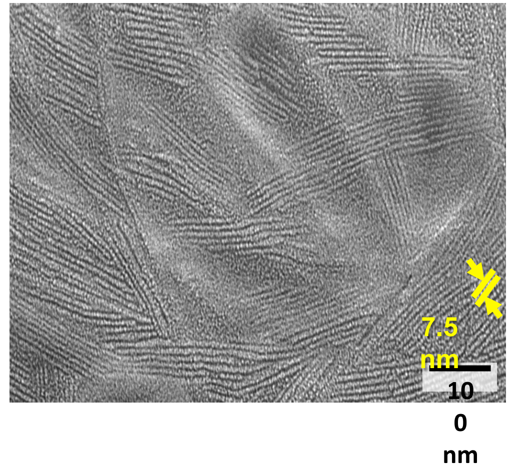


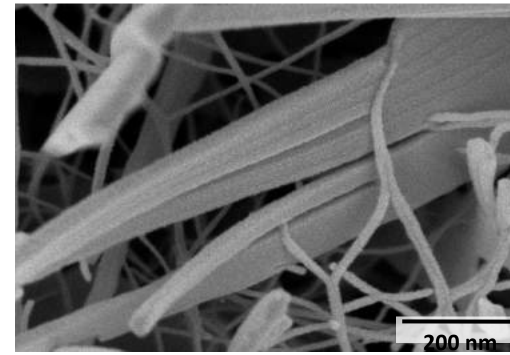


Images courtesy of S. Zhang and J. Mantei

Heat Induced Alignment
Only annealed PA leads to alignment

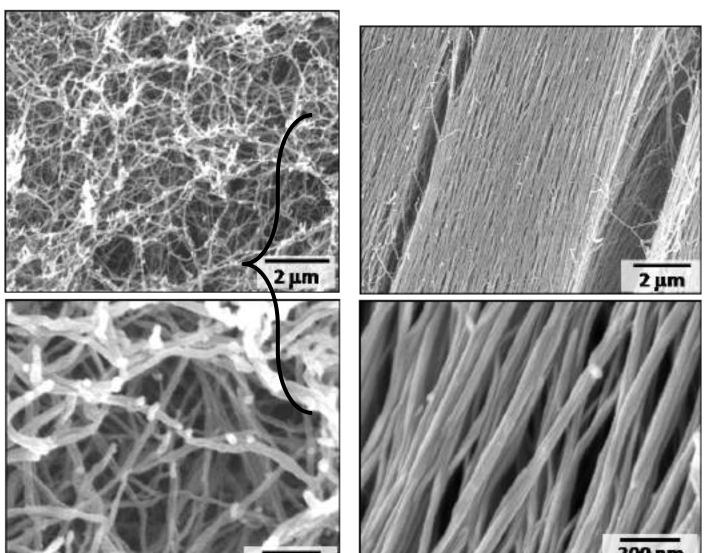
Cooling: Plaques break into bundles of fused fibers as water molecules rehydrate the PA

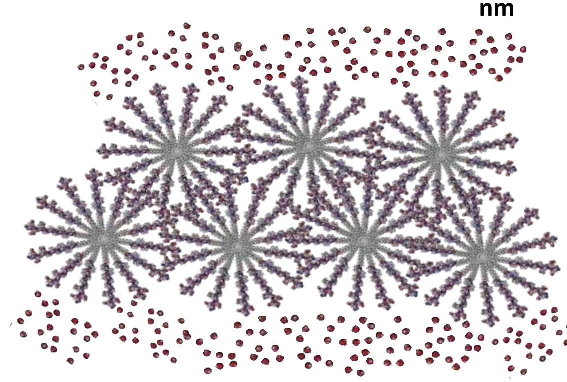


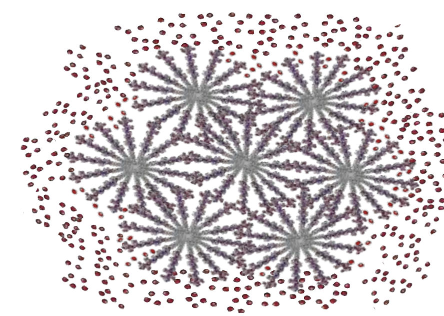


non-annealed PA solutions

Noodles with PA solutions **annealed** at 80 °C



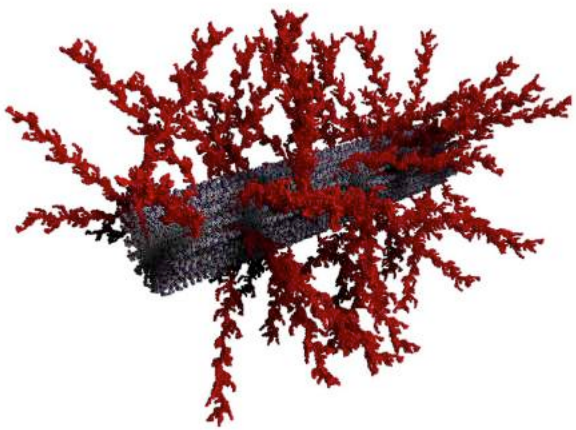




25 °C
fused PA fiber bundles

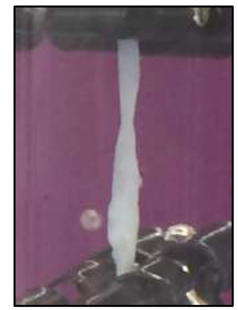
Images courtesy of Dr. A. Mata and Dr. R. Bitton

Peptide Amphiphile-Polymer Hybrid Materials



PA-polymer hybrids contracts at high T

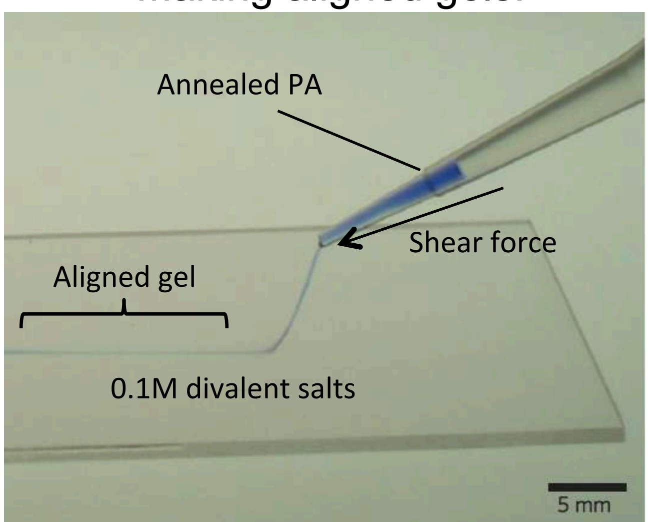
Polymerized aligned gels (15 mm x 2 mm) show anisotropic contraction



25˚C

47˚C

Making aligned gels:

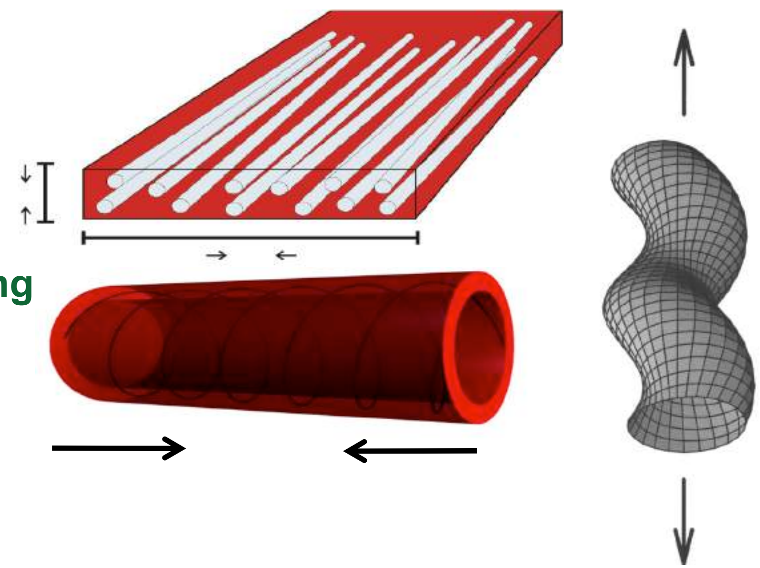


Nat. Mater. **2010**, *9*, 594

Next steps:

Control of gel shape and direction of contraction

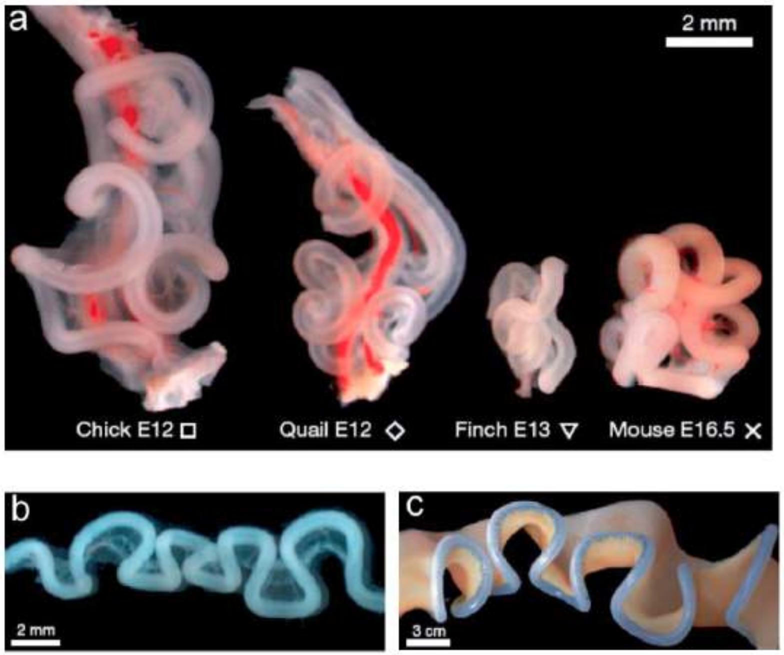
Analyze buckling of such heterogeneous system



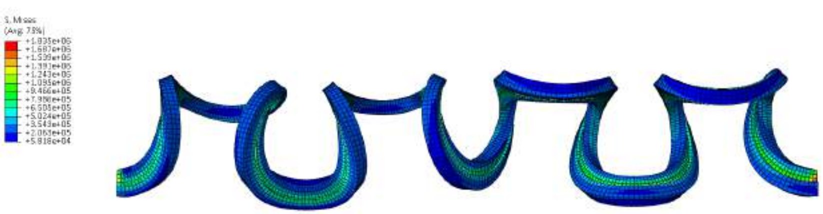
Buckling in Heterogeneous Elastomers

Bi-trips gels lead to looped patterns in gut tubes, which twists as a bi-layer gel

Gut tube and associated sheet tissue



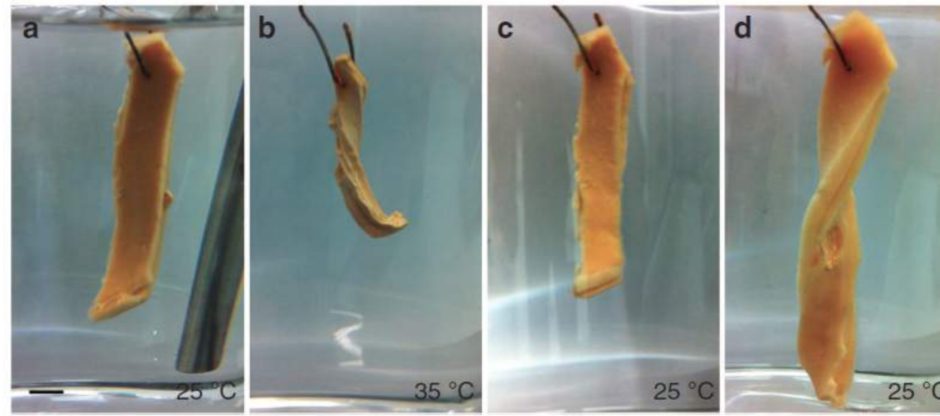
T. Savin et al. *Nature* 476 (**2011**), 57-62



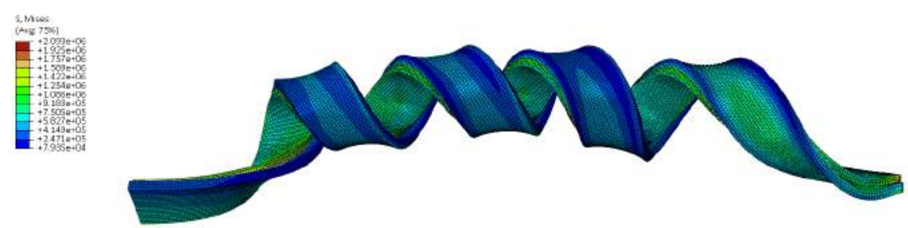
- -

+ +

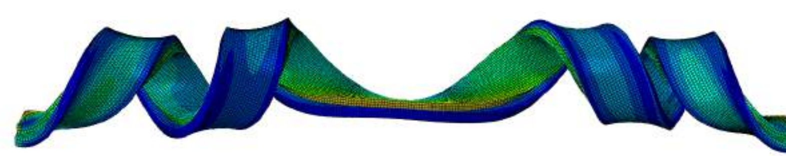
Bi-layer gel in poor solvent



R. Erb et al. *Nat. Commun.* 4 (**2013**), 1712



Top: Free end. Down: Fixed end

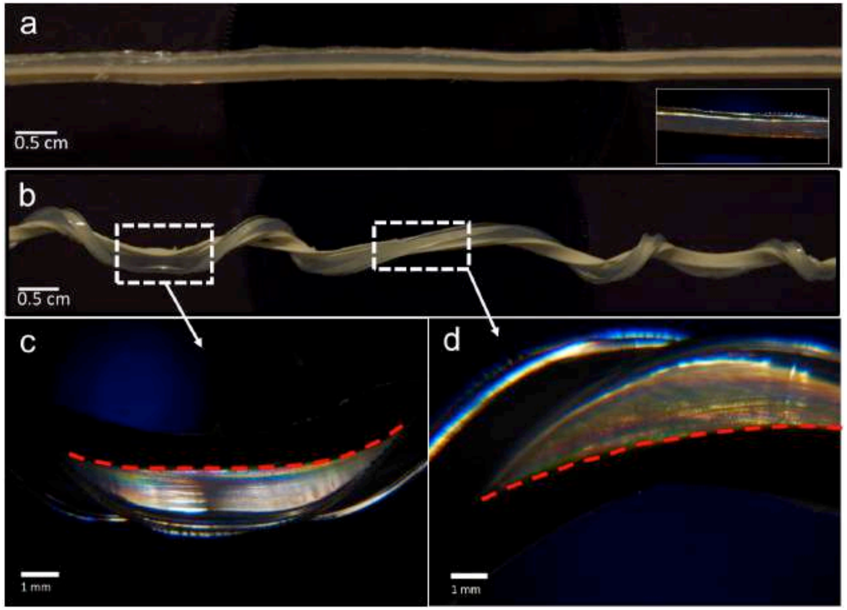


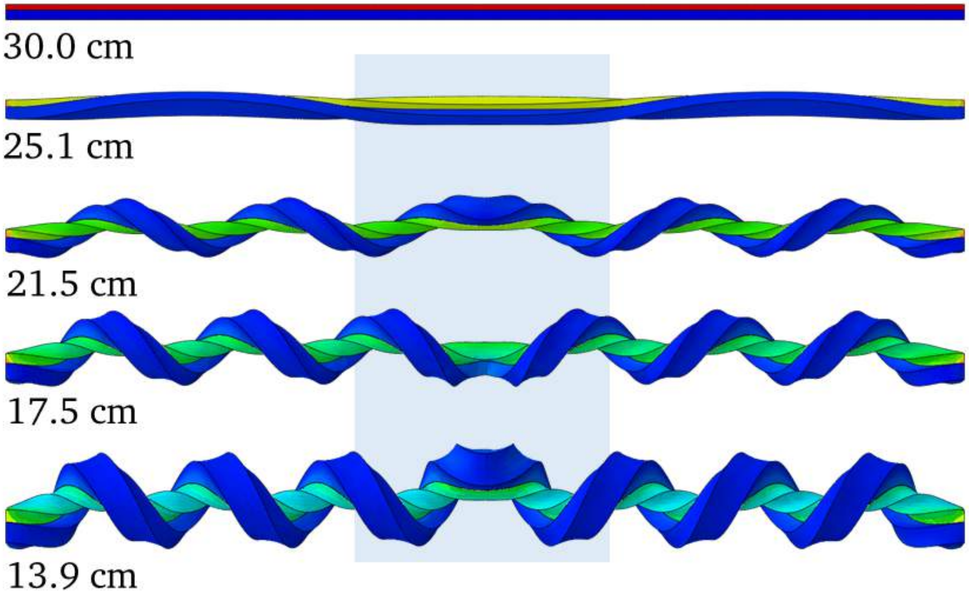
Simple Perversion

A perversion is a kink that connects two helices with opposite chirality observed in natural and artificial mechanical systems.

Perversions provide the fundamental mechanism of helical symmetry breaking and is an actuator.

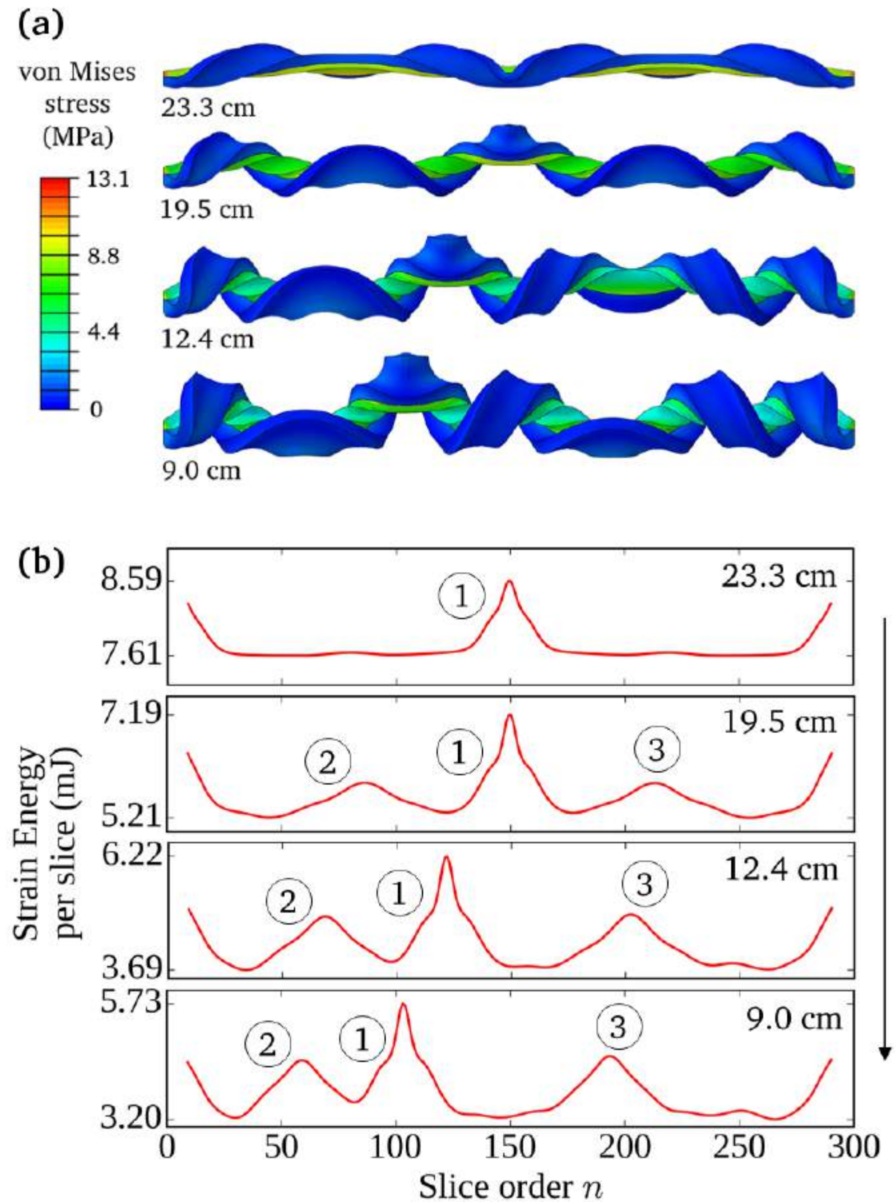
The elastic energy condenses around the perversion during buckling and at the interface corners





Multiple Perversions and Symmetry Breaking

- Symmetry breaking during buckling
  - Rightmost perversion wind before the other two
- Repulsive interaction between perversions 1 and 2

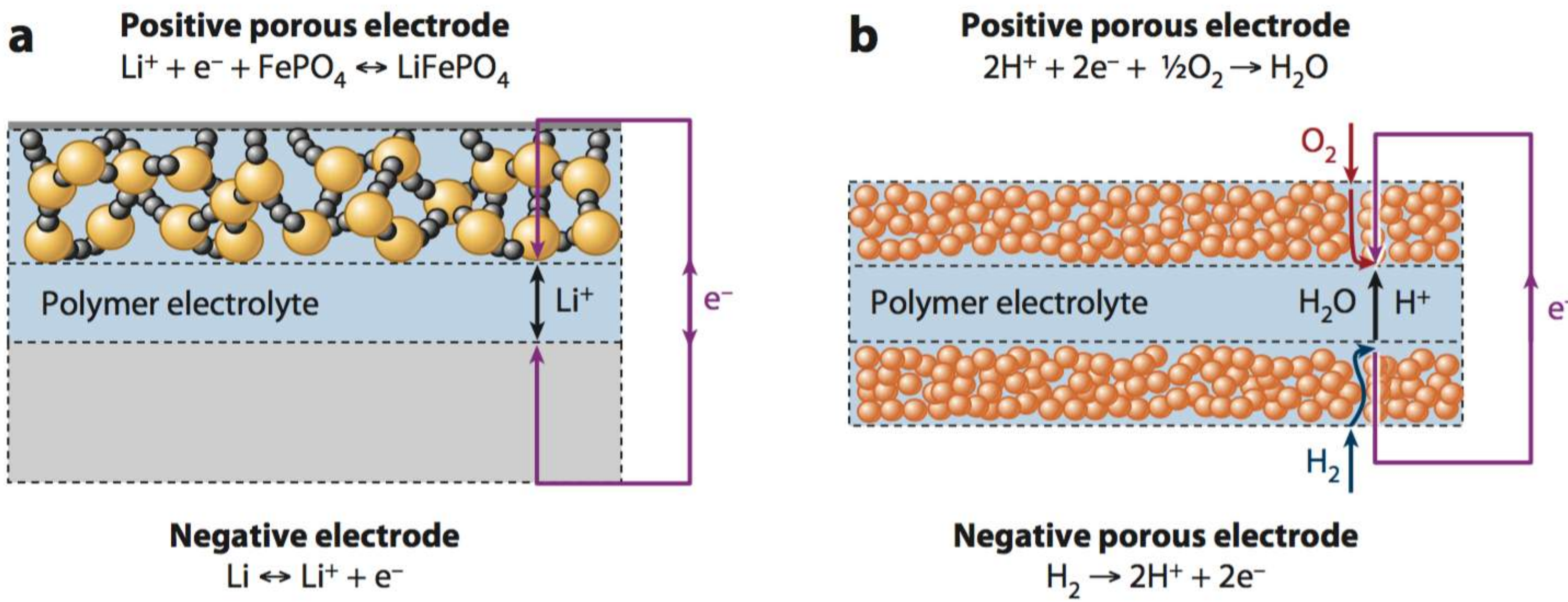


Liu et al PNAS 2016

Soft materials are integral to developments in organic electronics, such as energy harvesting organic photovoltaic devices (OPV) and new display and lighting technologies (OTFT, OLED), and to advanced medical devices and therapies (implants, tissue engineering, drug delivery, personalized medicine).

Molecular electrolytes and ion-containing polymers are the basis for products ranging from super-absorbents, separators, and membranes for advanced energy devices such as batteries and fuel cells.

Polymer electrolytes- Industrial applications



Hallinan Jr., D.T.; Balsara, N.P. *Annu. Rev. Mater. Res.* **2013**. 43:503.

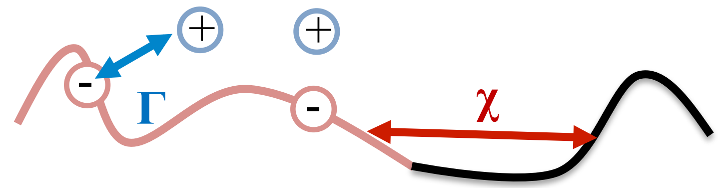
Polymer electrolytes

- Powerful Li-ion batteries can power entire factories
  - Heavy
  - Bulky
  - Expensive
  - Combustible
- Polyelectrolytes
  - Flexible
  - Lightweight
  - Low-cost
  - Recyclable
  - Space applications

Tesla. *www.testlamotors.com/powerwall*
C.E. Sing, J. W. Zwanikken, M. Olvera de la Cruz, *Nature Materials*, 13, 694-698, 2014.

Block co-polymer electrolytes

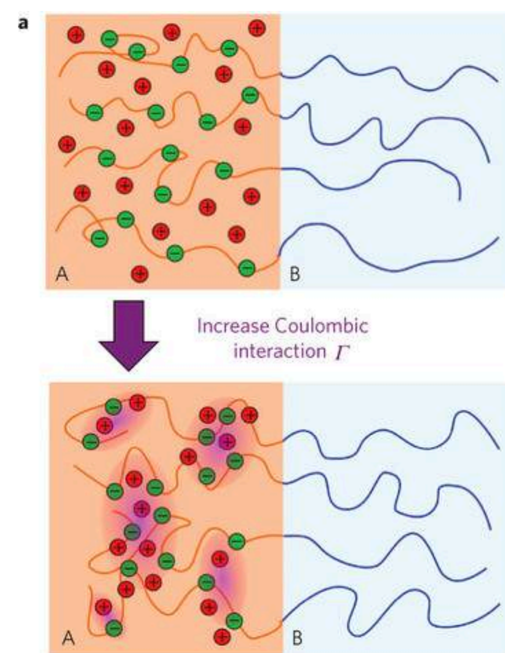
– Multi-scale interactions



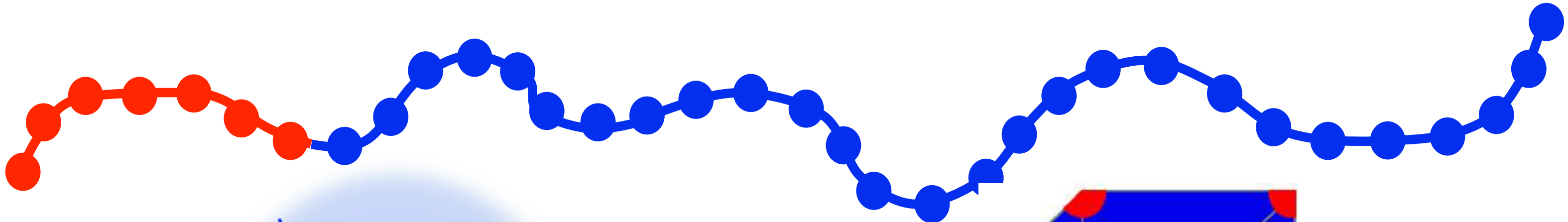
- Repulsion of polymer chains (10-100 nm)

- Coupling of opposite charges (1 nm)

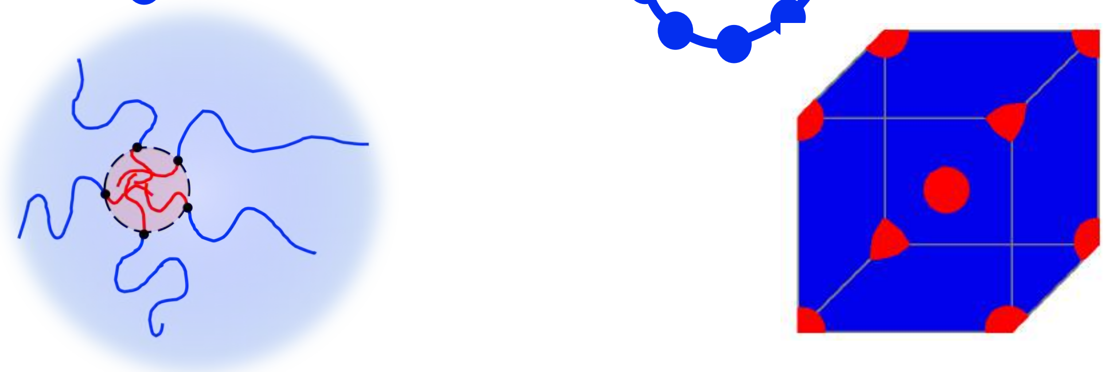
- Combine approach that bridges the two length scales (SCFT-LST)

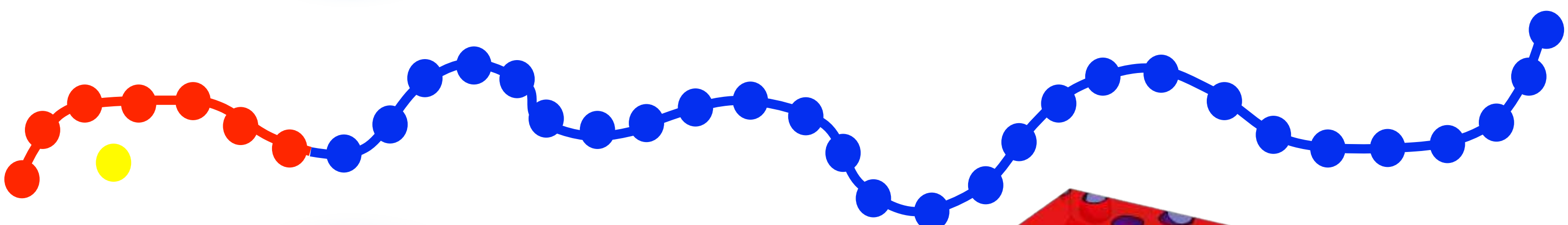


Ionic correlations drive self-assembly

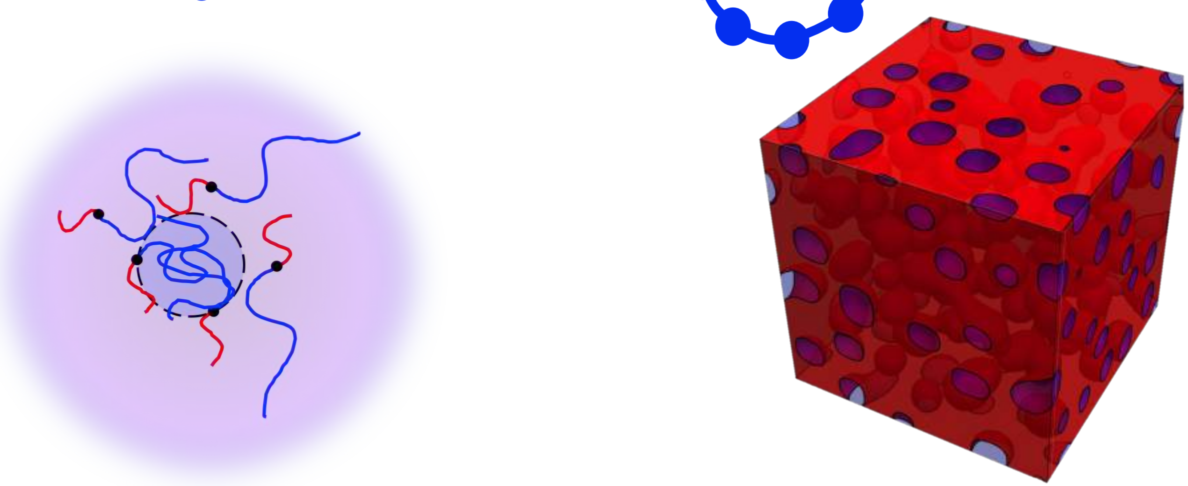


Neutral

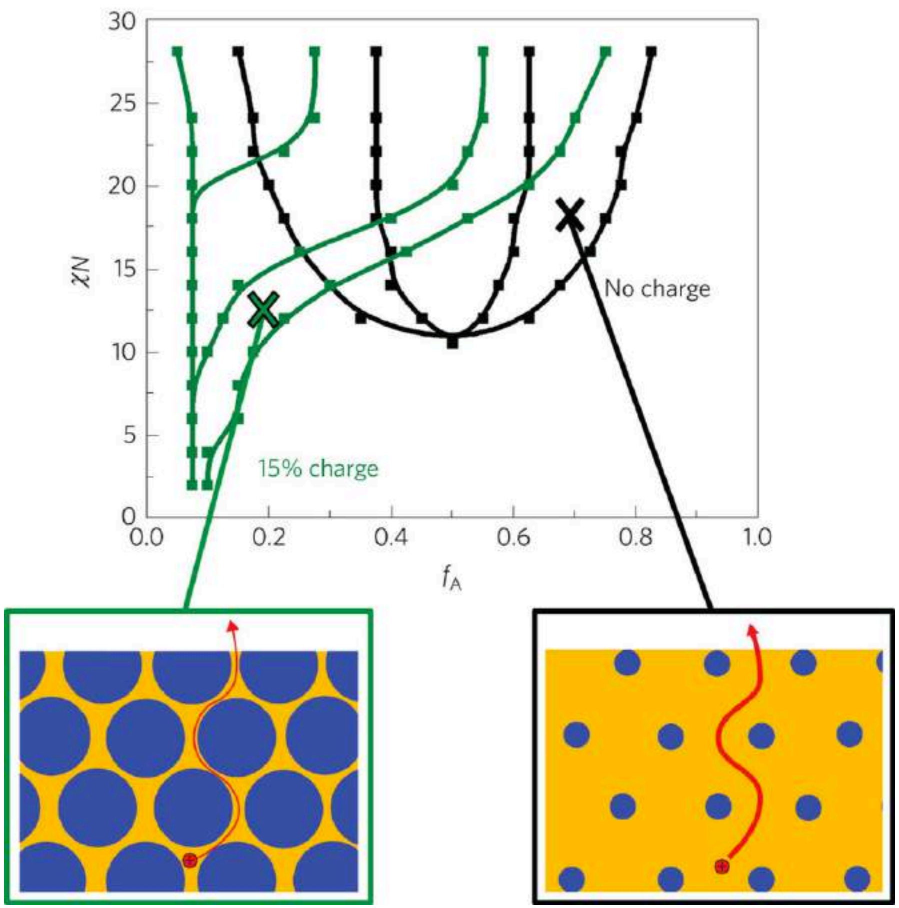


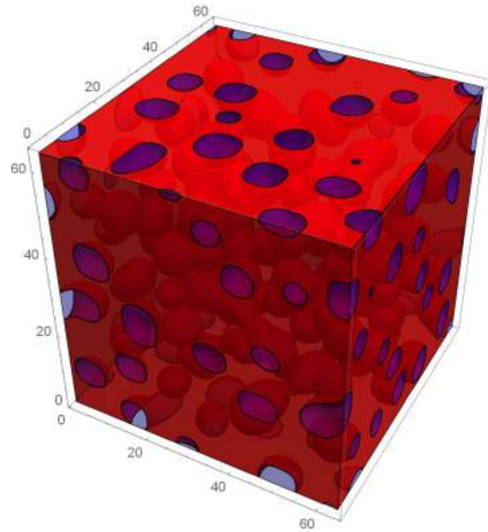


Charged

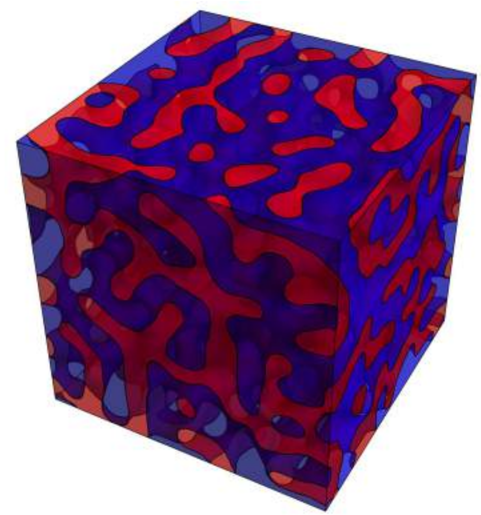


Self-assembly of inverted phases





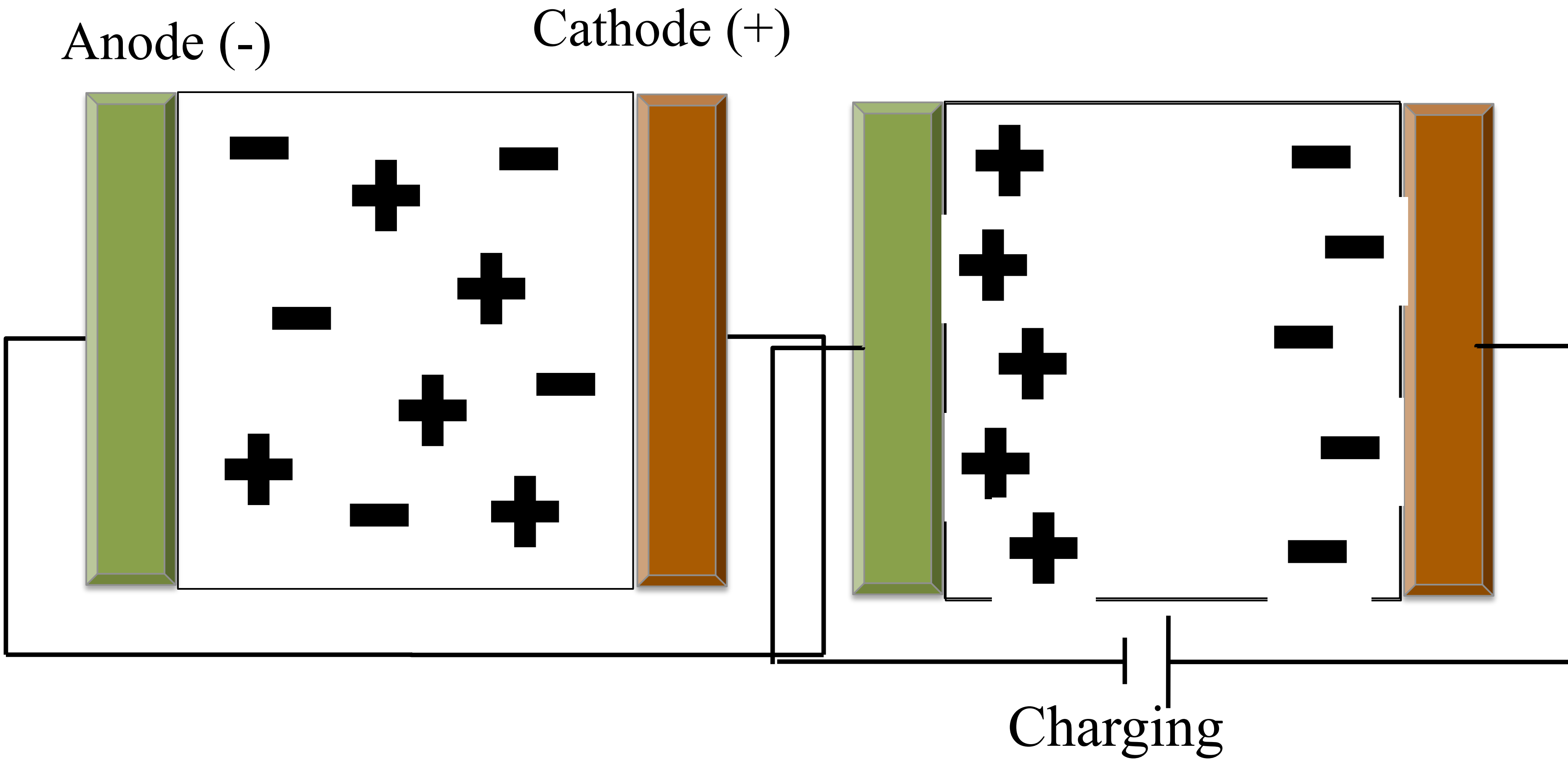
Inverted spheres



Gyroid

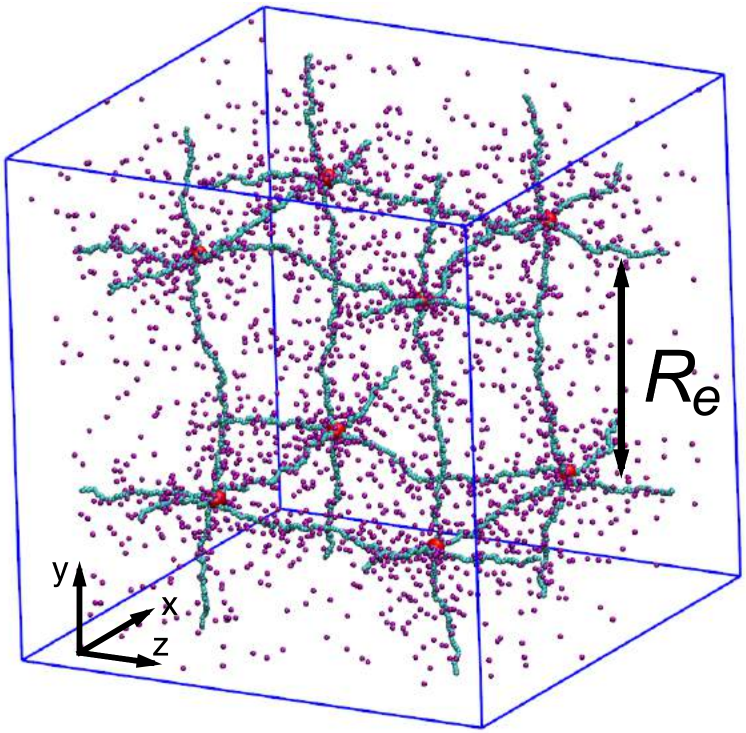
C.E. Sing, J. W. Zwanikken, M. Olvera de la Cruz, *Nature Materials*, 13, 694-698, 2014.

Dynamics of mobile ions



- Transport of ions through the polyelectrolyte nanodomain
- High ionic mobility required for high battery performance

Molecular Dynamics



Coarse-grained Model:

- bead-spring chain (N monomers)
- steric interaction (LJ)
- bond interaction (FENE)
- Coulomb interaction (PPPM)
- implicit solvent

Electrostatics:

- monomers q = +1;
- counterions, q = -1;
- Bjerrum length:

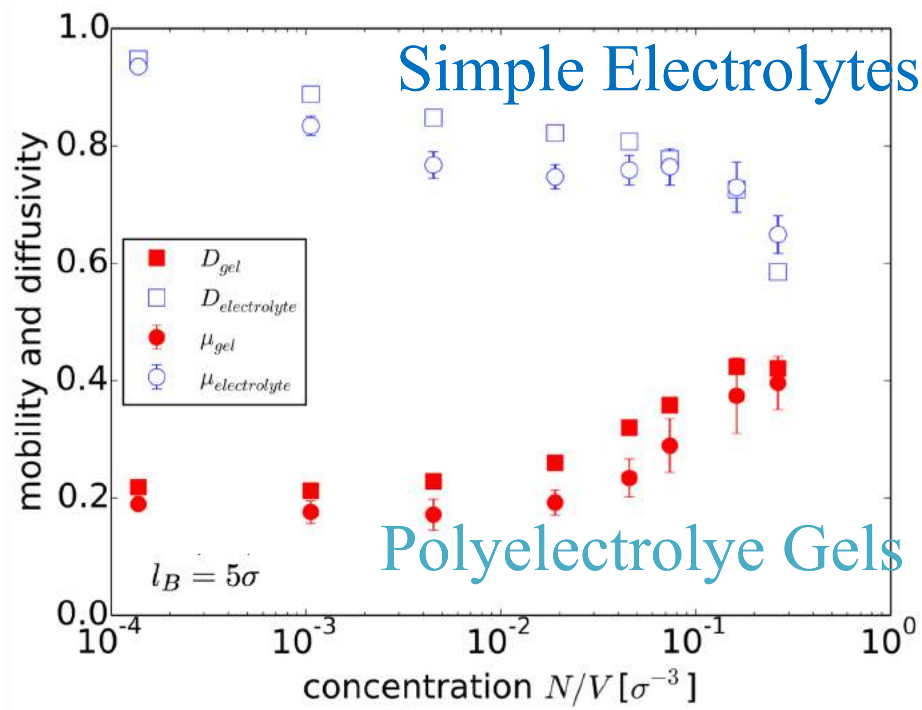
$$l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T}$$

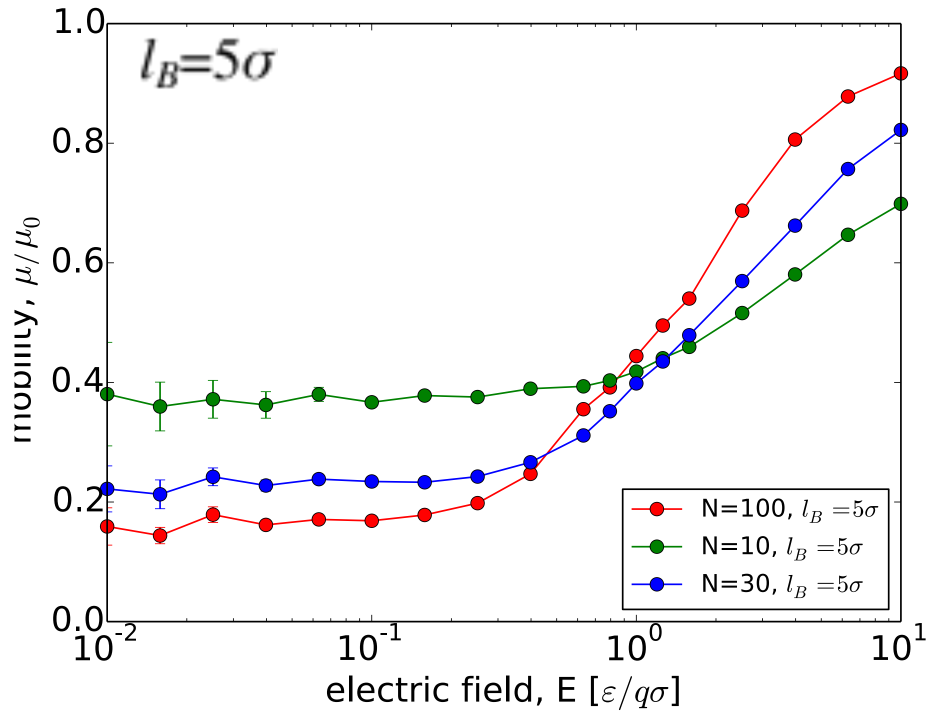
Counterion mobility

$$\mu = \frac{v_{drift}}{q\mathrm{E}}$$

Li et al Macromolecules 2016

Strong non-linear effects





- The mobility increases as the confinement/ concentration increases at low electric field E and it is E independent up to E=E* and or E> E* it increases with E until it saturates at E>>E*, qE*

Opportunities

- Soft materials will play a key role in the technologies that will underpin new business opportunities, employment, and economic vitality since they impact sectors of global energy, water, medicine, agriculture, and sustainability.

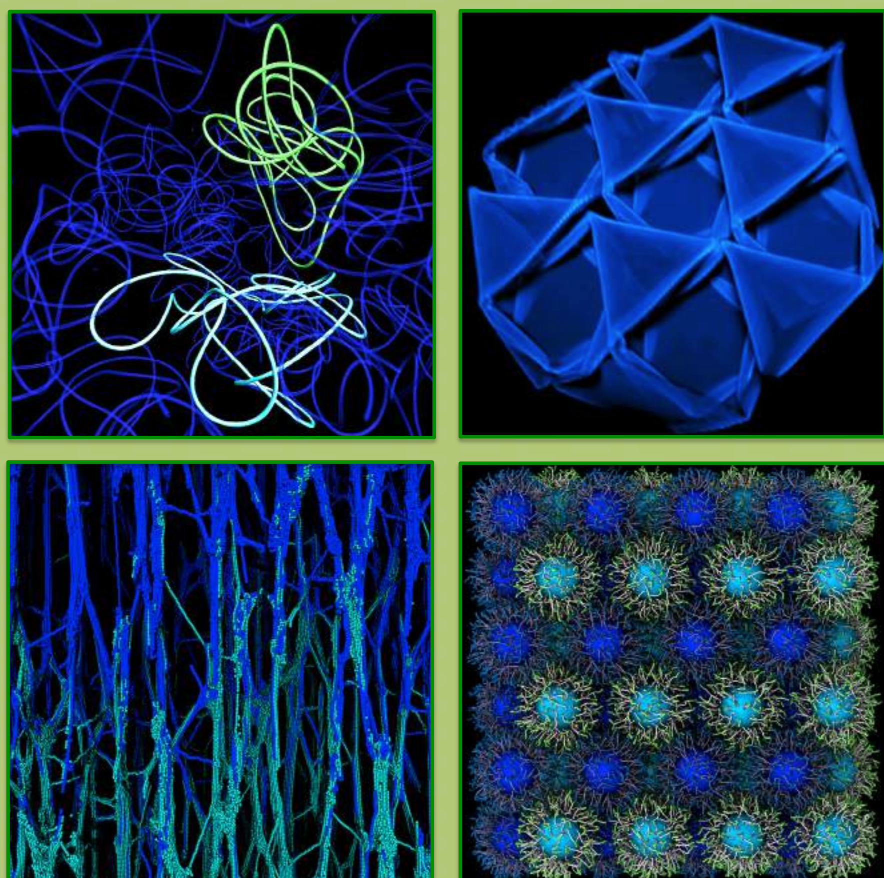
- There are many opportunities in energy production, storage and conversion, water purification and reuse, and biotechnology

Opportunities in Theoretical and Computational Polymeric Materials and Soft Matter

A National Science Foundation Sponsored Workshop

Chairs: Monica Olvera de la Cruz and Michael Rubinstein

Santa Barbara, California, October 20-22, 2013



Topics:

Reversing the Arrow: Materials by Design

Exploiting Geometry in Form and Function

Harnessing Non-Equilibrium Processes

New Paradigms Inspired by Nature

Bridging Scales in Space and Time

Liu et al Soft Matter, 11, 2326-32 (2015)

THANK YOU!