Polymer Morphology: you could spend an entire semester on this, but…

References:

Principles of Polymer Morphology by Bassett

Introduction To Polymers by Young

Hierarchical Structure—It's a long way from macromolecule to device.

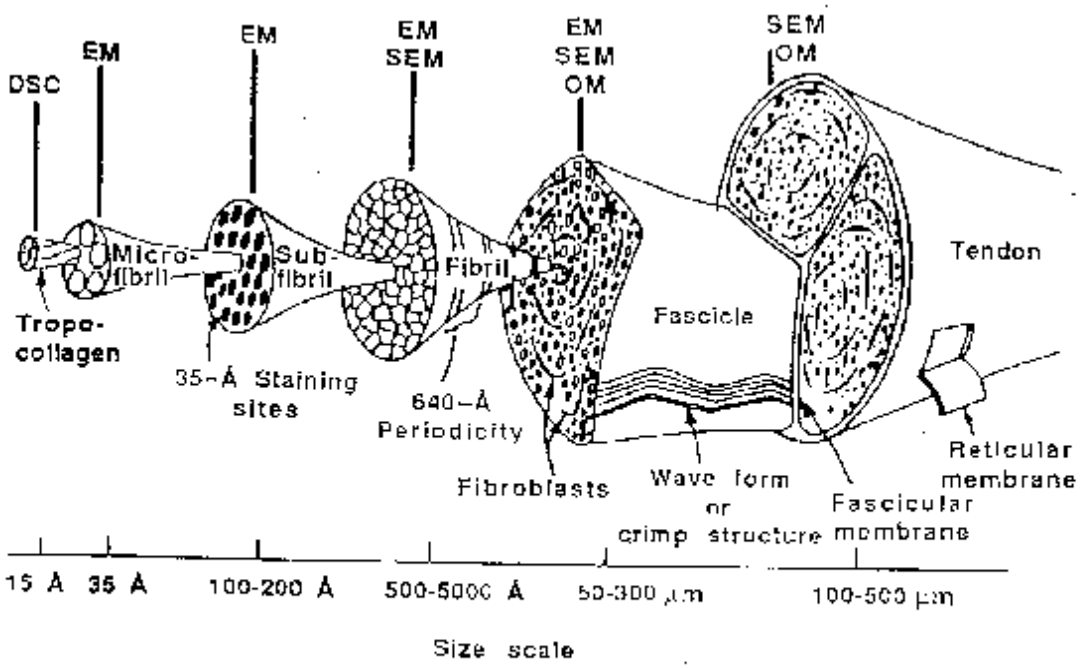


Fig. 9. Hierarchical model of tendon showing discrete levels of organization. Abbreviations: DSC, differential scanning calorimetry; EM, electron microscopy; SEM, scanning electron microscopy; OM, optical microscopy.

The major methods of morphology can be grouped into two classes.

- Microscopy
  - Get actual image
  - Sampling problems
  - Poor statistics
  - Requires vision and faith
- Scattering
  - Not the *molecular* scattering we discussed
  - No actual image
  - Everything inferred
  - Requires theory

Morphology originates in polymer structures.

Various forms of microscopy

TEM, SEM = Transmission or Scanning Electron Microscopy

POM = Polarized Optical Microscopy

SPM = Scanning Probe Microscopy

Pathways to Structures are tacticity, mesogens

Crystals: Lamellae, spherulites, shishkebabs

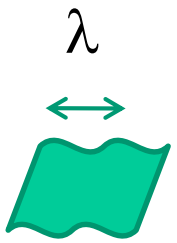
Gels are a nebulous type of morphology

Microphase separated structures

Colloid Connection: fractals

Resolution is limited by wavelength (but ingenuity sometimes trumps this limit).

It is hard for any microscope to separate two objects that are closer than about half the wavelength.



Light: $\lambda = 5000$ Å/2 → 2500 Å

Electron: $\lambda = h/mv = 0.04$ Å/2 → wow!

Actual resolution in EM is *much* less.

Two basic forms of EM are extremely important to morphologists.

(there are many subvarieties)

- SEM
  - Surfaces
  - Great depth of field
  - 3D looking
  - Can sorta do wet samples
  - Resolution 100 Å
  - Easy sample prep
- TEM
  - Looks through sample
  - Thin samples!
  - OsO_4 or other contrast agent often required

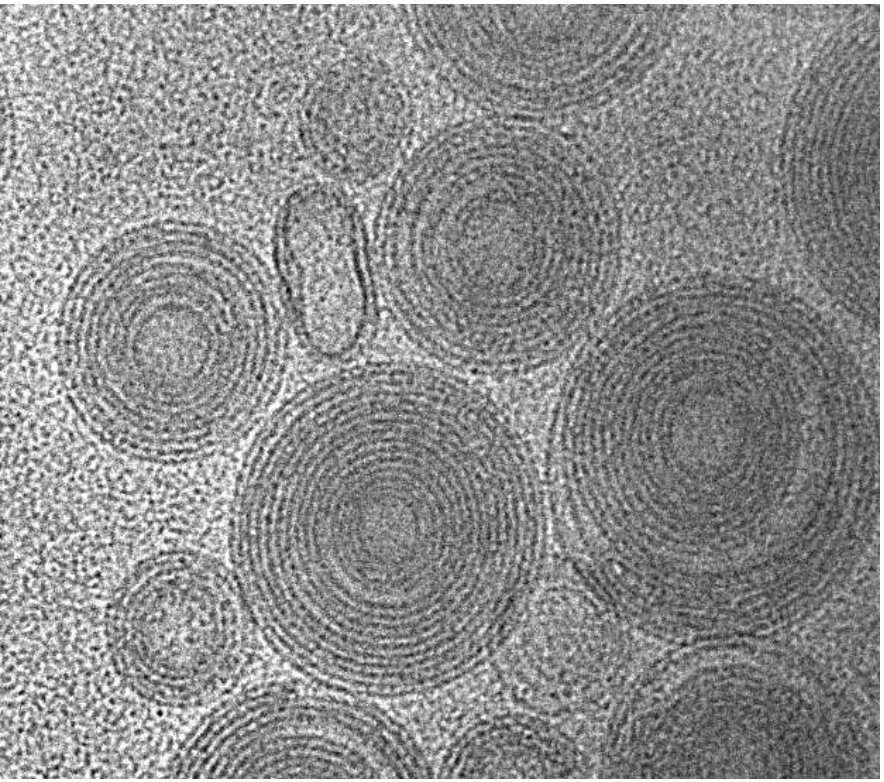
Some other EM varieties are valuable.

Secondary ion electron detectors

Scanning transmission

Freeze-fracture

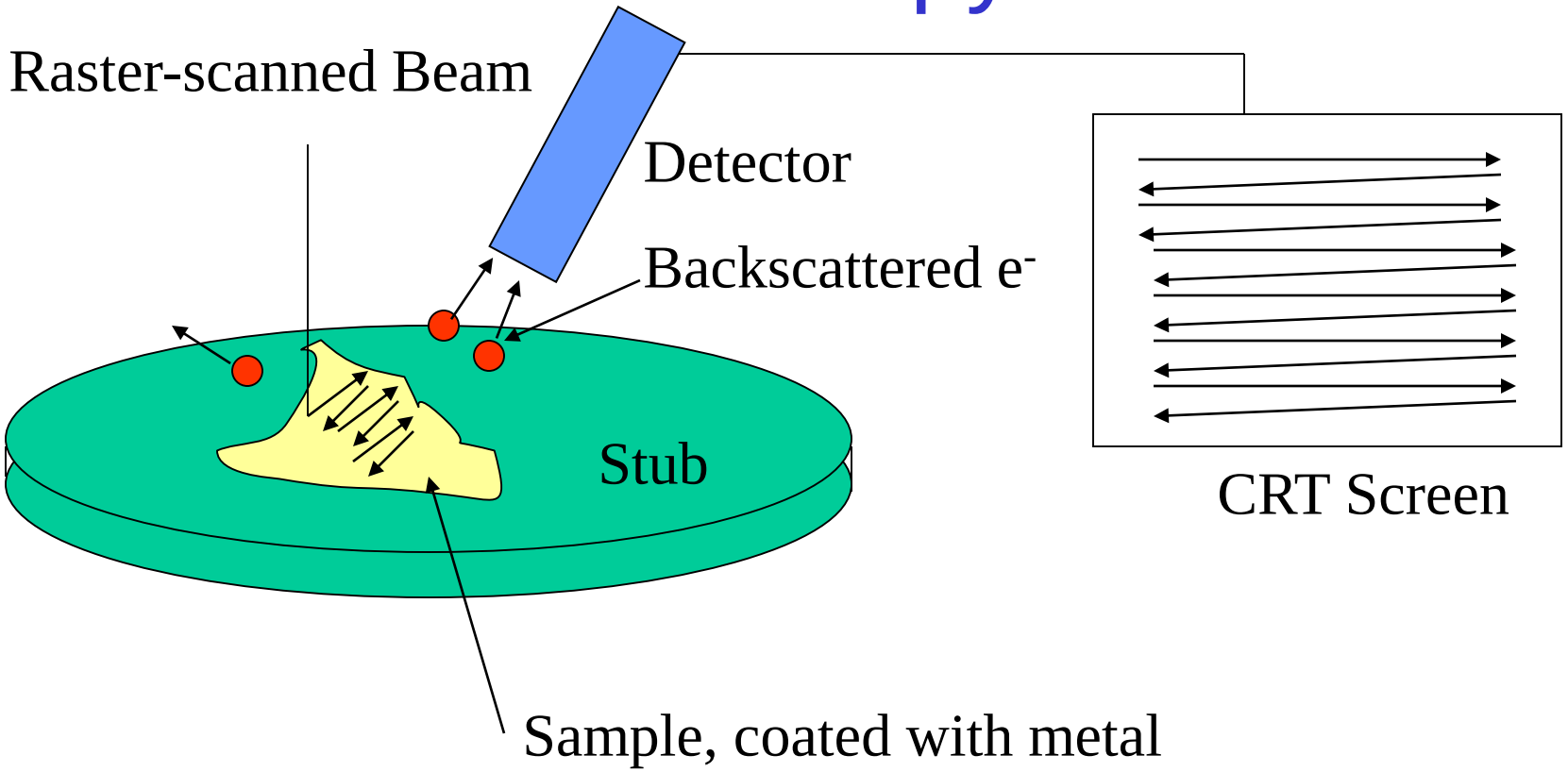
← Cryomicroscopy



Self-Assembly of Biological and Synthetic Amphiphiles Center of Excellence Funded by the Israeli Academy of Sciences.

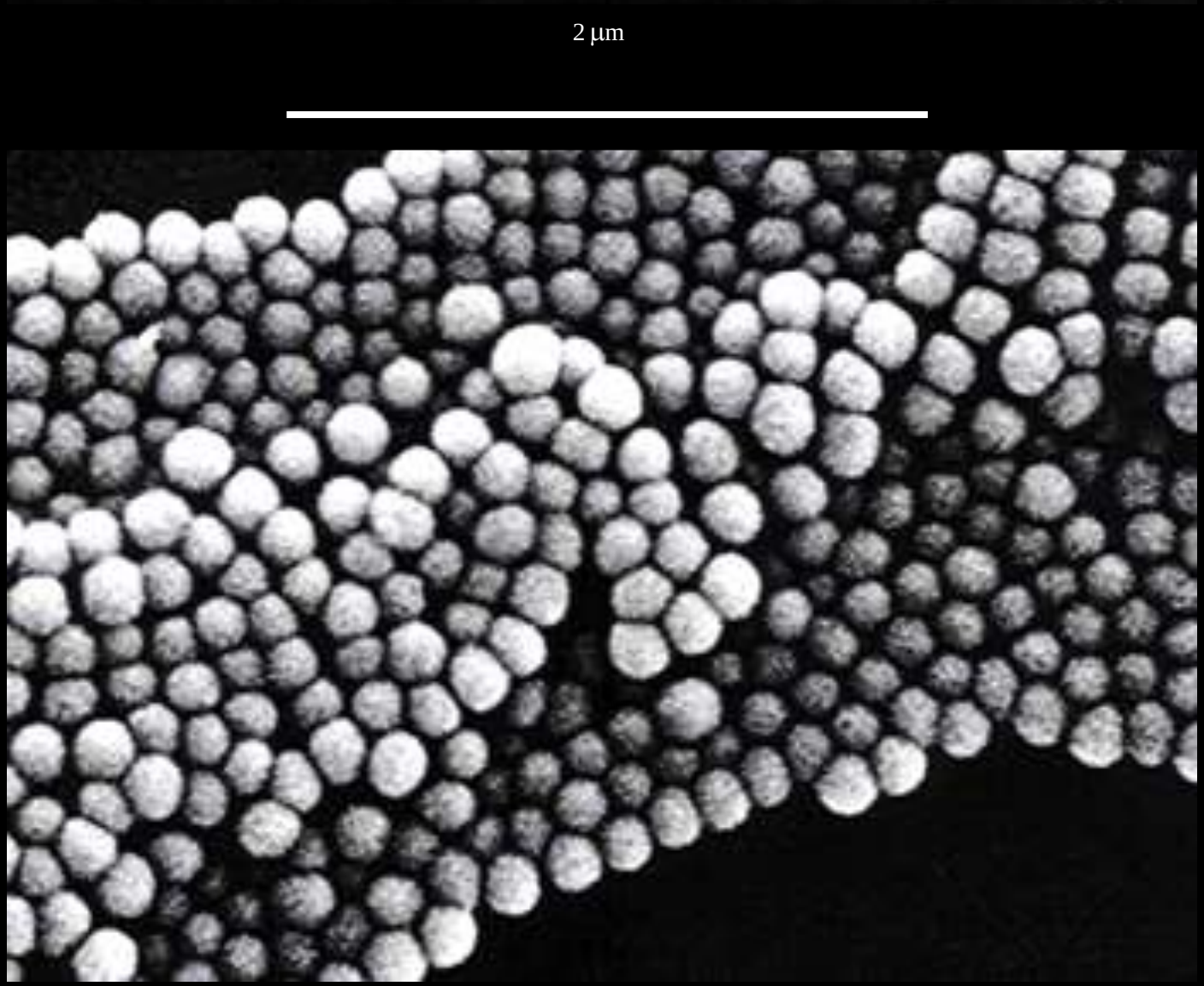
star.tau.ac.il/~andelman/moked_en.html

SEM=scanning electron microscopy.



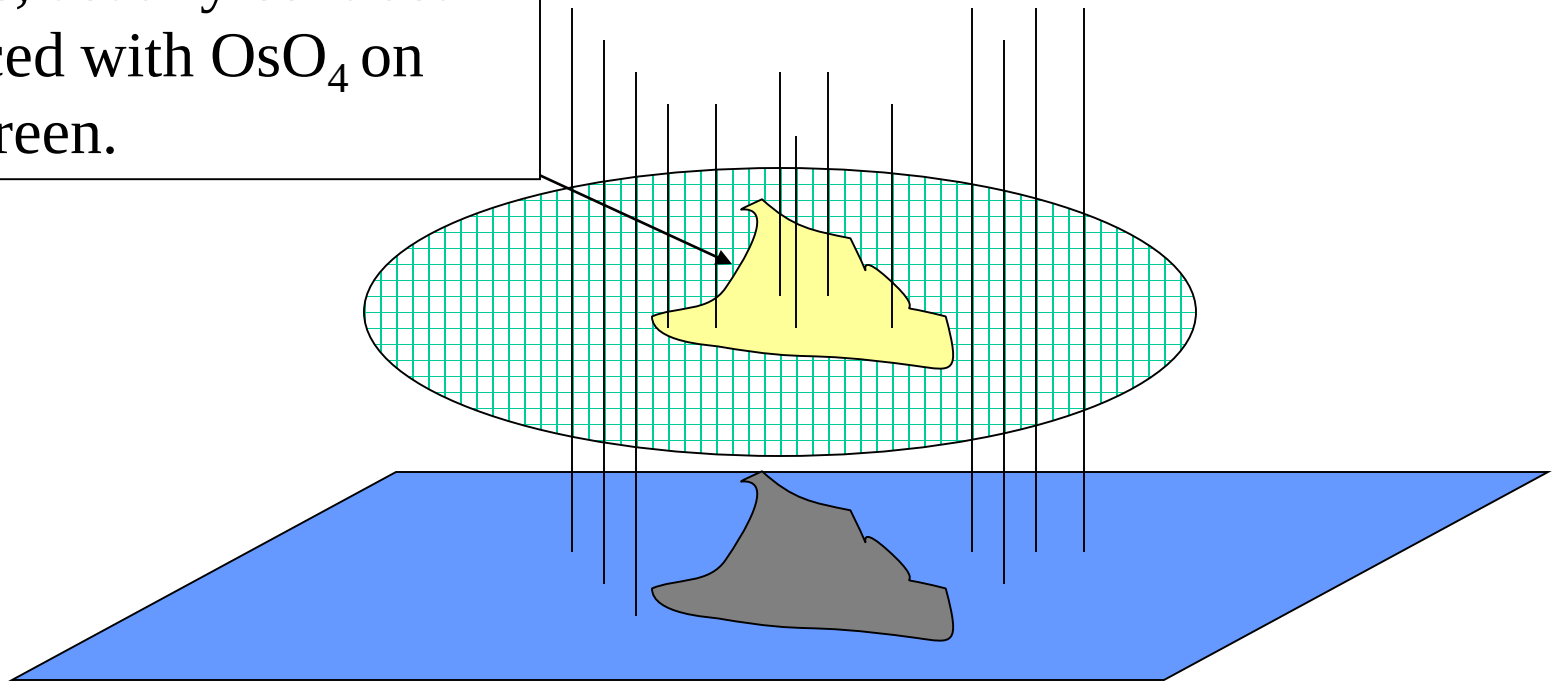
Fuzzballs: Silica-Polypeptide Composite Spheres

Fong, Turksen, Russo & Stryjewski



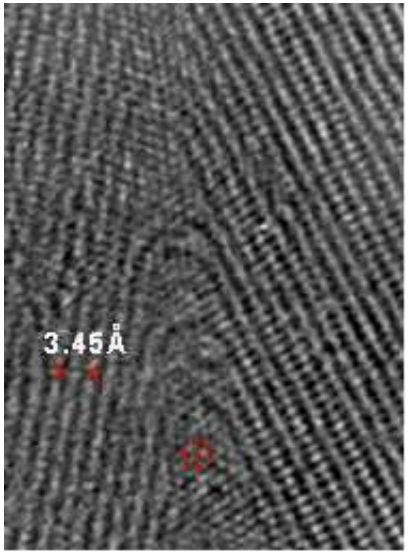
TEM=transmission electron microscopy.

Sample, usually contrast enhanced with OsO_4 on fine screen.

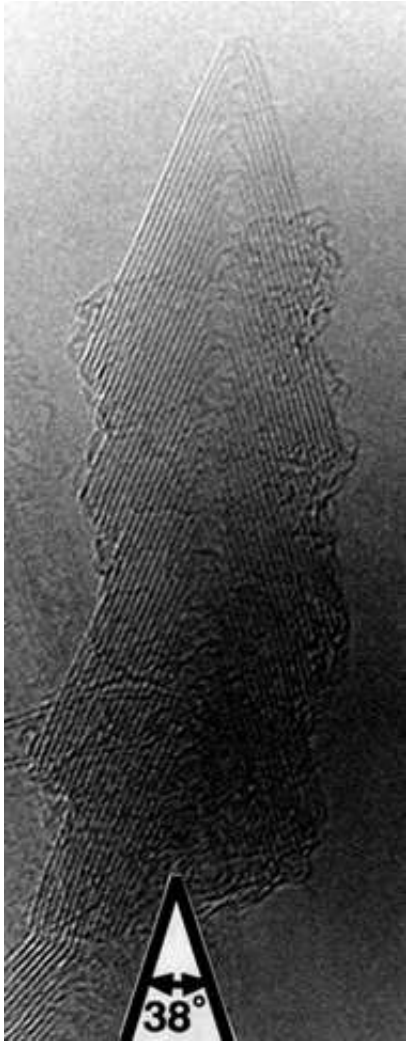


HRTEM Boron Nitride Nanocone

http://www-personal.monash.edu.au/~bourgeoi/ima_gall.html#nanocones



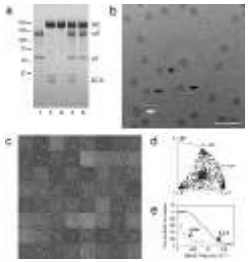
HRTEM and nanobeam DP of other nanocone. The hexagonal lattice fringes and the symmetry apparent in the DP are consistent with the cones being 240 deg. disclinations.



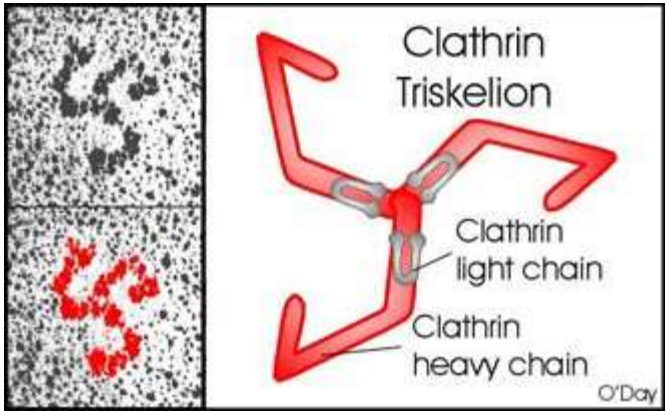
Temography.

http://www.jeolusa.com/PRODUCTS/ElectronOptics/TransmissionElectronMicroscopesTEM/Software/TEMographySoftware/tabid/332/Default.aspx

CryoEM is *still* not available at LSU….but Tulane has it.



http://en.wikipedia.org/wiki/Clathrin

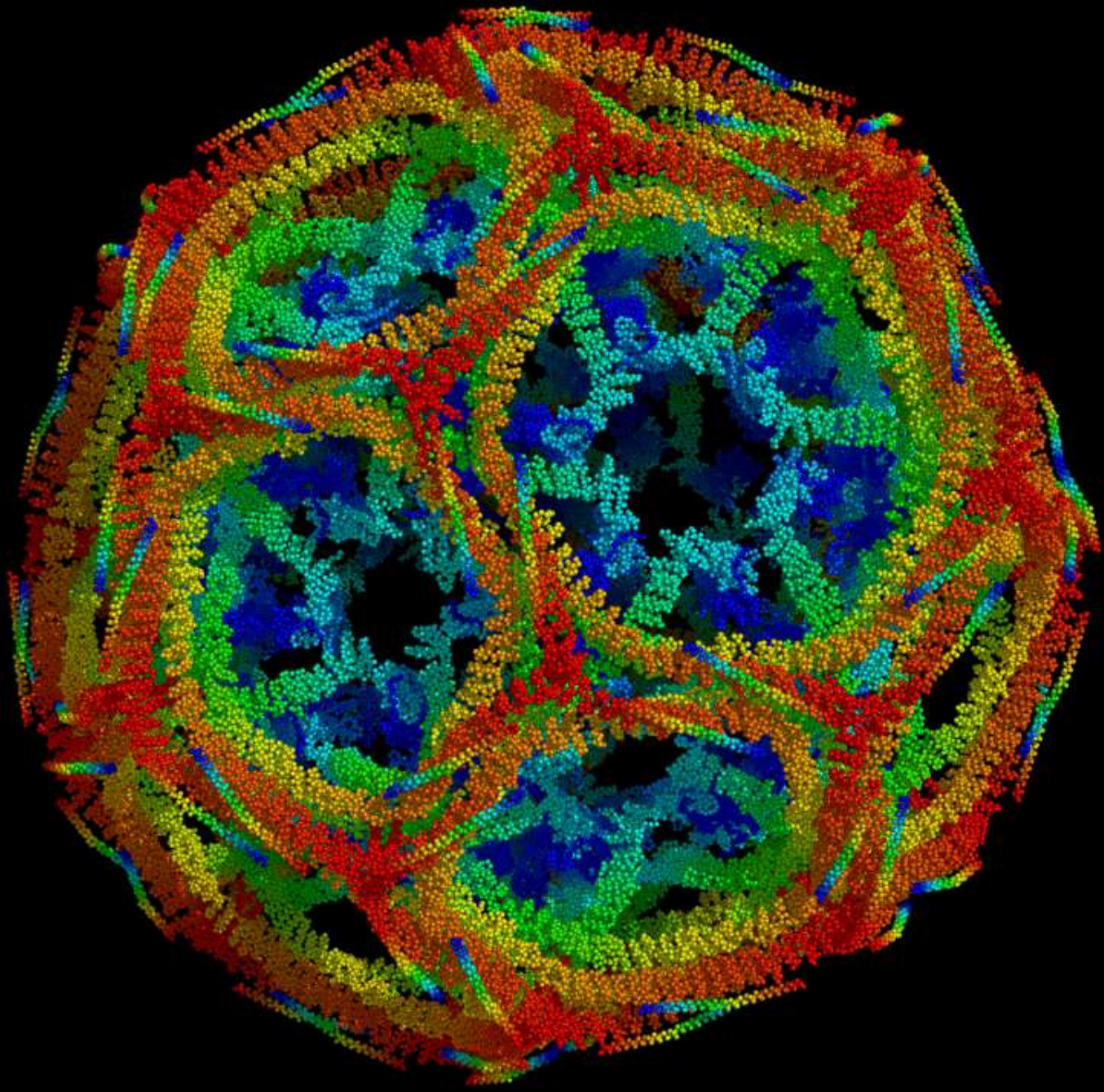


Clathrin Cryo-EM Image

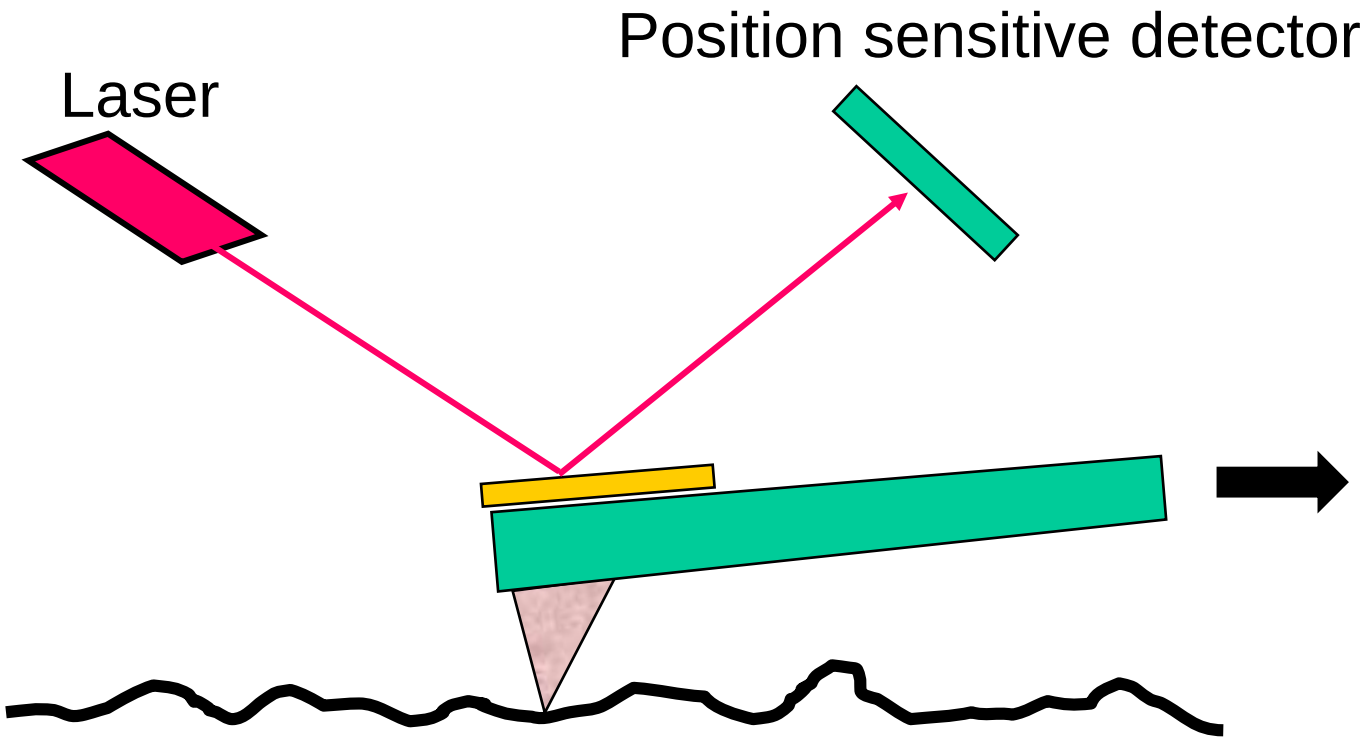
Molecular model for a complete clathrin lattice from electron cryomicroscopy
Alexander Fotin, Yifan Cheng, Piotr Sliz, Nikolaus Grigorieff, Stephen C. Harrison,
Tomas Kirchhausen and Thomas Walz
Nature 432, 573-579(2 December 2004)
doi:10.1038/nature03079

http://www.sp.uconn.edu/~bi107vc/images/cell/clathrin.jpg

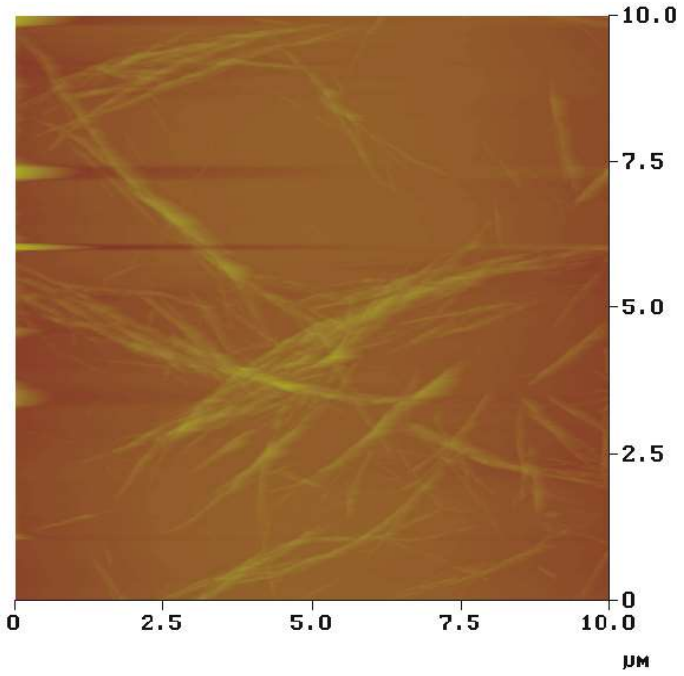
http://www.cbrinstitute.org/labs/kirchhausen/clathrinqt.html



Scanning Probe Microscopy = potentially simple idea; latest incarnations of surface probe microscopy (SPM) can be very sophisticated (Prof. Garno).



Amyloid fibrils have been visualized by the Alzheimer's team at LSU.

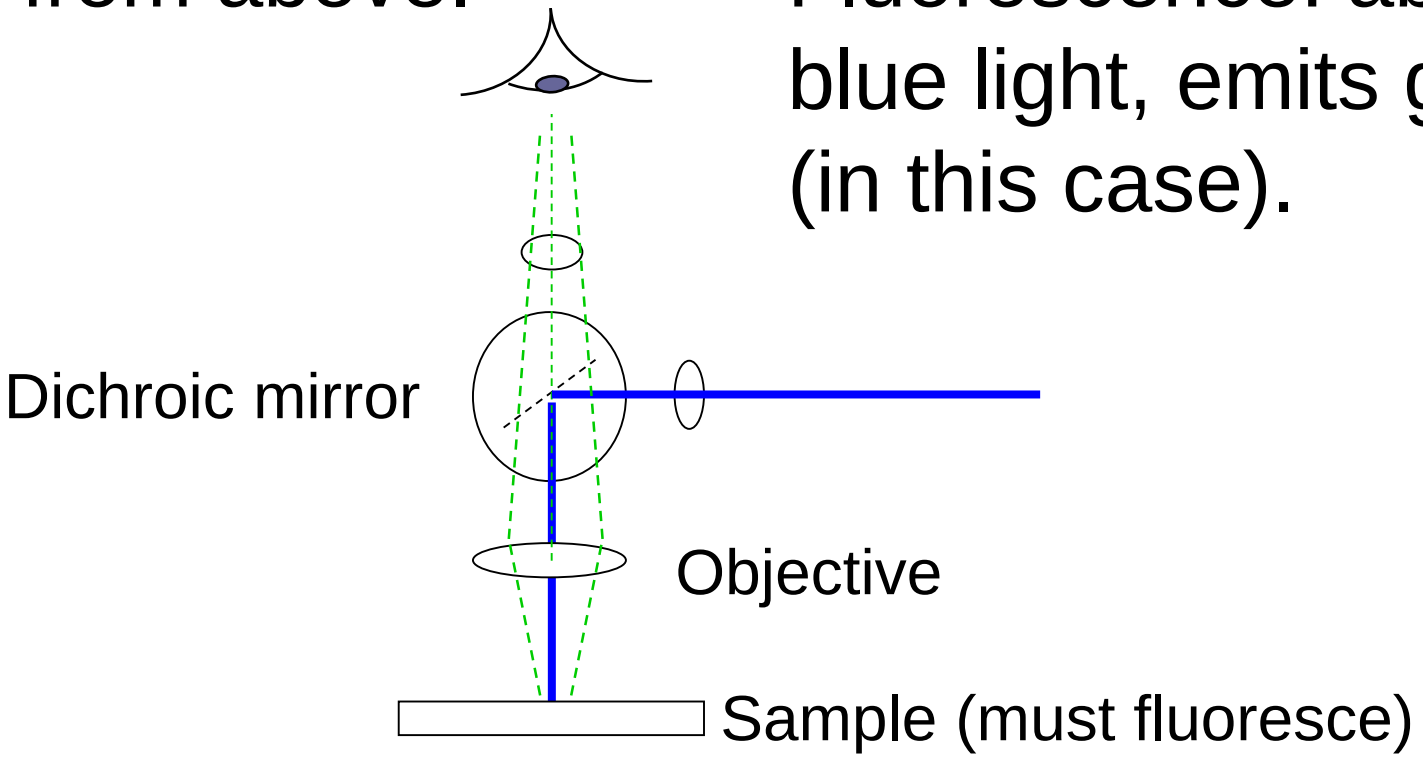


300 μM beta-Amyloid$_{10\text{-}35}$ in 70 mM KF and
10 mM phosphate buffer system at pH 4
22 days after sample preparation

Epifluorescence microscopy features extraordinary contrast, sensitivity and bioactive probes.

Epi: from above.

Fluorescence: absorbs blue light, emits green (in this case).



Samples not naturally fluorescent must be labeled; some possibility of damag

Polarized light microscopy responds to optical anisotropy.

The polarization of light is changed by some samples, especially some crystals.

You have to infer the structure based on the ability of certain structures to change the sense of light polarization.

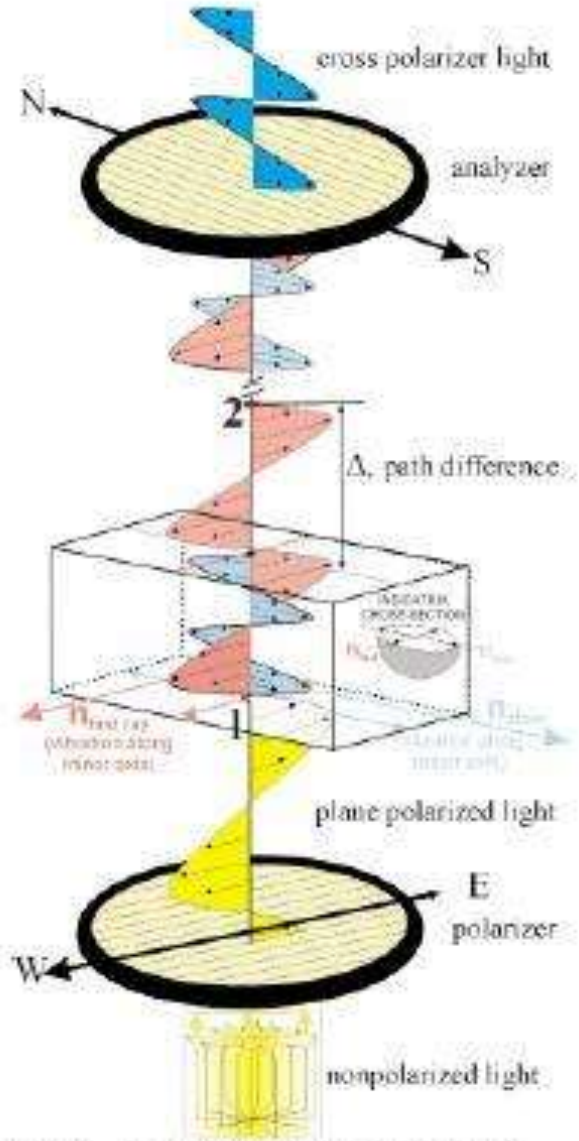
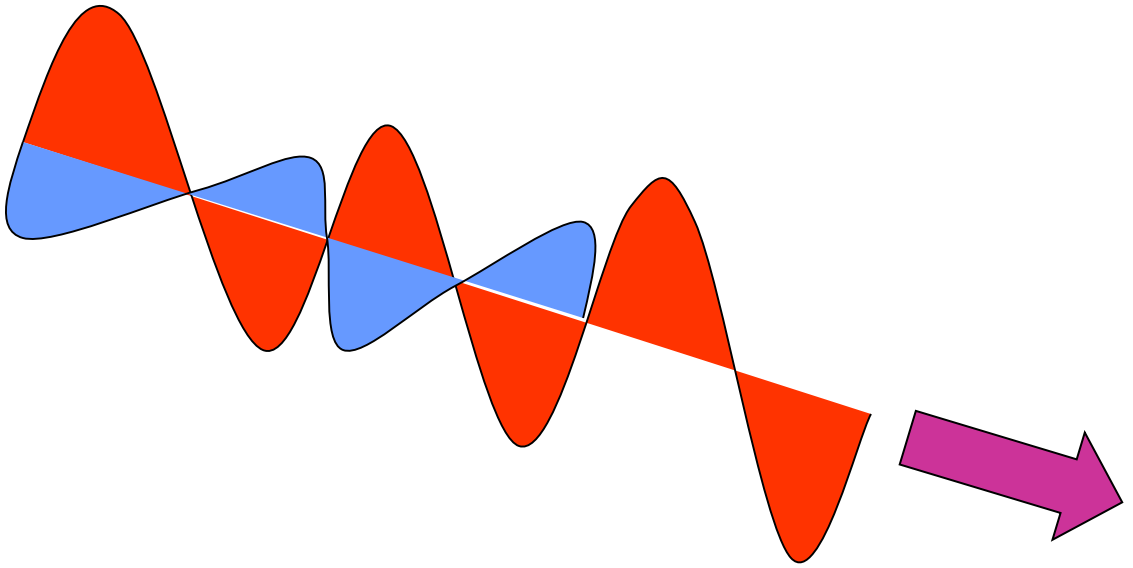


Figure 2 Interaction of polarized light with an anisotropic crystal (see text). Note that the PLM's rotating stage (not shown) allows one to place any vibration direction within the sample parallel to the east–west incident light so that its refractive index can be measured. Also note that the analyzer may be inserted for observation in cross-polarized light (XPL) or removed for observation in plane-polarized light (PPL).

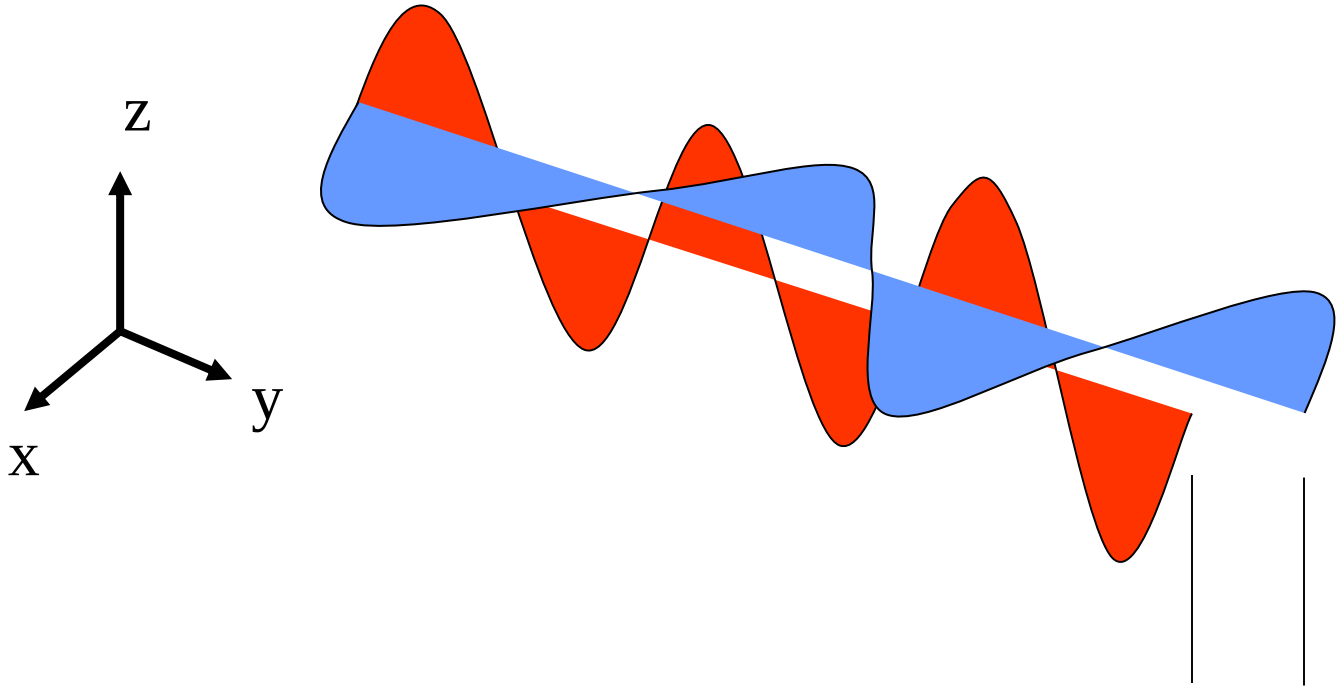
Phase shift builds up as light goes through crystal, splits into ordinary and extraordinary rays, recombines.

R. Weaver, Am. Lab, Oct. 2003

Light: $\underline{S} = \underline{E} \times \underline{H}$



Birefringence means two refractive indices in the same material: The electric fields of Extraordinary & Ordinary rays travel at slightly different speeds.

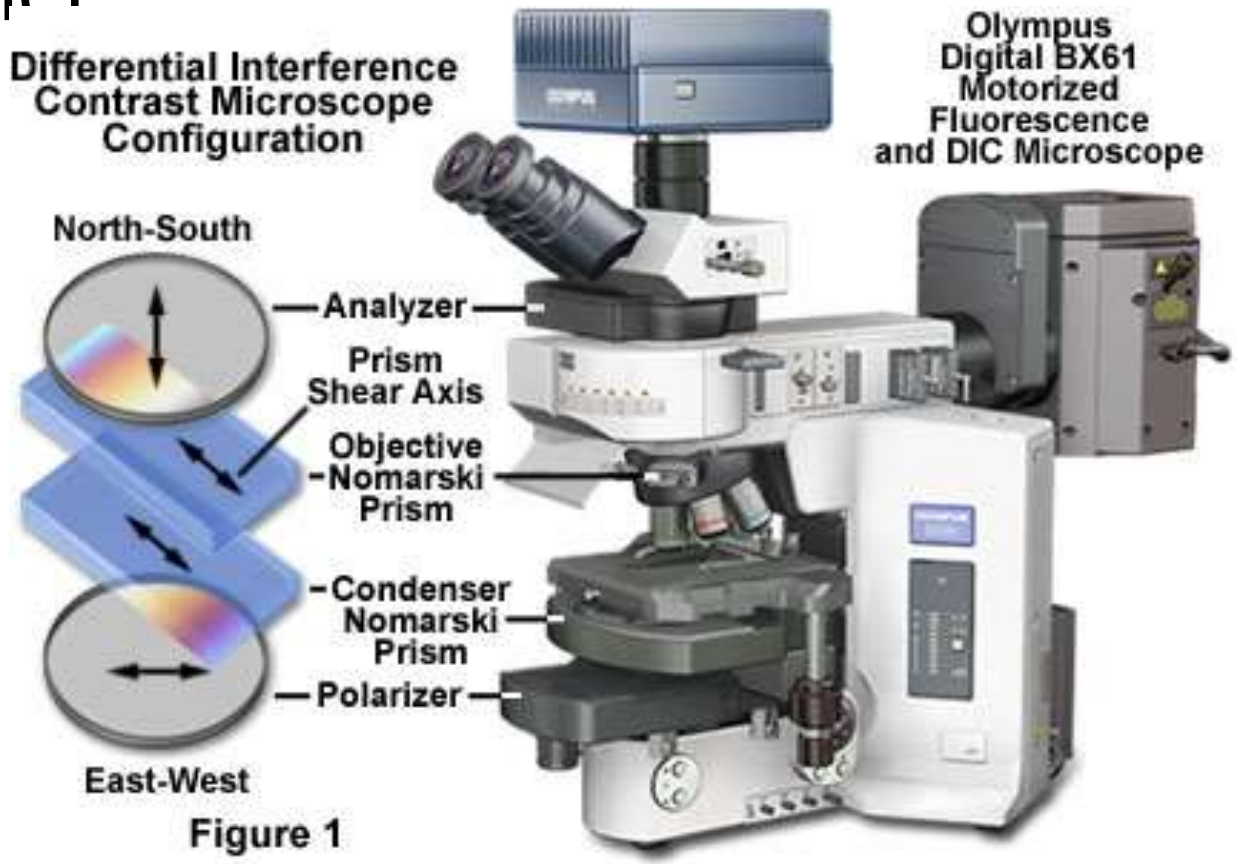


δ = phase shift $=(2\pi/\lambda)\Delta n \cdot d$

Nomarski (Differential Interference Contrast) microscopy also uses polarizers but also beam shearing—a displacement of a reference beam by a small amount.

- Can reveal features where there is not necessarily anisotropy, but at least a difference of refractive index, resulting in *optical* path difference.
- A form of polarized light microscopy that takes advantage of small phase shifts the light suffers as it goes through objects in your sample.
- The phase shifts are converted optically to a kind of shadow or “relief” providing in some cases a three-dimensional look.

The microscope in your montage assignment can do Nomarski. Here's another



http://www.olympusmicro.com/primer/techniques/dic/dicintro.html

Nomarski is the same thing as Differential Interference Contrast.

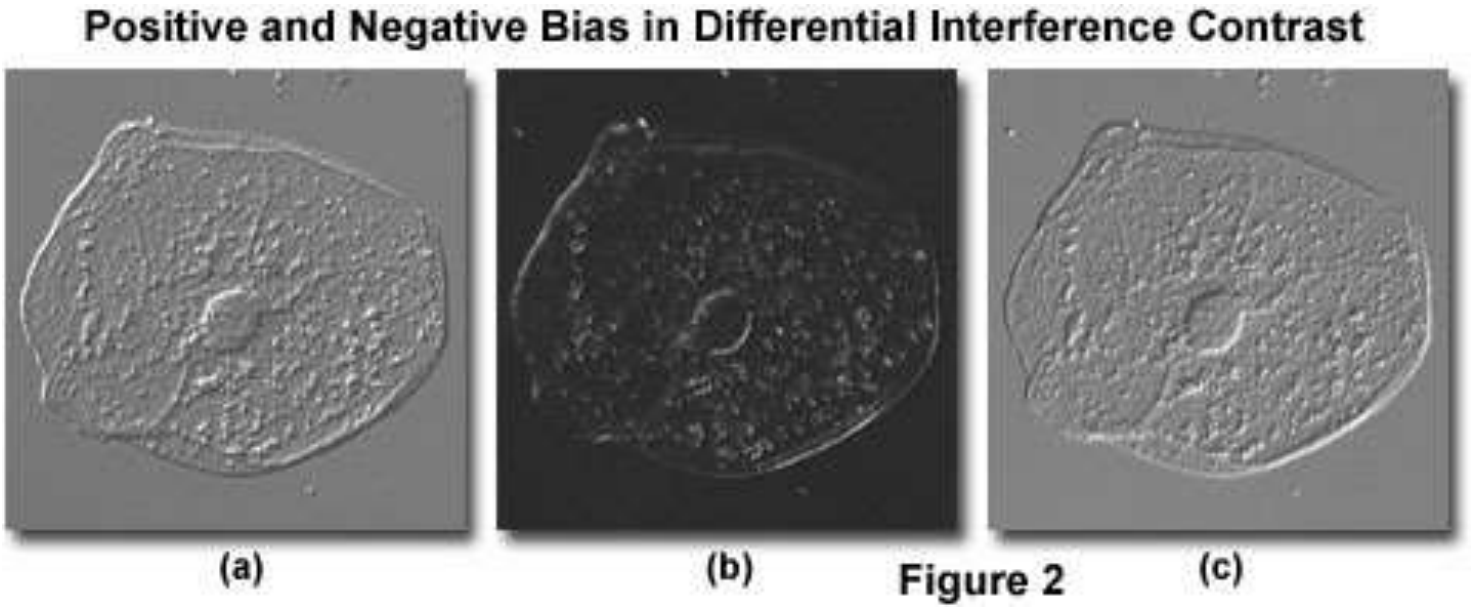


Figure 2

http://www.microscopyu.com/tutorials/java/dic/dicalignment/

Olympus Nomarski JAVA Simulator

Nikon Nomarski JAVA Simulators

FSU Microscopy Primer

Where would *structure* come from in simple polymers—e.g. random coils?

Tacticity is one answer.

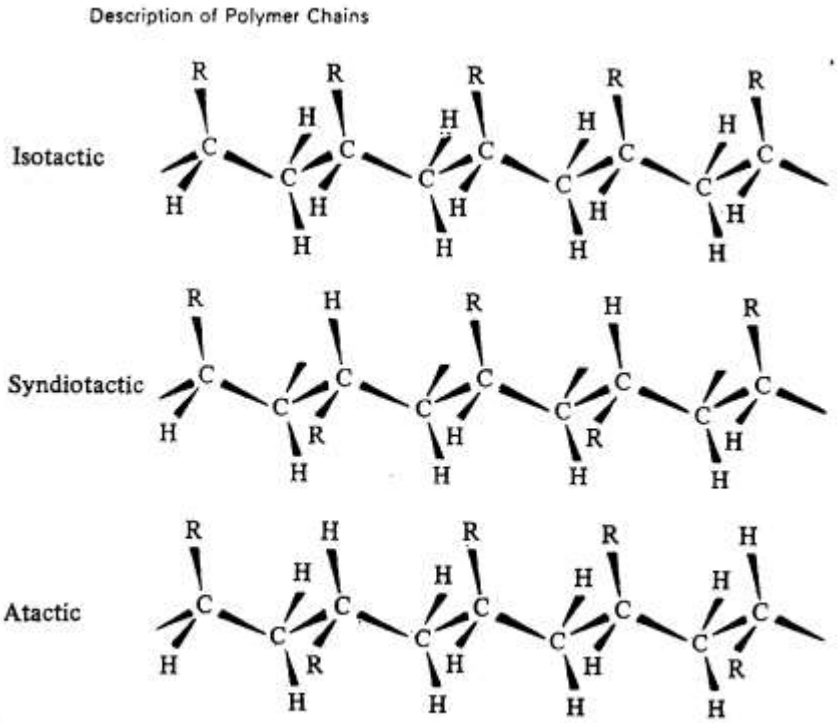
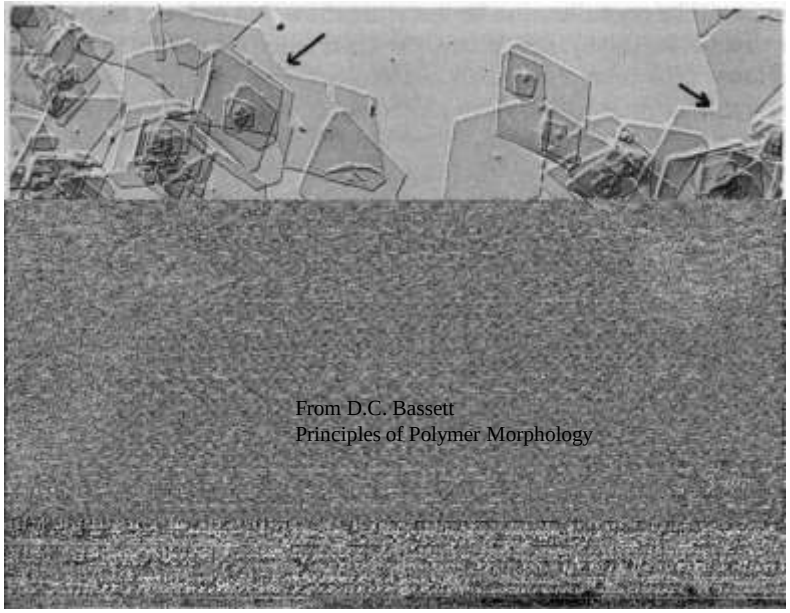


Fig. 1.5. Chain configurations in poly (α olefines). (From Schultz, 1974.)

From D.C. Bassett
Principles of Polymer Morphology

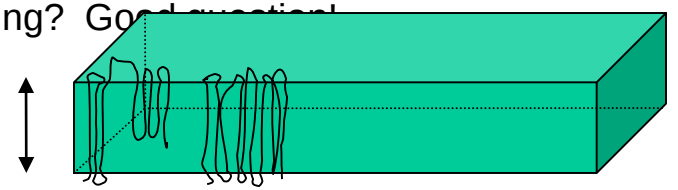
Tacticity can lead to crystallinity. Amazing: something large & wiggly can crystallize!

- SEM or TEM???
- The crystals at right were grown from a solution.
- You can also make crystals by cooling a polymer melt, but….some regions remain amorphous.
- People say things like "crystallizable polymer" because the actual percentage of crystals realized is a function of conditions.



Lamellar thickness <<< chain contour length so
Chain folding into lamella is required. Local (switchback) folding or remote (switchboard) folding? Good question!

l = ca. 50 – 100 Å



Thickness is controllable and increases when crystals made near T_m .

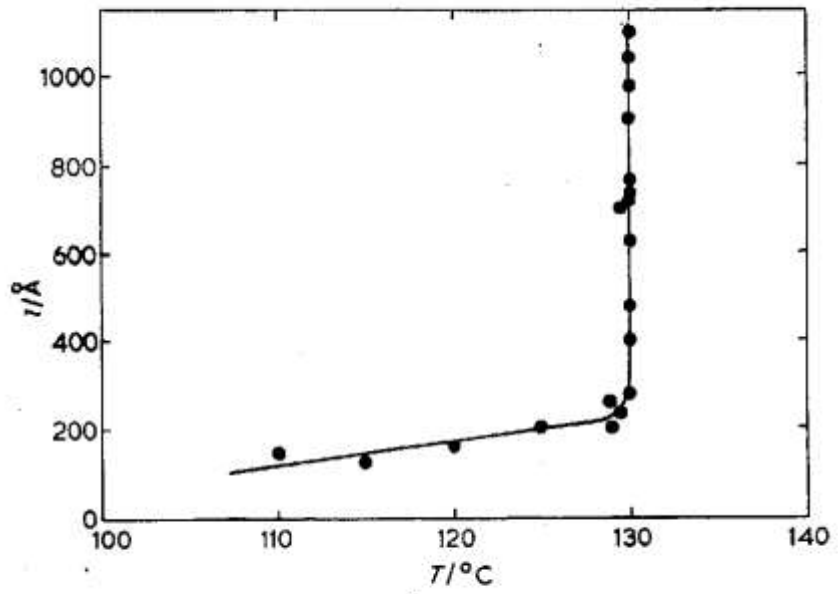
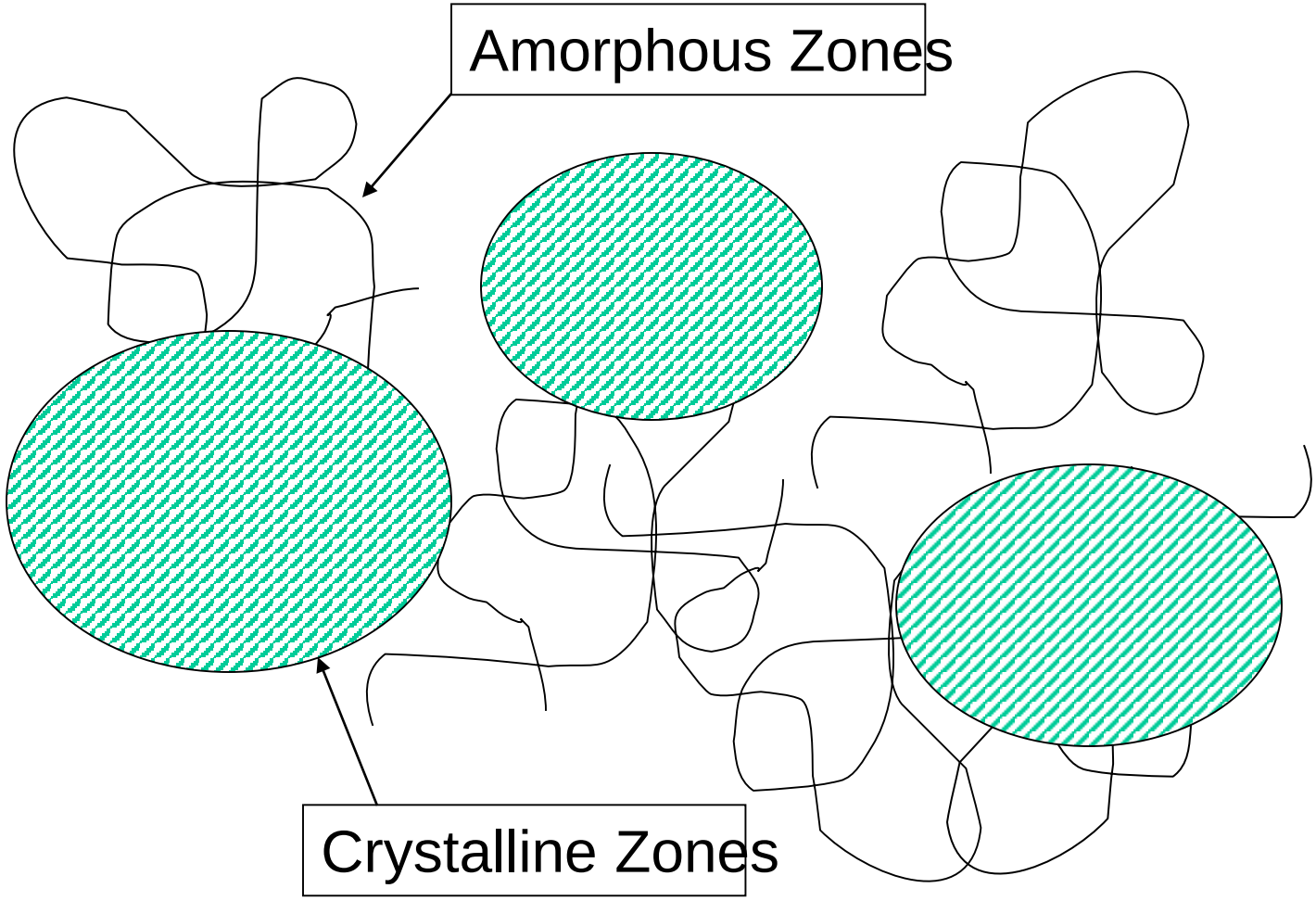


Fig. 4.20 *Lamellar thickness as a function of crystallization temperature for isothermally melt-crystallized polyethylene. (After Wunderlich).*

Polymers don’t always crystallize, and some never do!



There are many crystal motifs besides lozenges shown already—e.g. *spherulites.*

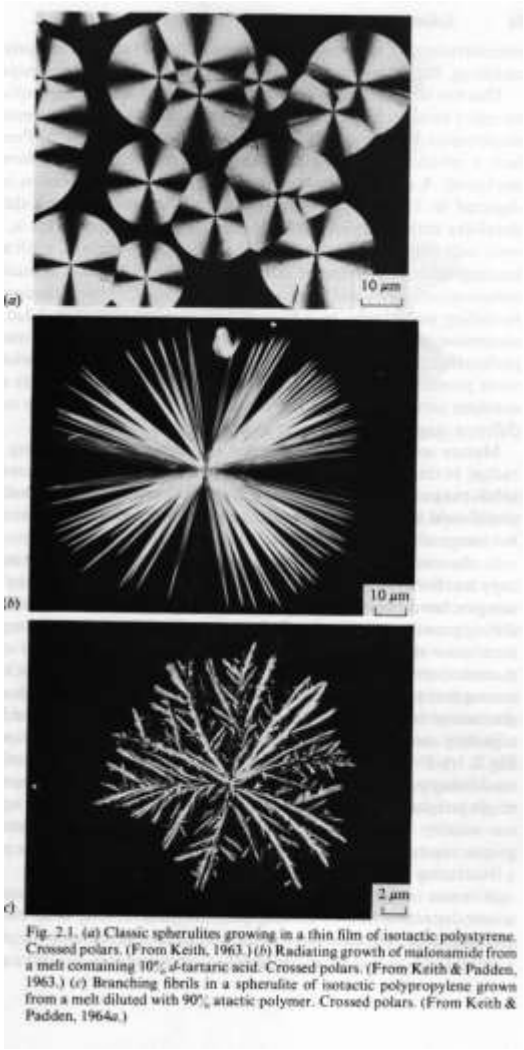
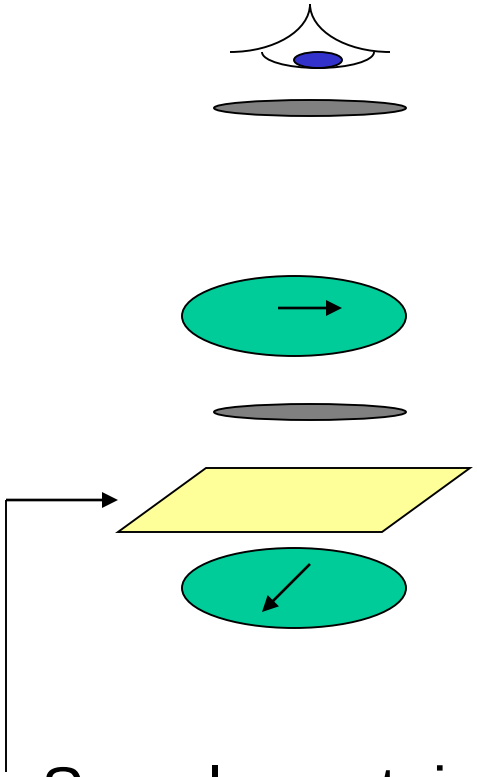


Fig. 2.1. (*a*) Classic spherulites growing in a thin film of isotactic polystyrene. Crossed polars. (From Keith, 1963.) (*b*) Radiating growth of malonamide from a melt containing 10% *dl*-tartaric acid. Crossed polars. (From Keith & Padden, 1963.) (*c*) Branching fibrils in a spherulite of isotactic polypropylene grown from a melt diluted with 90% atactic polymer. Crossed polars. (From Keith & Padden, 1964*a*.)

Polarizing Optical Microscopy (POM)

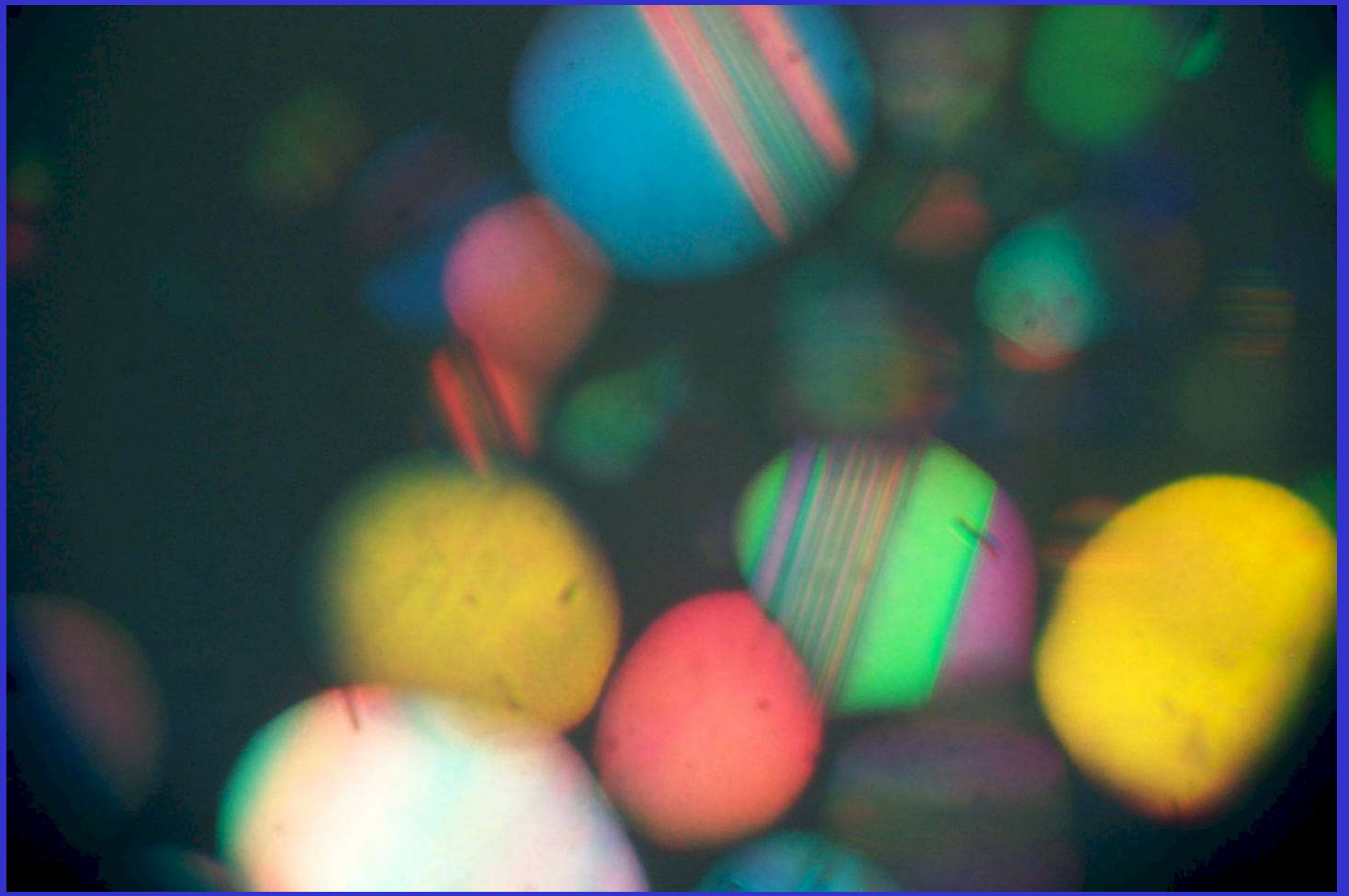


Analyzer East

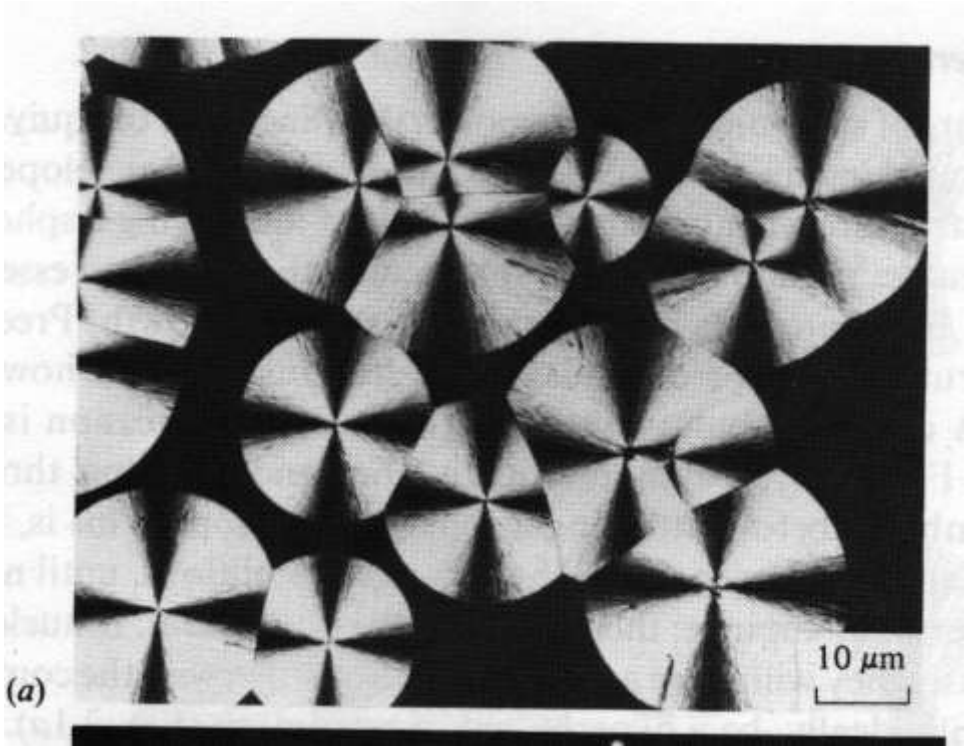
Polarizer North

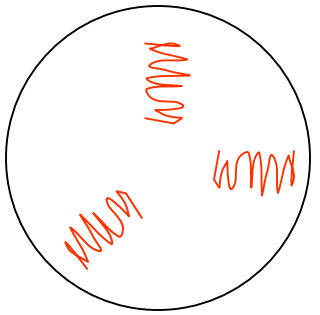
Sample containing spherulites

This spectacular image from our lab shows a colloidal crystal made of a hybrid inorganic core /organic polymer shell composite particle.



Why the maltese cross?





N can't "grab" light

E can grab it, but can't redirect it.

SW grabs and redirects

Polarizer N → Analyzer E

Grab light? Yeah, like gravity grabs you. In this case, it means light polarizes the electrons.

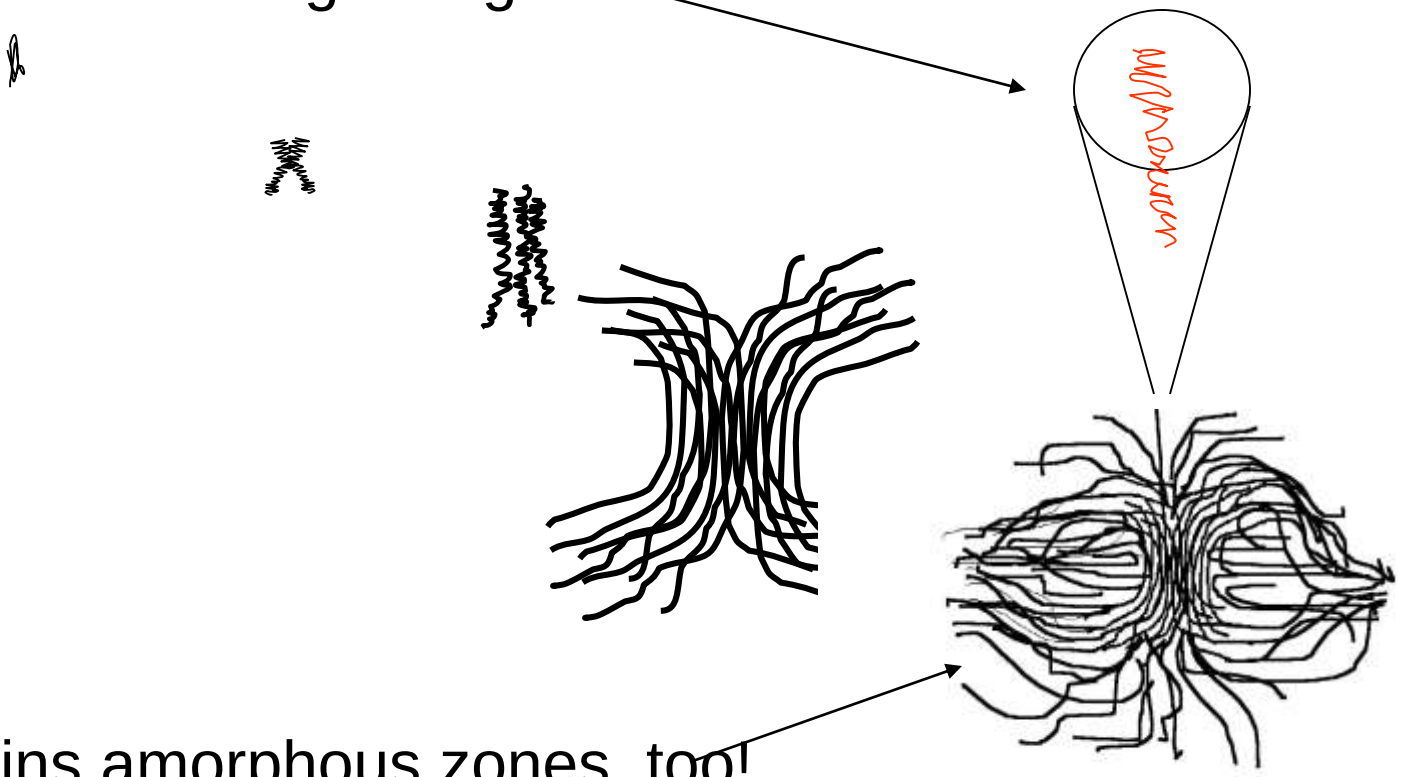
A Volkswagen on its wheels on flat ground can roll but doesn't unless motor running.

A VW lying on its door can't roll.

A VW on a hill will roll (or slide).

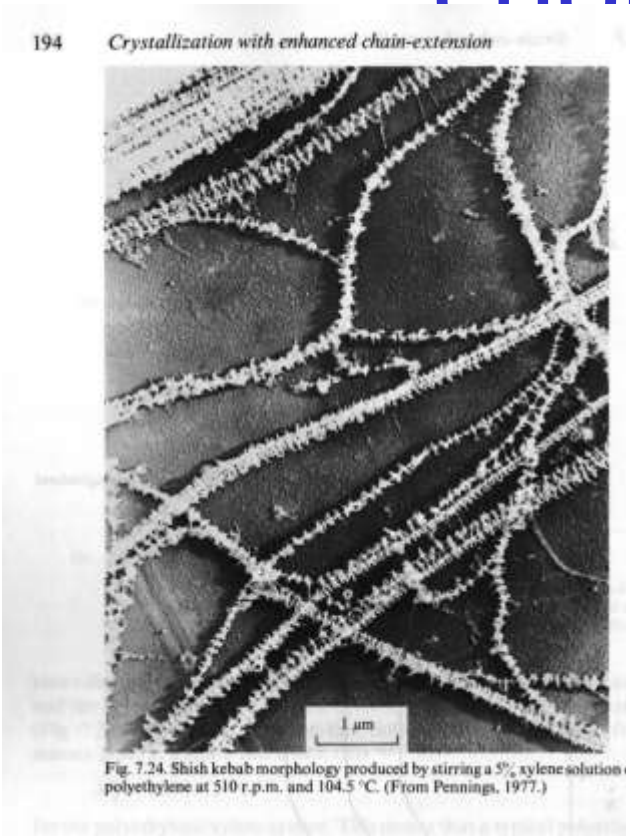
Spherulites grow from little seeds.

Branched fibrils with polymer chains folded at right angles.

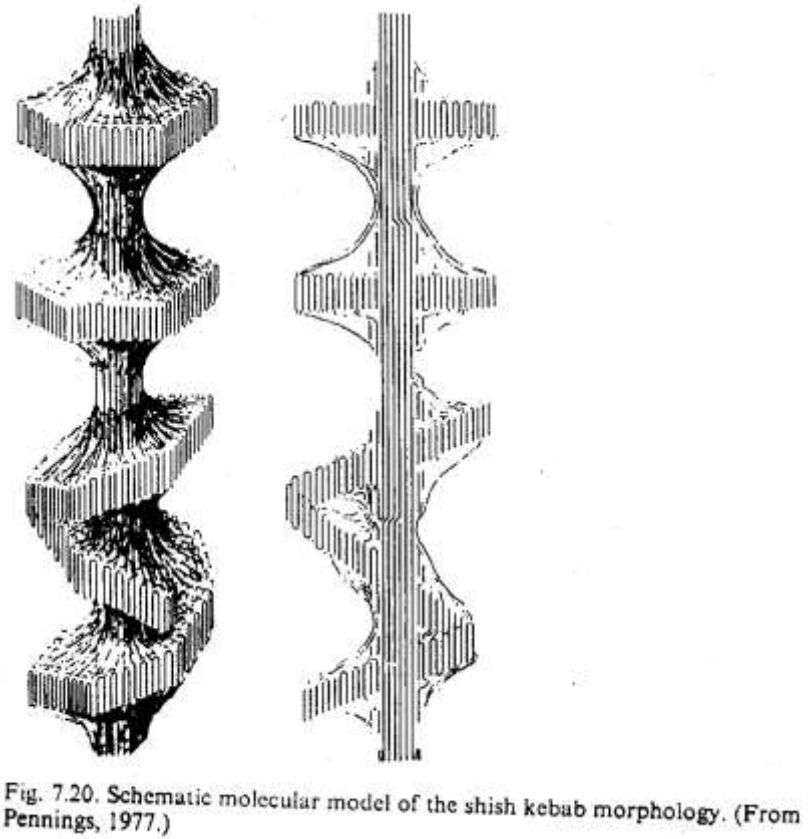


Contains amorphous zones, too!

Spherulites aren't the only choice

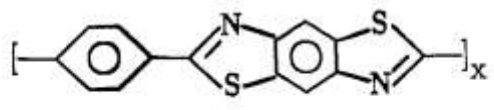


From Bassett



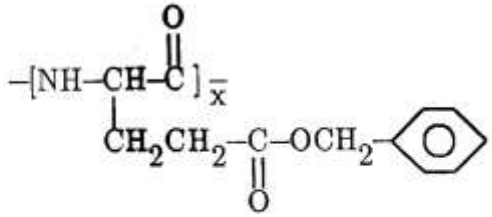
Shish kebab

Other polymer motifs can lead to structure—e.g., rods give liquid crystals that spawn structures.



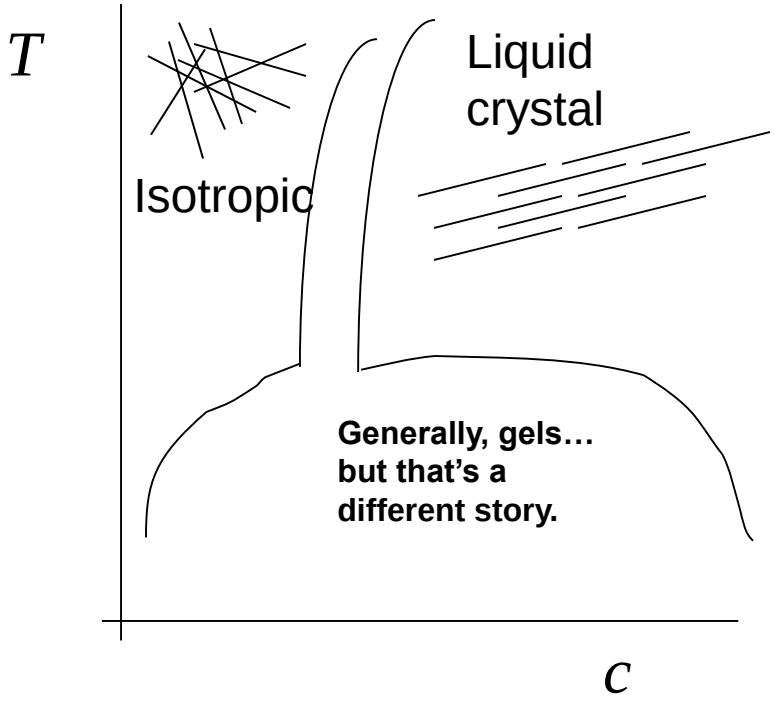
Mainchain conjugated rod

PBT poly(p–phenylenebenzobisthiazole)

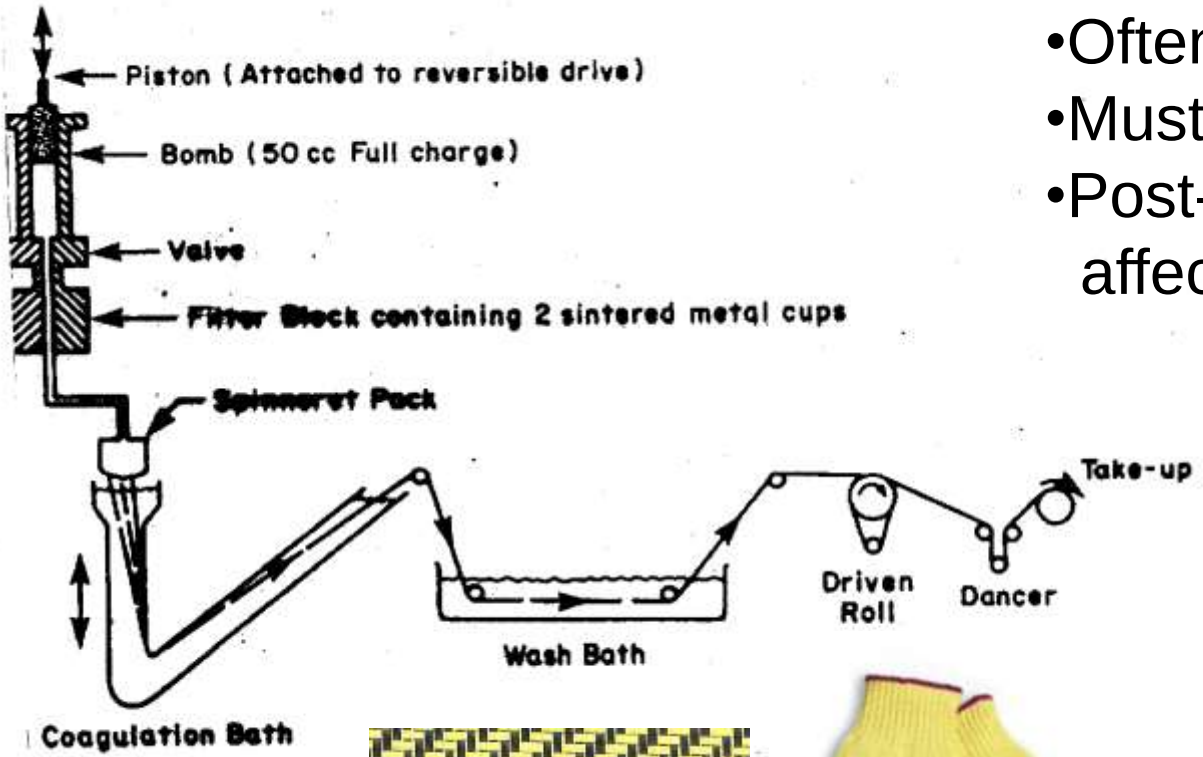


Helical rod

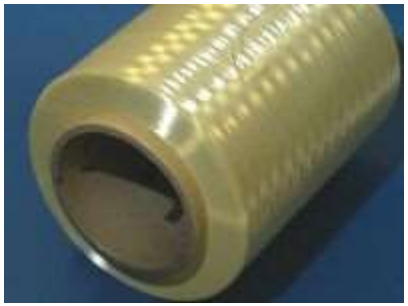
PBLG poly(γ–benzyl–α,L–glutamate)



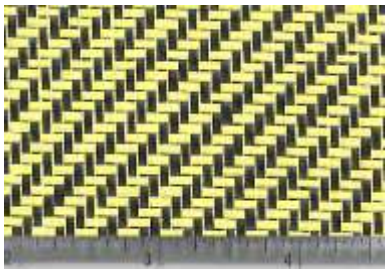
Polymer LC's—generally too slow for displays but facilitate fiber production



- Often awful solvents!
- Must remove solvents.
- Post-coagulation steps affect strength.

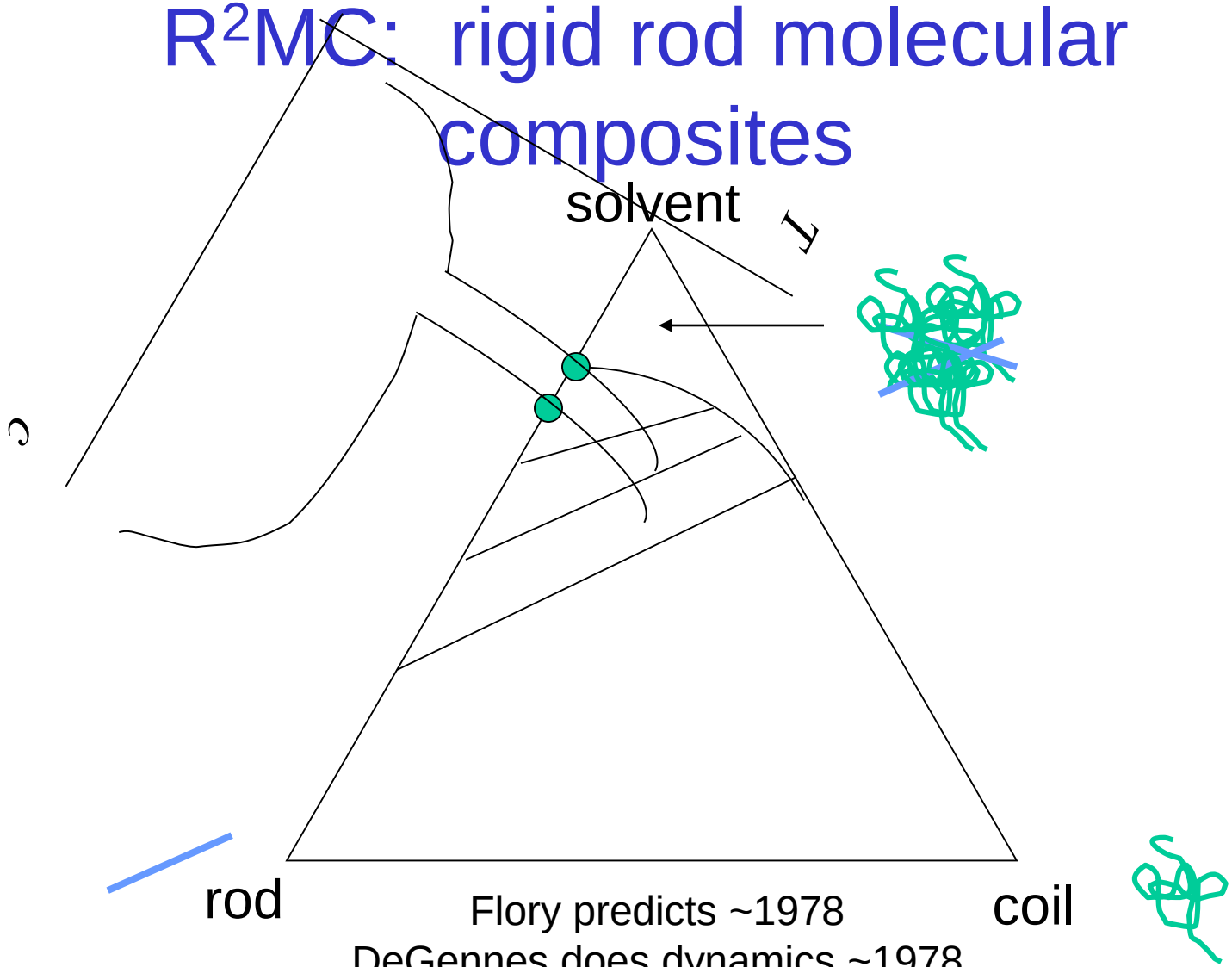


http://www.netcomposites.com/news.asp?4500



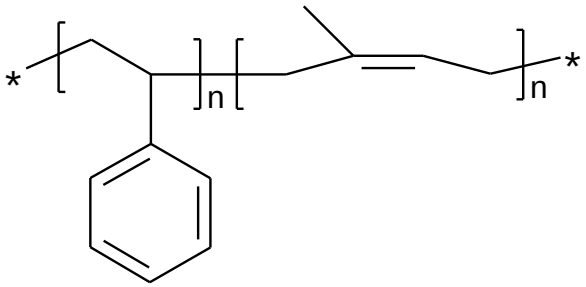
Co-woven with graphite

R^2MC: rigid rod molecular composites

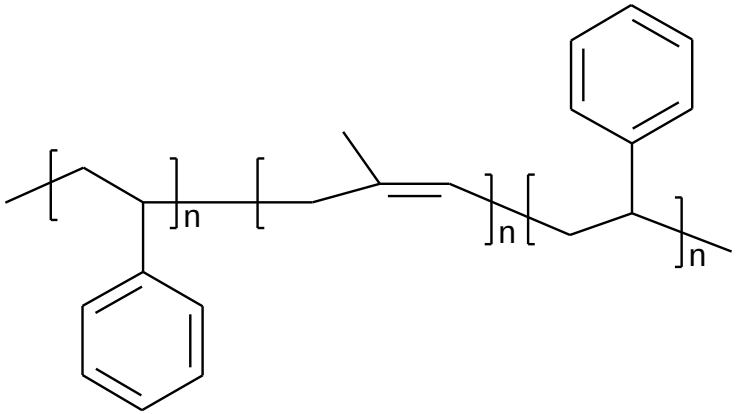


Flory predicts ~1978
DeGennes does dynamics ~1978
Experiments still hard to do!

Building (with) Blocks: Copolymers can also introduce morphology

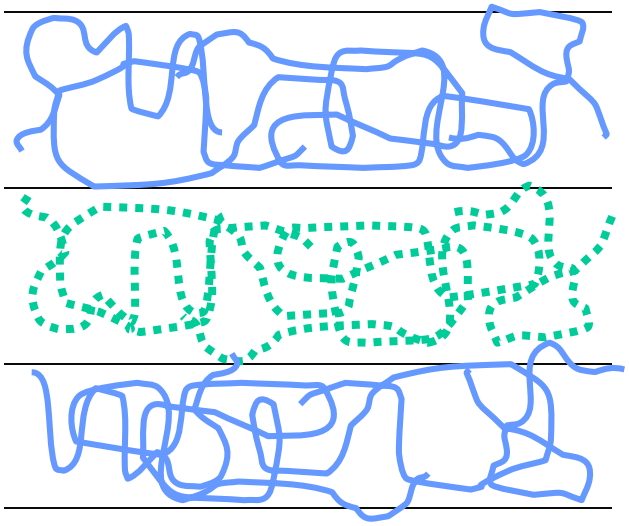


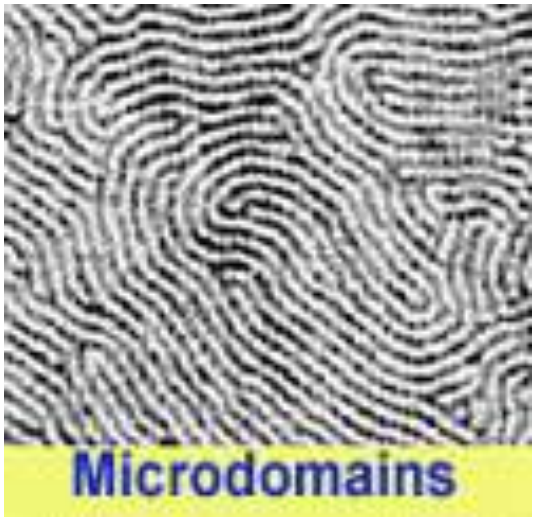
Styrene-Isoprene Diblock



Styrene-Isoprene-Styrene Triblock

Can’t we all just get along? No.





http://arnold.uchicago.edu/MRSEC/Nuggets/Stripes/index.html

Lamellar structure is hardly all.

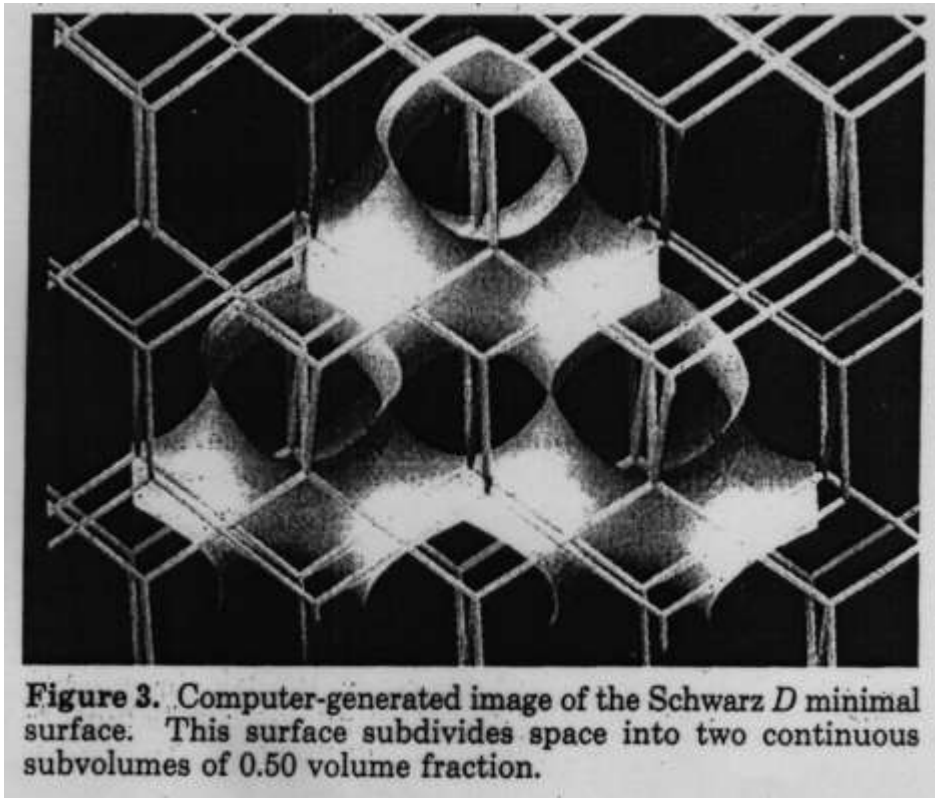
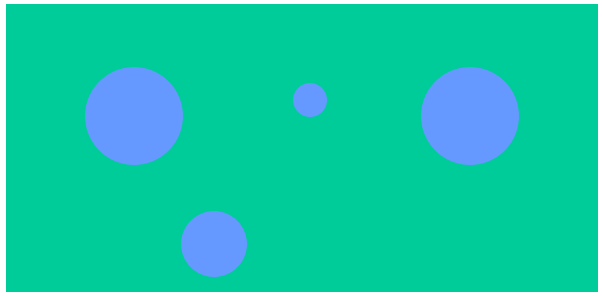


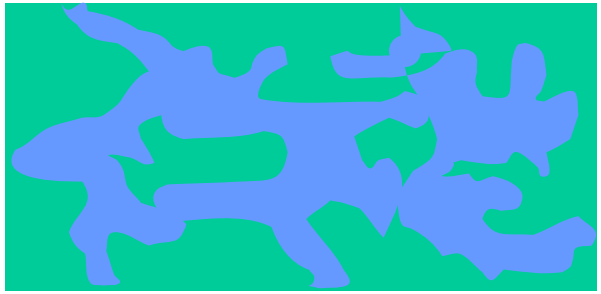
Figure 3. Computer-generated image of the Schwarz *D* minimal surface. This surface subdivides space into two continuous subvolumes of 0.50 volume fraction.

Many more structures exist. Chemical engineers and some scientists spend fortunes figuring out phase relations and the details of the internal structure. The one at left divides space into two continuous subvolumes.

Frustrated Phase Separation Can Produce Morphology



Initial structure in the metastable zone: nucleation & growth



Initial structure in the unstable zone: spinodal decomposition

Because of the incredible slowness of polymer systems,
The N&G or SD structures can be almost permanently trapped.

Gelation: dilute systems that don't flow can also introduce morphology.

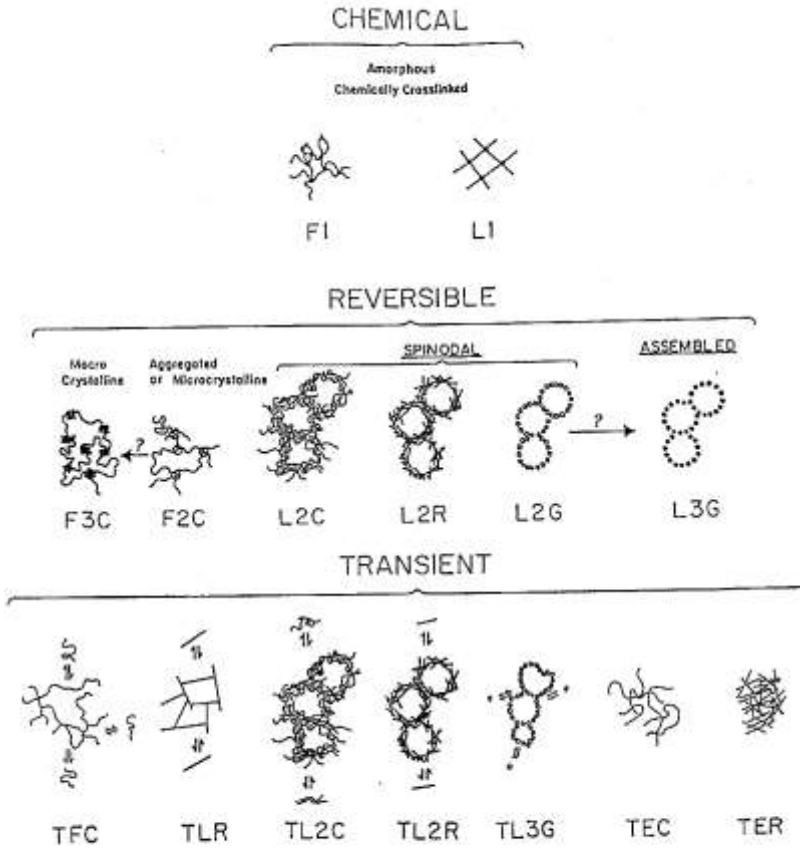


Figure 2. Structural classification scheme for polymer gels and related systems. Key: F = fishnet; L = lattice; T = transient; E = entangled; C = coil; R = rod; G = globular.

This figure, out of some guy's book on thermoreversible gels, tries to categorize gels. By a lot of different ways, it is possible to "freeze" a fluid with a small amount of polymer. The responsible structures can sometimes be retained even after the solvent is removed—for example, by supercritical fluid drying.

Breaking Stuff

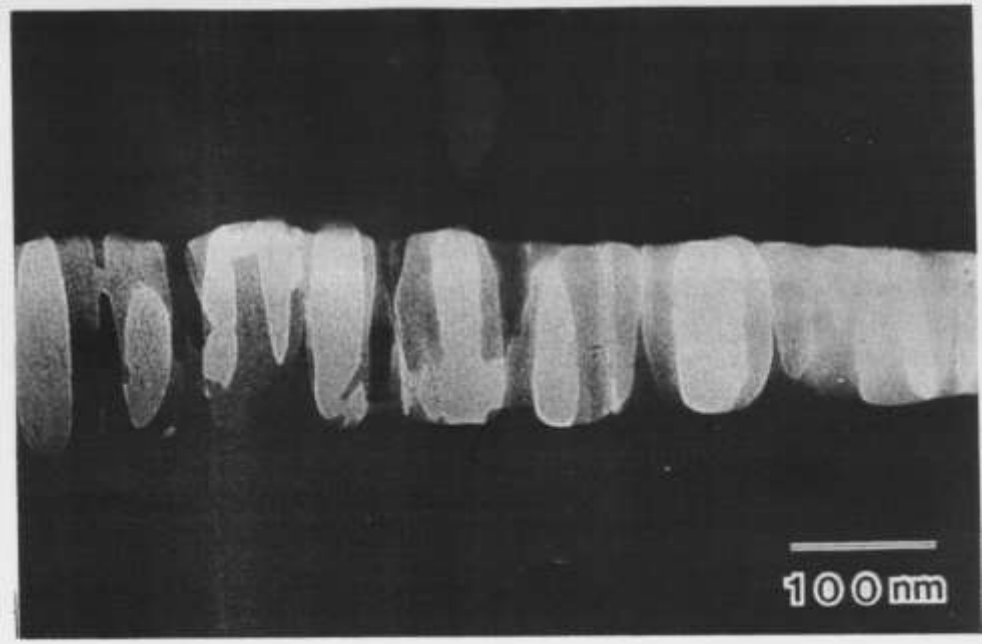
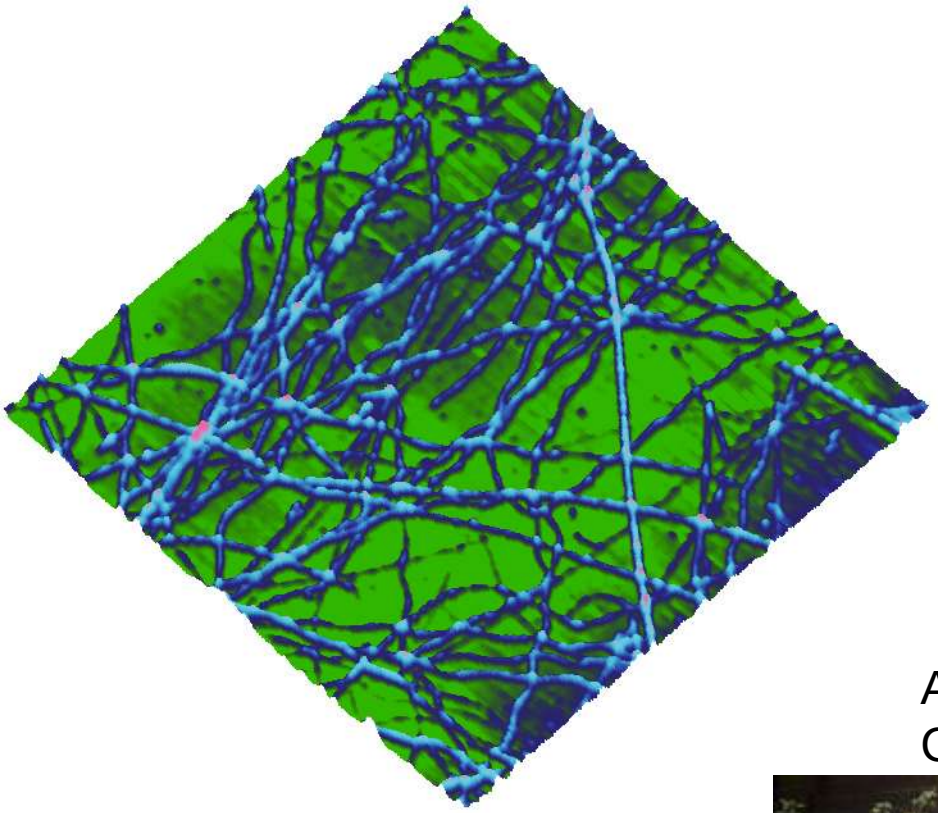


Fig. 1. Electron micrograph of a single craze in polystyrene. Thin fibrils, which are ~20 nm in diameter, are stretched across the craze boundaries. The applied strain is ~1%. Some of the fibrils have fractured; the remaining ones will break on further extension. This will lead to catastrophic crack development.

From Bassett

A *lot* of time and effort goes into determining when things break…and if one might sue as a result! Engineers and chemists get drawn into such debates. Example: was the M_w off specification for that product?

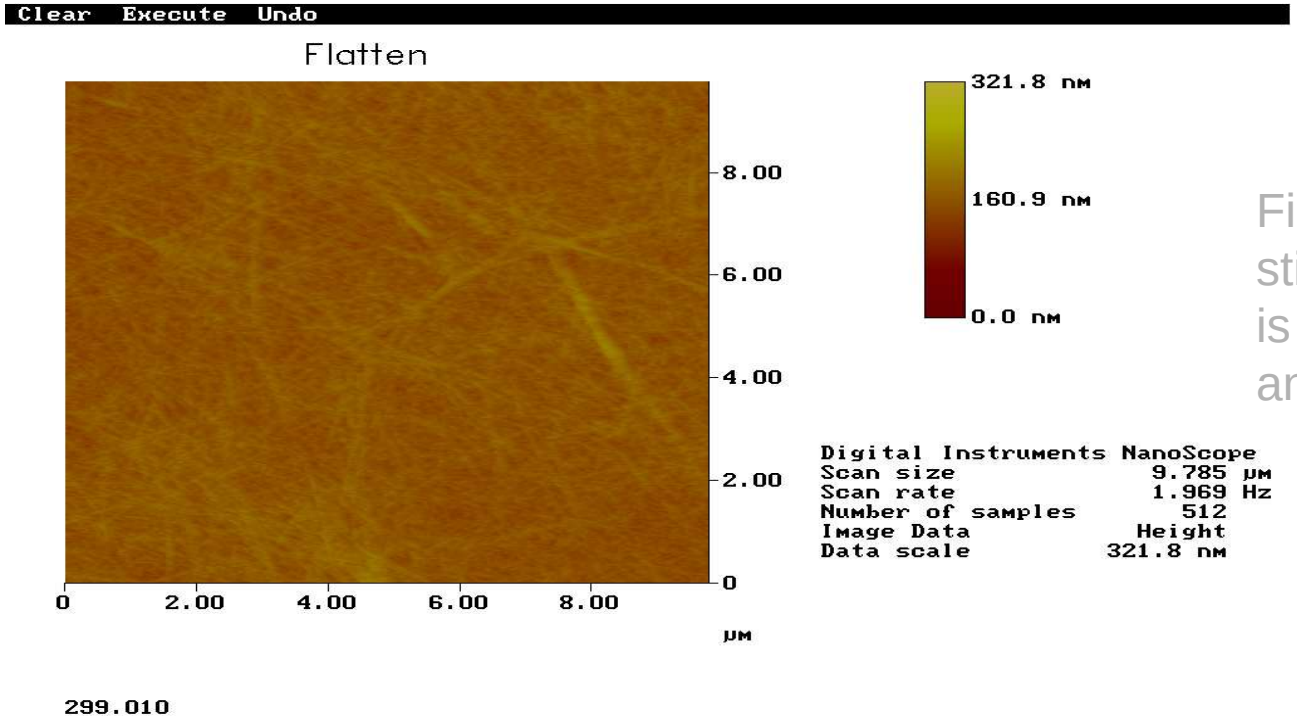


Amyloid fibrils by AFM
Courtesy LSU collaborators

Alzheimer's group in Krispy Kreme hats
September, 2003

AFM for 0.2% [9]-12-[9]

- AFM in contact mode for 0.2% [9]-12-[9]

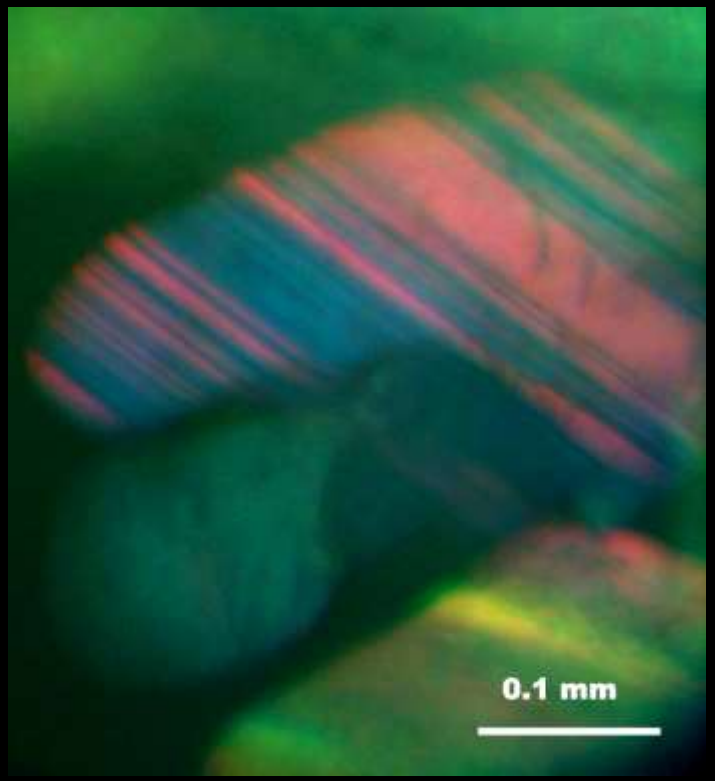


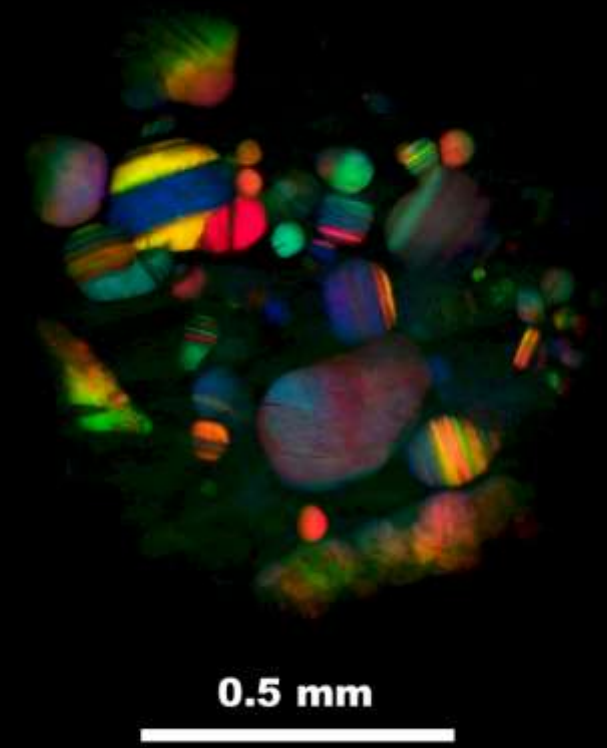
Fibers are still there, it is not a gel anymore.

Bundles stablize the gel.

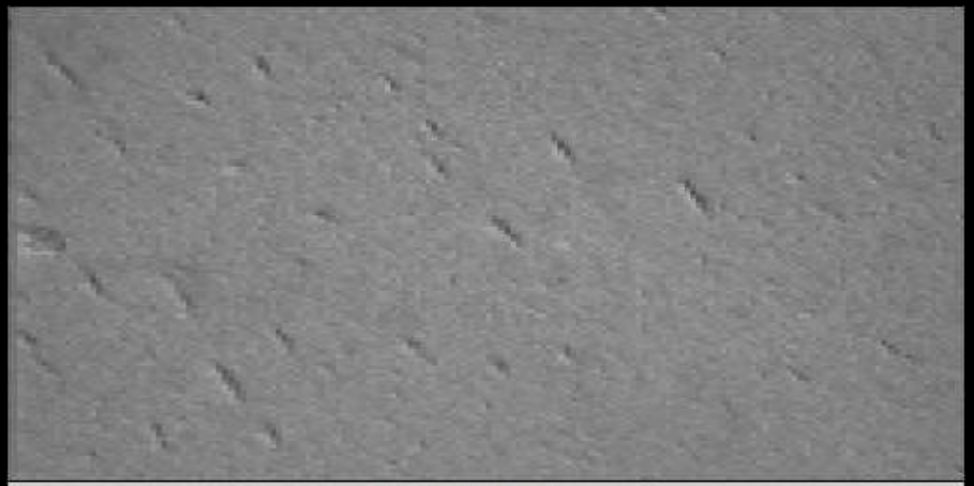
Colloidal Crystals

Fong, Turksen, Russo & Stryjewski
Langmuir 2004, 20, 266-269





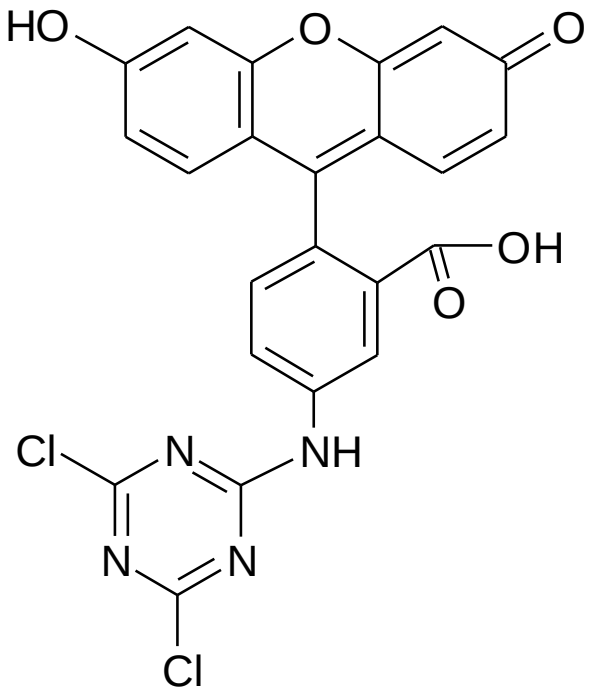
Magnetic chaining

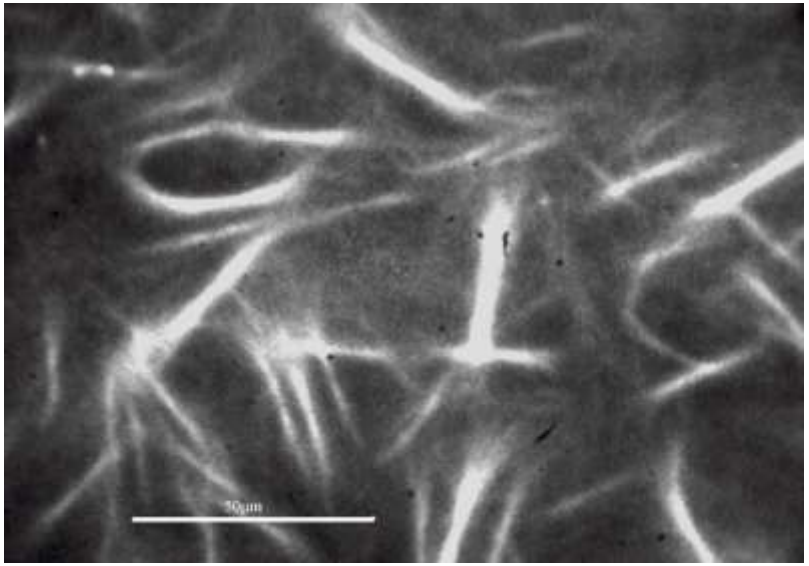


Field_ON_shorter

Fluorescence Label for Labeled [9]-12-[9]

5-DTAF 5-(4,6-dichlorotriazinyl)aminofluorescein





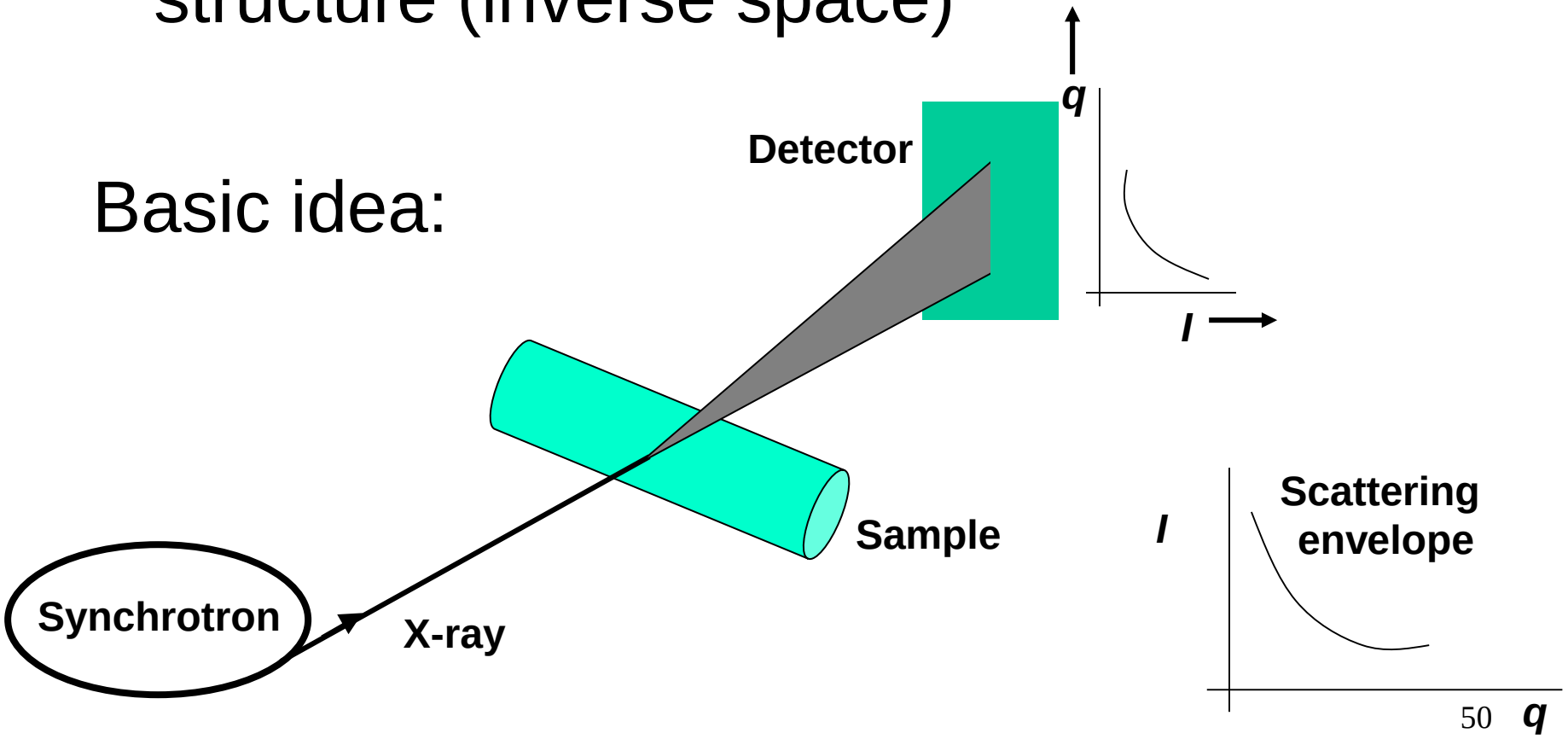
Microscopy ain't the be-all and end-all. We oven need scattering, an Inverse Space method.

- Not just LS like we used to size those latex particles.
- SAXS and SANS, too.
- Also, there is SALS
- Theory looks the same no matter what.
- Experimentation could hardly be more different!

SAXS

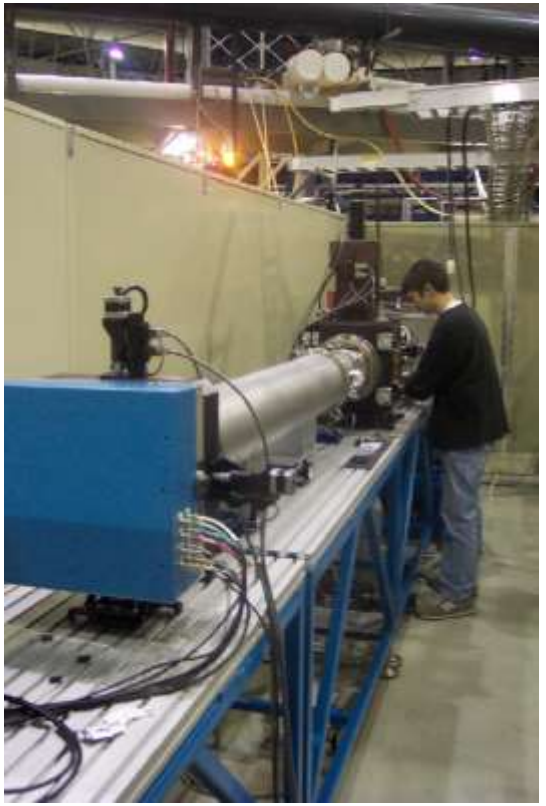
Small angle X-ray scattering: analysis of the structure (inverse space)

Basic idea:



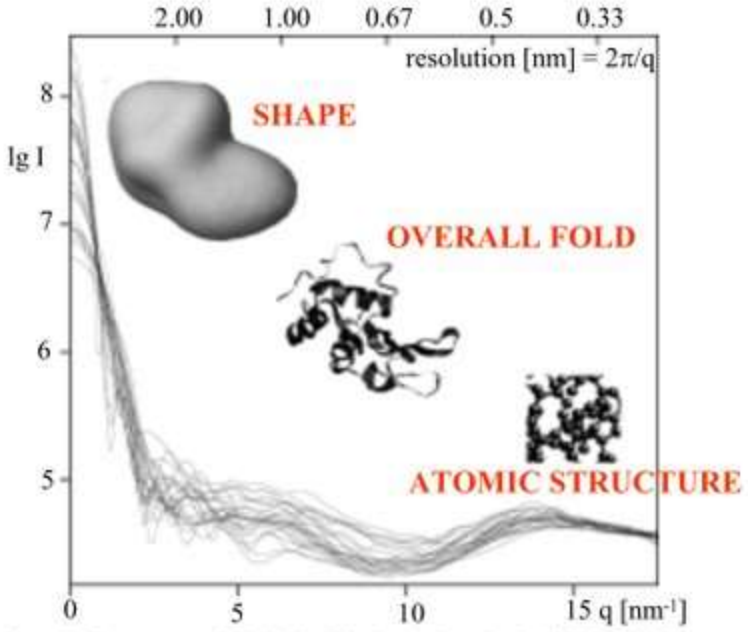
Doesn’t like the LS Machine in my lab or the Wyatt machines, right?

Some excellent SAXS builders in Brazil



Derek Dorman’s SAXS at CAM

Big angles = small details.

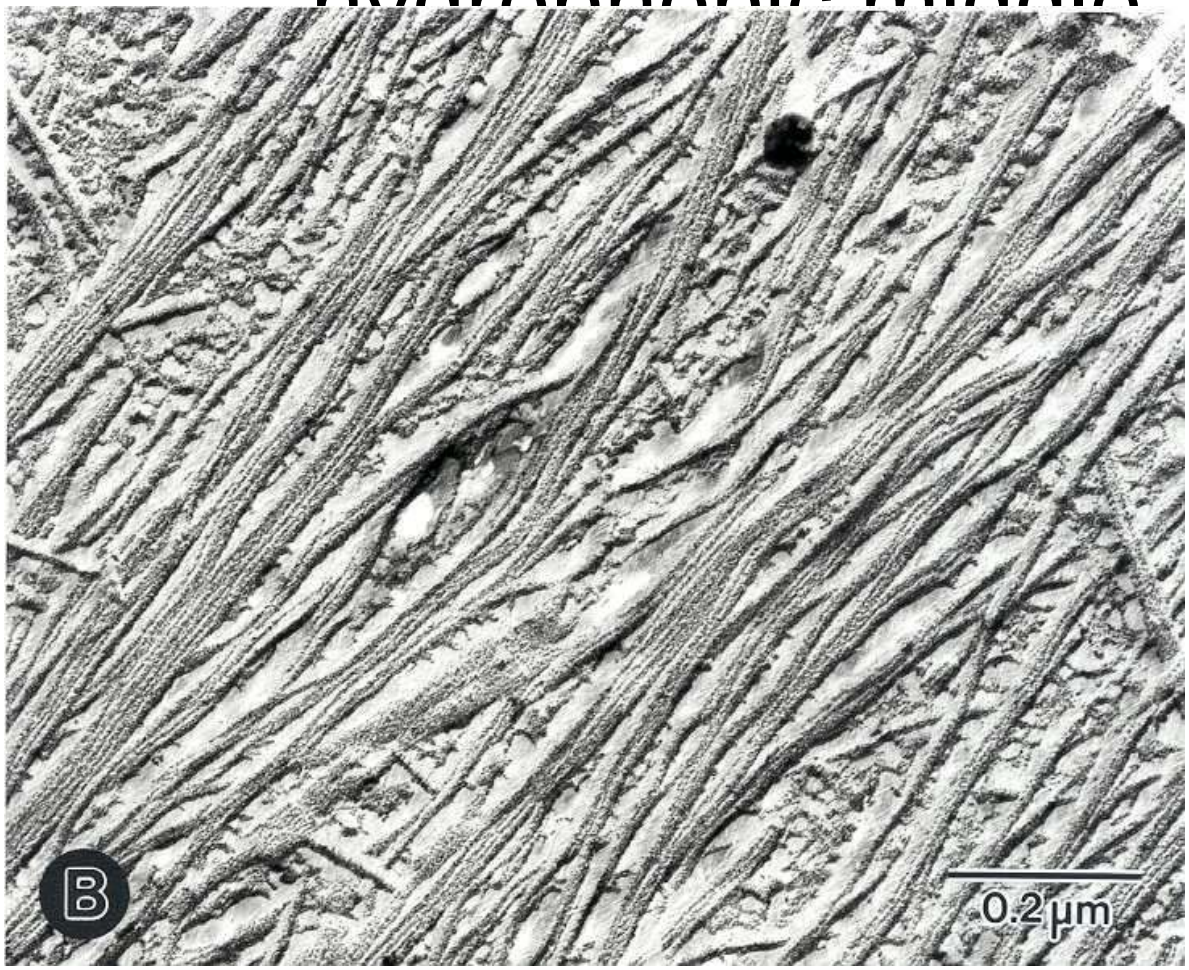


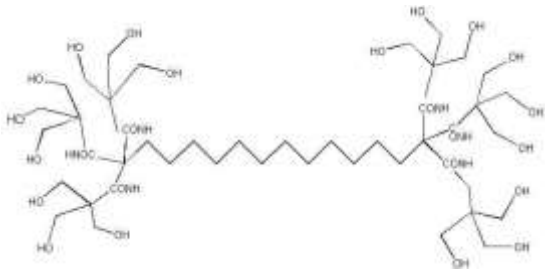
from D. Svergun and M. Koch, Biophysical methods (2002) 654-660

http://www.saxier.org/beamlines.shtml

From ESRF website

Arborols self-assemble into long fibrils in order to hide their hydrophobic middle

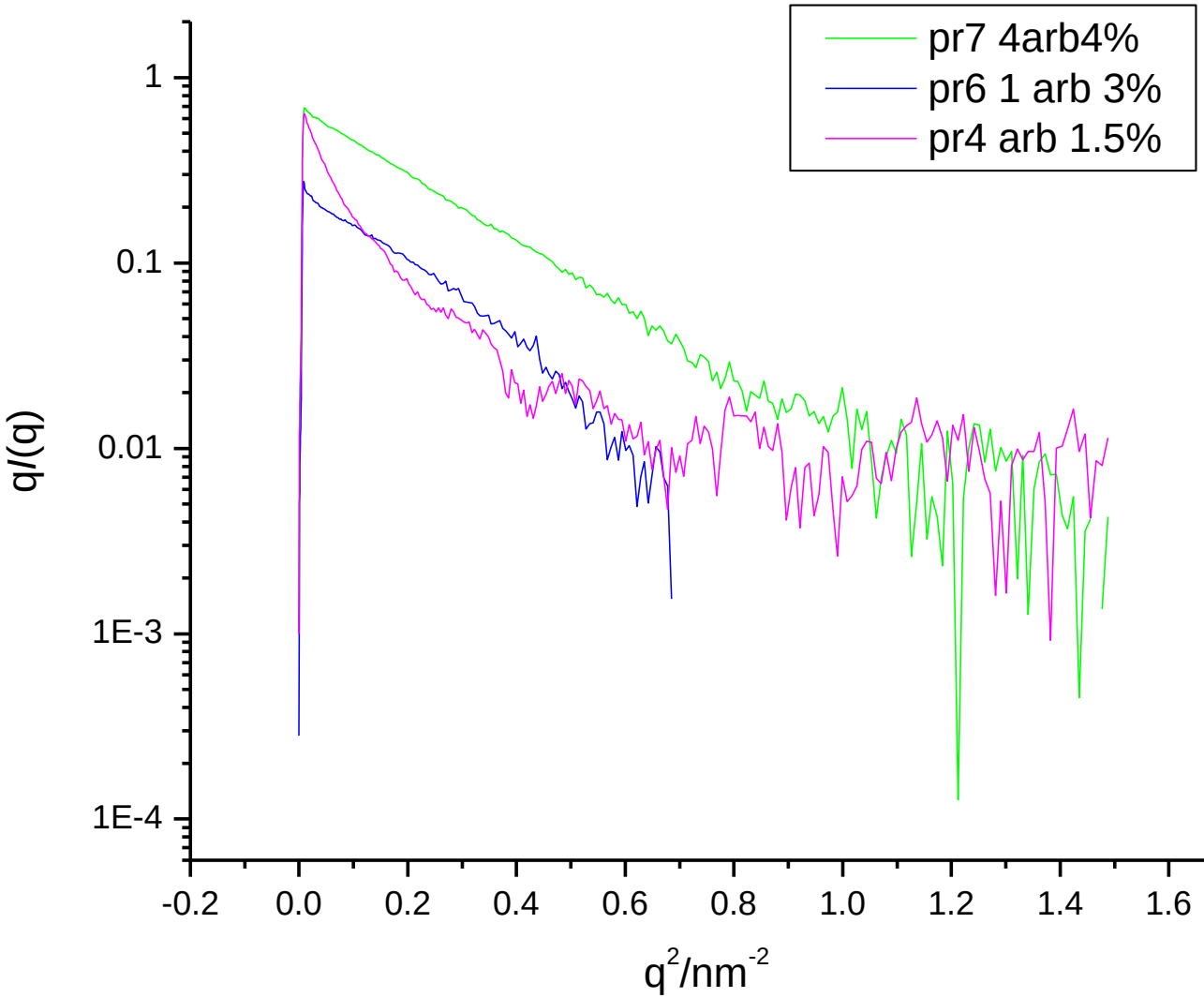




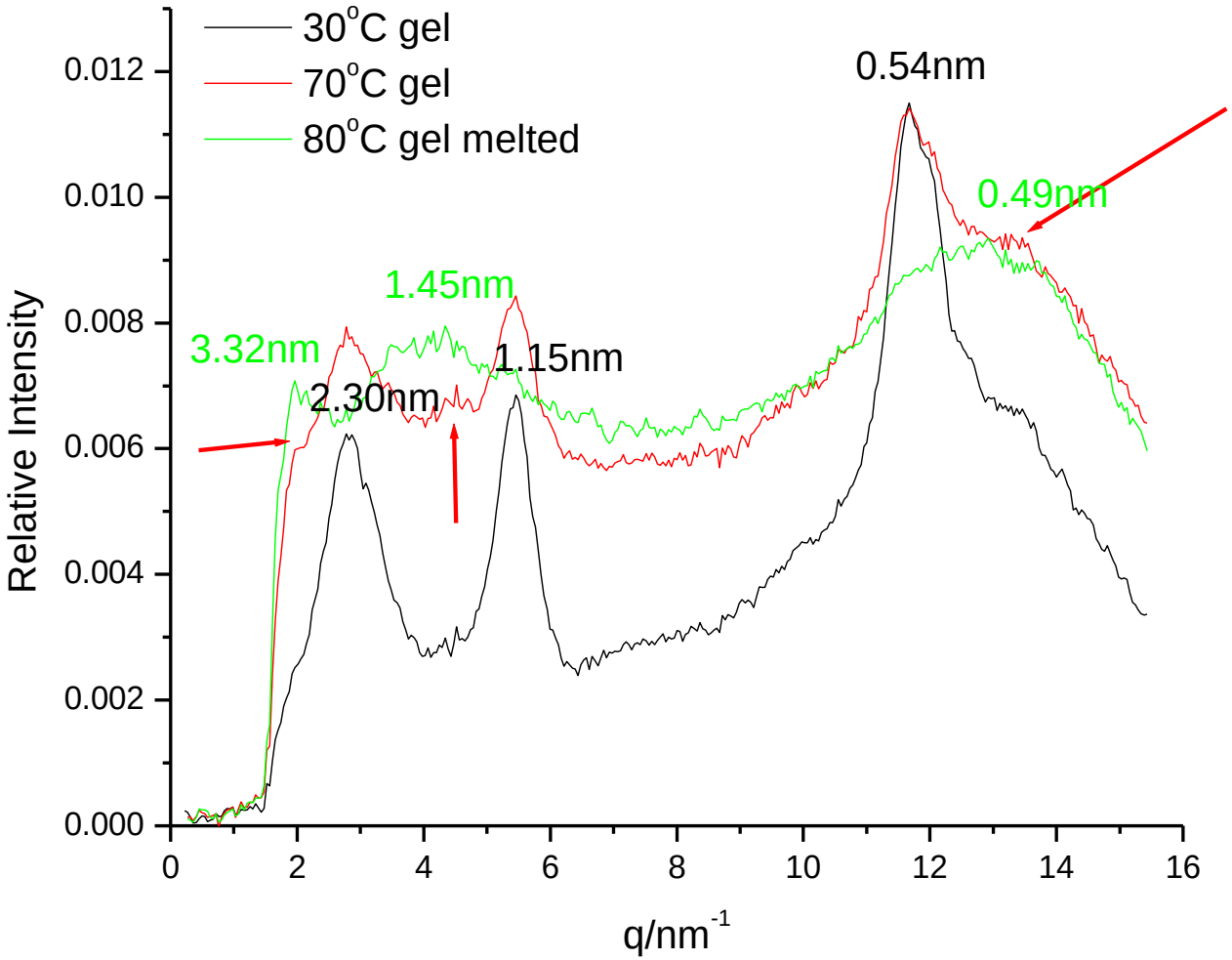
This is a special kind of TEM.

K.-H. Yu, P.S. Russo, L. Younger, W.G. Henk, D.-W. Hua, G. B. Newkome, G. Baker, *J. Polym. Sci.—Polym. Phys.*, 35, 2787-2793 (1997).

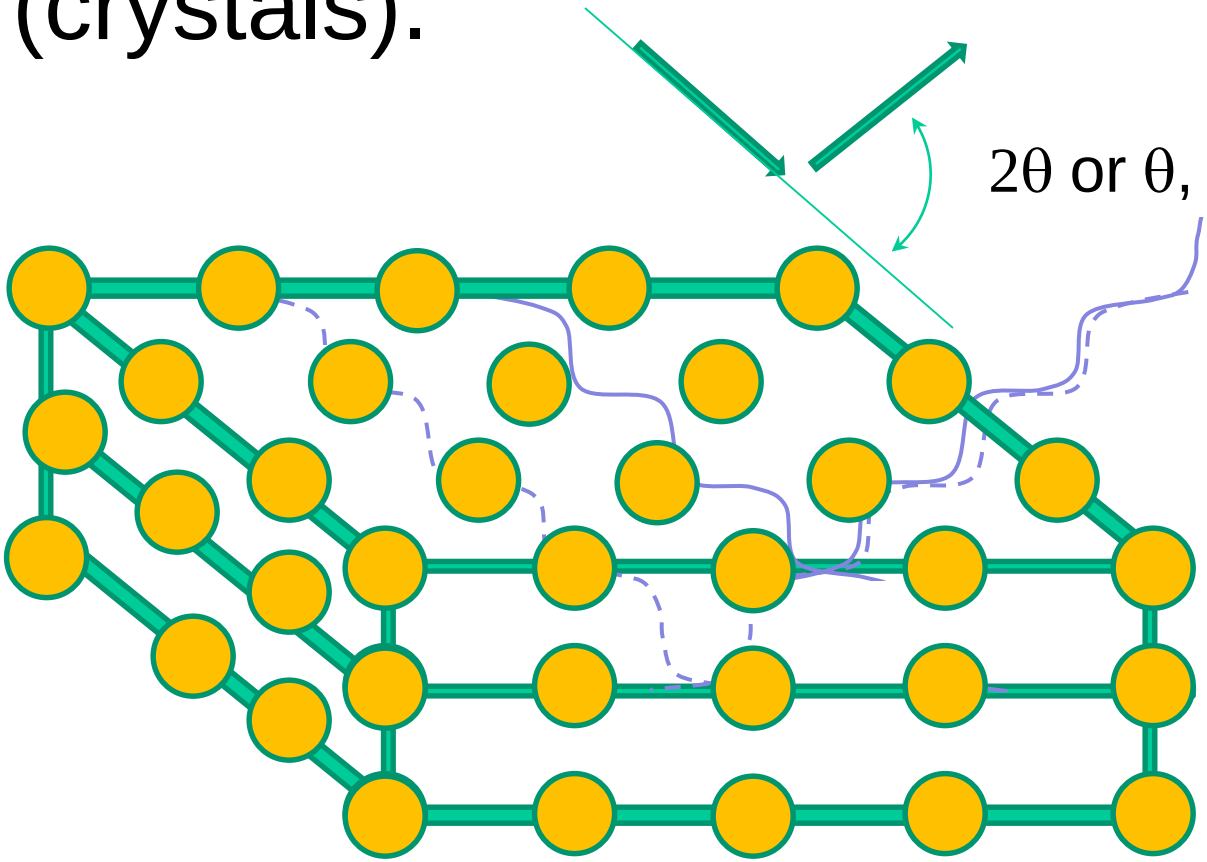
SAXS results confirm rodlike shape, show dependence on concentration and give a fibril thickness (about 5.4 nm).



WAXS for [6]-10-[6] in Water at Different Temperature



Bragg's law is a special case of scattering from regular structures (crystals).

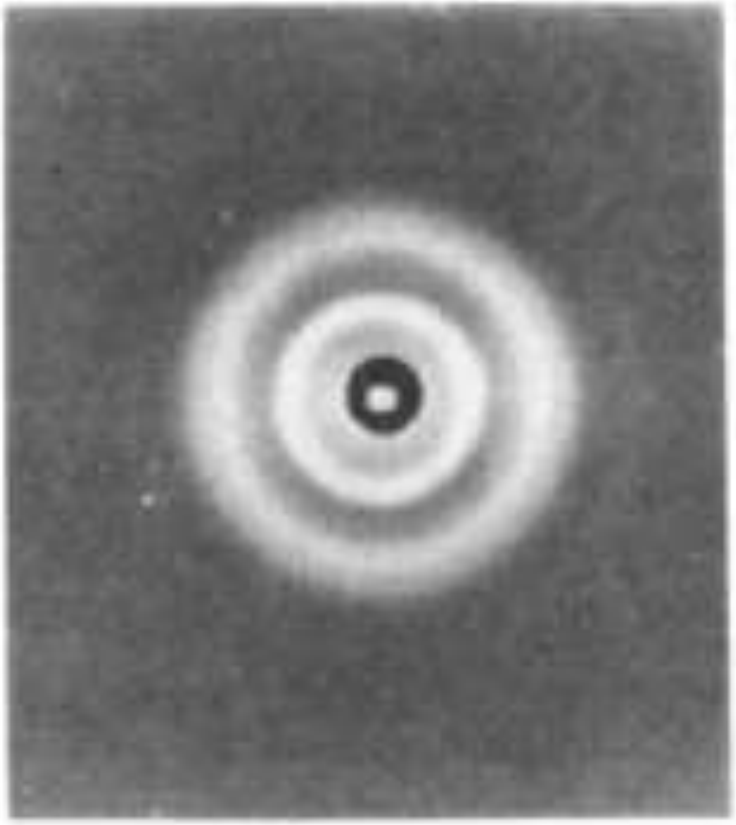


2θ or θ, depends on whether you call it diffraction or scattering

Bragg's law is the answer to the burning question: what combination of λ and θ results in constructive interference.

Let’s derive Bragg’s Law

Powder patterns: often, many crystallites are present, oriented randomly, which leads to a circular pattern.

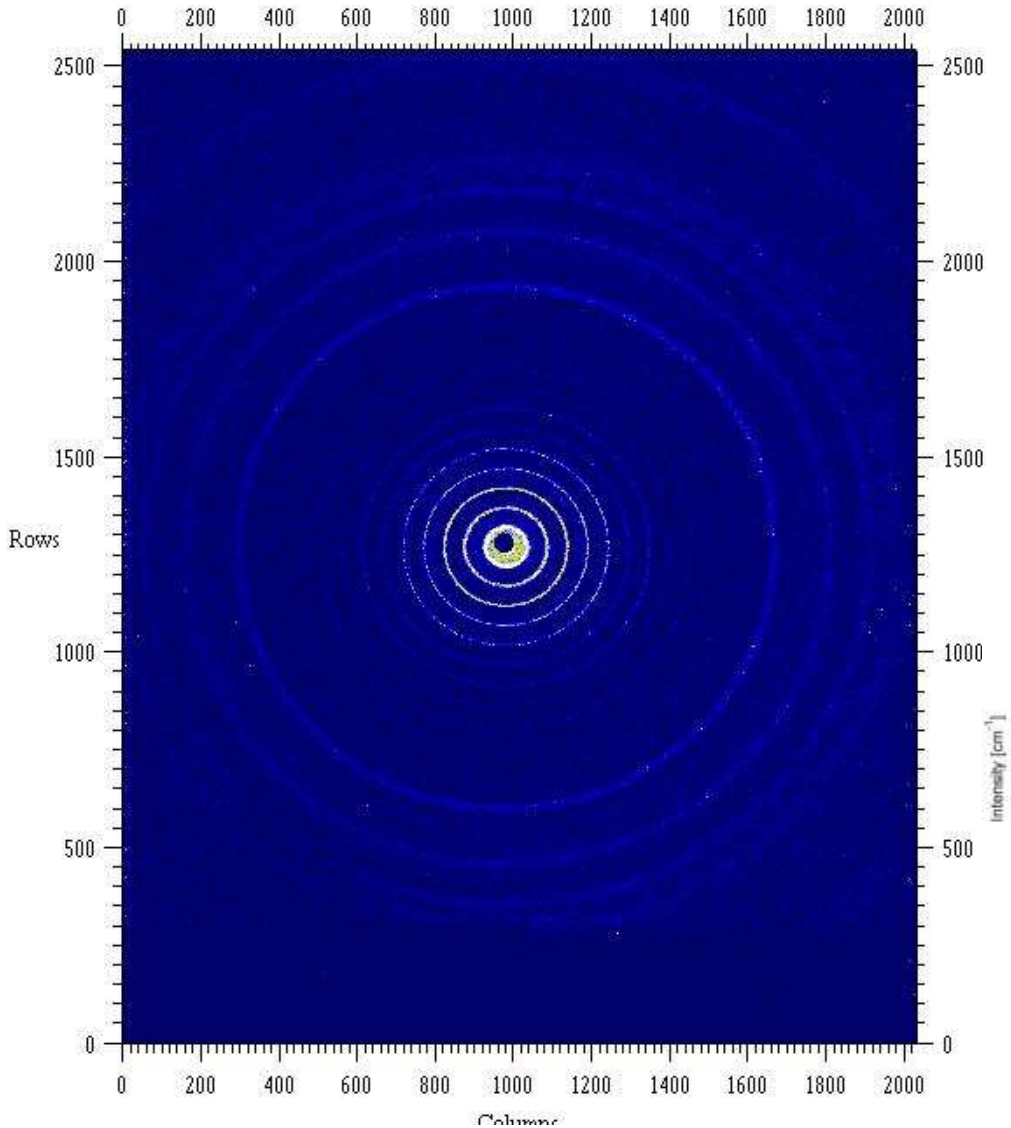


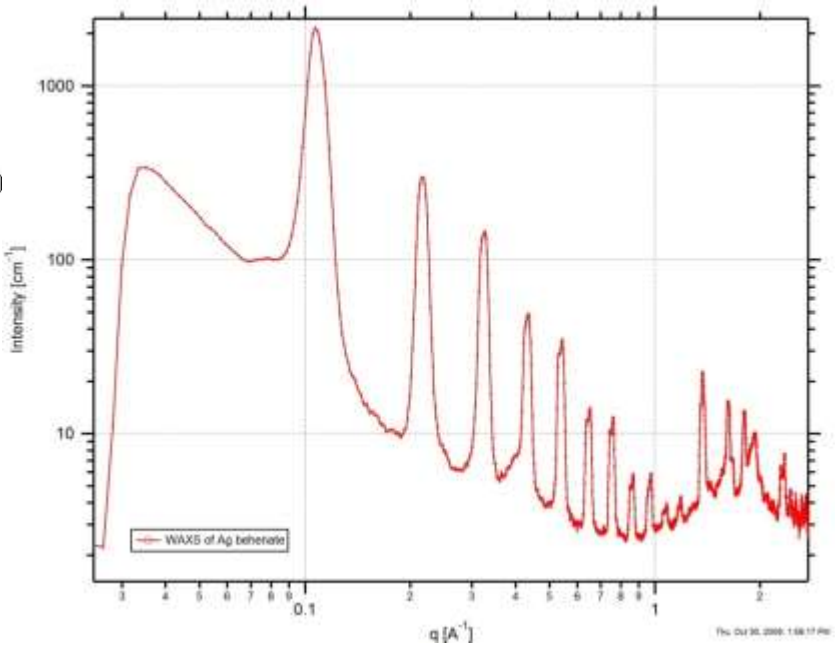
Macromolecules 1984,17, 1324-1331

←
This is a WAXS “powder pattern” for the “complex phase” of a rodlike polymer in an unusual, phase separated solid state, related to the liquid crystal.

Note: there is no “powder” in this sample. Polycrystalline would be a better word.

From CAMD's SAXS Image Plate





Other powder patterns.

Walking through snow on a moonlit night reminds me of X-ray crystallography. Various snowflakes come into a reflection geometry as you walk along.

http://www.selkirkwilderness.com/photos/optimized/CatSki.jpg

Miller indices tell you which (hypothetical) plane is responsible for a given (hypothetical) reflection.

A Miller index site can be viewed here.

Now this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.

We have just barely scratched the surface. The main point is to be aware of the strange and very *fun* things that polymers can do, in some cases that no other material can do. Looking back at the tendon on our first slide, we have a long way to go to achieve the kind of elegance that nature does regularly. The progress since, say, World War II has been phenomenal.