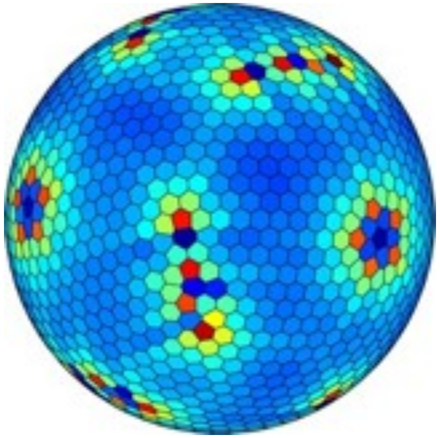
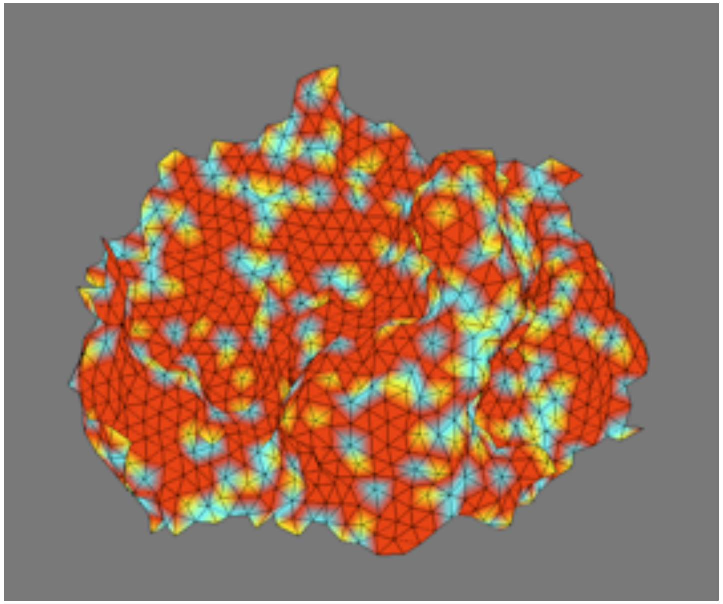
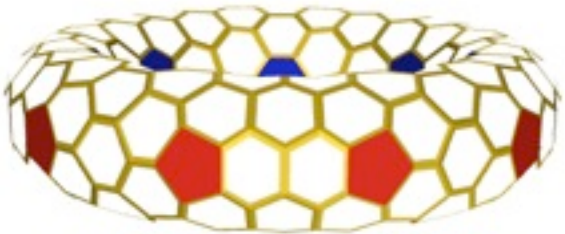
Defect-Driven Structures for Self-Assembly



JAKS 2012
Bangalore



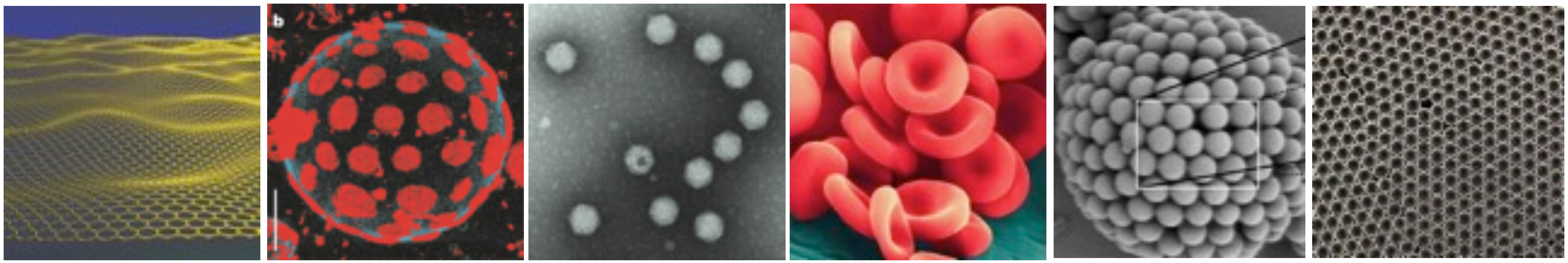
Mark Bowick
Syracuse University



MJB and L. Giomi, Adv. Phys. 58, 449-563 (2009) (arXiv:0812.3064)

Introduction

Among soft and biological materials there are many compelling examples of objects with curvature and intrinsic order. These systems span a very broad range of length and energy scales and the physical mechanisms that lead to their assembly and mechanical stability can be very different.



Lengths (in meters)

1.42×10^{-10} 5×10^{-9} 1.2×10^{-8} 10^{-7} 10^{-6} 10^{-3}

Energy ranges between hundreds of $k_B T$ (sp^2 bonds in graphene) to 1 $k_B T$ (Van der Waals interactions).

Suppose we want to design nano to meso scale building blocks (super-atoms) for creating super-molecules and subsequent 3D structures without the restrictions of quantum mechanics

Requirements:

- Distinguished regions for the attachment of ligands
- High degree of specificity

For small scale objects the surface to volume ratio is large so surface topological defects can provide the distinguished regions

The effective **valence** will then be determined by the number of defective regions and the type of **directional bonding** will be determined by the relative arrangement of the defects.

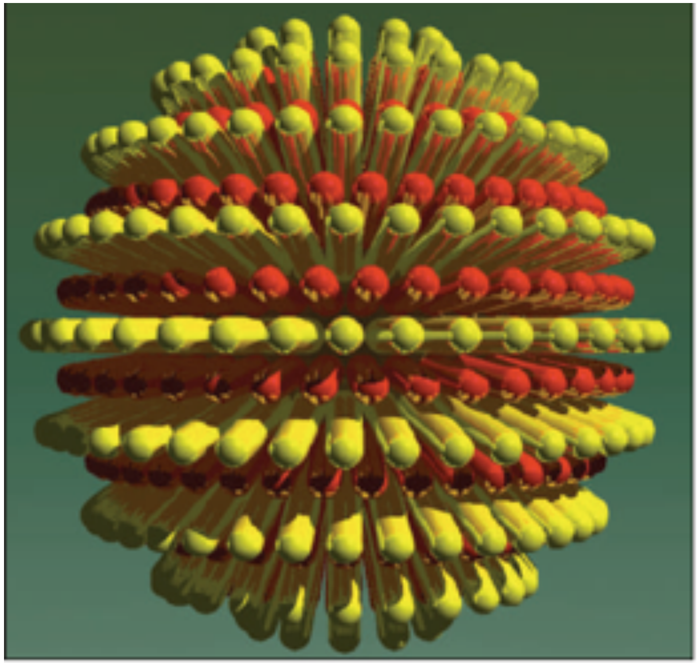
Lubensky & Prost (1992)

The number of defective regions is an energetic question with underlying topological constraints

Strategy:

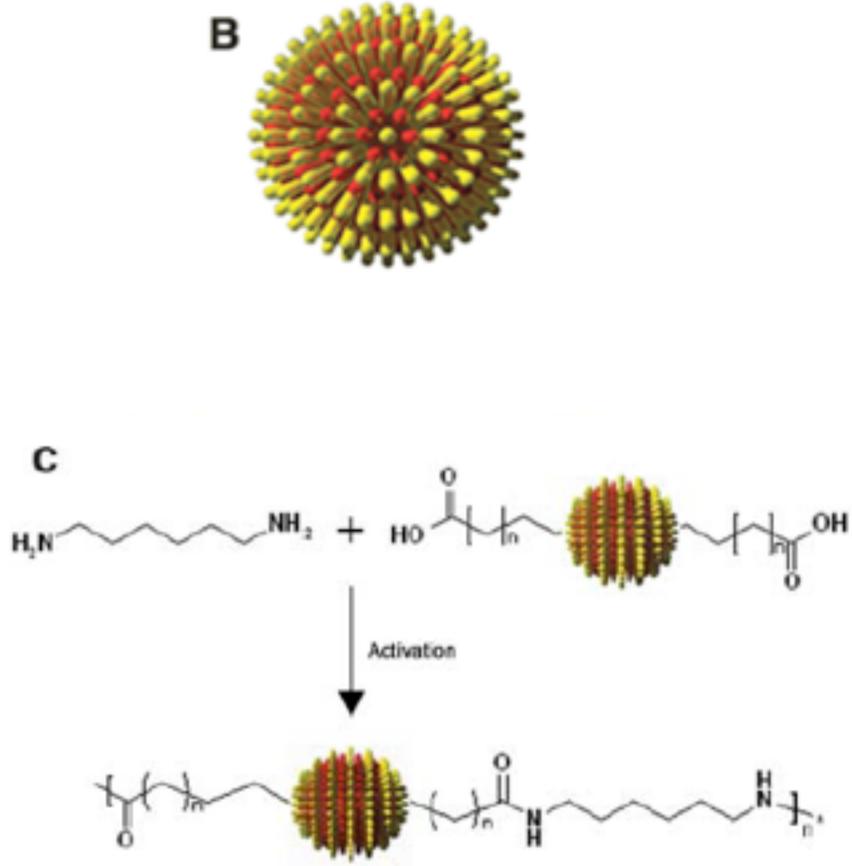
- Take a set of microscopic objects interacting on some fixed surface
- Map to an effective interacting defect problem by treating everything but the defects as a continuum
- Find the ground state of the defect Hamiltonian

Example: Divalent Metal Nanoparticles

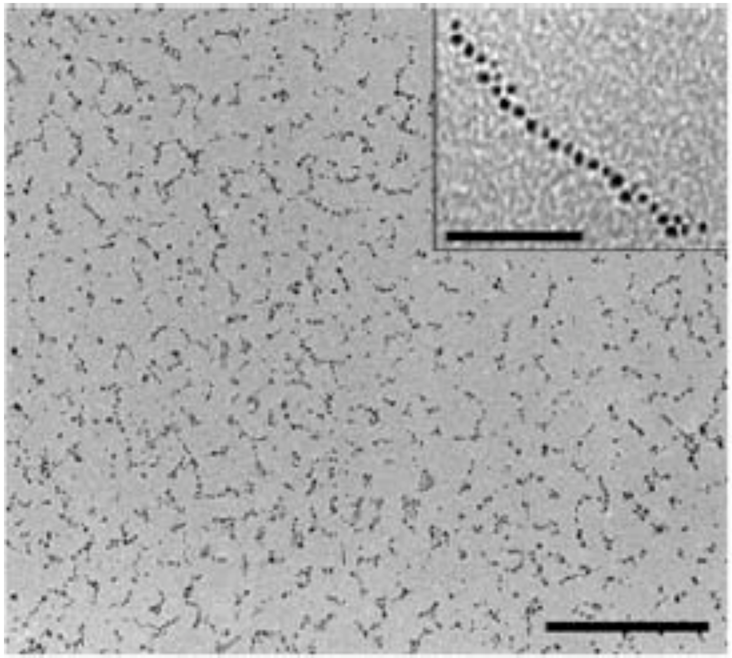


SAM consisting of 2 types of thiol-terminated ligands (1-nonanethiol and 4-methybenzenethiol) on Au

DeVries et al (Stellacci): Science (2007)

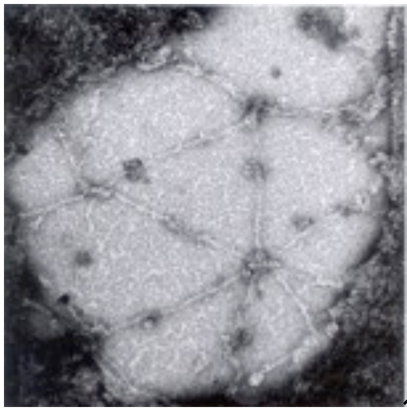


Functionalization by MUA plus linking by DAH

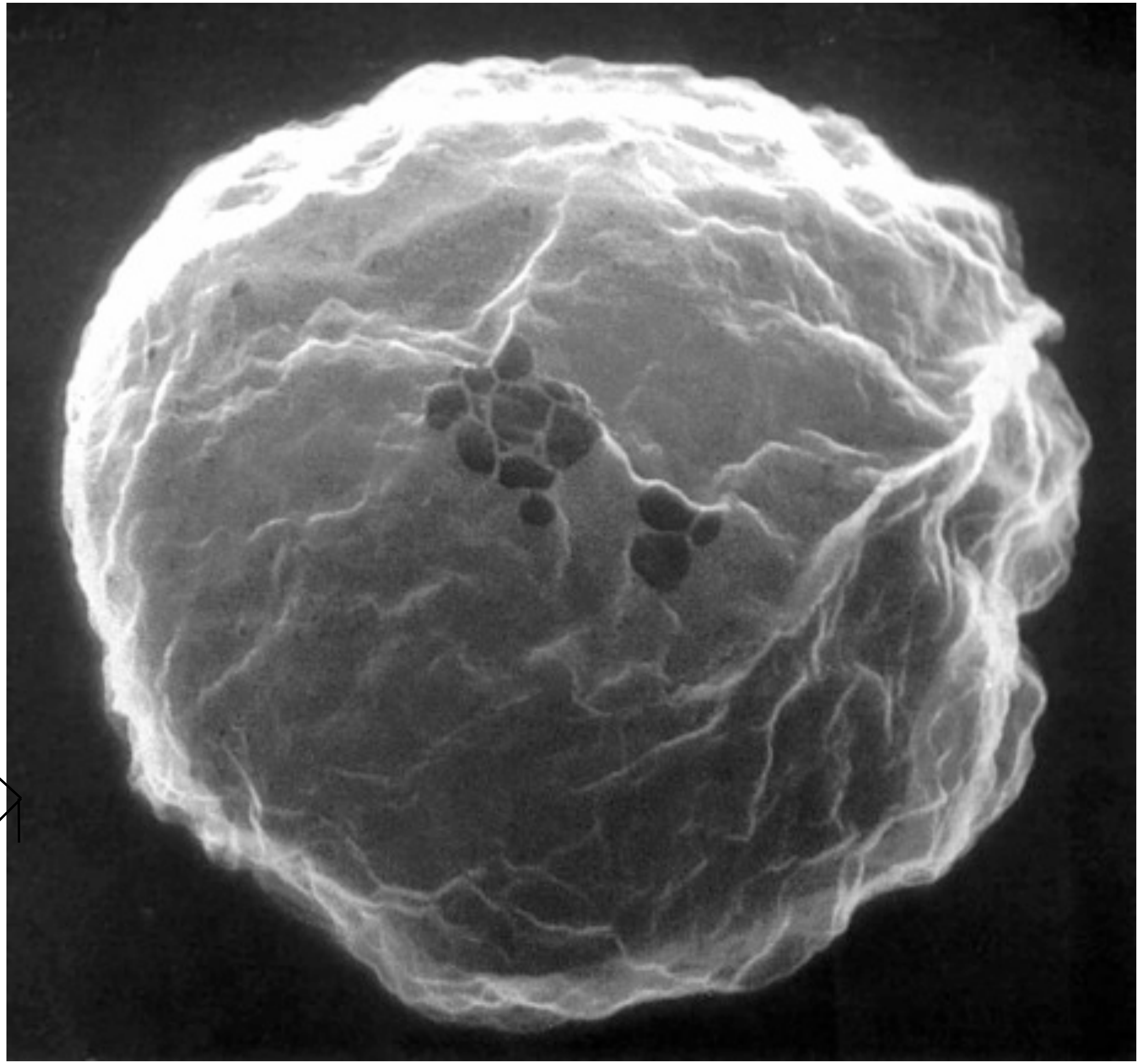


Redo all of polymer physics with nanoparticles!

Membranes



365,000X



J.F. Hainfeld and T.L. Steck, J. Supramol. Struct. **6**, 301 (1977)

(courtesy Leo Van Hemmen) 10,000X

Membranes

Crystalline (elastic) membranes

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

2d Elasticity of Sheet + Shape Change from Height Fluctuations

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

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

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

$$\text{Energy minimized when } u_{ij} \approx 0$$

$$\Longrightarrow \partial_j u_i + \partial_i u_j = -\partial_i h \partial_j h$$

BUT

This is impossible for single-valued phonon fields $u_i(x_1, x_2)$

Defects, e.g; disclinations and dislocations, are an essential part of the ground state!

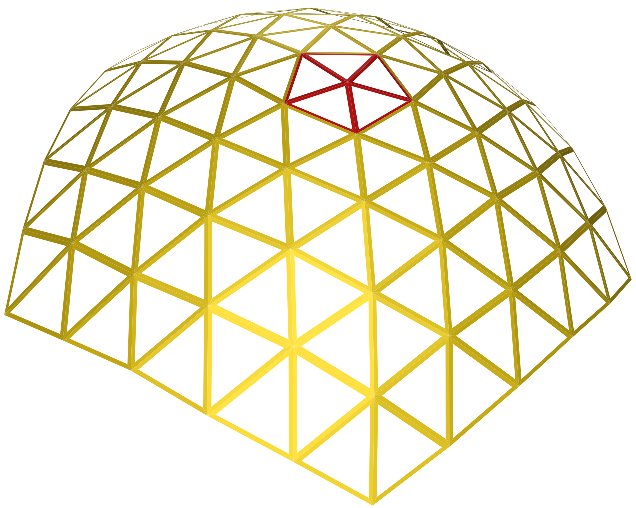
In fact,

$$\frac{1}{2}\epsilon_{im}\epsilon_{jn}\partial_m\partial_n(\partial_j u_i + \partial_i u_j) = \underset{\uparrow}{s(x_1, x_2)} = det(\partial_i\partial_j h) = \underset{\uparrow}{K(x_1, x_2)}$$

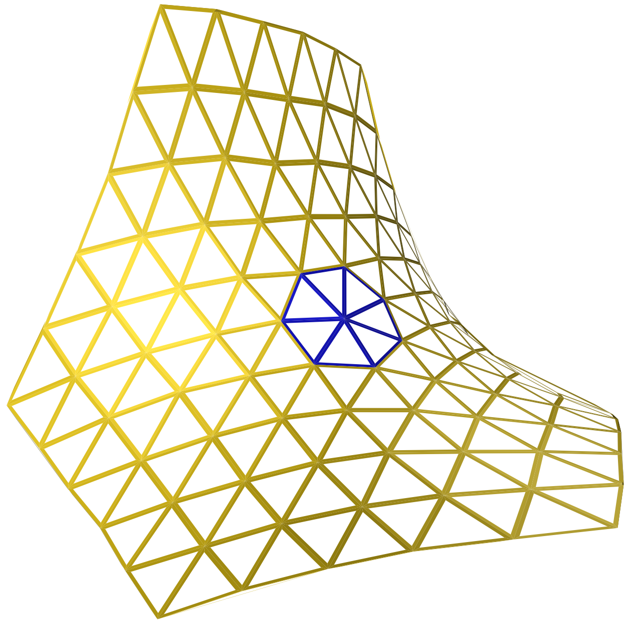
defect density **Gaussian curvature**

What are the defects?

1. Disclinations= Bond-Orientation Defects



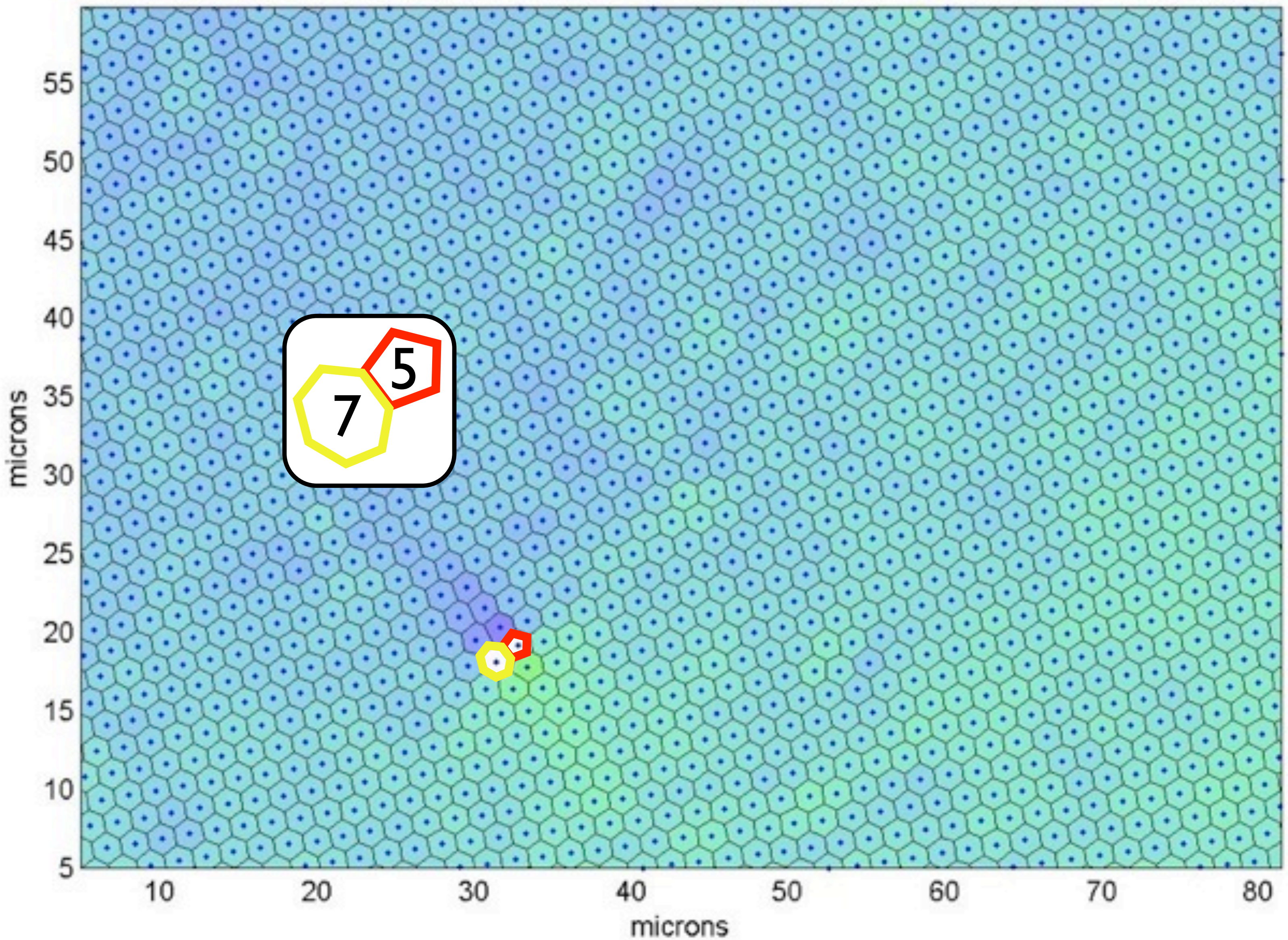
5=+1



7=-1

$$E \sim R^2$$ (planar)

2. Dislocations (translational defects) ≡ 5-7 dimers



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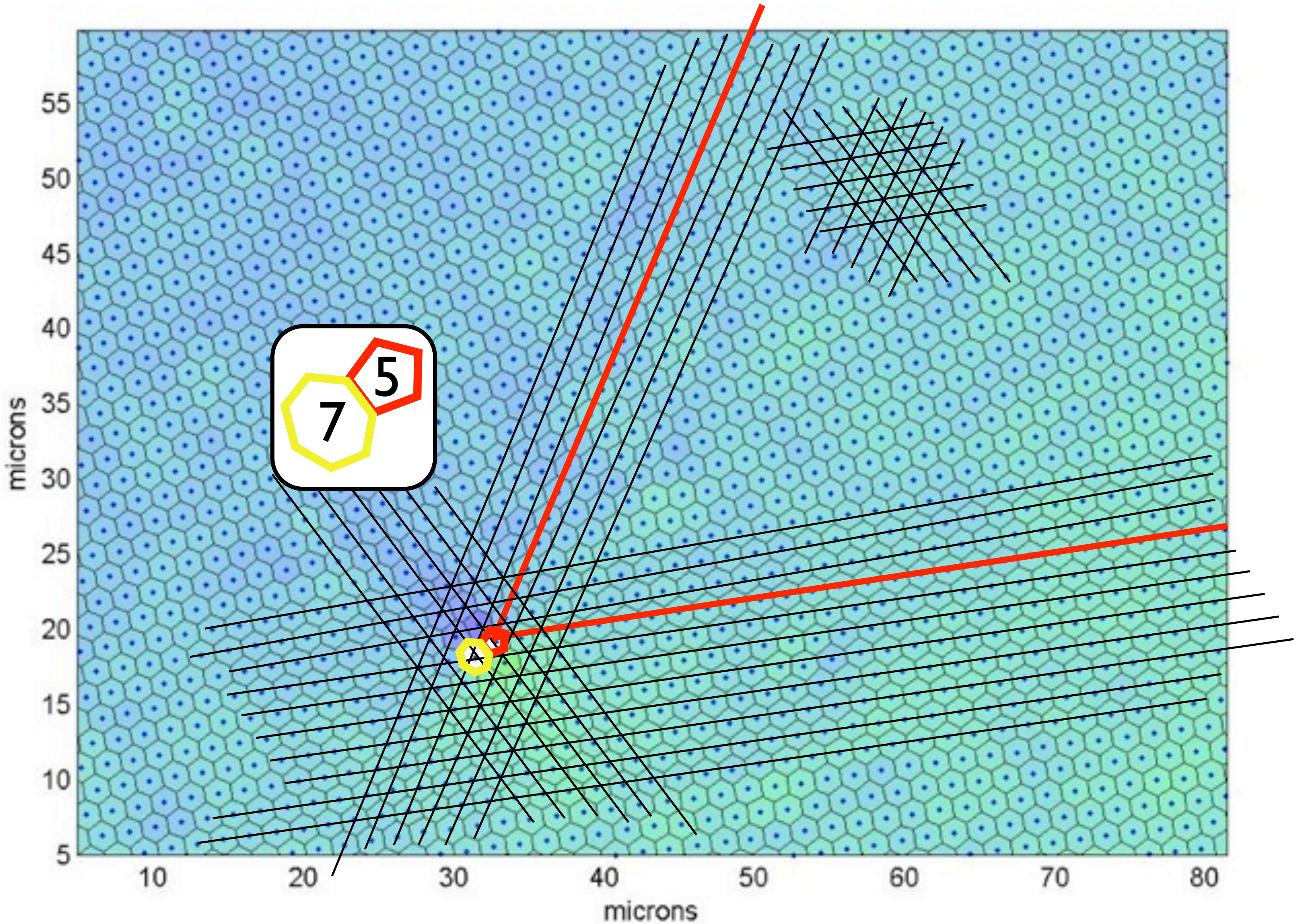

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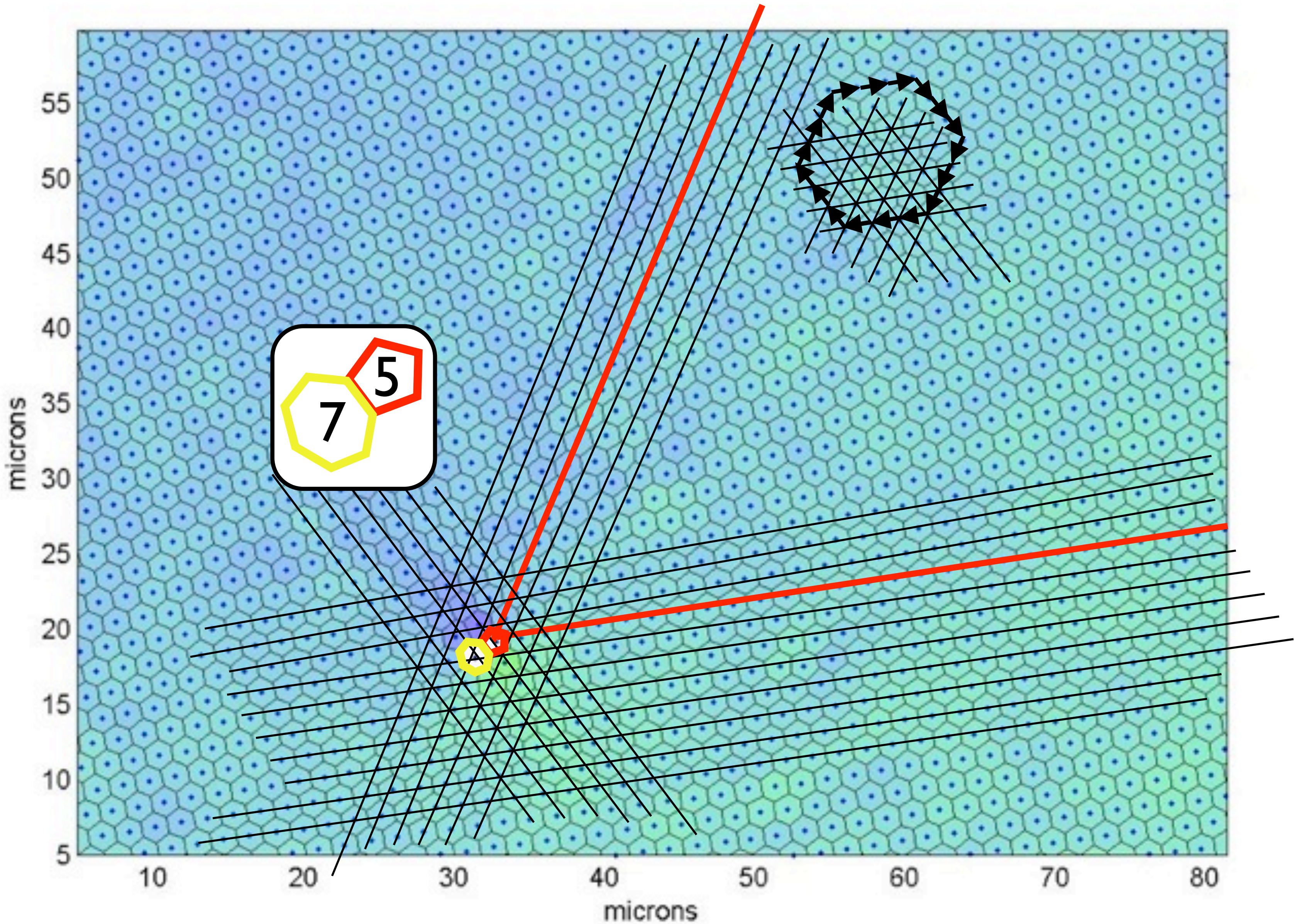

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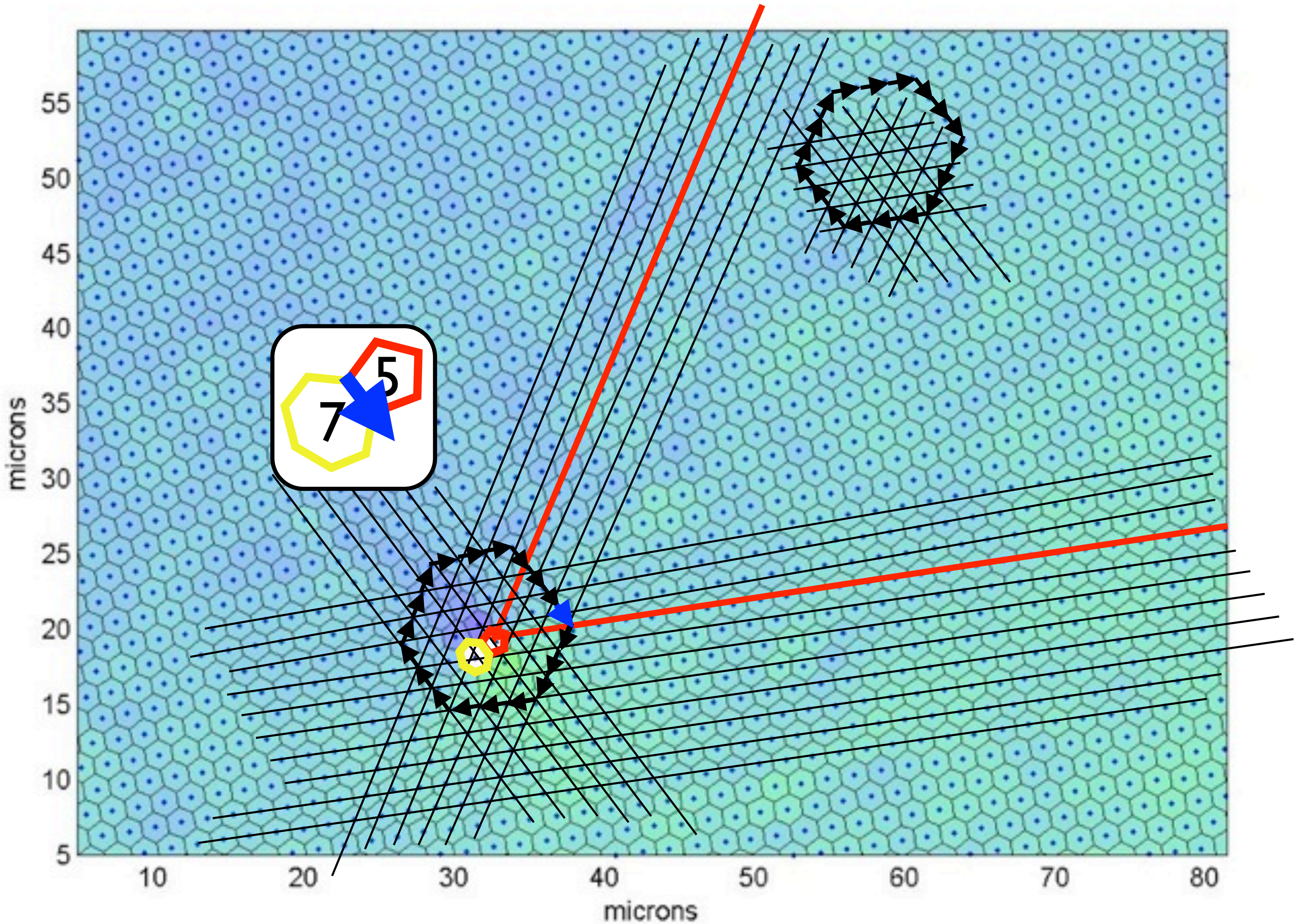


Integrating out the phonons one finds

$$E = \frac{Y}{2}\iint d^2x\, d^2y\, [K(x)\frac{1}{\Delta^2(x,y)}K(y)] + \kappa E_{bending}$$

$K(x) = \text{Gaussian curvature}$ $\quad Y = \dfrac{4\mu(\mu+\lambda)}{2\mu+\lambda}$ (2D Young's Modulus)

$$E = \frac{Y}{2}\iint d^2x\, d^2y\, [K(x) - s(x)]\frac{1}{\Delta^2(x,y)}[K(y) - s(y)] + NE_c + \kappa E_b$$

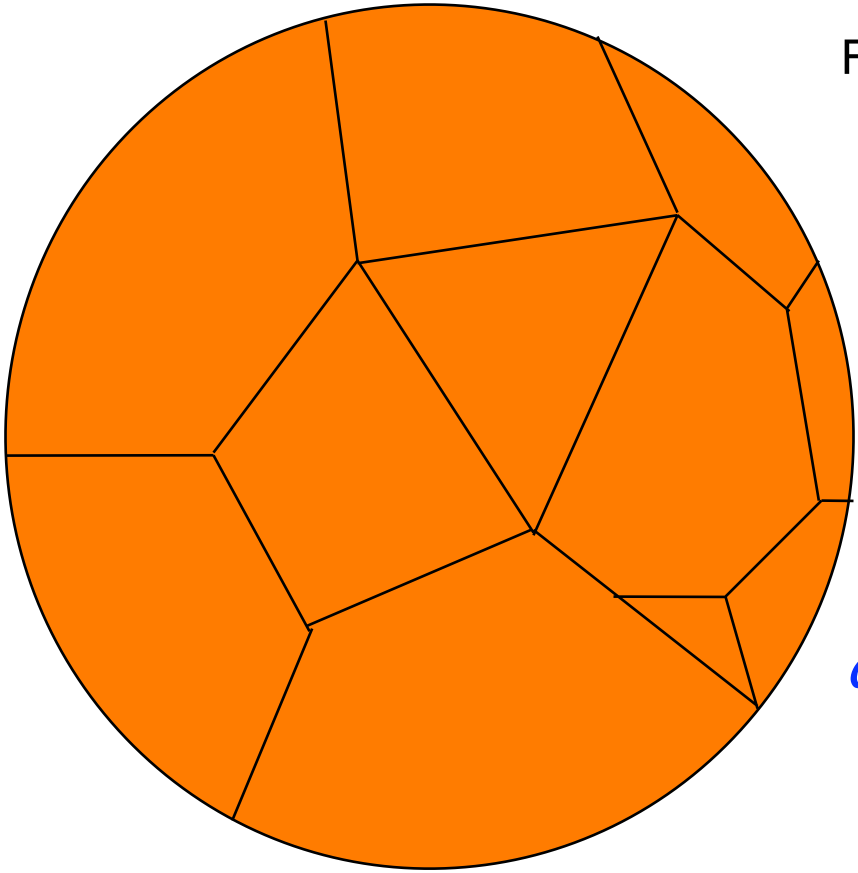
$$s = \frac{\pi}{3}\sum_{i=1}^{N} q_i \delta(x, x_i)$$

$$G(x,y) = \frac{1}{\Delta^2(x,y)} \sim |x-y|^2 \ln|x-y|$$

MJB, D.R. Nelson and A. Travesset (ISU) : PRB **62** (2000) 8738

MJB, A. Cacciuto (Columbia), D.R. Nelson and A. Travesset, PRB **73** (2006) 024115

From planar packing to spherical packing: topological constraints



$$V - E + F = \chi = 2$$

For triangulations (2E=3F) this implies

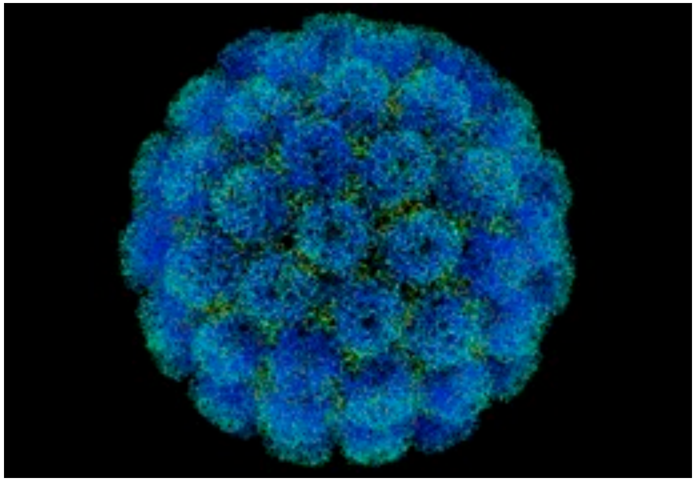
$$\sum_i \left(1 - \frac{c_i}{6}\right) = 2$$

c_i = degree of vertex i

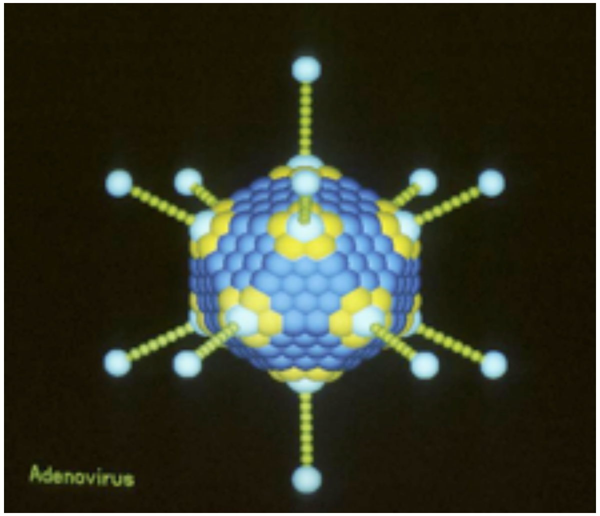
$q_i = 6 - c_i$ = disclination charge

$$Q_{tot} = \sum_i q_i = 12$$

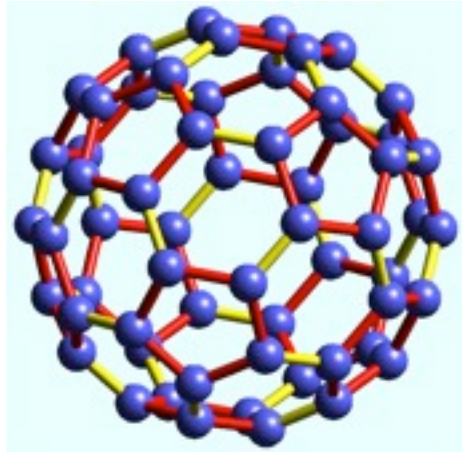
More specimens from sphereland



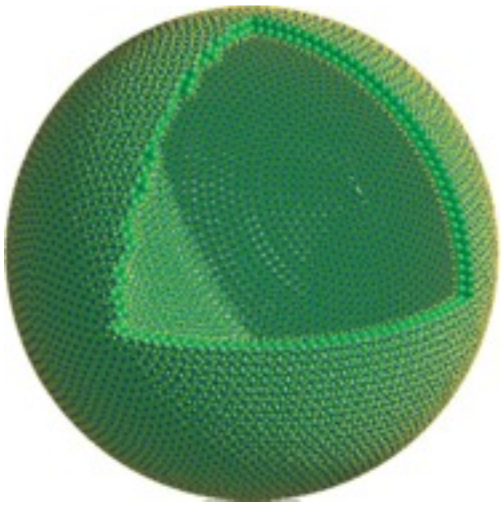
SV40 Viral Capsid



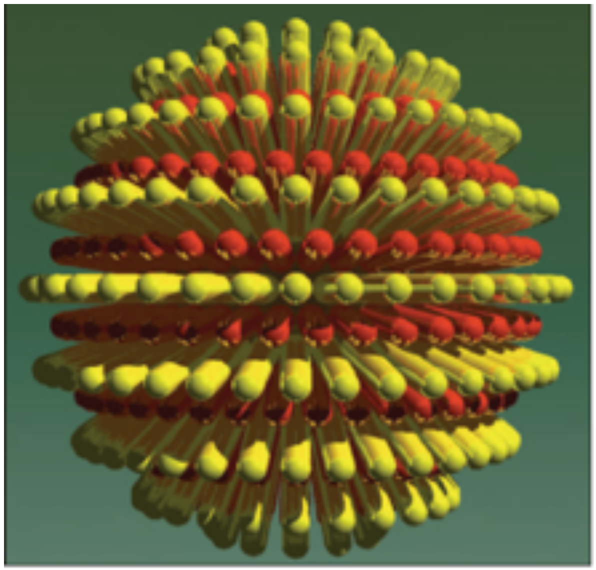
Adenovirus



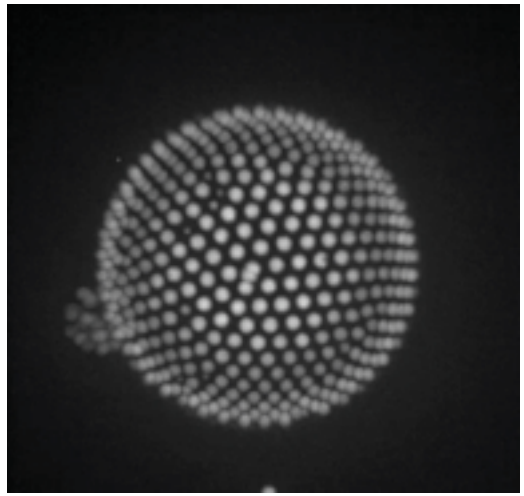
C60



Bilayer vesicle of Ph5C60K molecules:
Zhou et al



MP AuNP: DeVries et al (Stellacci)



Irvine & Chaikin

Shape of defective regions

Map particle interaction to (universal) defect Hamiltonian in a continuum elastic background with 2 parameters: bulk modulus Y and core energy E_c

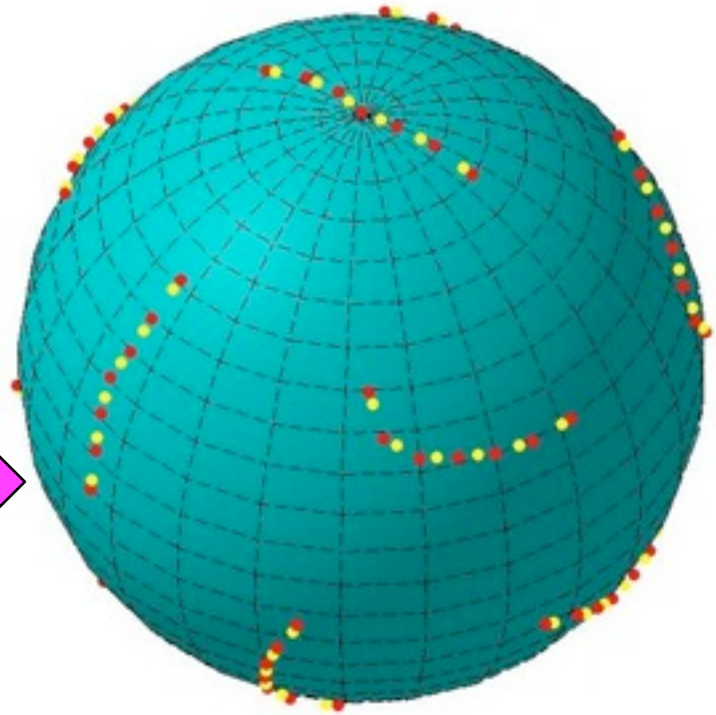
Constant positive Gaussian curvature $K(x) = 1/R^2$

Disclination elastic energies grow like R^2

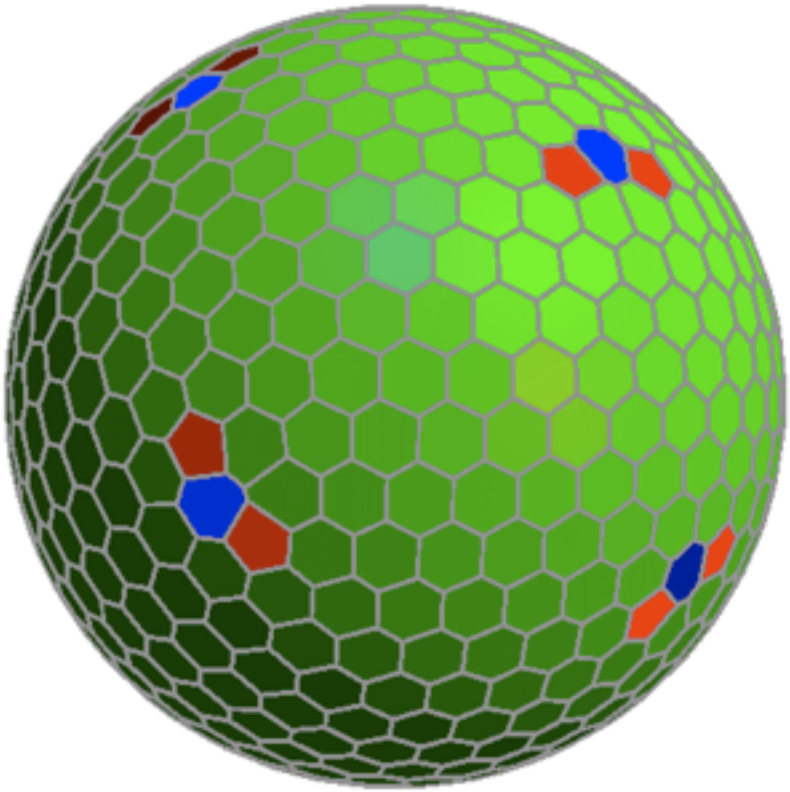
For **small** R/a (<5) the disclinations are **localized** – isolated point-like disclinations as in 2d melting from the hexatic to the fluid

For **large** R/a the disclinations are **delocalized** - leads to formation of freely terminating linear defect arrays

SCARS



Large Scale Simulations



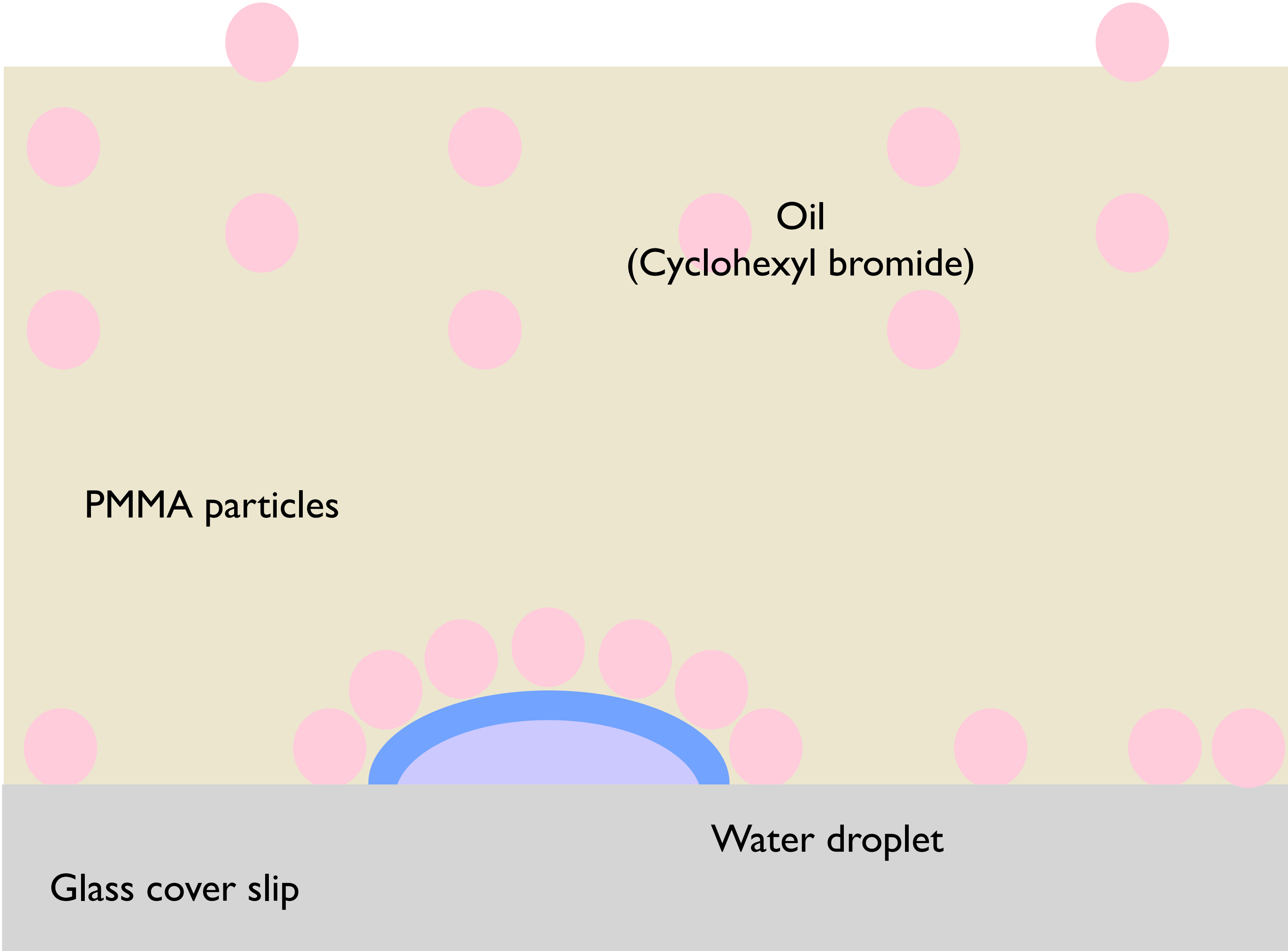
N=752 (V=1/r)

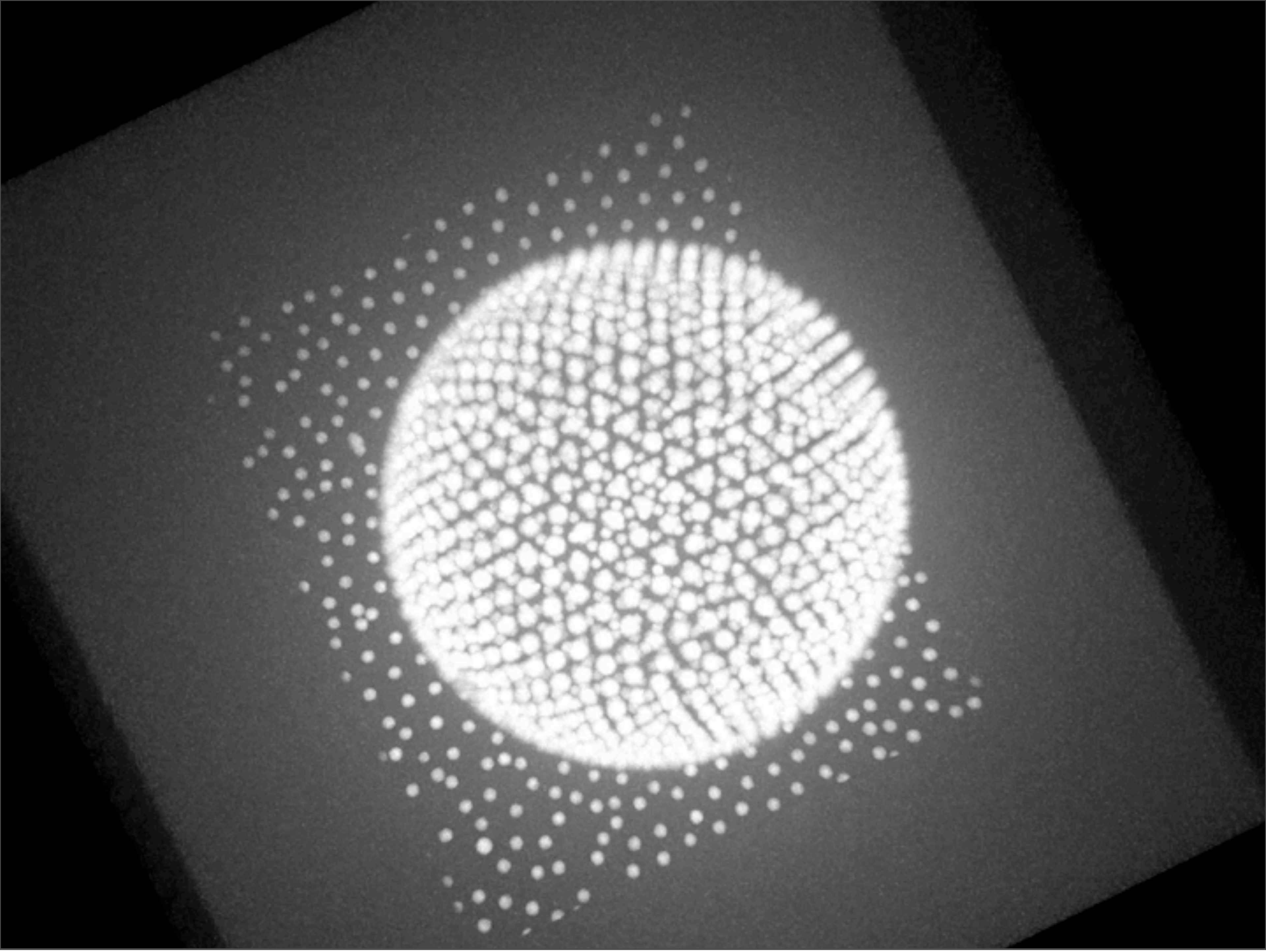
D.J. Wales, H. Mackay and E.L. Altshuler, PRB (2009)

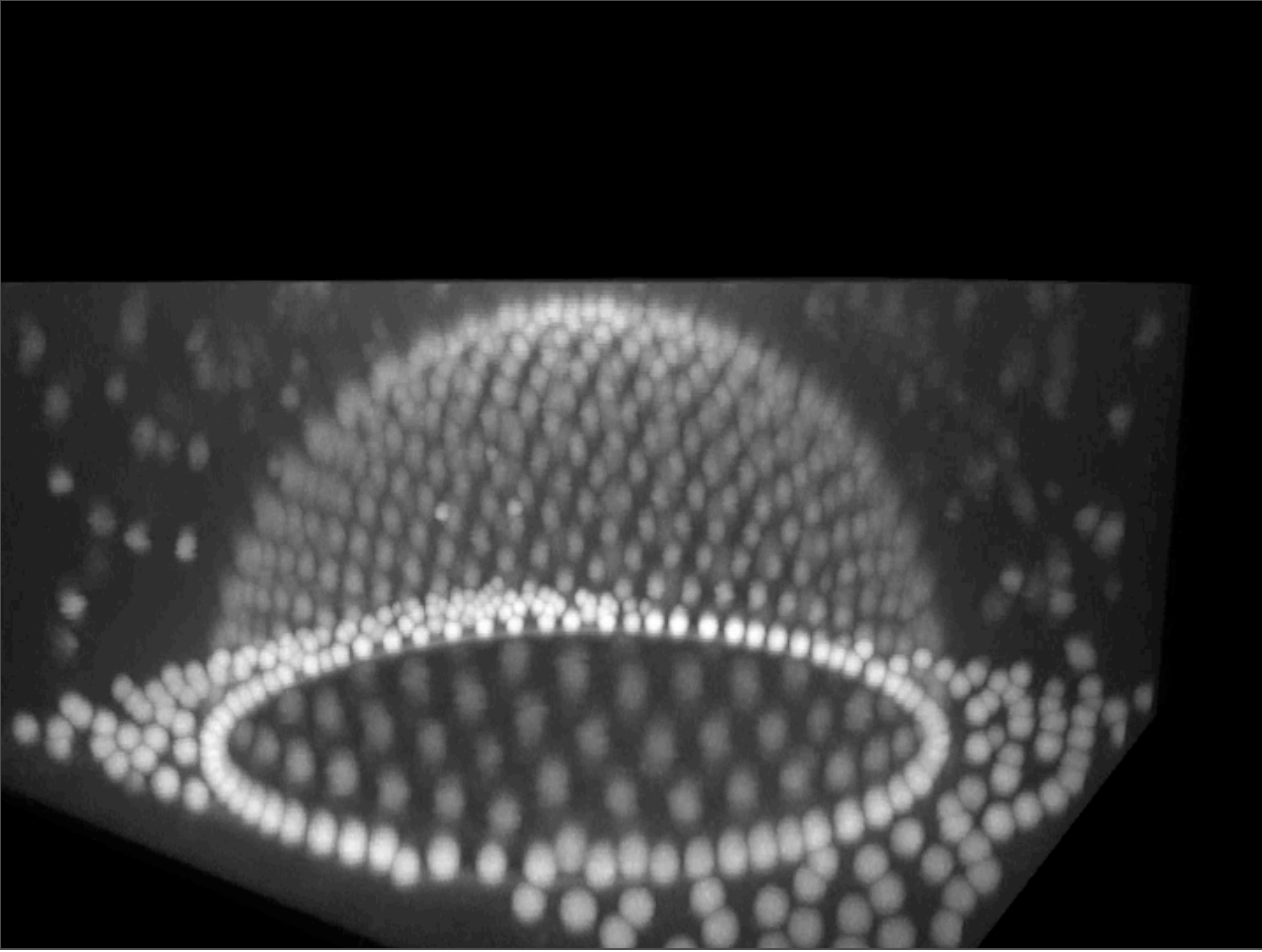
http://www-wales.ch.cam.ac.uk/~wales/CCD/Thomson2/table.html

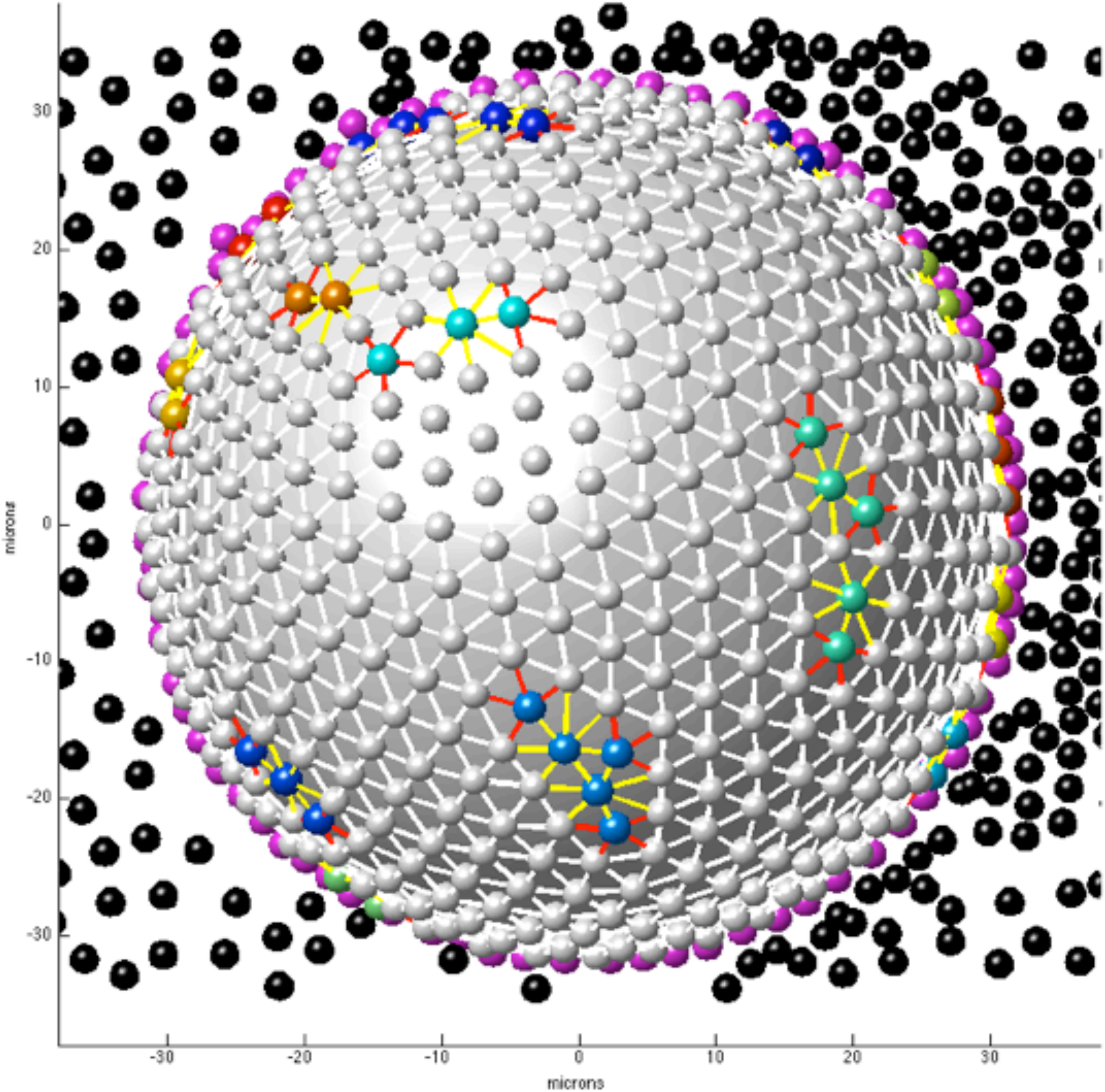
Thomson Applet: http://thomson.phy.syr.edu/thomsonapplet.htm
MJB, C. Cecka (Harvard) and A.A. Middleton (Syracuse)

PMMA particles on curved surfaces, imaging and reconstruction (Charge stabilized: Chaikin & Irvine: NYU)





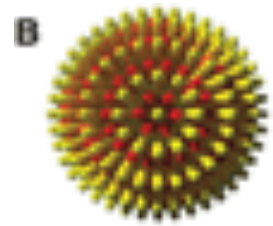


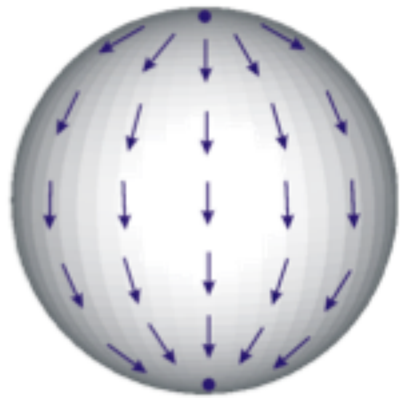

30
20
10
0
-10
-20
-30
microns
-30
-20
-10
0
10
20
30
microns

Changing the Order

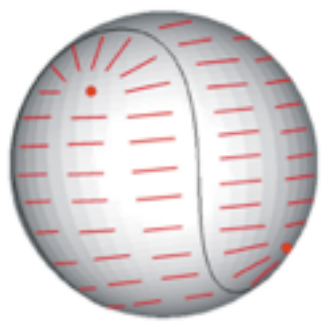
For **p**-fold order the total number of distinct defective regions is 2**p**

p	Local order	Valence
6	Crystalline	12
2	Nematic	4
1	Vector	2
4	Tetradic	8





p=1



p=2

Spherical nematics (p=2) give rise to 4 elementary +1/2 defects.

Lubensky & Prost (1992)

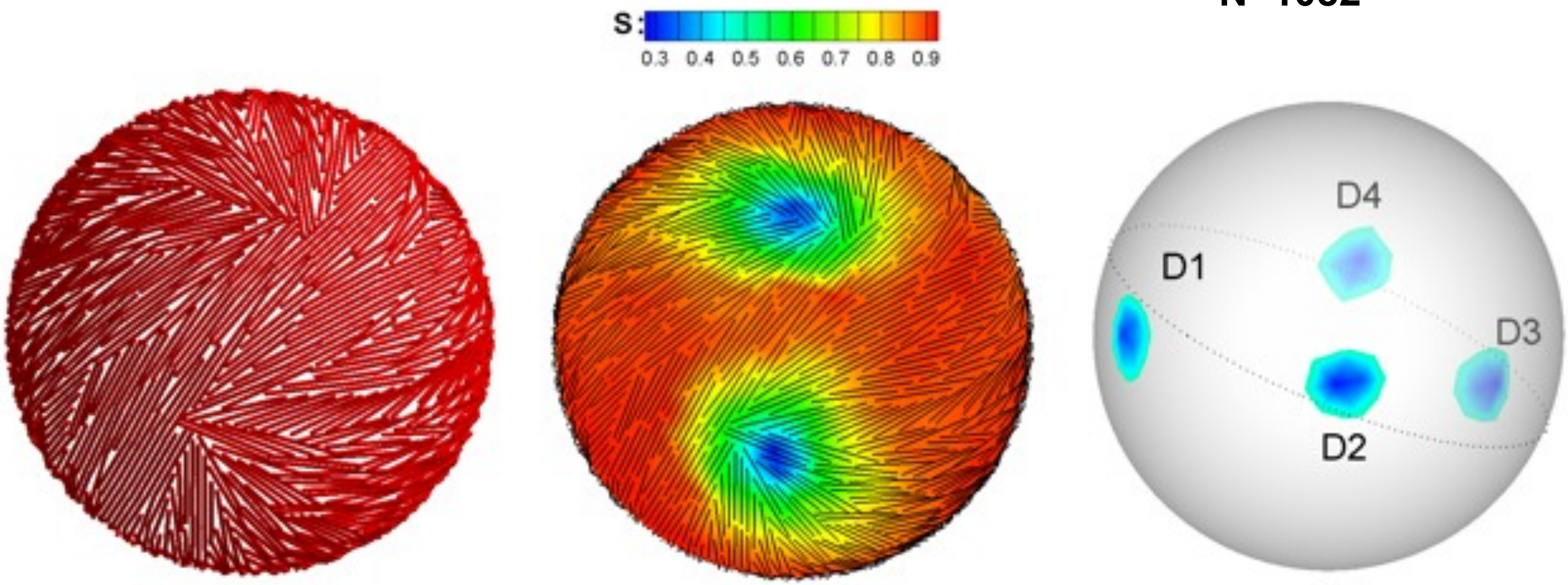
D.R. Nelson, Nano Lett.2 (2002) 1125

In the isotropic (one Frank constant) approximation the +1/2 defects would sit at the vertices of a tetrahedron

H. Shin, MJB and X. Xing: Phys. Rev. Lett. **101** (2008) 037802

Hard and soft rod MC fluid simulation produces jammed splay-dominated nematic state with four defects lying on a great circle!

N=1082



(a) (b) (c)

$$F = \frac{K_1}{2}\int (D\cdot n)^2 + \frac{K_3}{2}\int (D\times n)^2$$

For hard rods splay is preferred over bend

Take the extreme limit of pure splay deformations

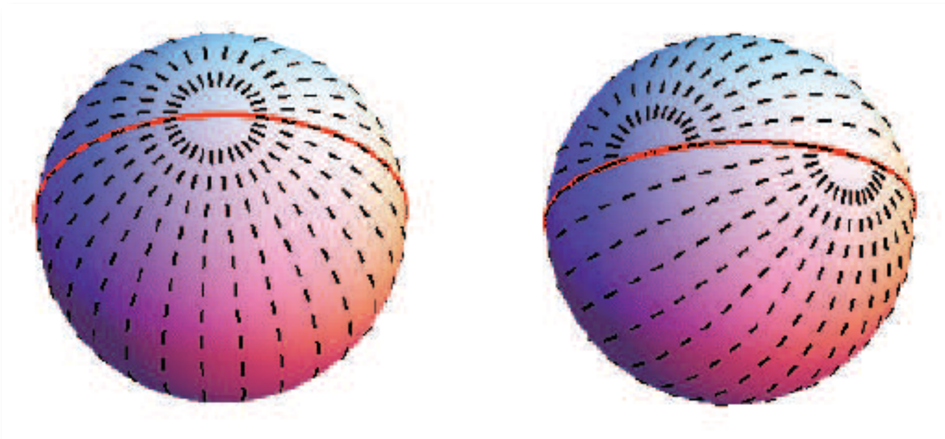
$$D\times n = 0 \implies (\vec{n}\cdot\vec{D})\vec{n} = 0$$

Director is a completely determined integral curve
(follows geodesics)

+1 disclinations are degenerate with 2 +1/2s

Why are all defects on a great circle?

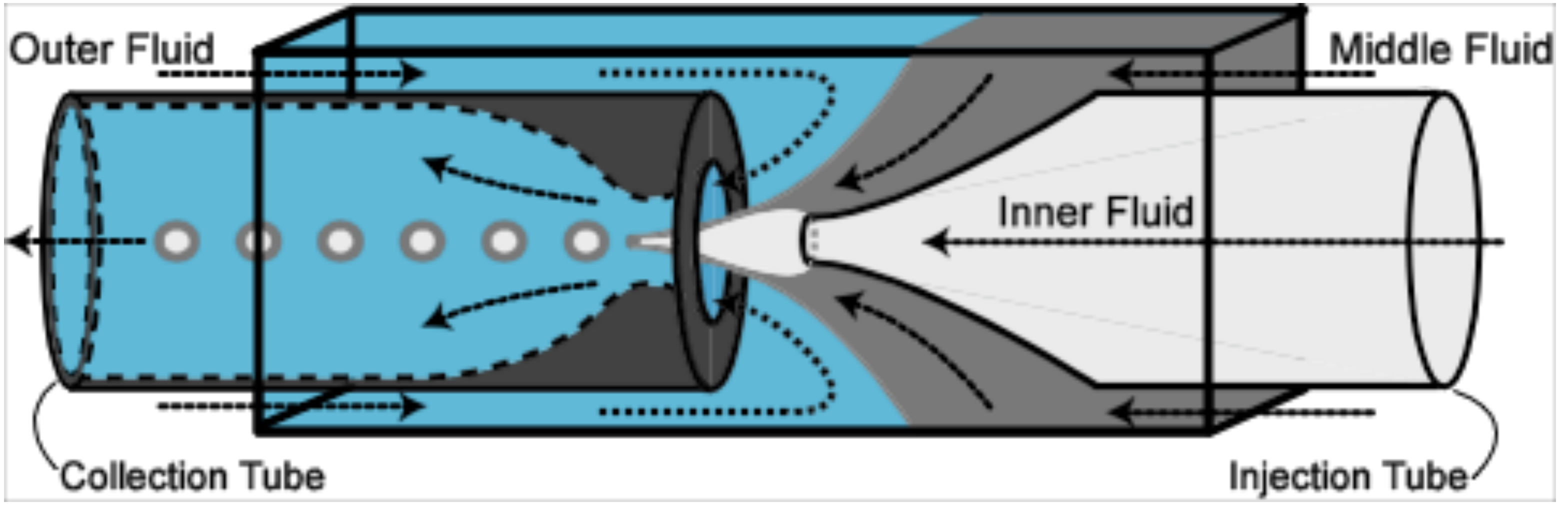
There is a special bending-free ground state



Cut and rotate by an arbitrary angle
Director field is continuous after surgery, except at defect cores
All four ½ defects form a rectangle of arbitrary aspect ratio
One parameter family of degenerate ground states

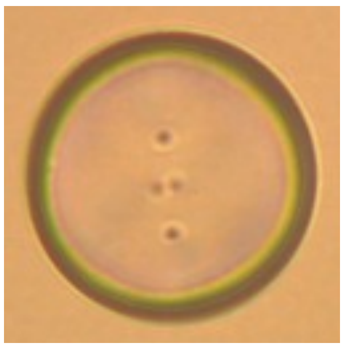
Making nematic shells: double emulsions

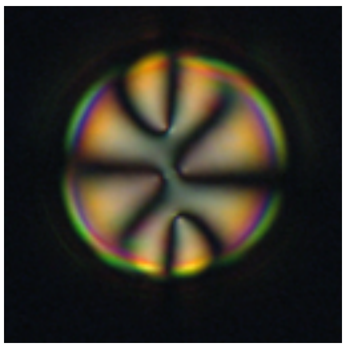
Fernandez-Nieves et al; PRL (2007); Vitelli and Nelson, PRE (2006)



Material selection

- Outer liquid: Glycerol + water + PVA
- Middle liquid: Chloroform + LC (5CB)
- Inner liquid: **Water + PVA**





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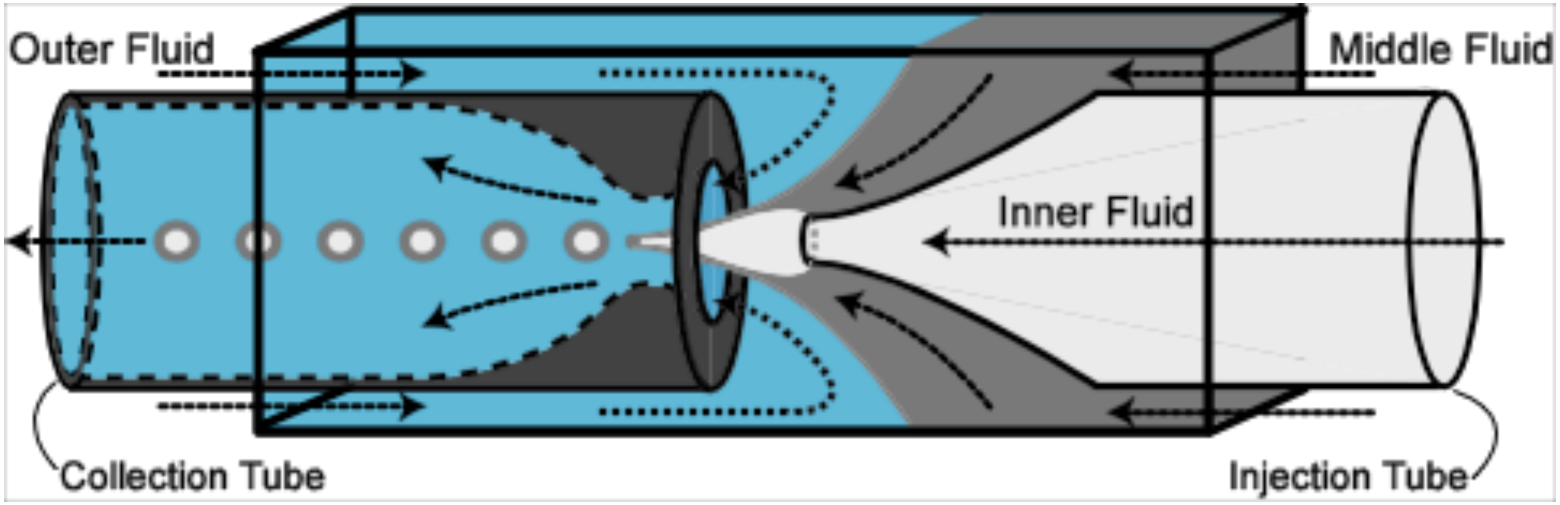

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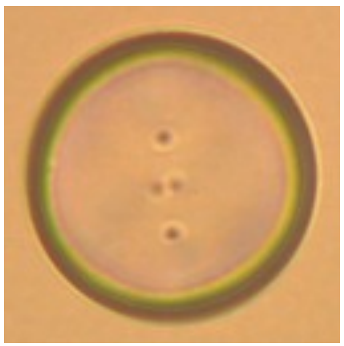
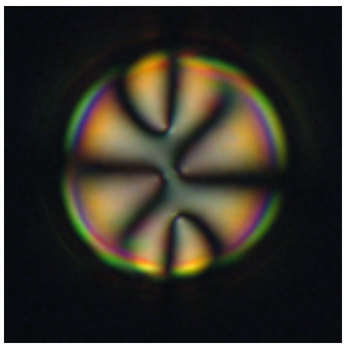
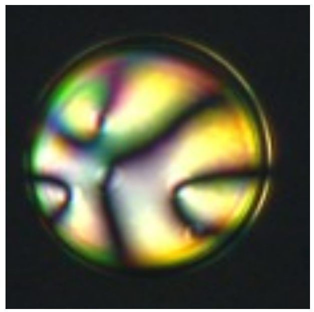
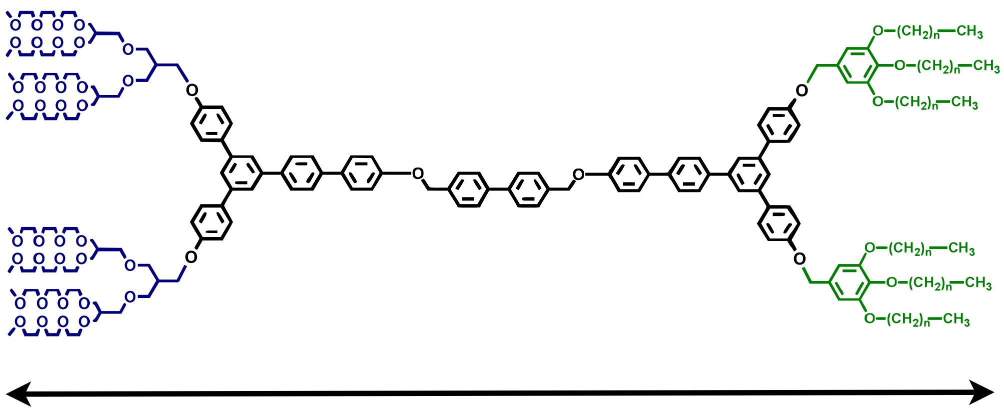




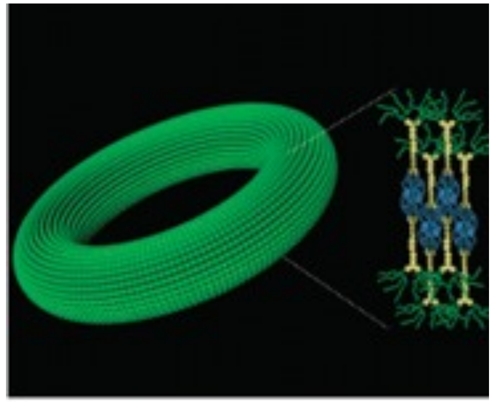


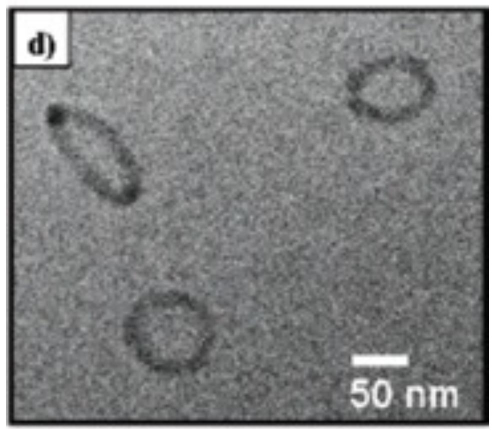
Toroidal Crystals

Toroidal crystals are two-dimensional crystalline assemblages of monodisperse objects on a torus. Example: toroidal micelles from self-assembly of amphiphilic dumbbell molecules (Kim *et al* 2006)



8 nm

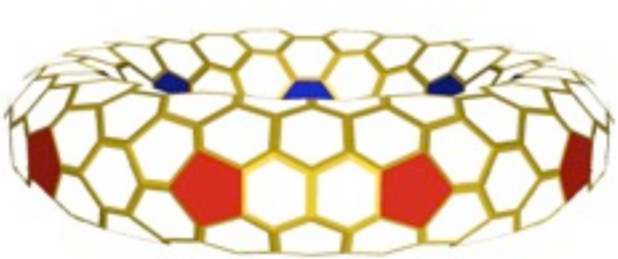




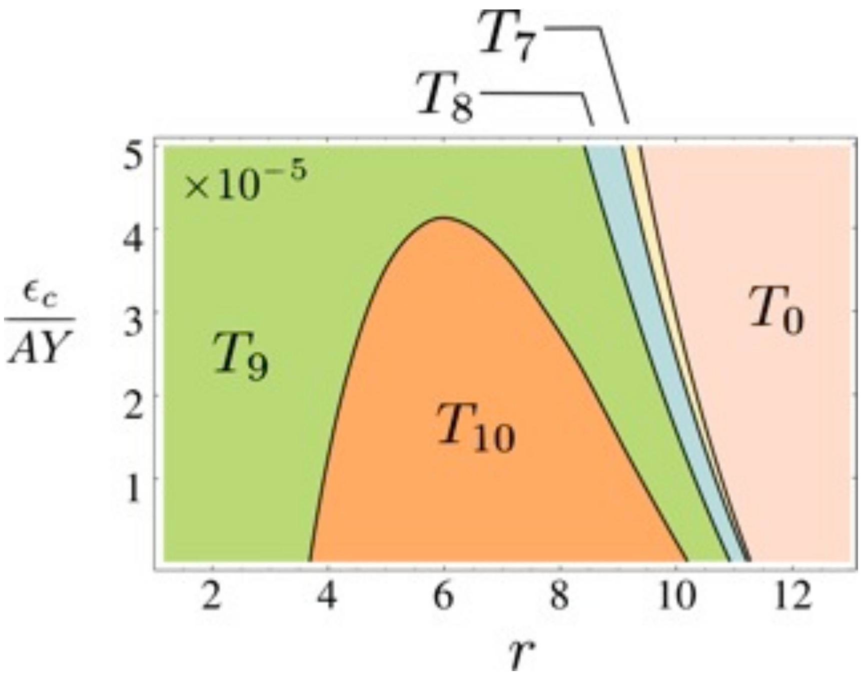
Amphiphiles form double-dumbbells of 16 nm in length and self-assemble in spherical and uncapped cylindrical micelles. These turn into toroidal micelles in the course of a week. Diameters: D_1=70-300 nm, D_2=16 nm.

Changing the Manifold: T^2

Although defects not required topologically $(\chi = 0)$ they appear as **minimizers**



Valence 10

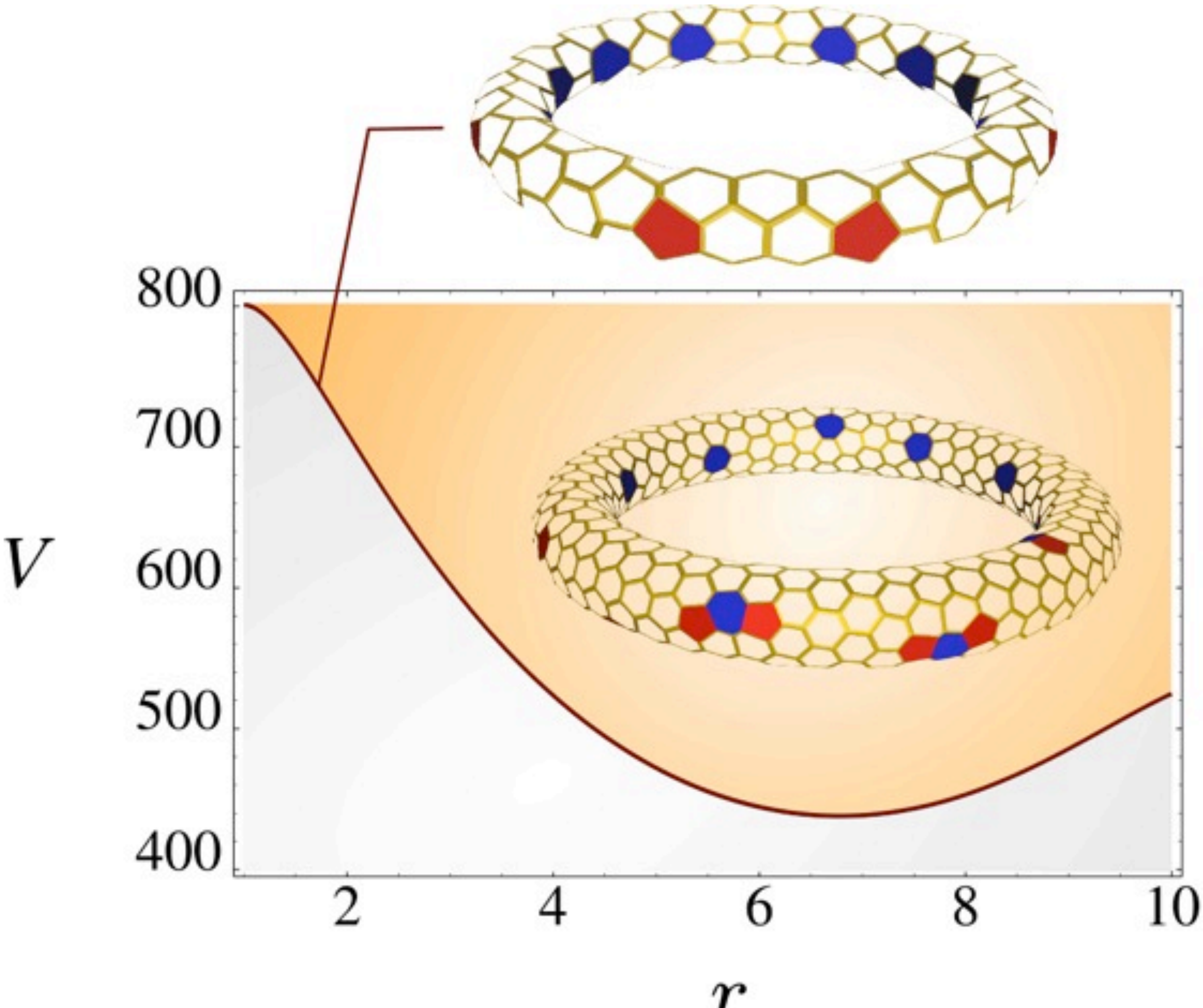


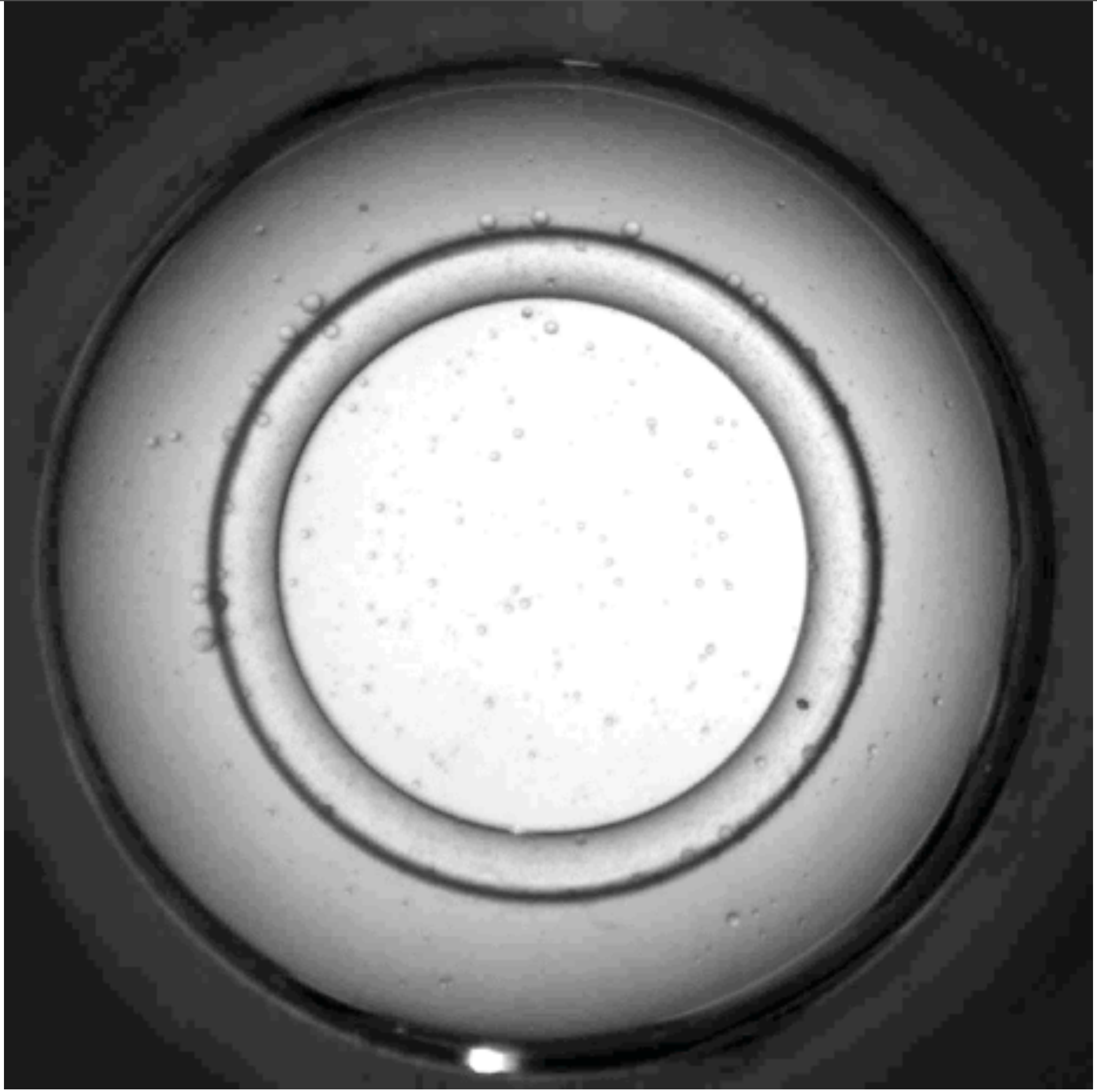
Geometrically Tunable Valence!

Luca Giomi and MJB

Phys. Rev. E 78, 010601(R) (2008); Eur. Phys. J. E27, 275 (2008)

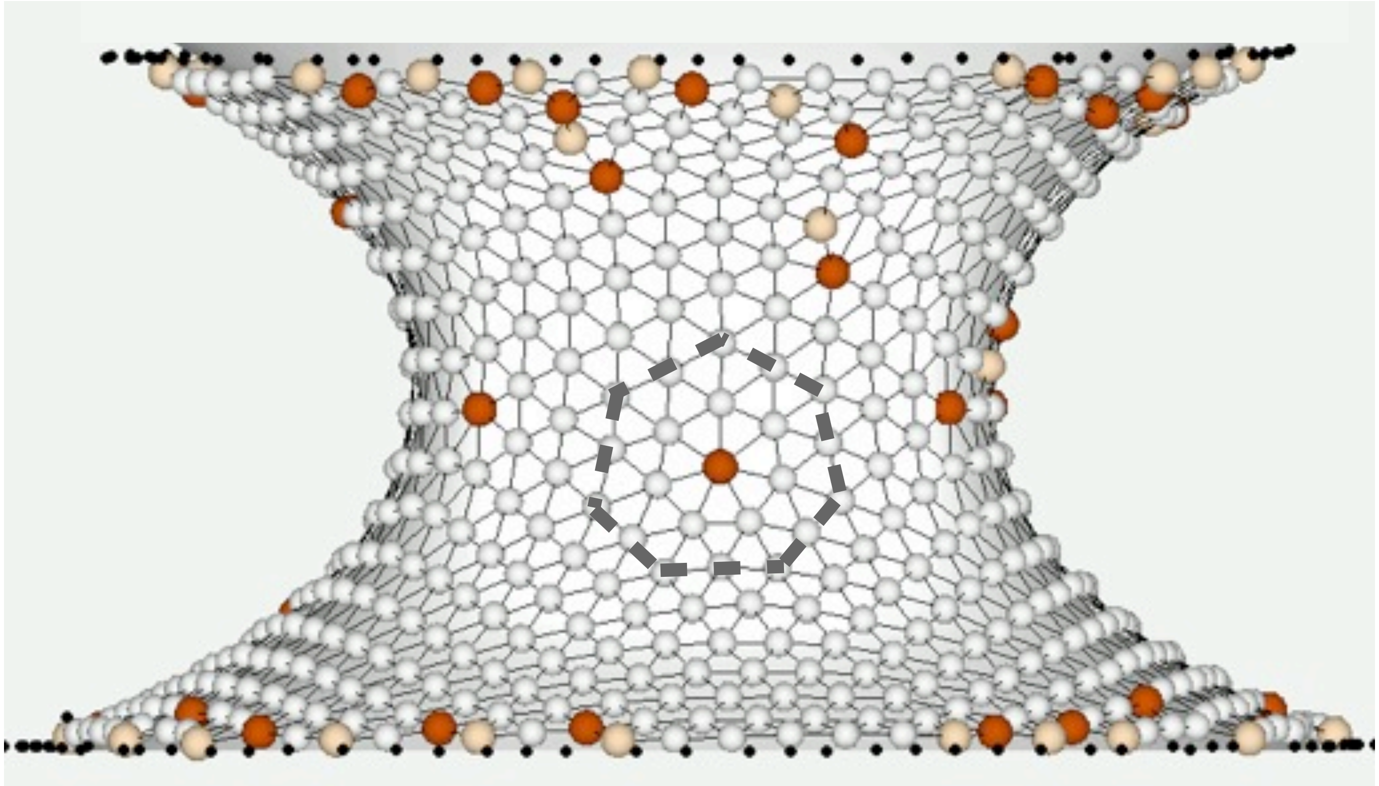
Toroidal Scars





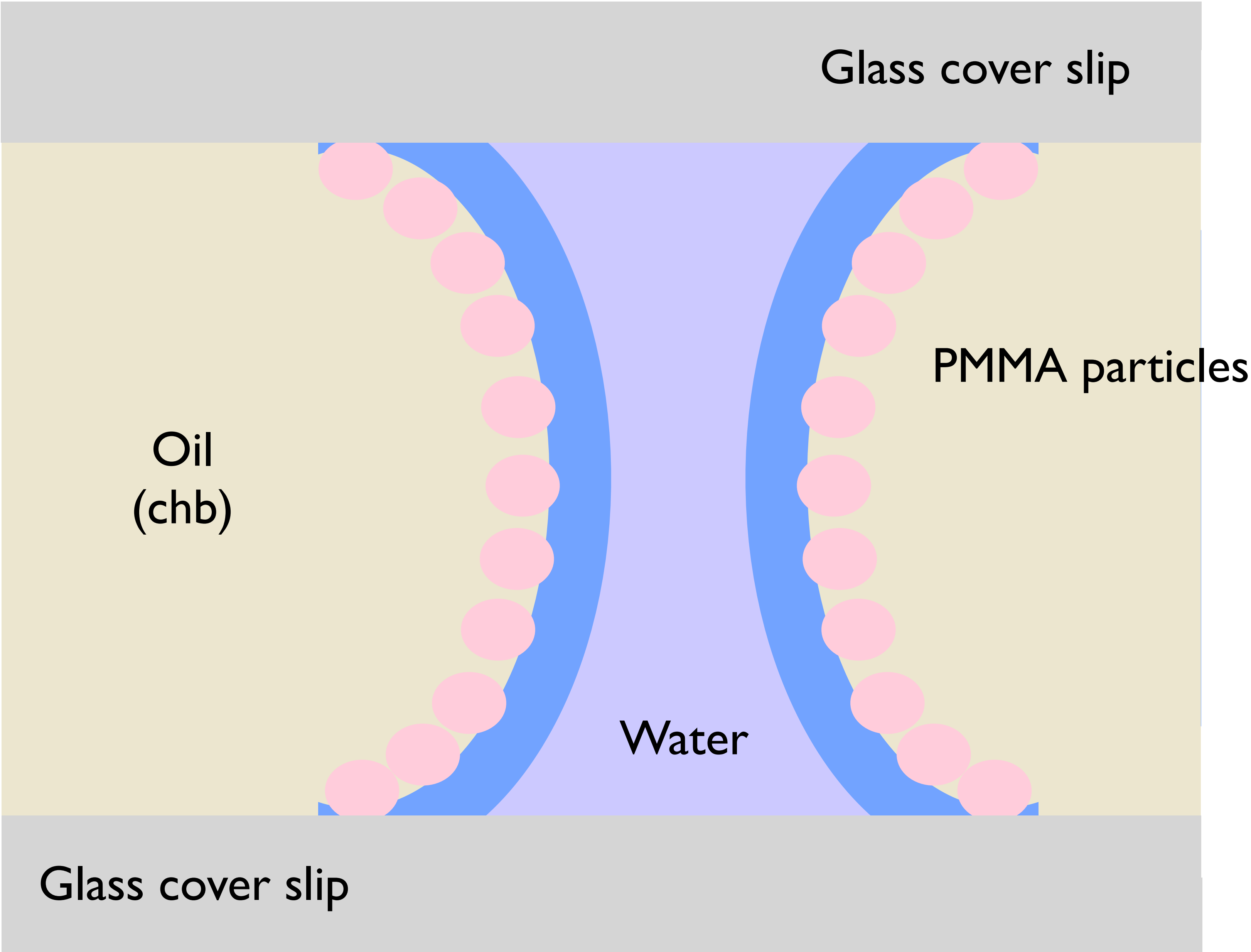
E. Pairam and A. Fernandez-Nieves PRL 102, 234501 (2009)

Crystalline Order on CMC Delaunay surfaces

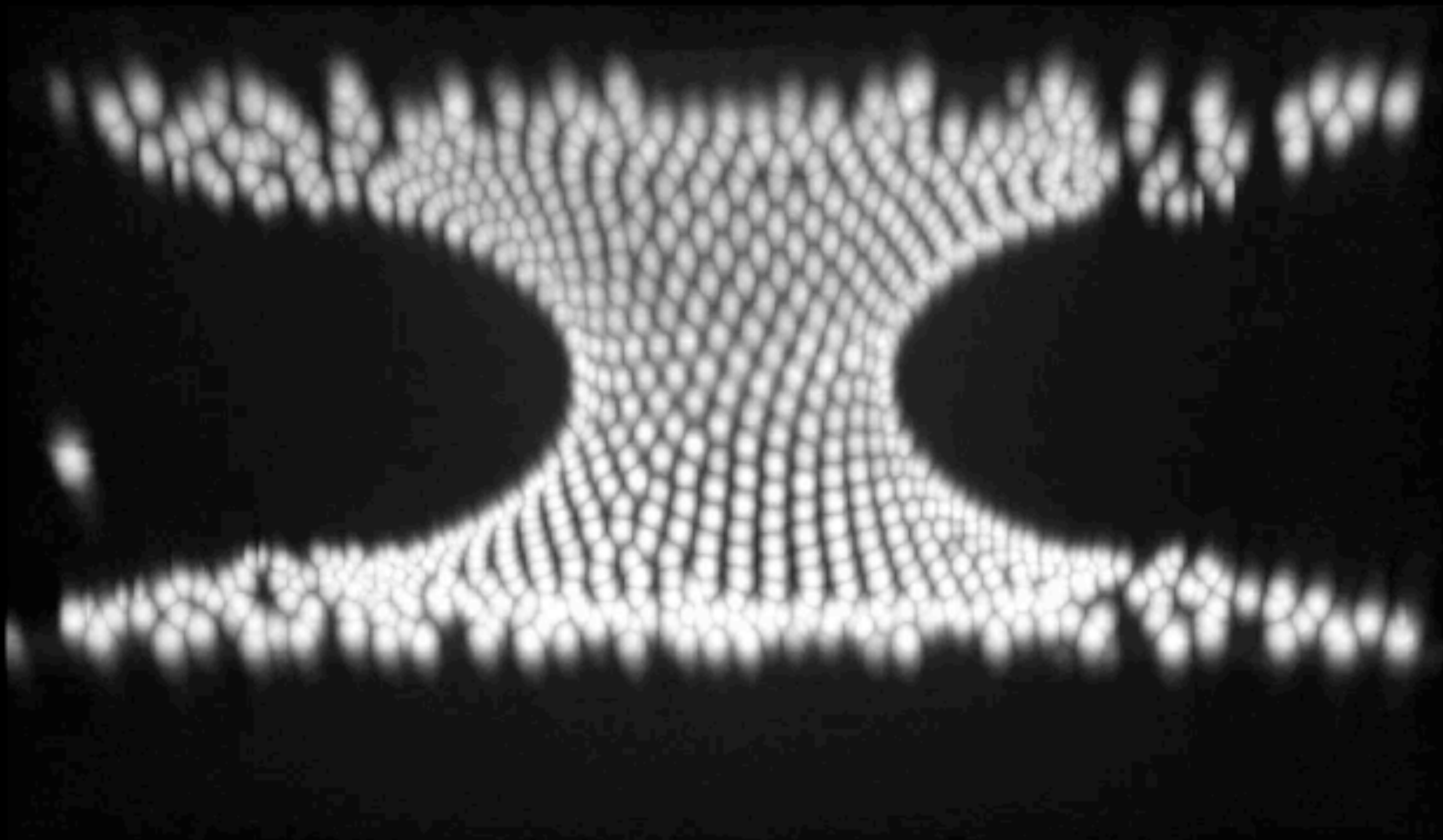


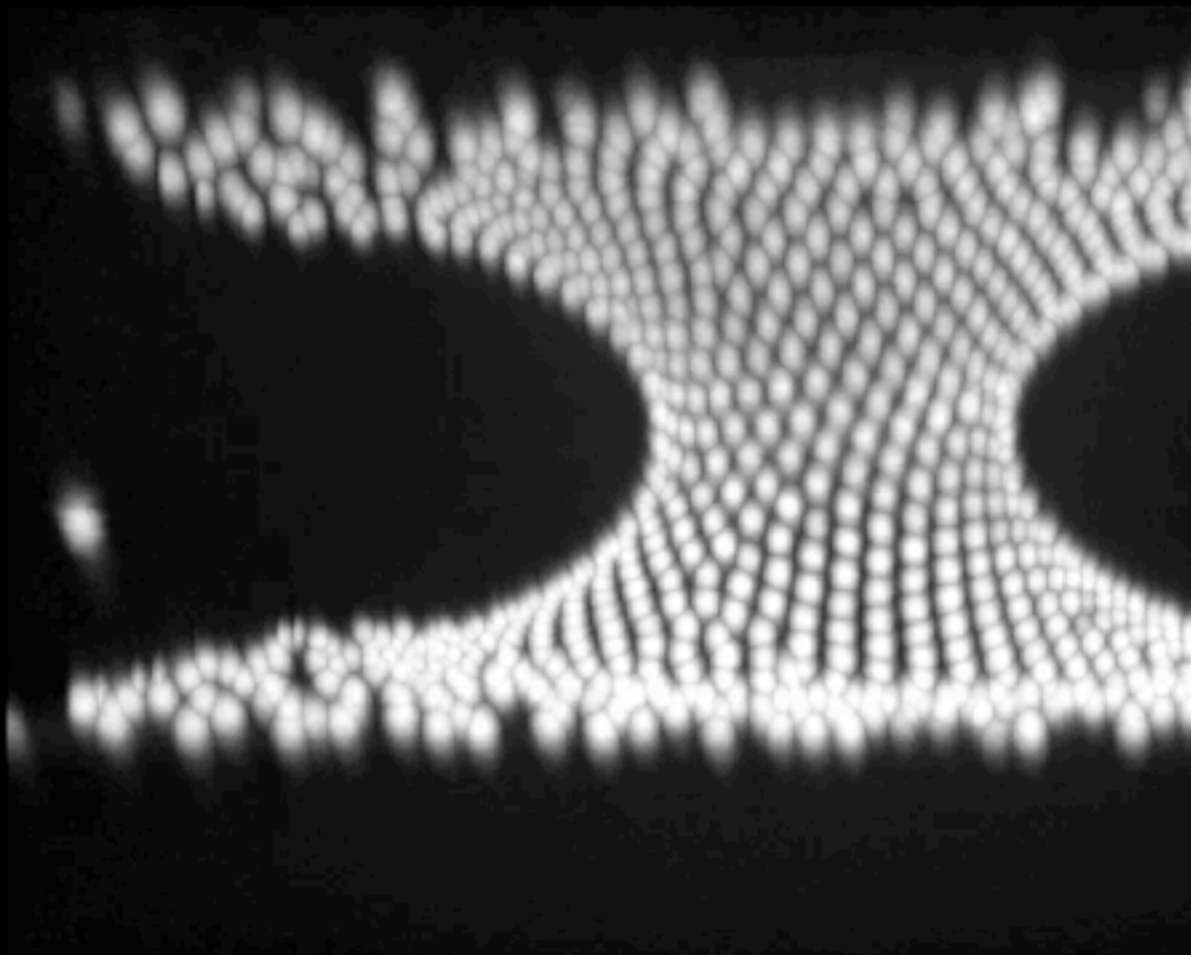
Irvine, Vitelli and Chaikin, Nature (2010)
MJB, Z. Yao, EPL (2011)

Catenoids



Glass cover slip
PMMA particles
Oil
(chb)
Water
Glass cover slip





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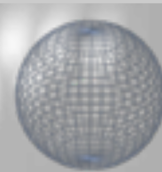
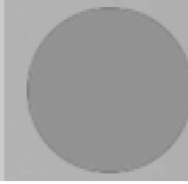
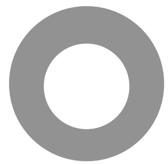
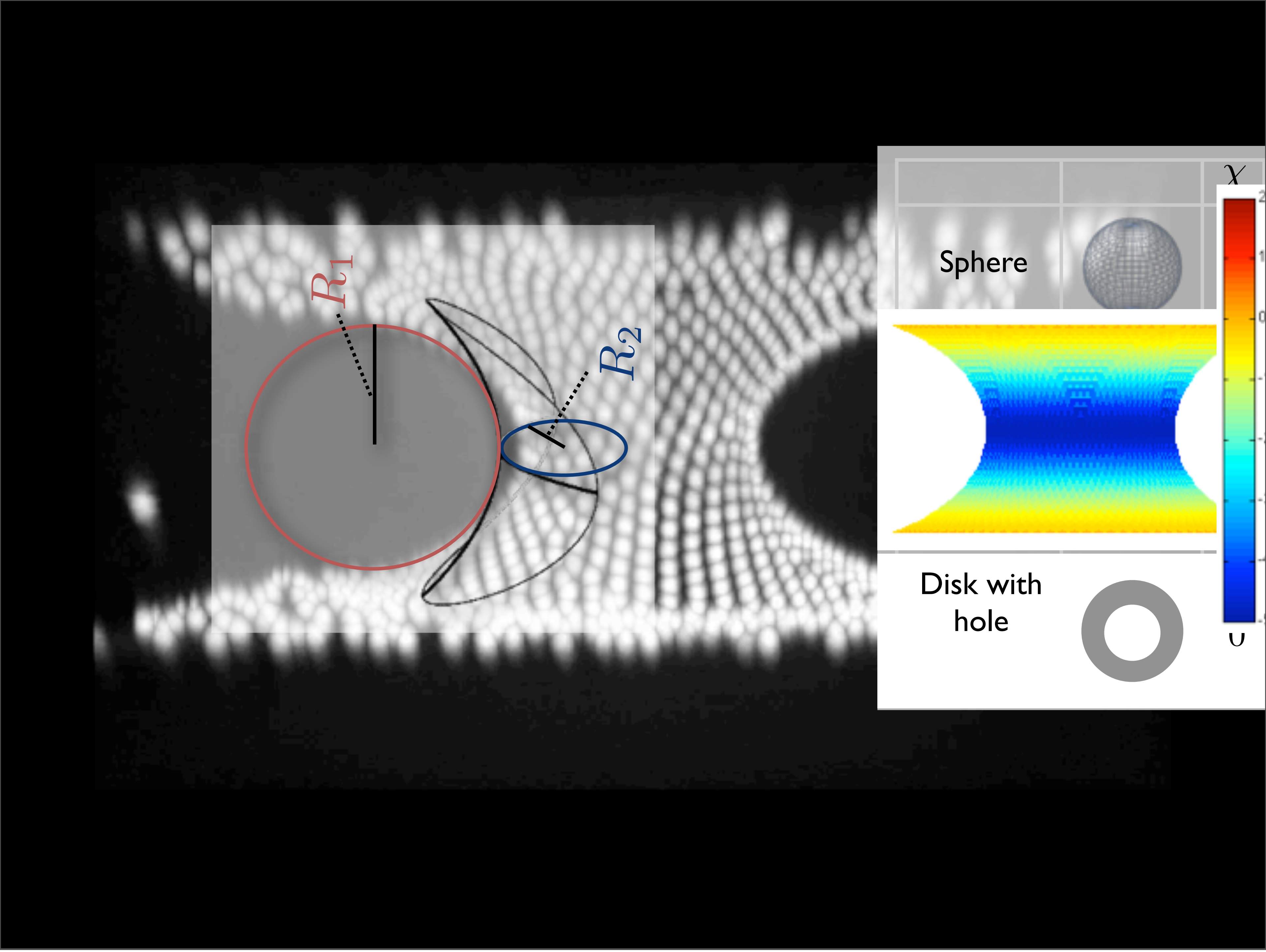
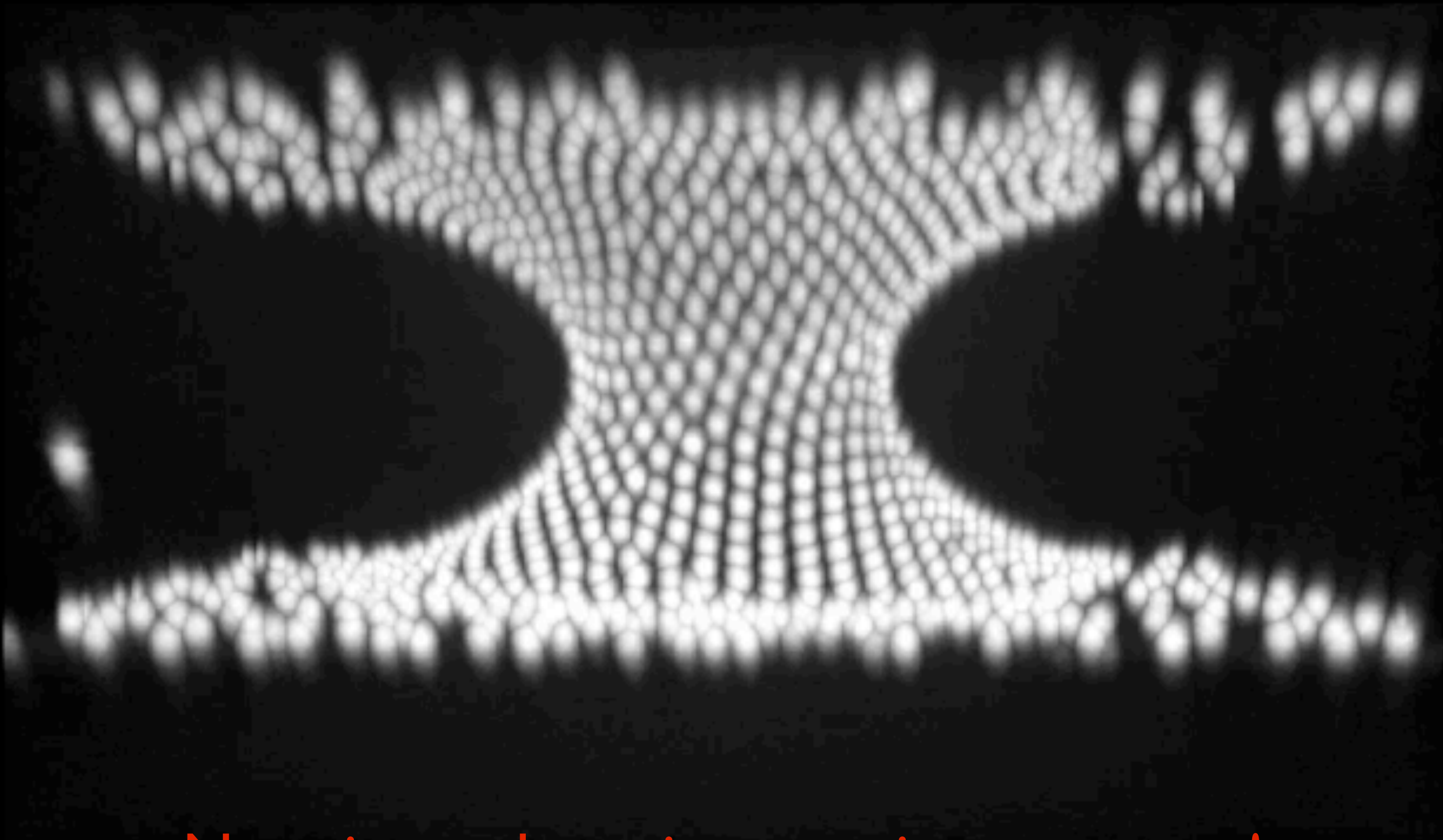
Sphere		2
Torus		0
Disk (or dome)		1
Disk with hole		0

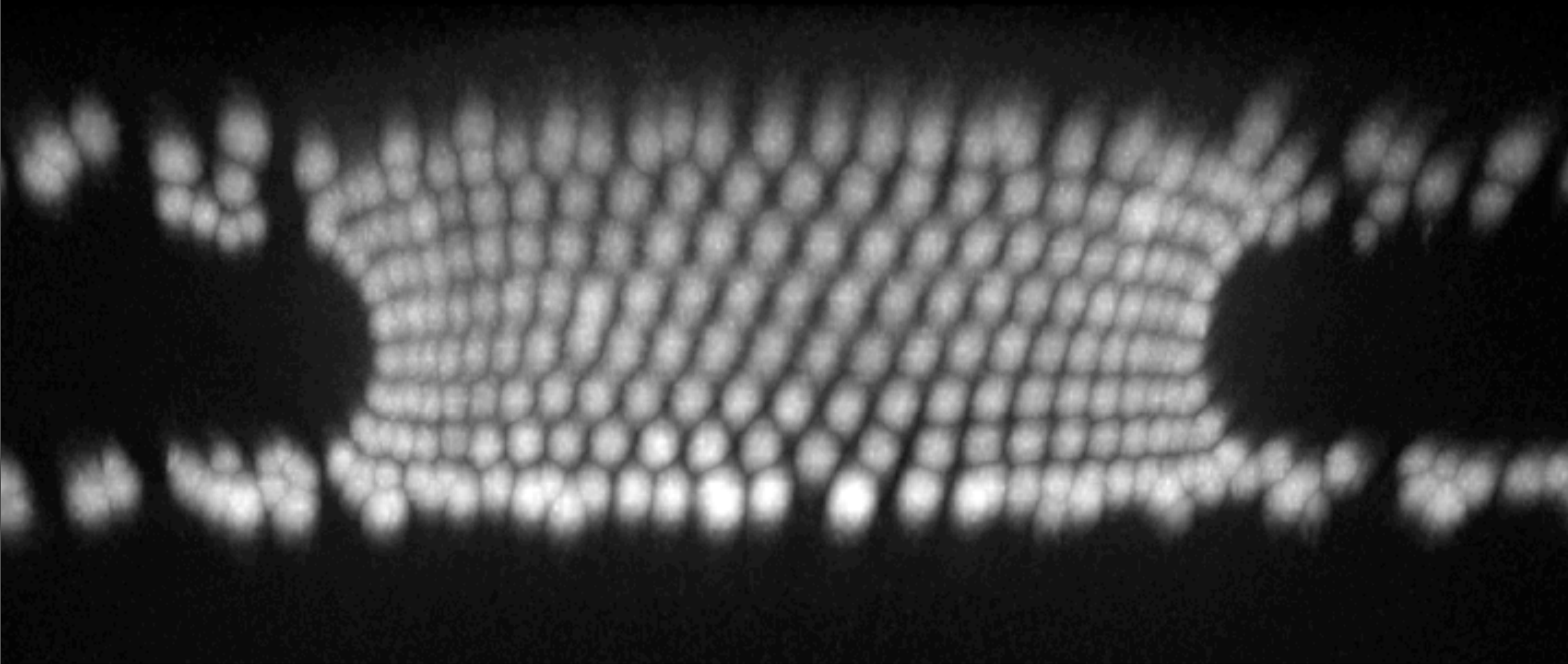

R_1
R_2
Sphere
Disk with hole
χ

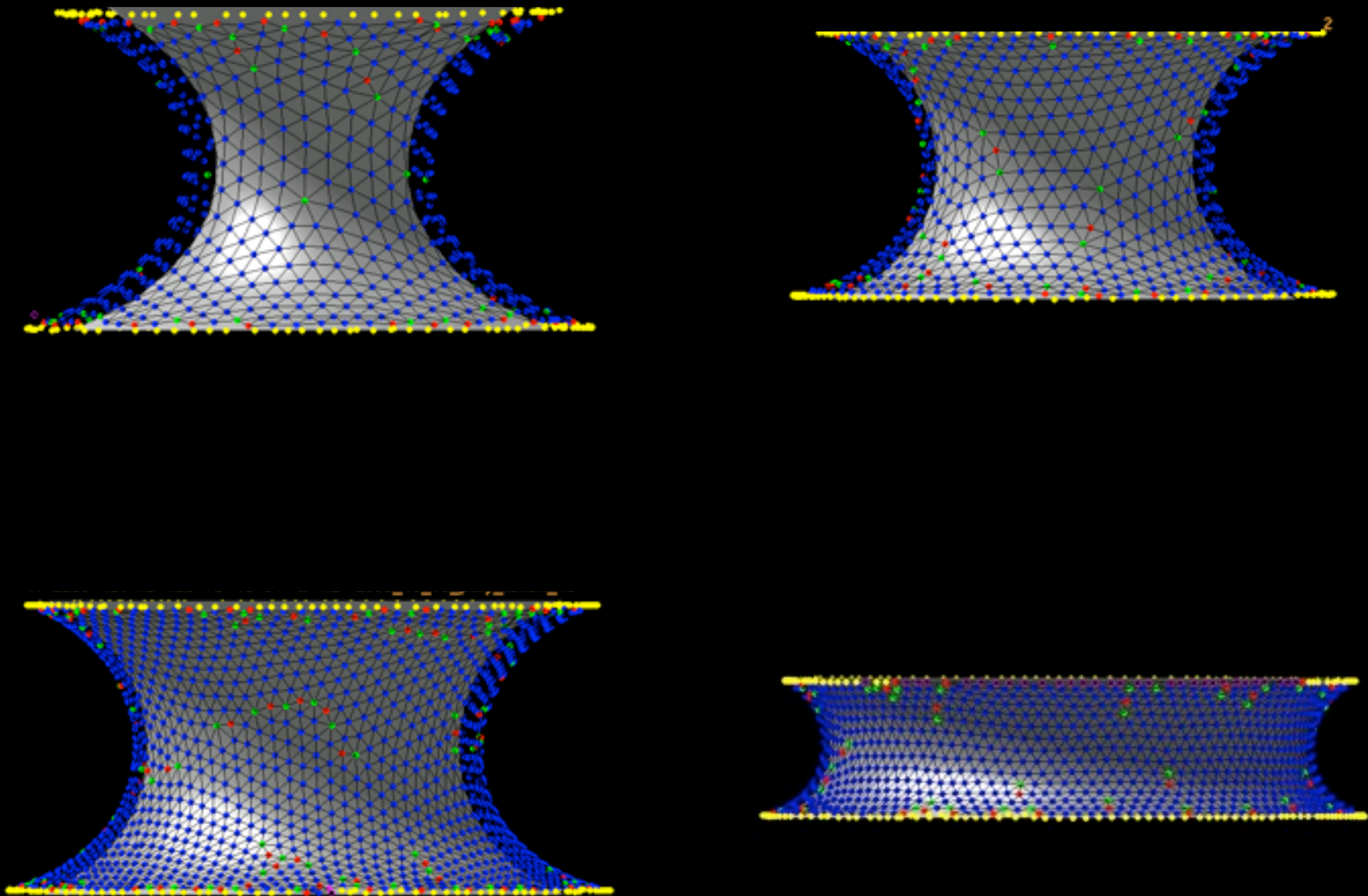
Euler number 0



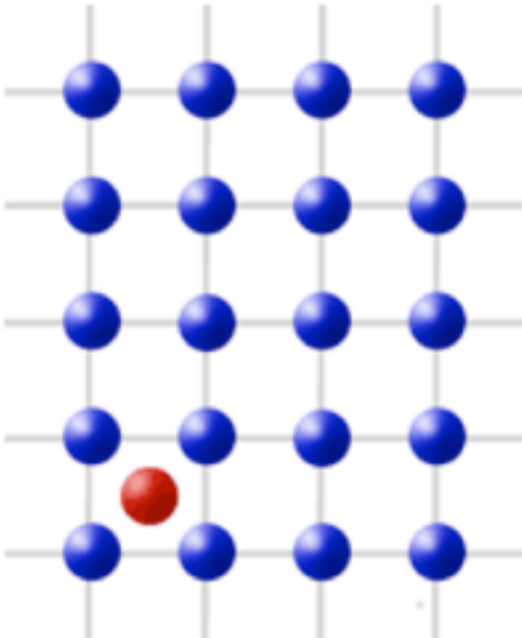
Negative and varying gaussian curvature!

Stretching a capillary bridge





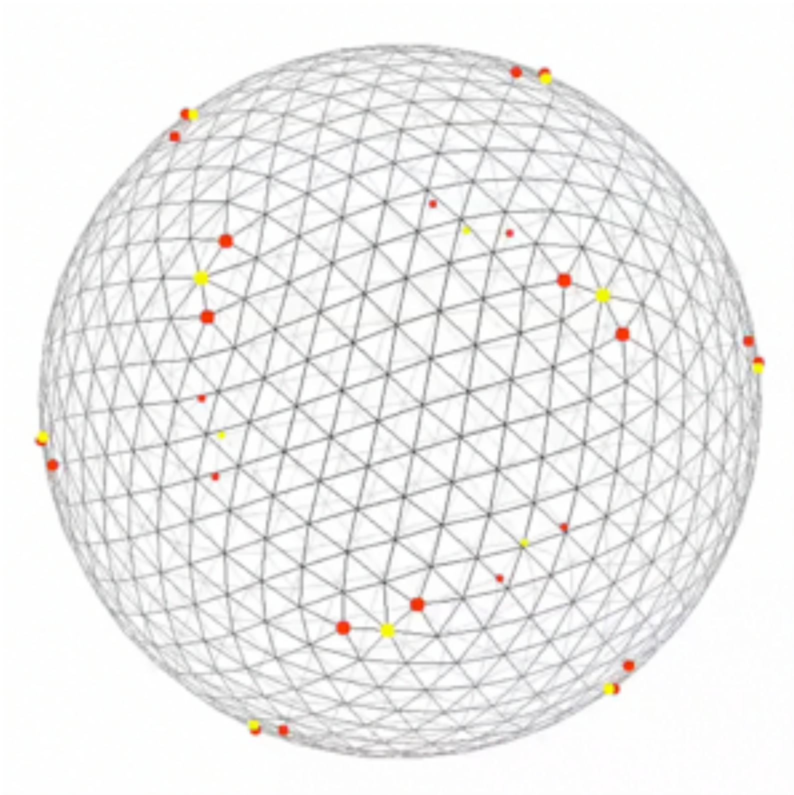
Self-interstitials (MJB, Irivine & Chaikin)

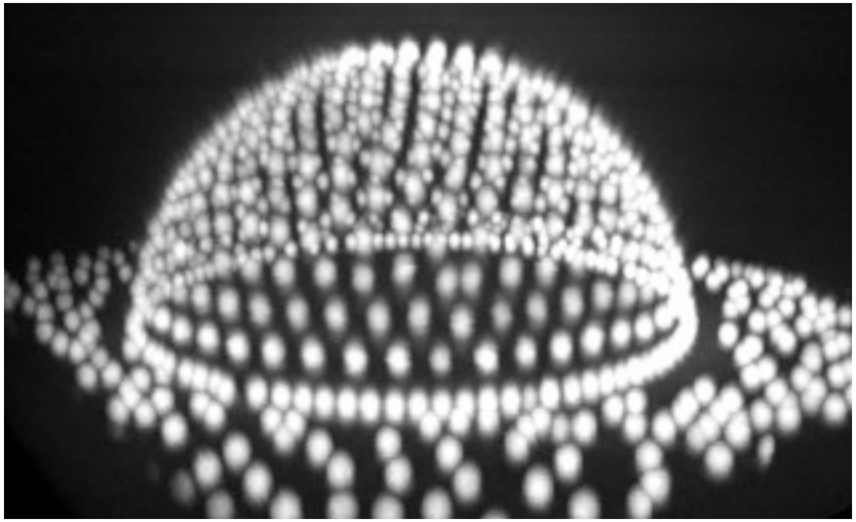


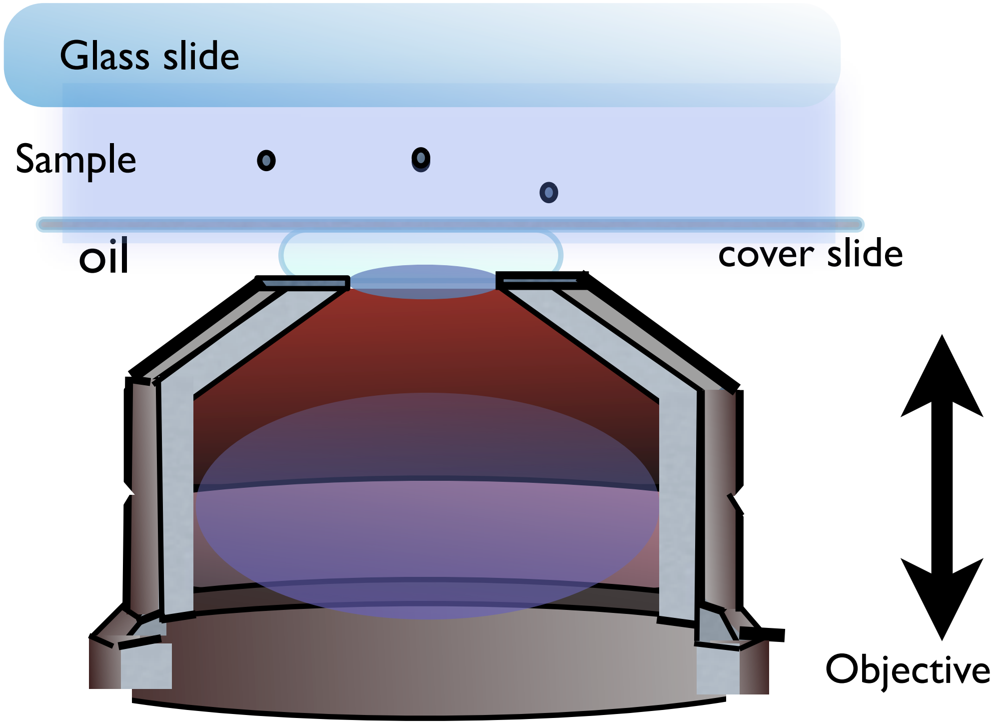
Curvature driven fractionalization

- MJB, H. Shin and A. Travesset, PRE 75 (2007) [cond-mat/0610819]
- MJB, D. R. Nelson and H. Shin, Phys. Chem. Chem. Phys. (2008) [arxiv:0707.1909]

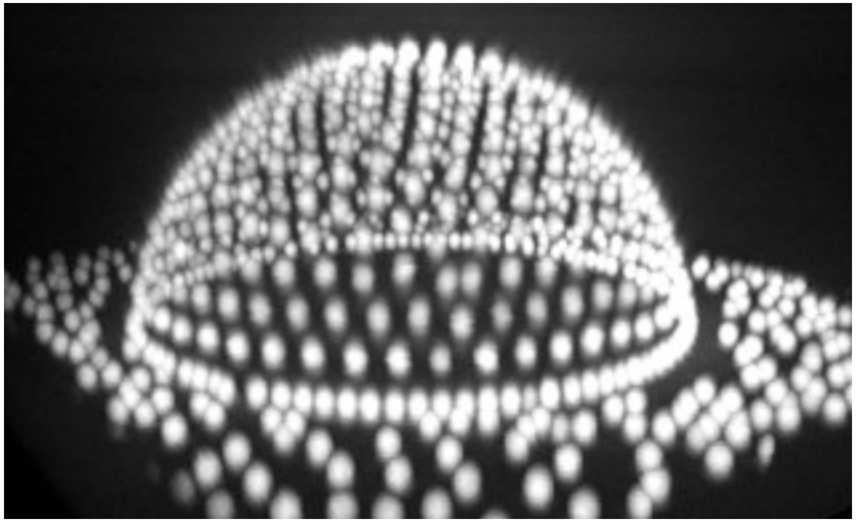
http://thomson.phy.syr.edu/thomsonapplet.htm

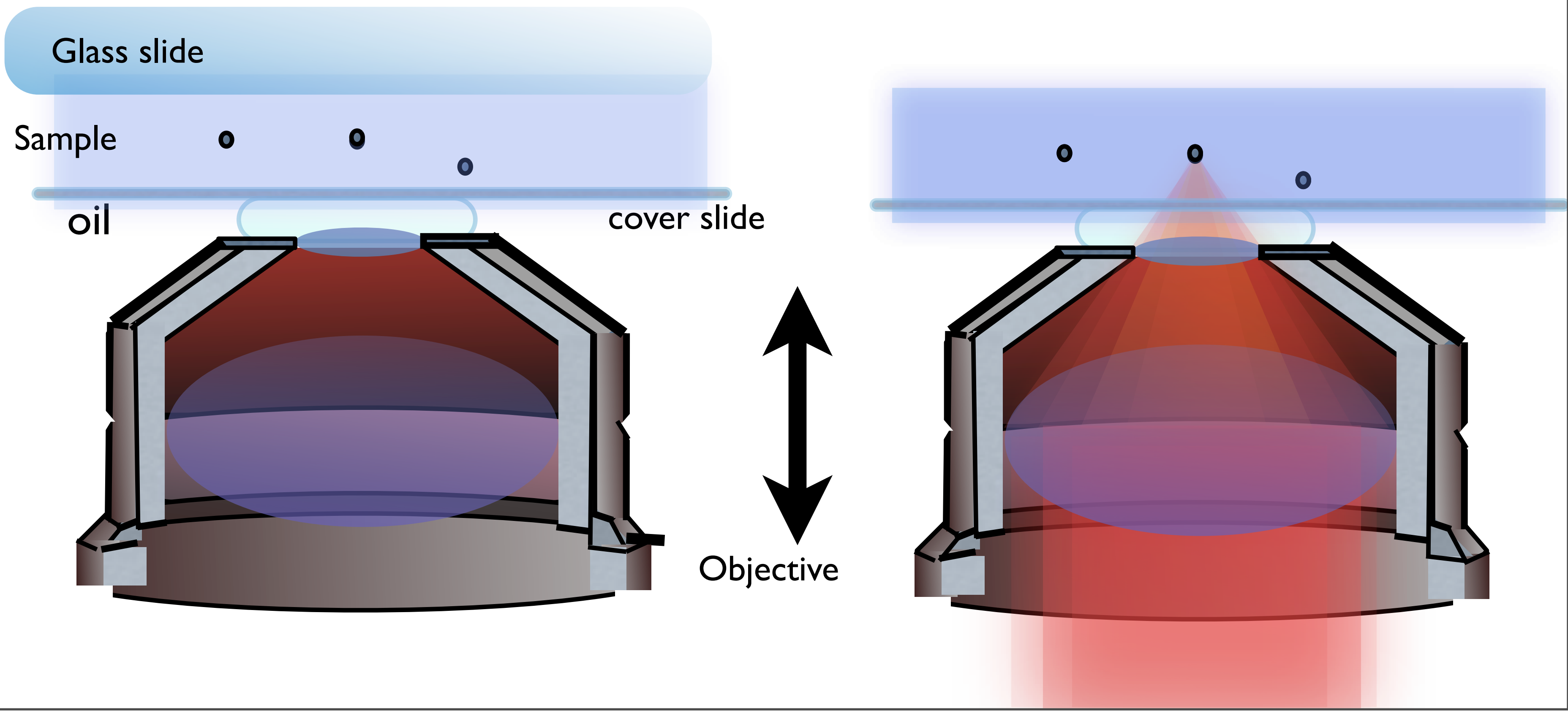


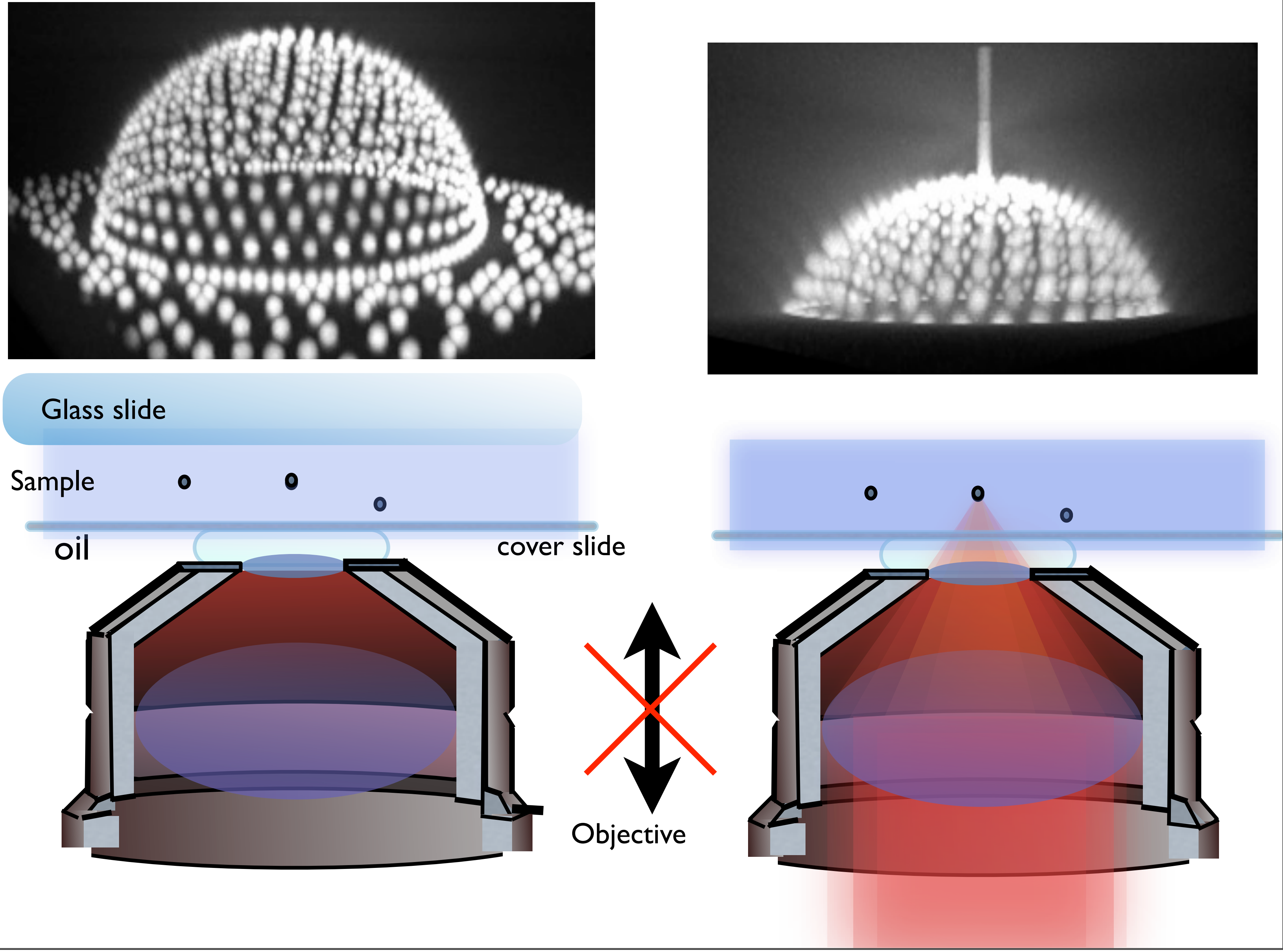


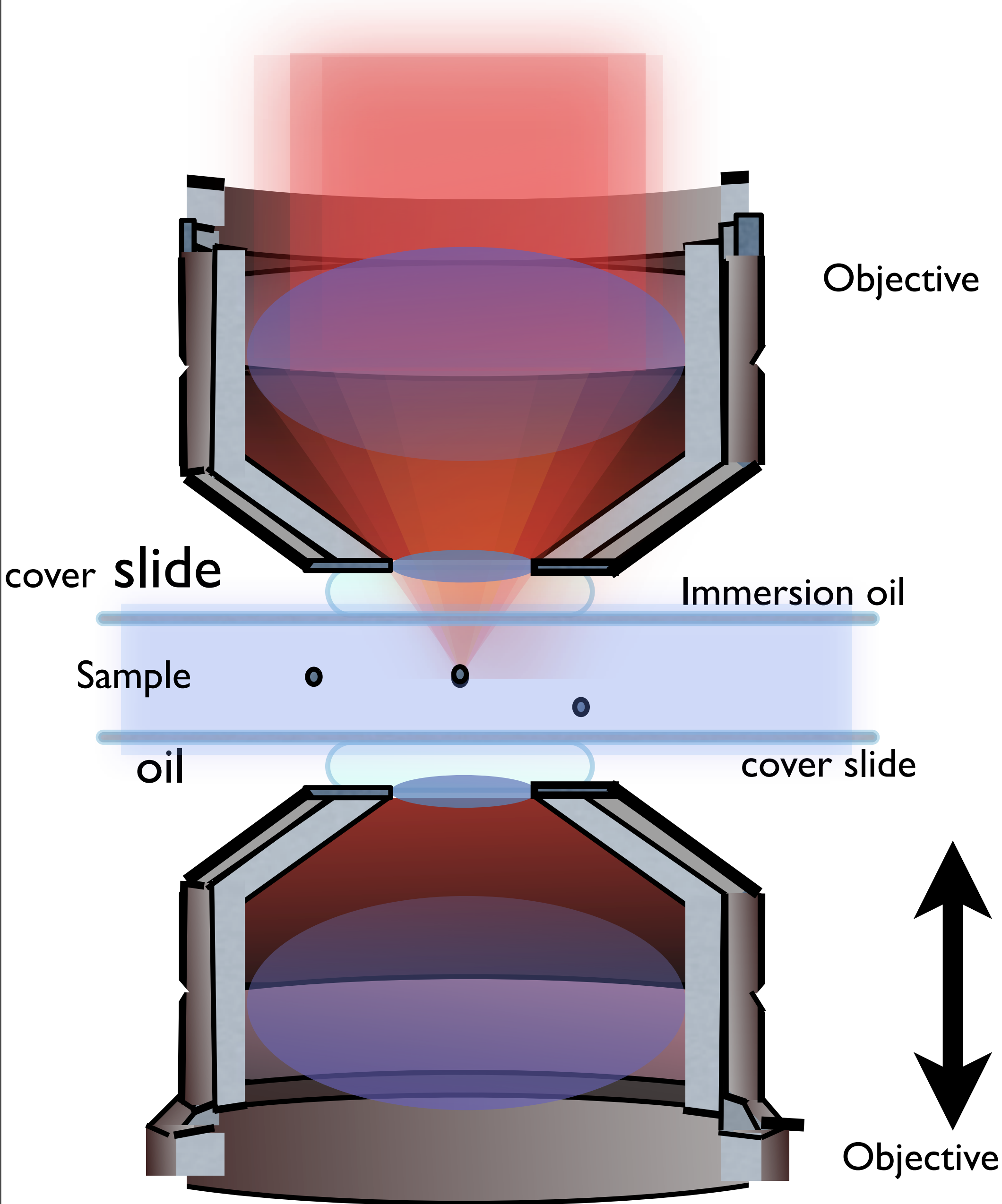


Scan objective
up and down
for confocal operation




Glass slide
Sample
oil
cover slide
Objective


Glass slide
Sample
oil
cover slide
Objective

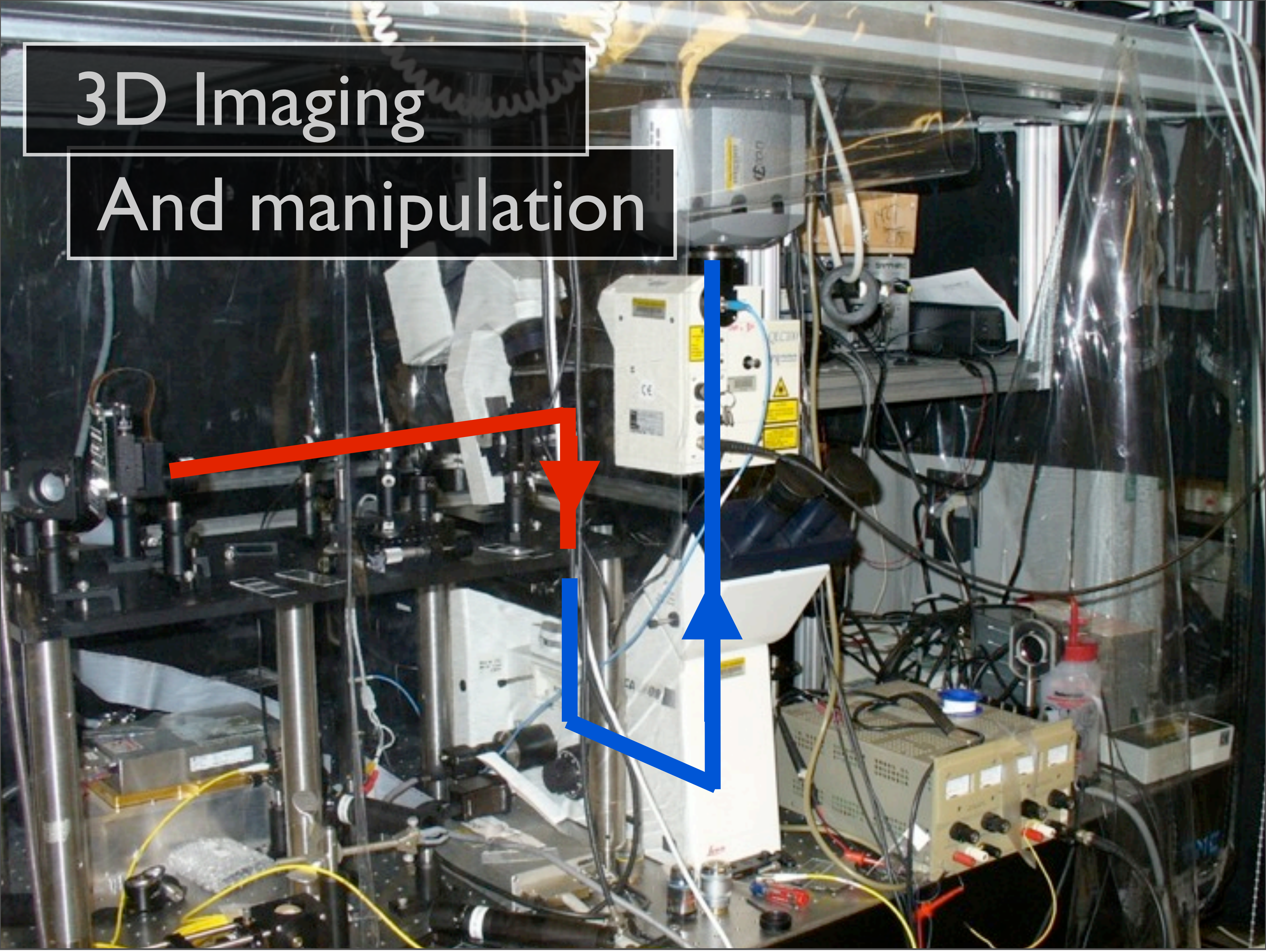


Manipulate independently

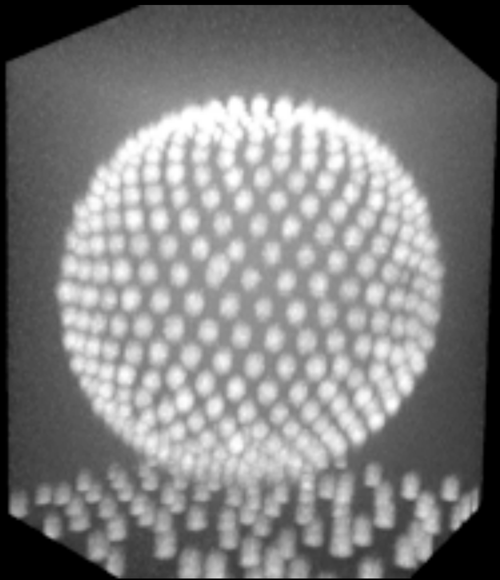
Scan objective up and down for confocal operation

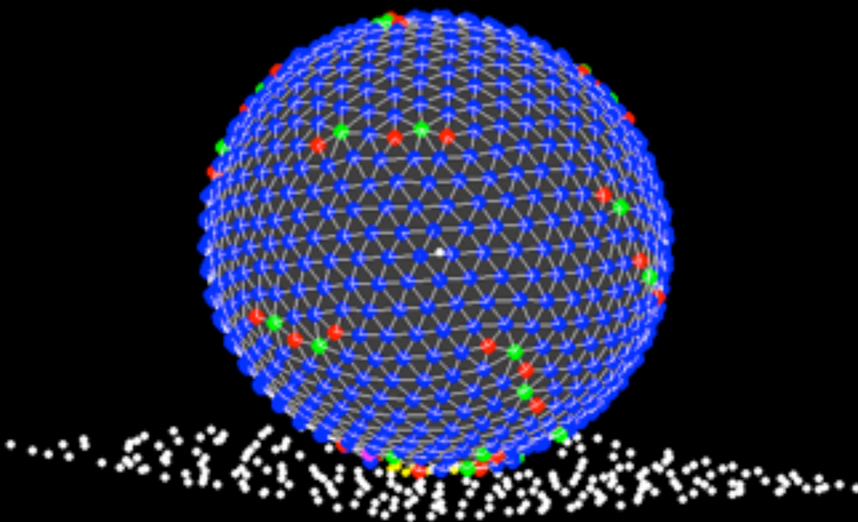
3D Imaging

And manipulation

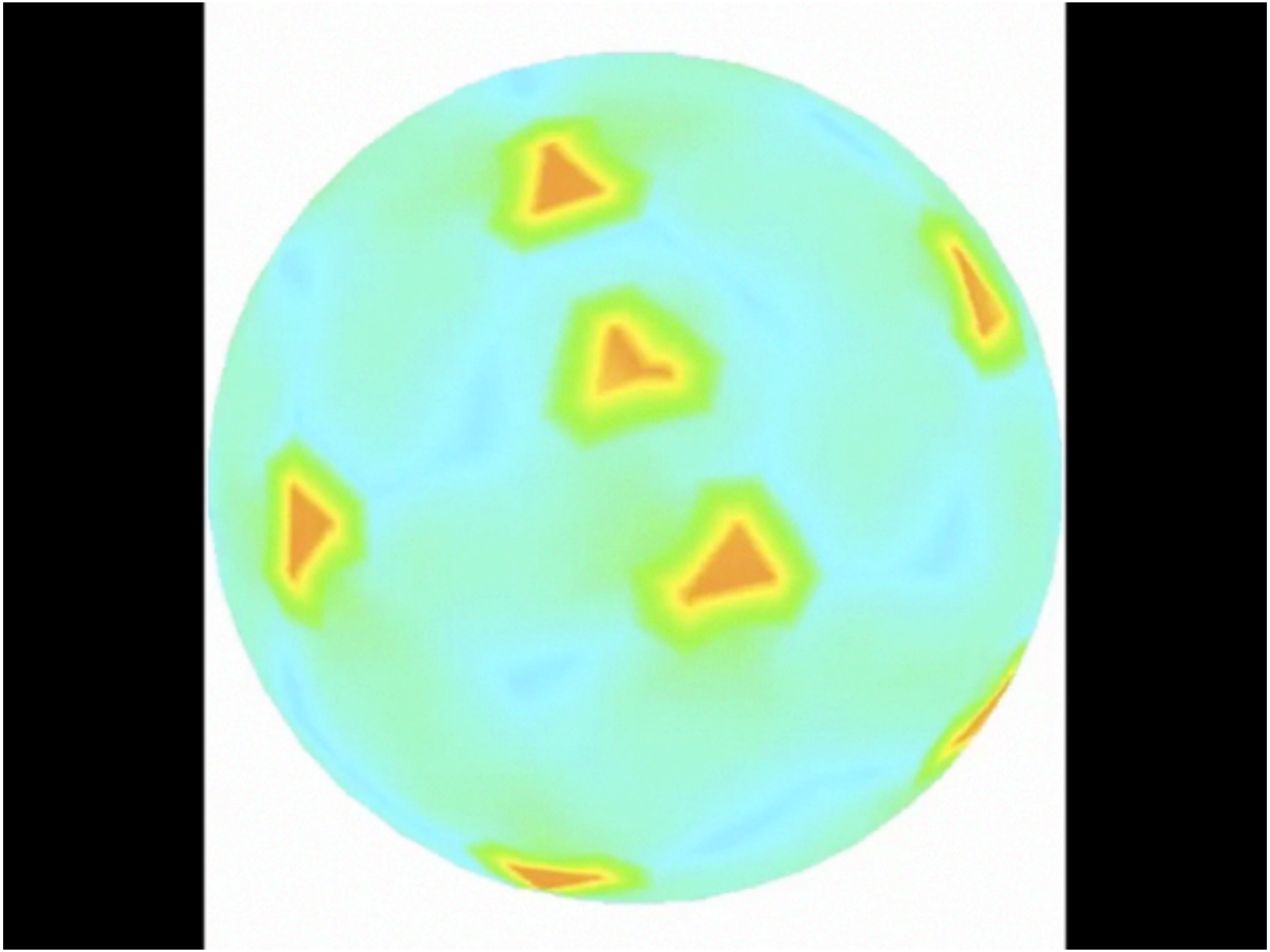


Thursday, February 2, 12

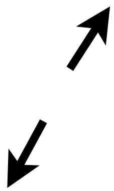




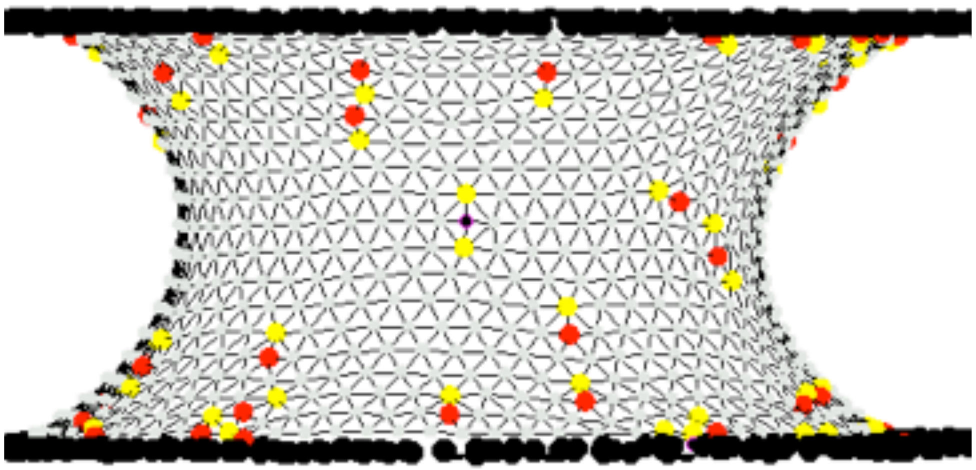
Where did the particle go?



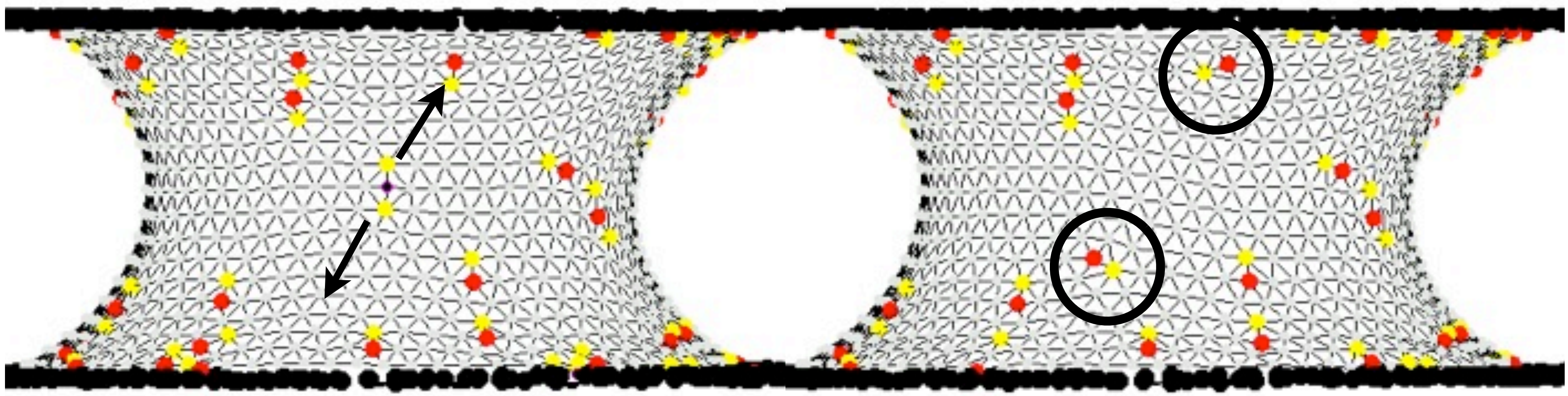
Interstitial fractionalization on a catenoid



Interstitial fractionalization on a catenoid



Interstitial fractionalization on a catenoid



Conclusions

- Topology determines broad structure of ground state
- Energetics determines the detailed structure = shape of defective regions

Curvature-driven effects

- Disclination delocalization
- Novel structures (disclinations) in ground state

Defects allow design of superatoms
Defective regions = valence
Global Geometry of Defective regions determines type of directional bonding available (controllable via elastic moduli)

Structure controls shape in some cases: faceted liquid crystalline vesicles from block copolymers