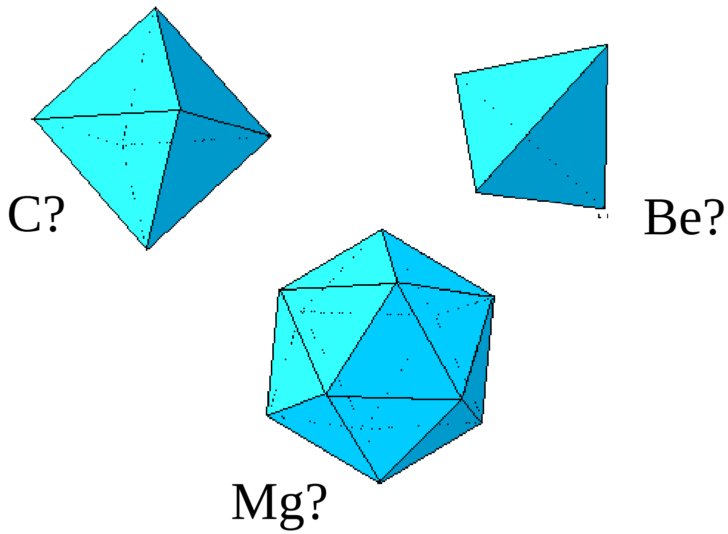
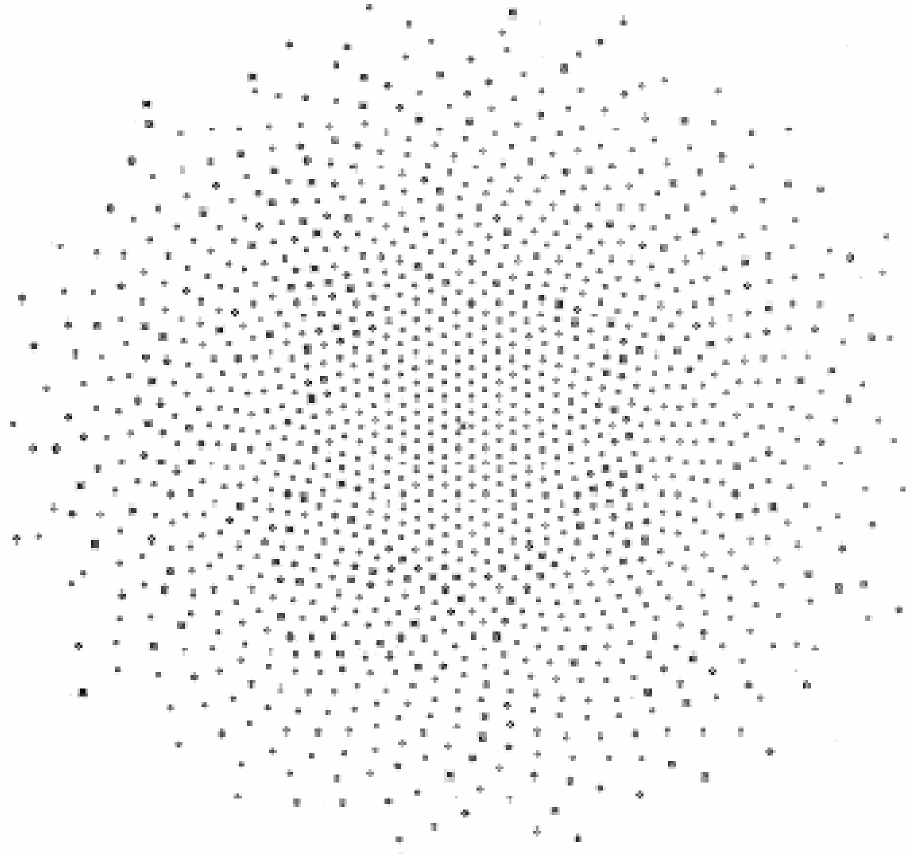
The Thomson Problem

What is the ground state of interacting particles on a sphere for R/a >> 1? (R = sphere radius, a = particle size)

1904: J.J. Thomson's attempt (Phil. Mag. 7, 237) to explain the periodic table in terms of *rigid* electron shells fails….



"The analytical and geometrical difficulties …of corpuscles…arranged in shells are much greater… and I have not as yet succeeded in getting a general solution." J.J. Thomson



nucleation and growth on a sphere:
$R/a = 10$; 1314 particles
M. Rubinstein and drn *($N_5 - N_7 = 12$)*

Spherical Crystallography: Virus Buckling and Grain Boundary Scars

Particle packings on curved surfaces – *"geometrical frustration"*

--Thomson problem: 'theory' of the periodic table (circa 1904)

--Icosahedral packings in virus shells $(N_5 - N_7 = 12)$

--Theory of disclination buckling in viruses

--Theory of crumpling at high "Foppl-von Karman number

Grain boundary scars and colloids on water droplets

--*What happens when shells cannot buckle? grain boundaries!!*

--*Experiments: 'colloidosomes' on water droplets (A. Bausch et al.)*

--*Grain bounaries in ground state terminate inside curved media….*

Liquid crystal textures on curved surfaces

--*Colloids with a valence*

--*Baseball textures: 'sp^3 hybridization' on a micron scale….*

--*Ordered states on bumps and torii*

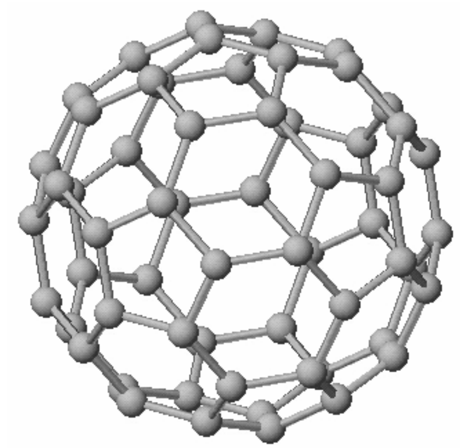
M. Rubinstein
S. Sachdev
S. Seung

L. Peliti

J. Lidmar
L. Mirny

M. Bowick
A. Travesset
V. Vitelli

20^{th} century solutions of the Thomson problem….

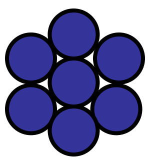


Fullerene molecule; (1,1)

Geodesic Dome

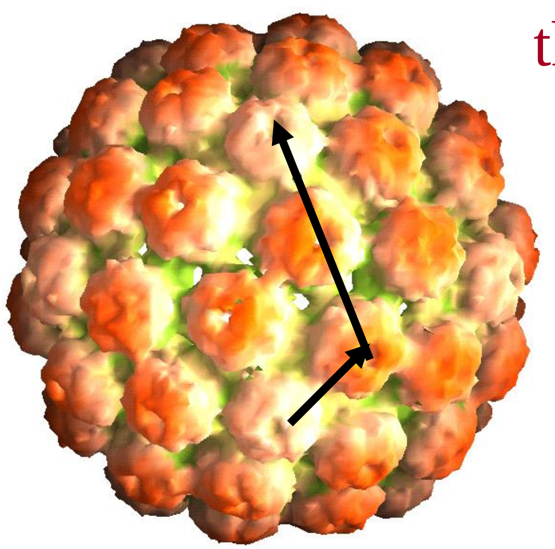
Geodesic house

Biological solutions of the Thomson problem …..



•Flat surface: Triangular lattice tiles the plane

•Ordering on a sphere: ‘geometric frustration’ forces at least twelve 5-fold disclinations into the ground state…

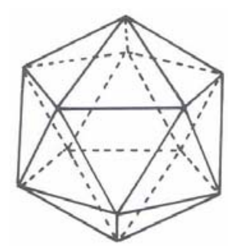


Simian virus SV40

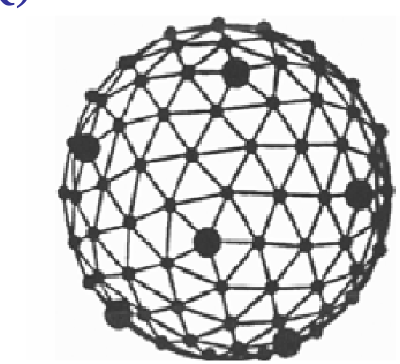
(P, Q) = (1,2)

-Icosadeltahedral solutions of the Thomson problem for *intermediate* particle numbers are exhibited by the capsid shells of *virus* structures for ‘magic numbers’ of protein subunits indexed by pairs of integers (P,Q)

D. Caspar & A. Klug,
Cold Spring Harbor Symp.
on Quant. Biology **27, 1 (1962)**



$(P,Q)=(1,0)$

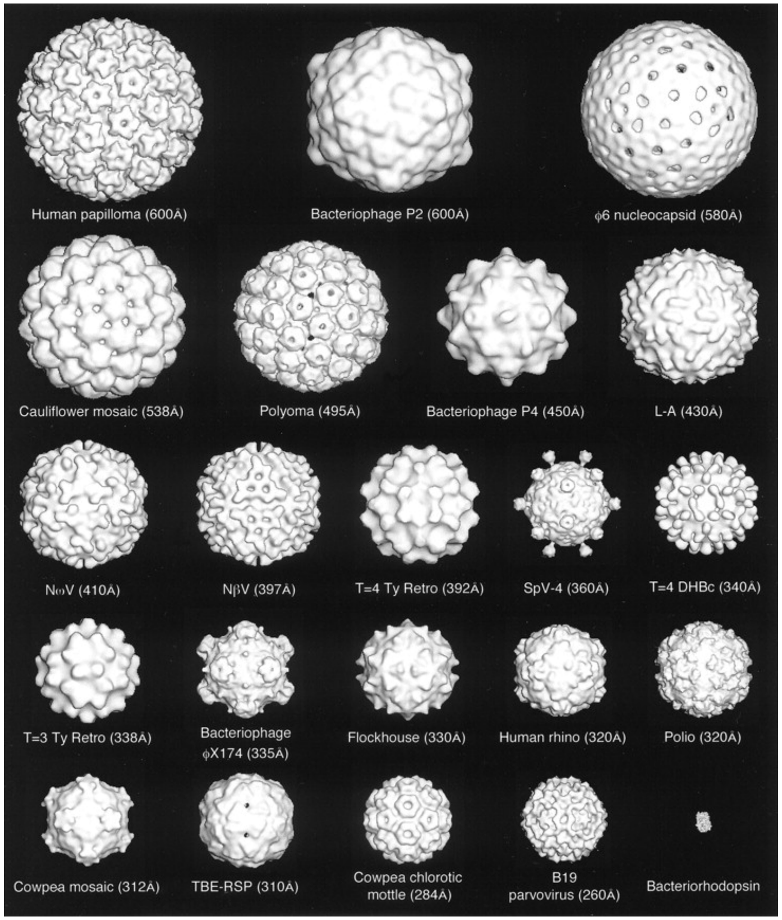


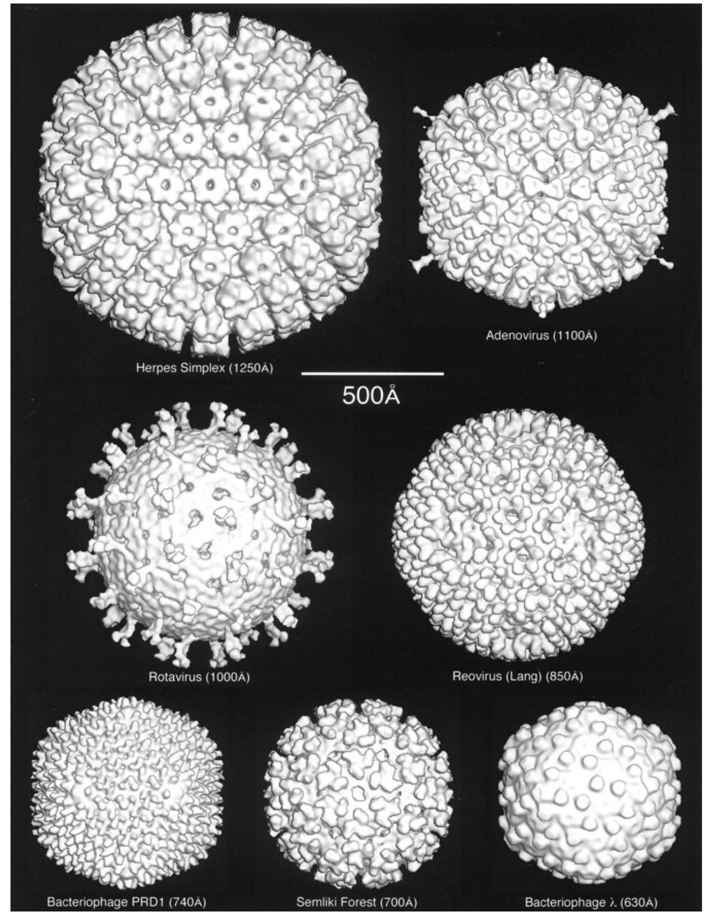
$(P,Q)=(3,1)$

$$N = \textit{particle number} = 10(P^2+Q^2+PQ)+2$$

A gallery of viruses…

T.S. Baker et al., Microbiol. Mol. Biol. Rev. **63**, 862 (1999)

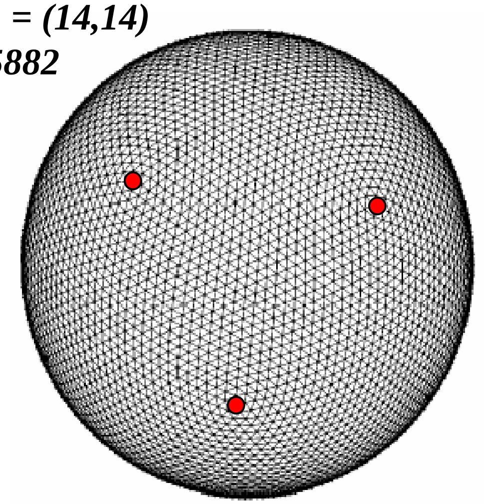


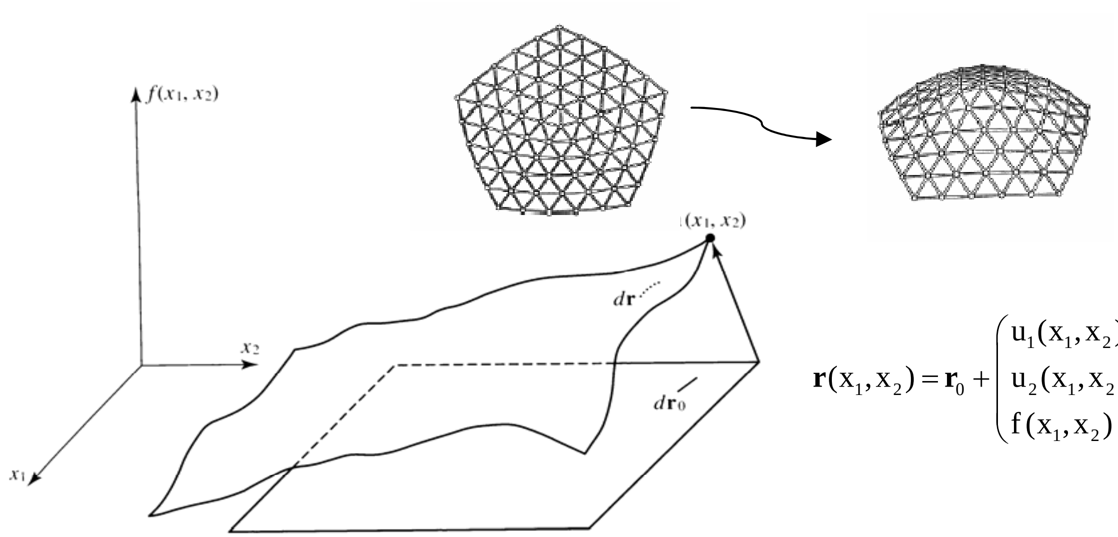


◆ The small viruses are round and large ones are facetted…

Strain relaxation via disclination buckling in large viruses…

(P,Q) = (14,14)
N = 5882

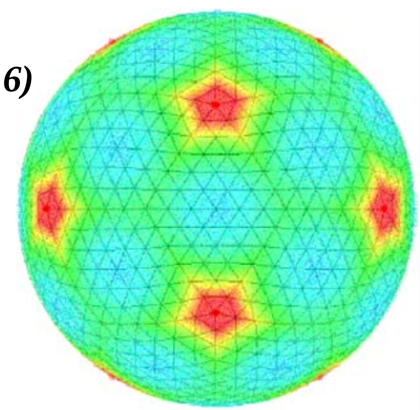




$$\mathbf{r}(x_1,x_2)=\mathbf{r}_0+\begin{pmatrix}u_1(x_1,x_2)\\ u_2(x_1,x_2)\\ f(x_1,x_2)\end{pmatrix}$$

(P,Q) = (6,6)
N = 1082

Strain energy



M. Bowick, A. Cacciuto, A. Travessett and drn, Phys. Rev. Lett. **89**, 185502 (2002)

Solve for ground state via a 'tethered surface' floating mesh triangulation …..

S. Seung and drn, Phys.Rev. A38, 1055 (1988)

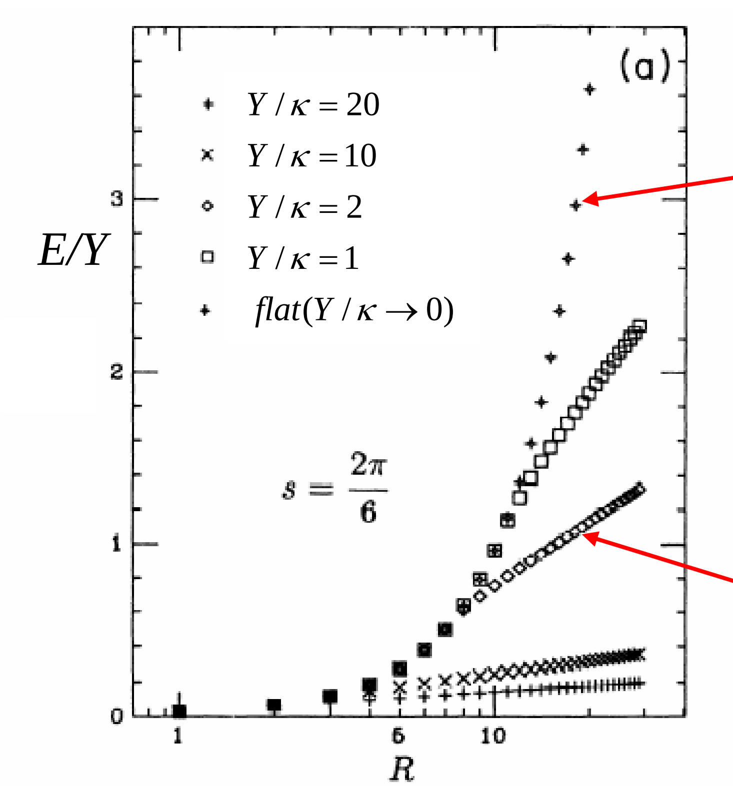
Disclination buckling transition

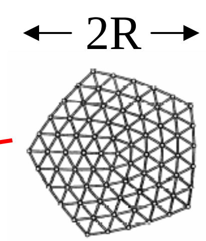
To solve von Karman equations must, in an Eulerian representation, minimze the ***nonlinear*** *elastic energy:*

$$E = \frac{1}{2}\int d^2x[\kappa(\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})]$$

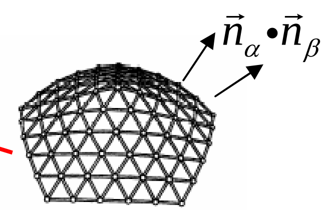
where,

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$





E ~ Y R^2*, R < R*$_b$



E ~ κ ln (R/R$_b$*), R> R*$_b$

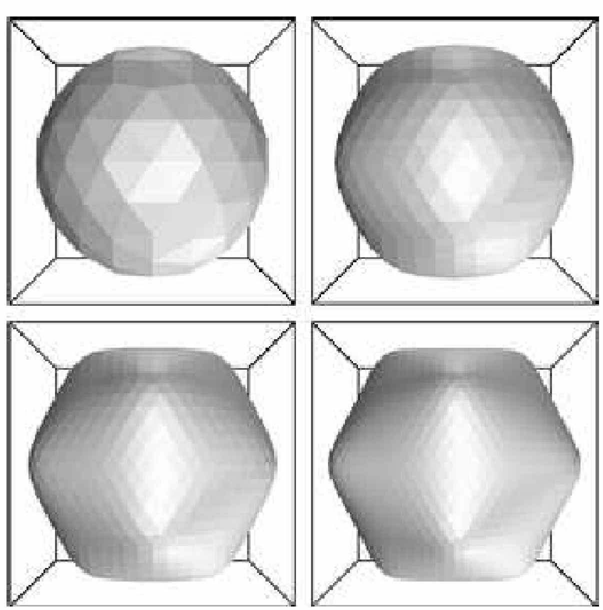
Disclinations buckle above a critical radius R$_b$ *such that*

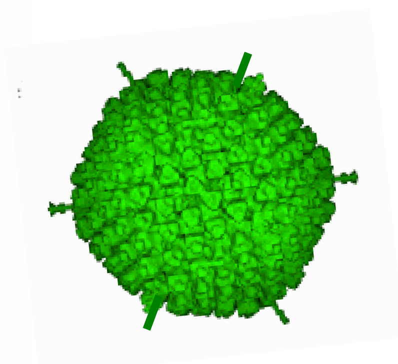
$YR_b^2/\kappa = 154\ldots.$

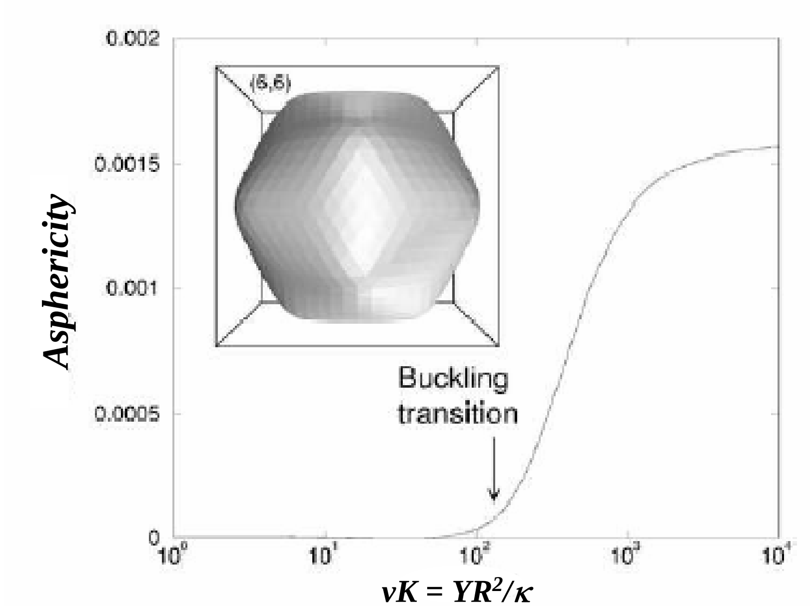
But what about 12 *interacting* disclinations on a sphere?

Solution of the Foppl-von Karman equations for viruses (arbitrary vK!)

- *Shape depends only on the 'von-Karman number'* $vK = YR^2/\kappa$
  - κ = *bending rigidity of shell*
  - Y = *Young's modulus of shell*
  - R = *mean virus radius*
- $(vK)_c = 154$ *in flat space….*

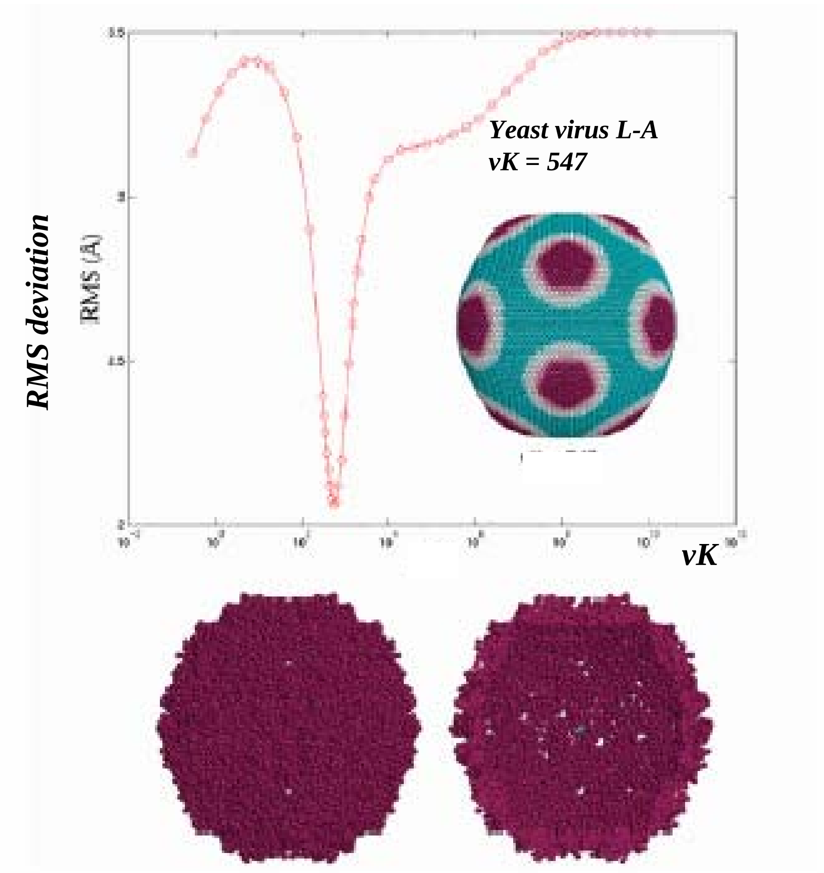


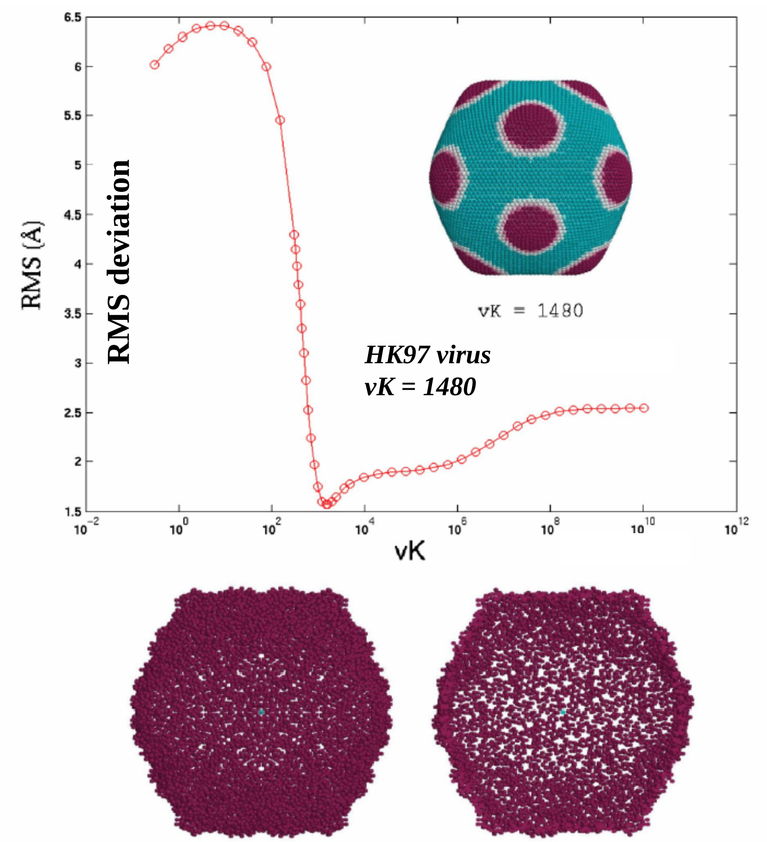




J. Lidmar, L. Mirny and drn, Phys. Rev. E**68**, 051910 (2003)

Fits to specific viruses





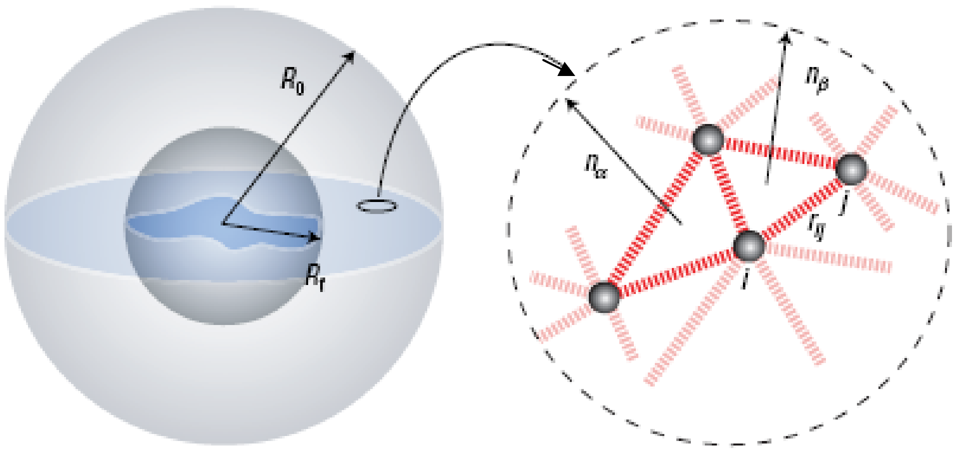
$$vK = YR^2 / \kappa$$

The precursor, capsid, or "prohead", of HK97 is more spherical, in constrast to the larger, more facted mature form shown here.

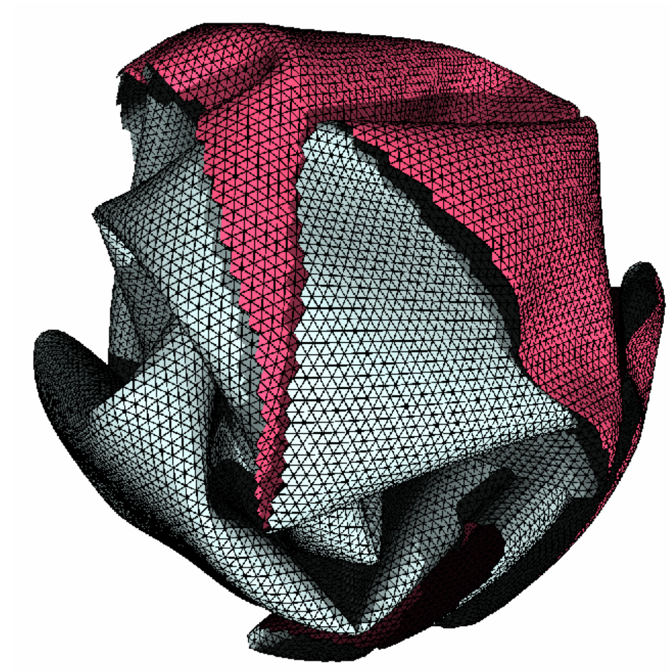
Evidence for a buckling transition ….

Large vK: Computer Simulations of Crumpling

G. A. Vliegennthart and G. Gompper, Nature Materials (in press)



A flat self-avoiding disk is crushed inside a hollow sphere from initial radius R_0 to a final radius R_f by application of an inward radial force F….



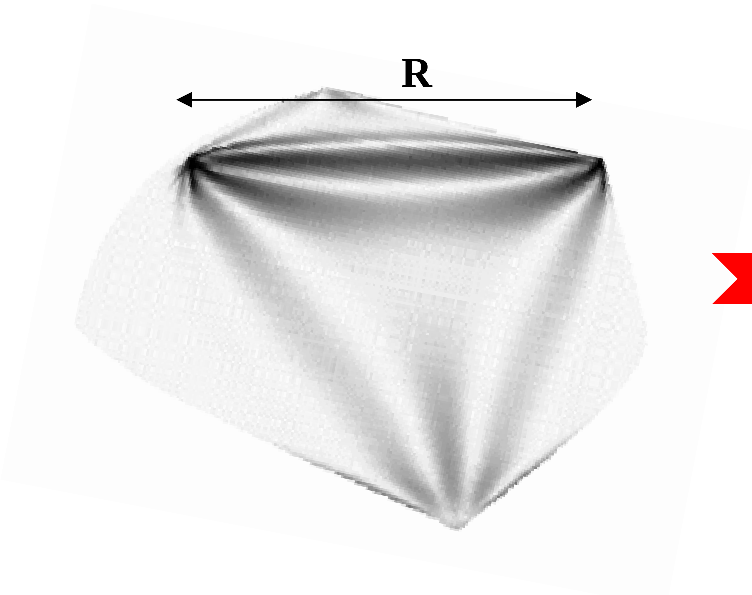
Crushed triangular lattice, N = 61816 particles…

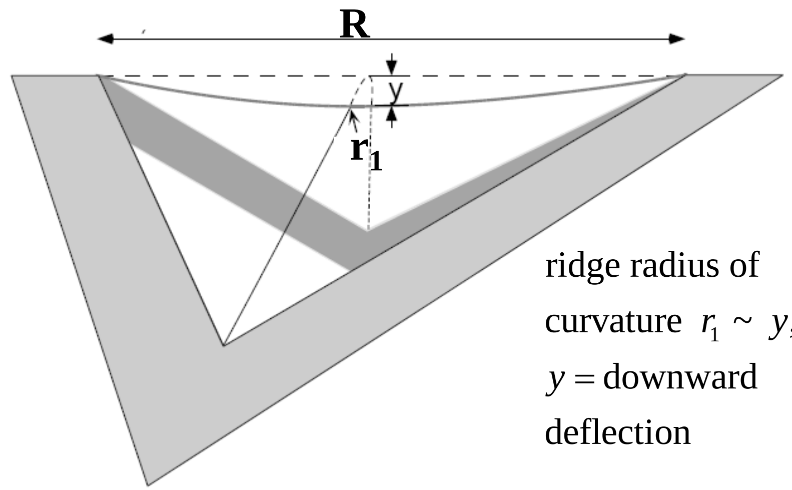
How does the energy of the creases depend on size?

What is the effect of self-avoidance?

Two interacting disclinations with separation L

[A. Lobkovsky and T. Witten, see Physica A**313**, 83 (2002)]





ridge radius of curvature $r_1 \sim y$, y = downward deflection

$$E_{tot} \approx \kappa \int da \left(\frac{1}{r_1} + \cancel{\frac{1}{r_2}} \right)^2 + Y \int da (\varepsilon)^2; \quad r_2 >> r_1 \sim y, \quad \varepsilon \sim (y/R)^2, \quad \int da = yR$$

~ 0

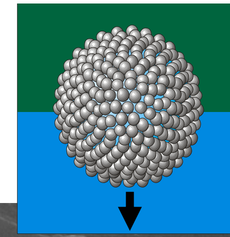
$$E_{tot}(y) \approx \kappa \frac{R}{y} + Y \frac{y^5}{R^3} \quad \rightarrow \quad y^* \approx \left(\frac{\kappa}{Y} \right)^{1/6} R^{2/3}, \; E_{tot}(y^*) \approx \kappa \left(\frac{Y}{\kappa} \right)^{1/6} R^{1/3}$$

$$y \sim R/(vK)^{1/6}, \quad E_{tot}(y) \sim \kappa (vK)^{1/6}, \quad vK = YR^2/\kappa \gg 1$$

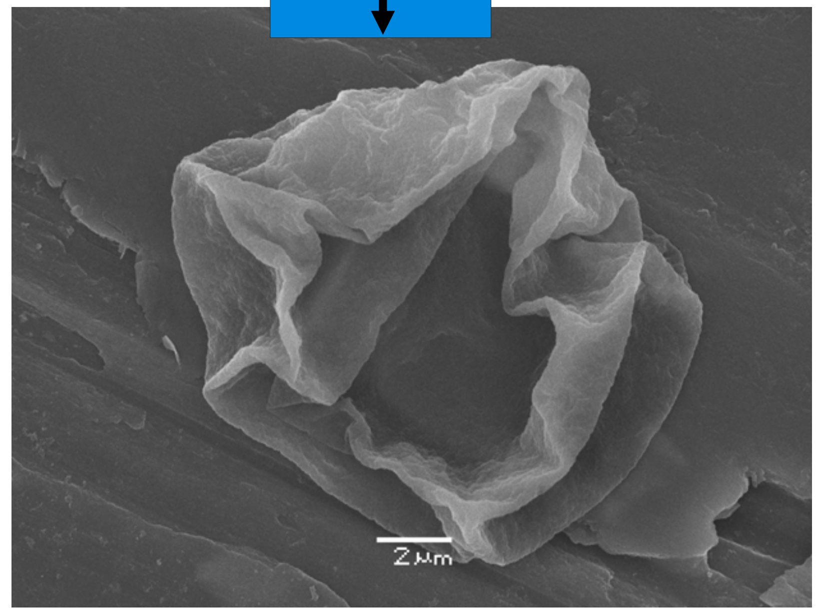
YR^2/κ = vK = Foppl-von Karman number is a kind of "Reynolds number" for crumpling…

Osmotic Crushing of Amorphous Shells

Experiments by Andreas Bausch, Tech. Univ. of Munich



$vK \approx 10^7$



- Amorphous colloidal assemblies formed on water droplets in oil. The exterior oil is replaced by water and the resulting shell crushed osmotically (bottom) to produce a crumpled object with vK = 10^7

- In the presence of thermal fluctuations, the bending rigidity and Young's modulus become strongly dependent on length scales

$$\kappa_R(l) \approx \kappa (l / l_{th})^{\eta}, \qquad Y_R(l) \approx Y (l / l_{th})^{-\eta_u}$$

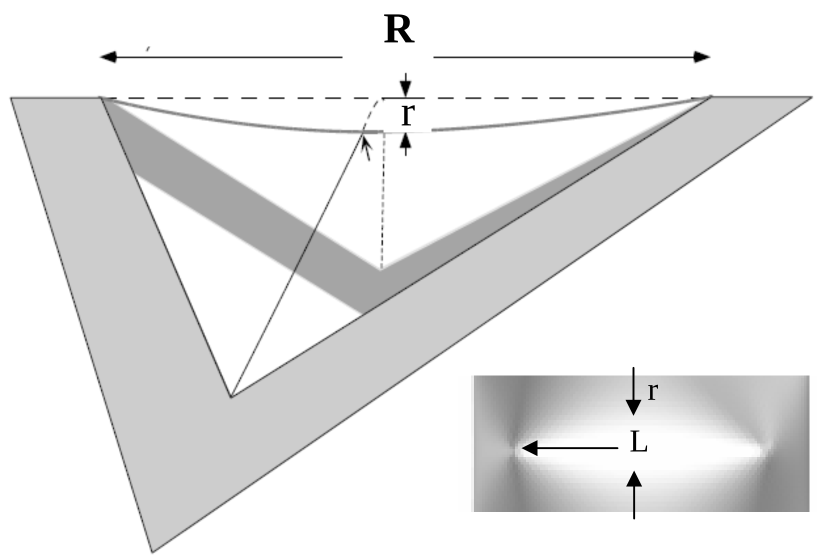
$$\eta \approx 0.75 - 0.80 \qquad \eta_u \approx 0.36 - 0.50$$

$$l_{th} = \sqrt{4\pi^3 \kappa^2 / (k_B T Y)} \qquad l_{th} \approx 40nm$$

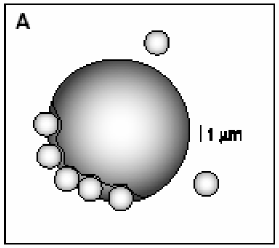
$$r \sim R^{(4+\eta_u)/(6-\eta)} \sim R^{0.76},$$

$$E \sim R^{(2+3\eta-\eta_u+\eta\eta_u)/(6-\eta)} \sim R^{0.74}$$

(without thermal fluctuations, $r \sim R^{2/3}, E \sim R^{1/3}$)

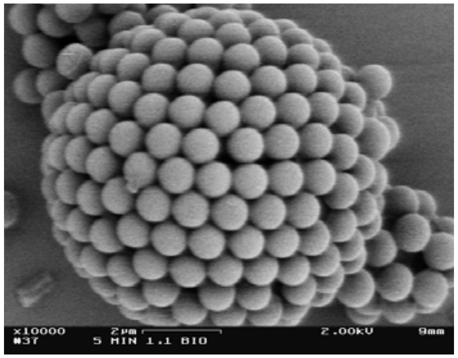


Spherical crystallography of 'colloidosomes' (see also "Pickering emulsions")



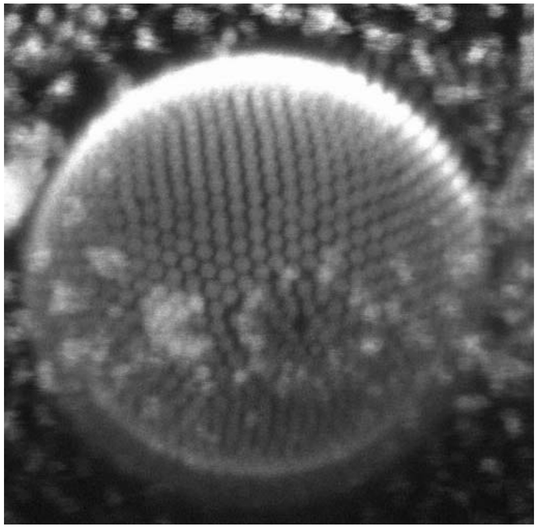
- ✱ Adsorb, say, latex spheres onto lipid bilayer vesicles or water droplets
- ✱ Useful for encapsulation of flavors and fragrances, drug delivery

  [H. Aranda-Espinoza e.t al. Science **285**, 394 (1999)]
- ✱Strength of colloidal 'armor plating' influenced by defects in shell….
- ✱ For water droplets, surface tension prevents buckling….



"Colloidosome" = colloids of radius ***a*** coating water droplet (radius ***R***) -- Weitz Laboratory

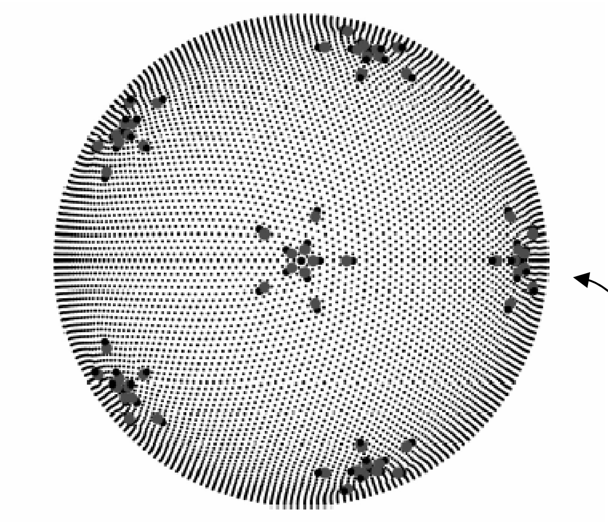
Ordering on a sphere ➔ a minimum of 12 5-fold disclinations, as in soccer balls and fullerenes -- what happens for $R/a >> 1$?

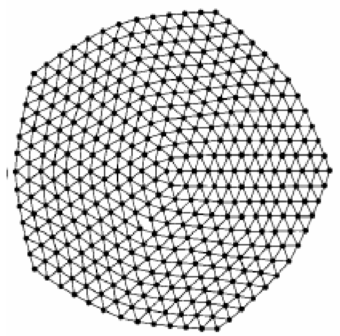


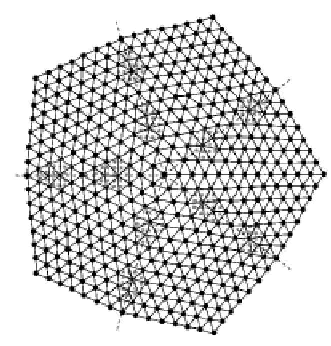
Confocal image: P. Lipowsky, & A. Bausch

Grain boundary instabilities

✱If droplet surface tension enforces spherical shape, disclination buckling is **replaced** by an instability towards grain boundaries….







✱can insert the required dislocations into the ground state by hand….

M. J. W. Dodgson and M. A. Moore, Phys. Rev. B**55**, 3816 (1997)
Perez-Garrido, M.J.W. Dodgson and M. A. Moore, Phys. Rev.B**56**, 3640 (1997).
Alar Toomre (unpublished)
A. Perez-Garrido and M. A. Moore, Phys.Rev. B**60**, 15628 (1998)

✱or construct a continuum elastic theory of topological defects on the sphere…:

M. J. Bowick, A. Travesset and drn, Phys. Rev. B**62**, 8738 (2000)

Continuum elastic theory of defects on spheres

- **Finding the ground state of ~26,000 particles on a sphere is replaced by minimizing the energy of only ~ 250 interacting disclinations, representing points of local 5- and 7-fold symmetry.**

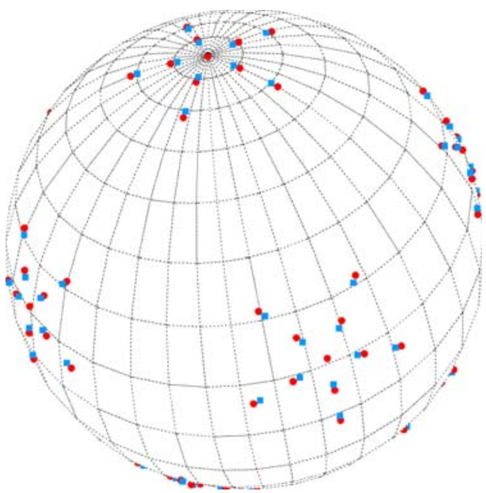
Dislocation = 5-7 pair =

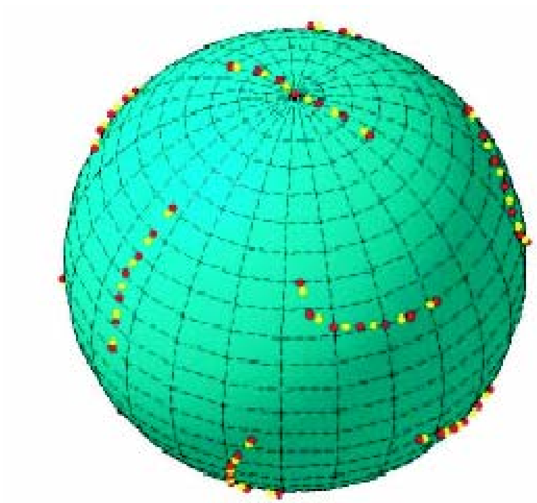
Grain boundary = 5-7 5-7 5-7 …
= …

$$E(\mathrm{Y}) = \frac{\pi \mathrm{Y}}{36} R^2 \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j \, \chi(\theta^i, \phi^i; \theta^j, \phi^j) + N E_{core}$$

$$\chi(\theta^a, \phi^a; \theta^b, \phi^b) = R^2 \left(1 + \int_0^{(1-\cos\beta)/2} dz \frac{\ln z}{1-z} \right)$$

[χ Solves biharmonic eq. on a sphere]





Continuum elastic theory of defects on spheres

⬣ **Finding the ground state of ~26,000 particles on a sphere is replaced by minimizing the energy of only ~ 250 interacting disclinations, representing points of local 5- and 7-fold symmetry.**

Dislocation = 5-7 pair =

Grain boundary = 5-7 5-7 5-7 …
= …

$$E(\Upsilon) = \frac{\pi \Upsilon}{36} R^2 \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j \, \chi(\theta^i, \phi^i; \theta^j, \phi^j) + N E_{core}$$

$$\chi(\theta^a, \phi^a; \theta^b, \phi^b) = R^2 \left(1 + \int_0^{(1-\cos\beta)/2} dz \frac{\ln z}{1-z} \right)$$

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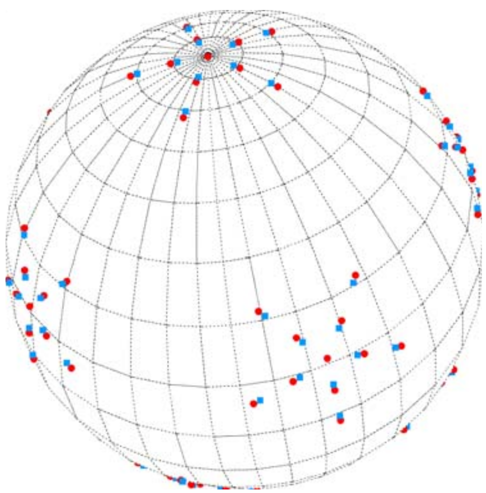
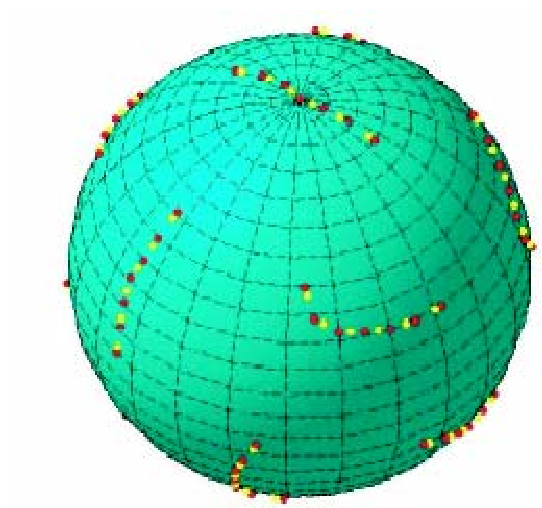
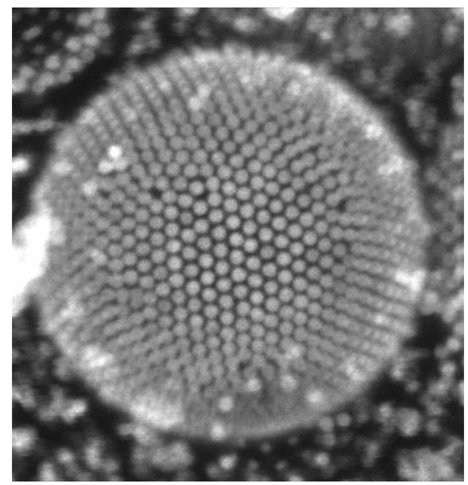


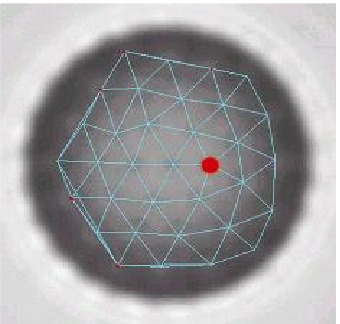


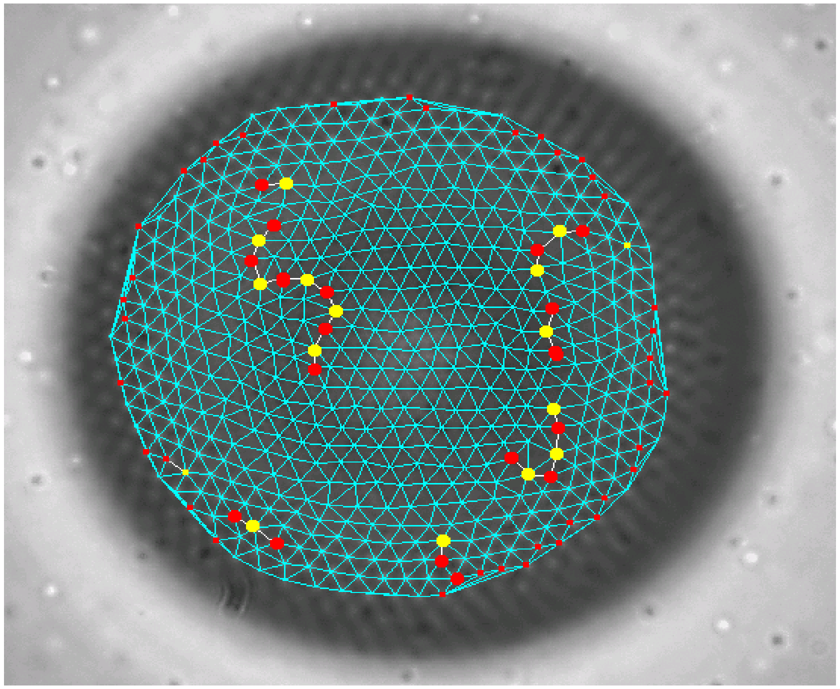


What happens for real ***colloidosomes****?*
(silanized silica beads)

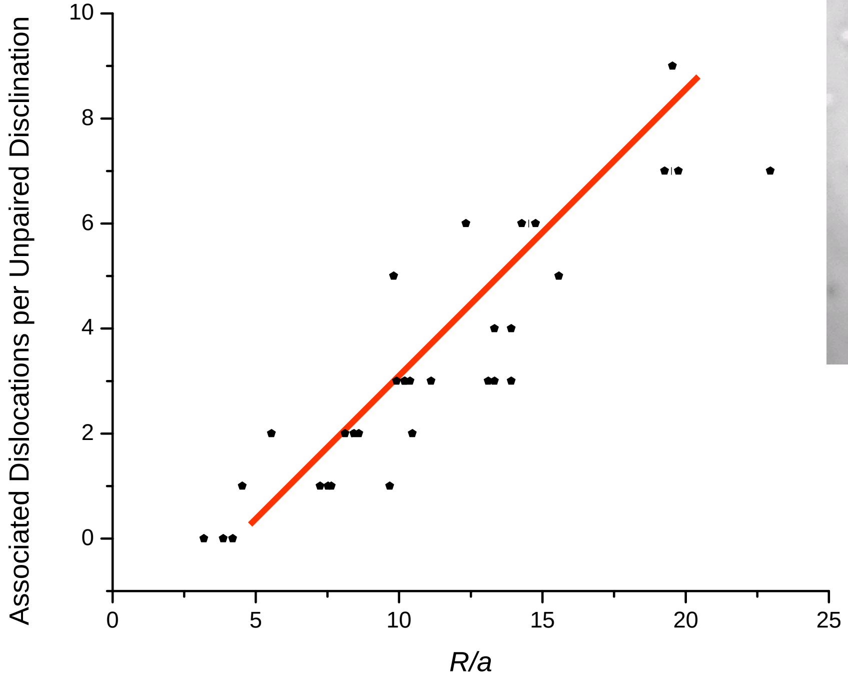
R/a >> 1: Grain Boundaries in the Ground State!!

Bausch et al. Science 299, 1716 (2003)
polystrene beads on water….



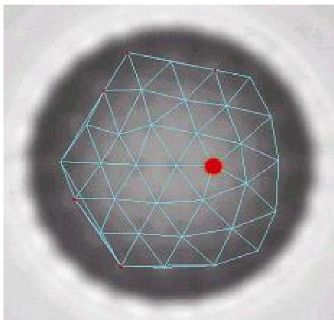


Defect Screening as a Function of *R/a*

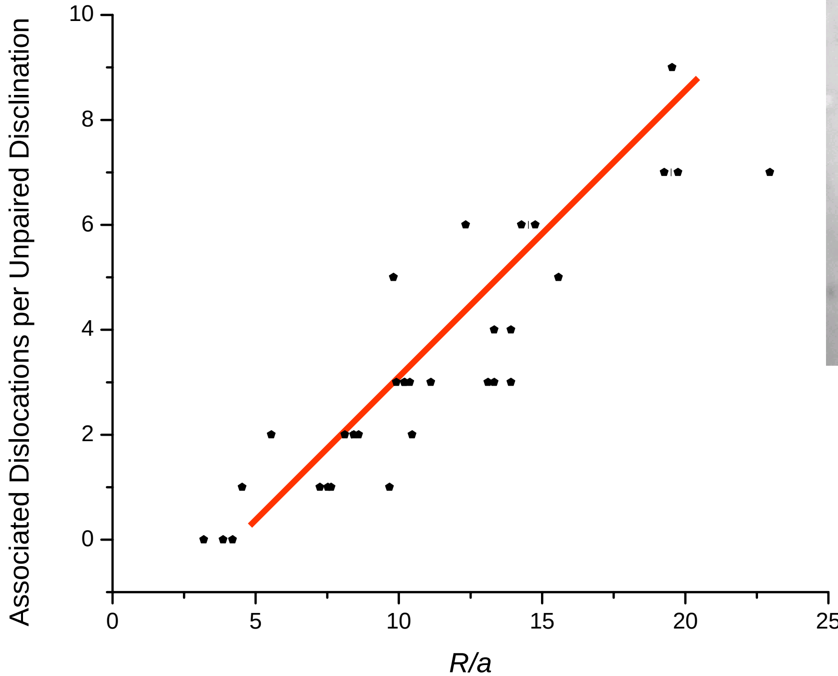


$(R/a)_c \approx 5$, determined by dislocation core energy

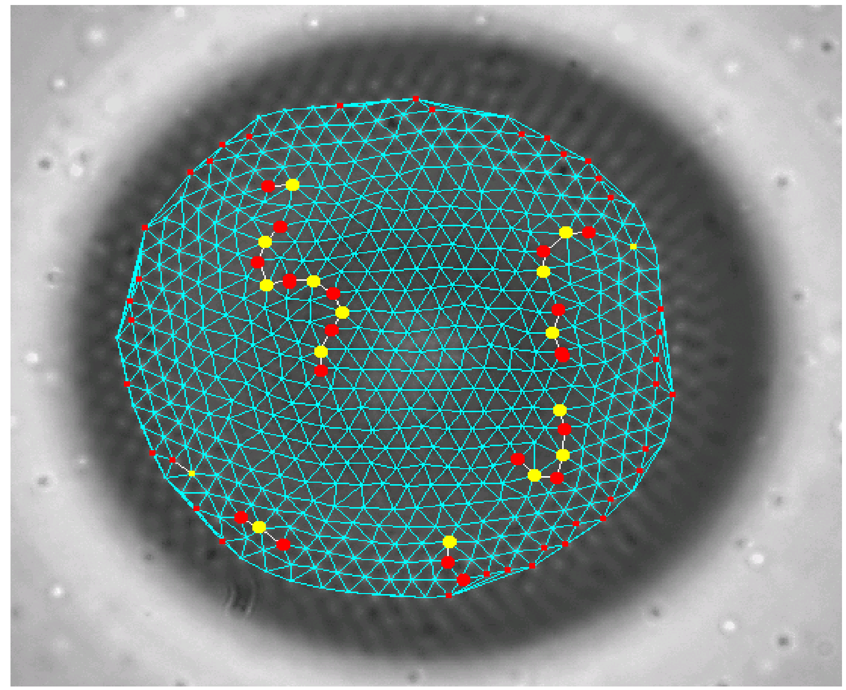
R/a >> 1: Grain Boundaries in the Ground State!!



Defect Screening as a Function of *R/a*



Bausch et al. Science 299, 1716 (2003)
polystrene beads on water….

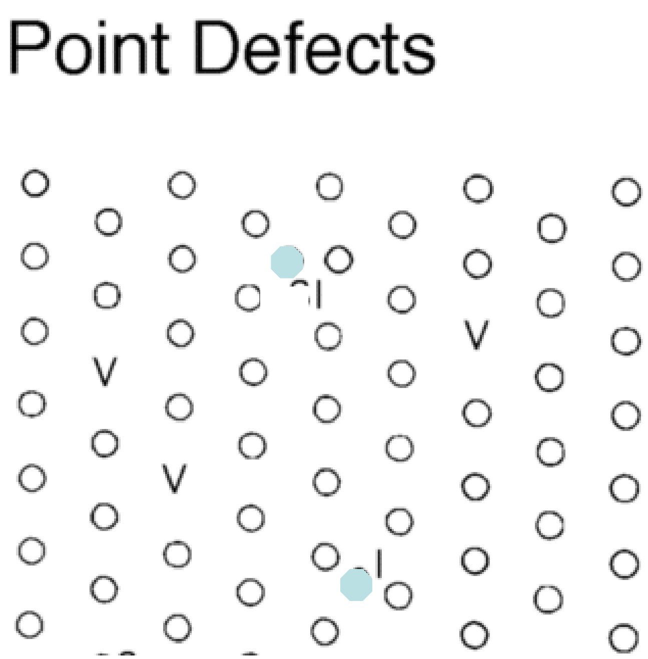


$$Slope = \frac{\pi}{3}\left[\sqrt{11} - 5\cos^{-1}(5/6)\right] \approx 0.41$$

$(R/a)_c \approx 5$, determined by dislocation core energy

Vacancies and interstitials on curved surfaces

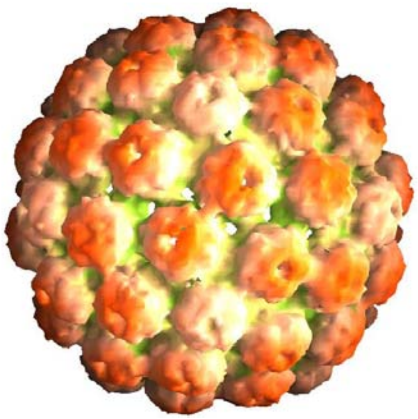
interstitial movie, courtesy of Mark Bowick, Cris Cecka and Alan Middleton; see also, http://www.phy.syr.edu/condensedmatter/thomson/



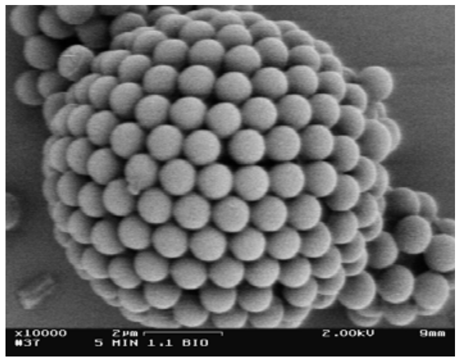
V = vacancies
I = interstitials

The Thomson Problem and Spherical Crystallography

1904: J. J. Thomson asks how particles pack on a sphere – relevant to viruses, colloid-coated droplets, and multielectron bubbles in helium



Simian virus SV40



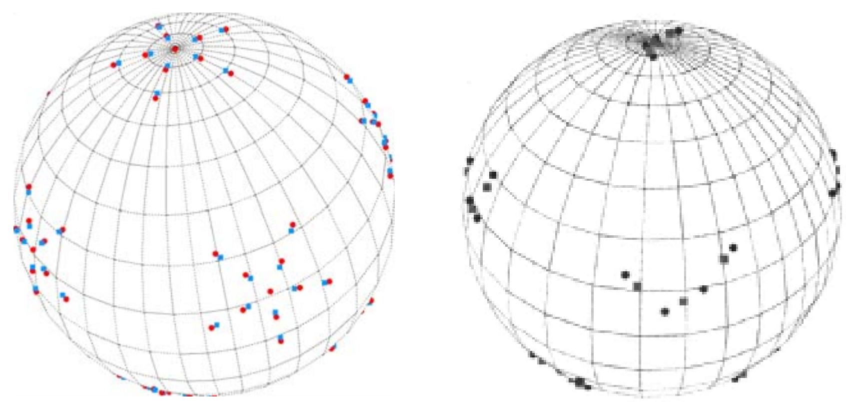
“Colloidosome” = colloids of radius ***a*** coating water droplet (radius ***R***) -- Weitz Laboratory

- **Continuum elastic theory (with M. Bowick and A. Travesset) shows that the 5-fold disclinations become unstable to unusual *finite length* grain boundaries (strings of dislocations) for R/a >> 1.**

- **Finding the ground state of ~26,000 particles on a sphere is replaced by minimizing the energy of only ~ 250 interacting disclinations, representing points of local 5- and 7-fold symmetry.**

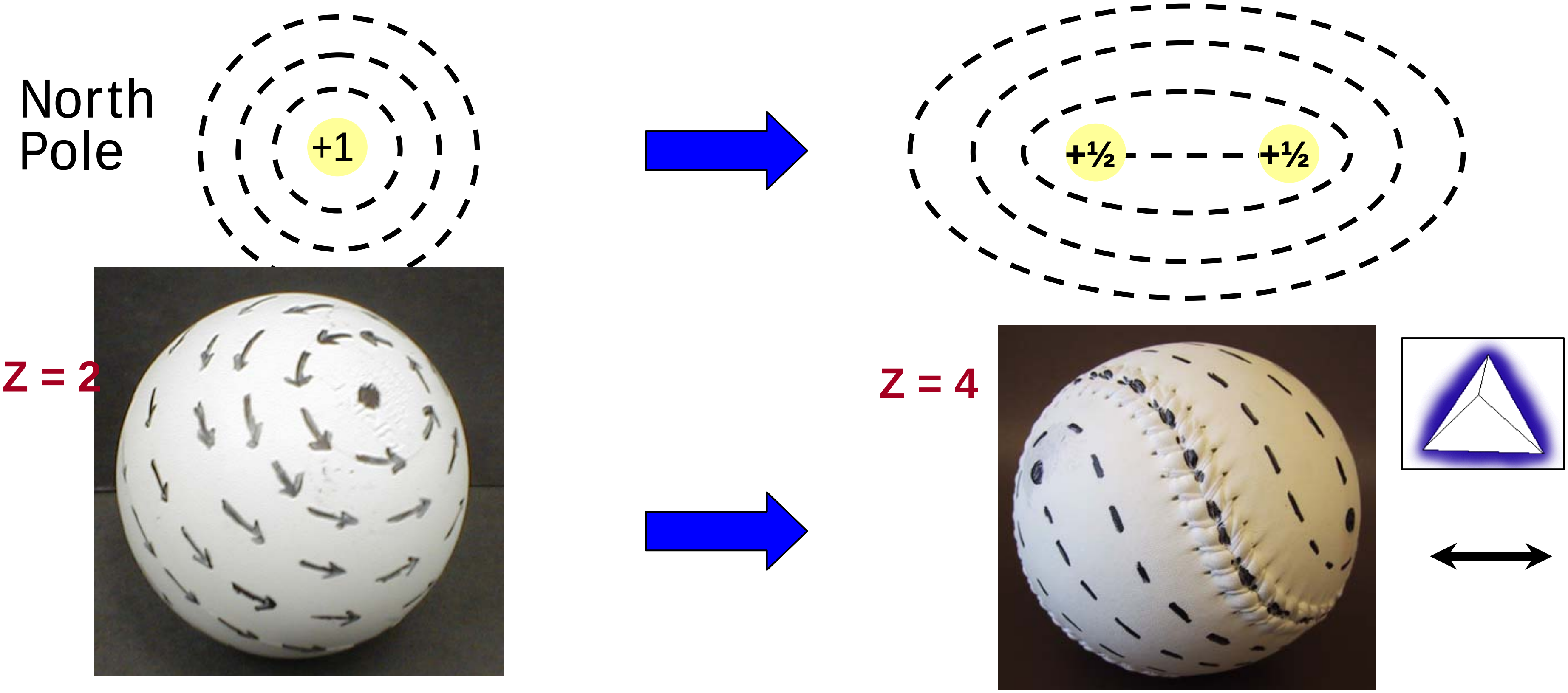
- **Grain boundaries in ground state for R/a > 5-10 have important implications for the mechanical stability and porosity of colloidosomes, proposed as delivery vehicles for drugs, flavors and fragrances.**

Ordering on a sphere ➔ a minimum of 12 5-fold disclinations, as in soccer balls and fullerenes -- what happens for *R/a >> 1* ?



Dislocations (5-7 defect pairs) embedded in spherical ground states

Nematic textures on spheres: toward a tetravalent chemistry of colloids… [drn, NanoLetters, **2**, 1125 (2002)]



$$E_{\text{total}} = 2\pi K \ln\left(R/a\right) + c$$

$$E_{\text{total}} = \pi K \ln\left(R/a\right) + c'$$

Long-range repulsion $\Rightarrow$

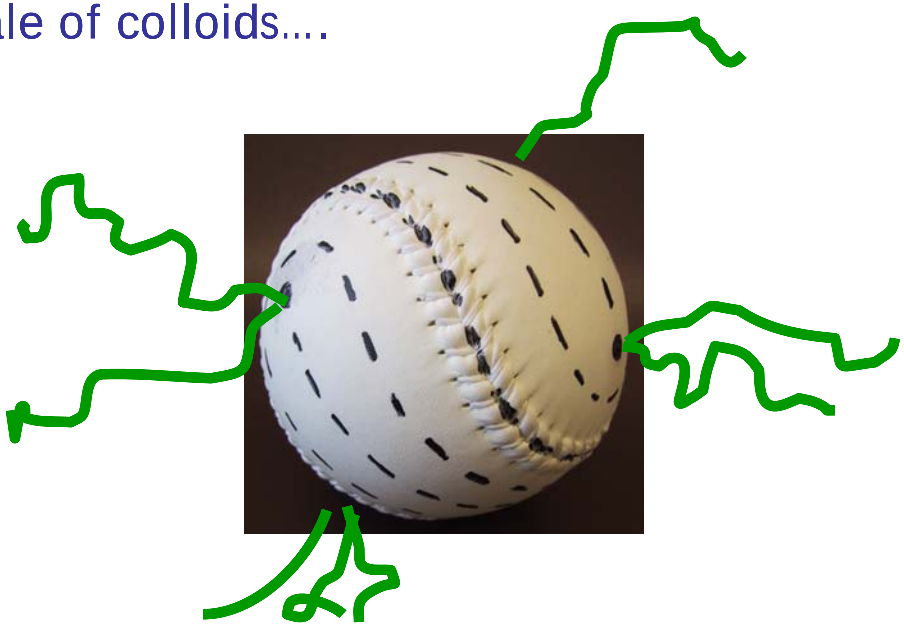
TETRAHEDRAL DEFECT ARRAY

Linking colloids with a valence

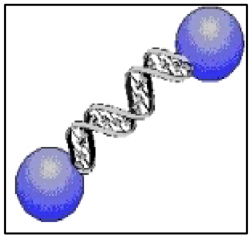
Possible nematogens include gemini lipids, (say, on an oil droplet), triblock copolymers, and CdSe nanocrystals.

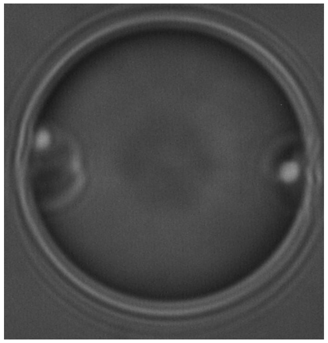
• The four unique “bald spots” on a nematic-coated sphere can be functionalized with DNA linkers…

• may be possible to reproduce the quantum chemistry of **sp^3** hybridization on the micron scale of colloids….



functionalize colloidal particles with , e.g., DNA…



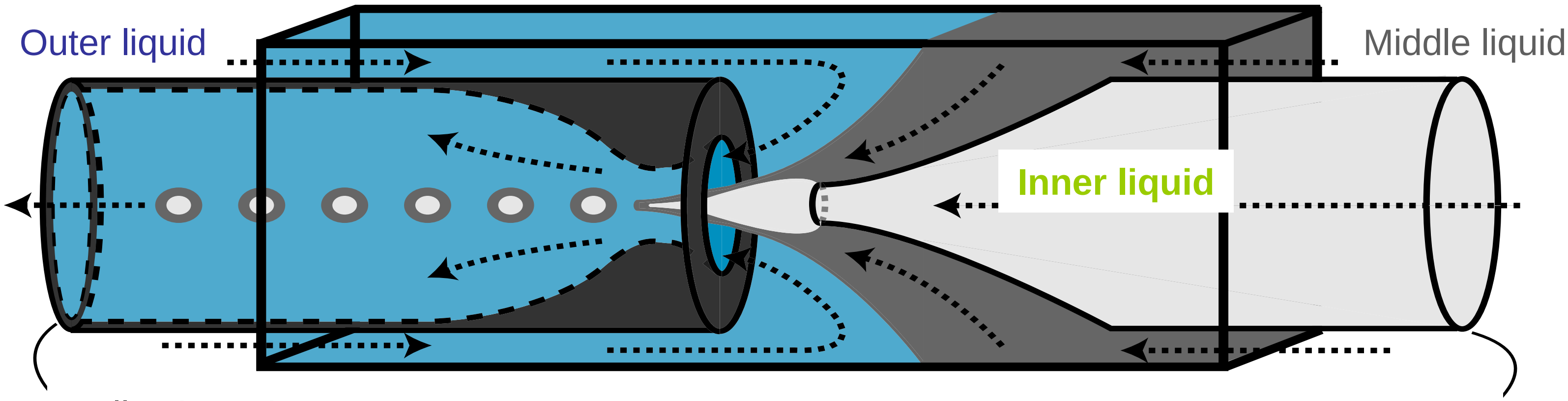


Fluoresent beads on nematic droplet colloidal analogue of sulfer…

Z. Cheng, D. Link and P. Lu, Weitz group

Experiments: Alberto Fernandez-Nieves, Weitz Laboratory

Making nematic shells: double emulsions



Anchoring at inner and outer surface: PLANAR

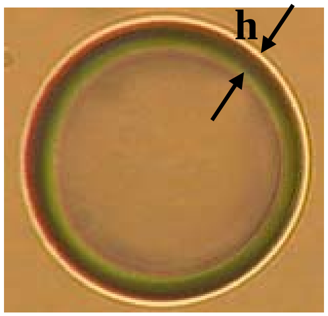
Viscosities: $\eta_{outer} > \eta_{inner}$, η_{middle}

Outer liquid: Glycerol + water + PVA

Middle liquid: Chloroform + LC (5CB)

Inner liquid: **Water + PVA**

Water droplet coated with a nematic shell of thickness h

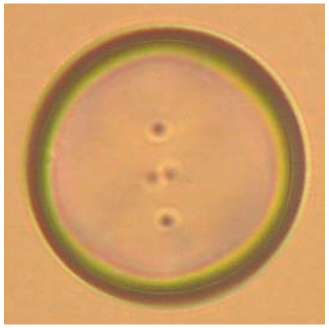


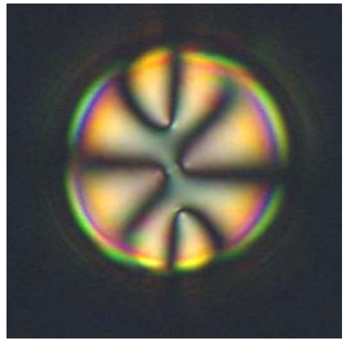
LC+chloroform shell

In fact, valences Z = 4, 3 and 2 are possible….

Z =4

110 micron droplet; shell ~ 6-8 microns

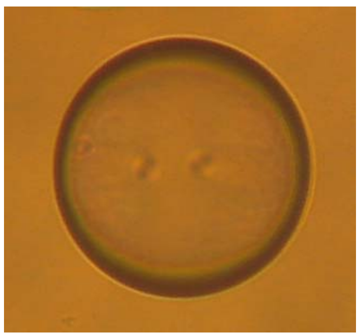


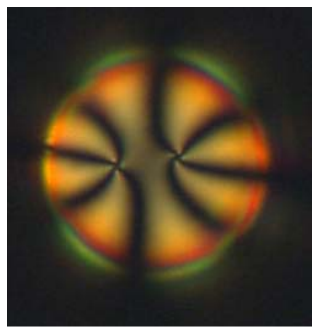


4 defect shell (Inhomogeneous shell thickness distorts perfect tetrahedron…)

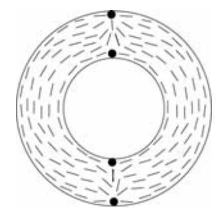
Z = 2

100 micron droplet; shell ~ 6-8 microns





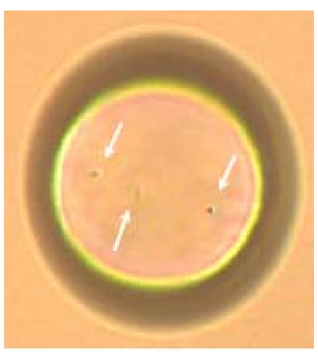
2 defect shell

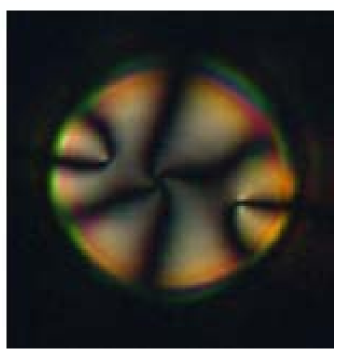


(See M. Kleman and O. D. Lavrentovich)

Z = 3

90 micron droplet; shell ~ 4-7 microns





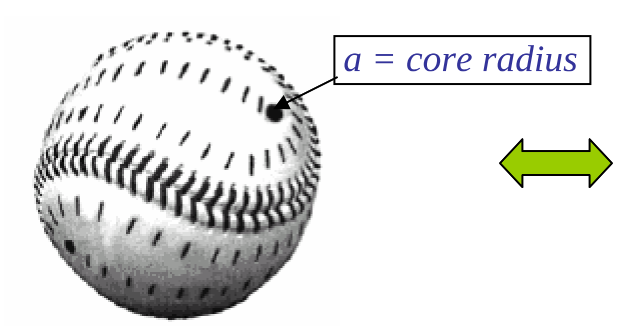
3 defect shell!!

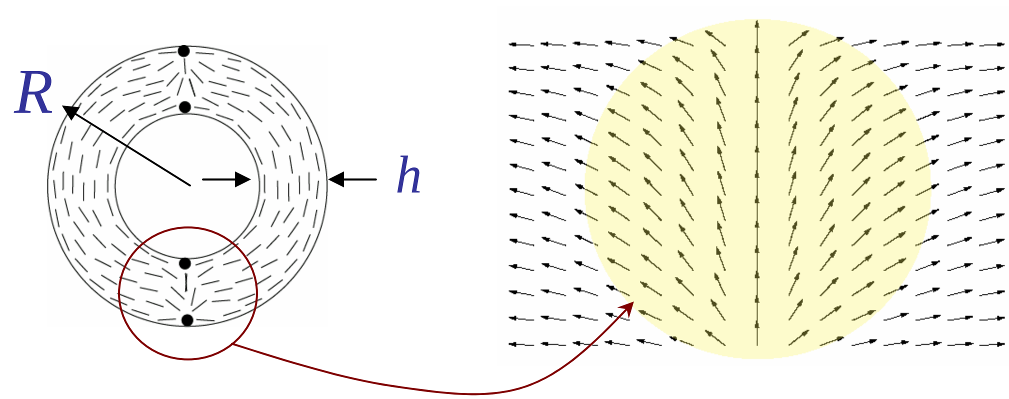
disclinations (thin films) vs. ½ - hedgehogs (thick films)

Assume a homogeneous thickness h and a single Frank constant K…..

Z = 4 shell
(four s = ½ disclinations)

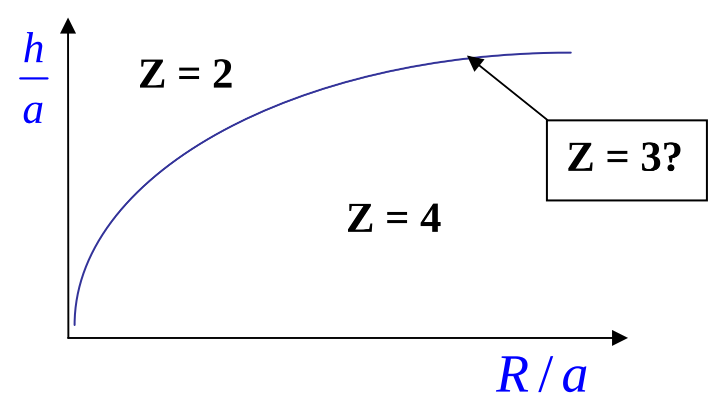
Z = 2 shell
(two pairs of ½-hedgehogs…)





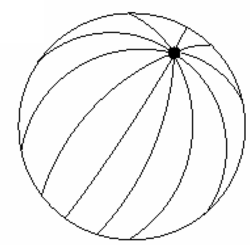
$$E_4 = 4\times(\pi K/4)Kh\ln(R/a)+\ldots \qquad E_2 = 2\times(\pi K)h\ln(R/h)+\ldots$$

- ½-hedgehog defects preferred for $h > h_c$, such that $E_4(h) > E_2(h)$
- this leads to $h_c = const.\times\sqrt{Ra}$



Colloids with nematic shells of thickness h….

Which surface texture dominates?

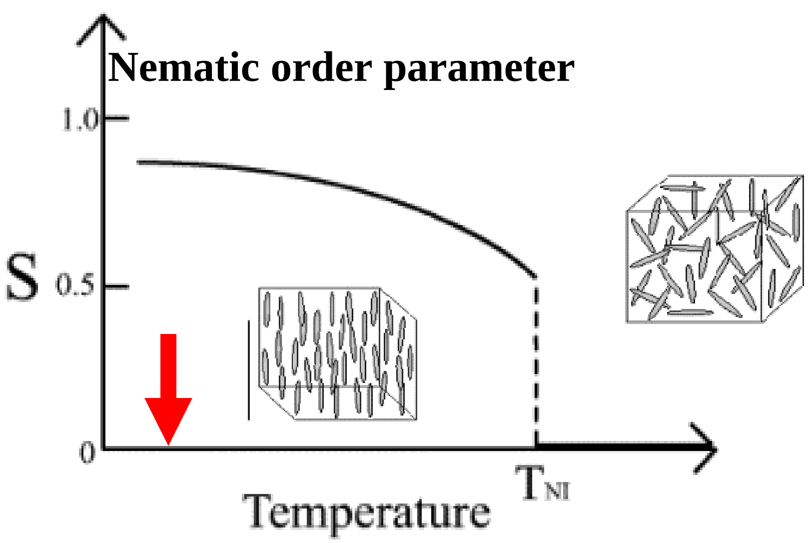


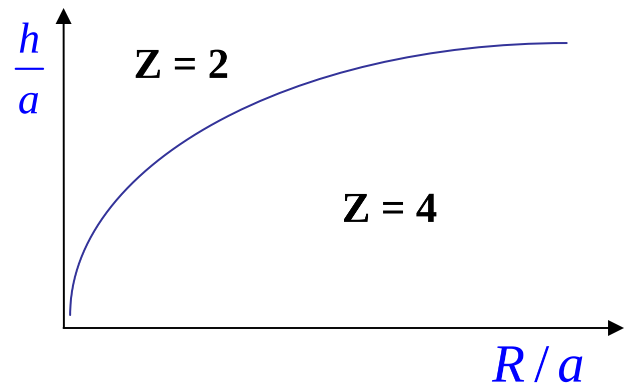
OR

?

**Colloids with Z = 4 are always energetically preferable for thin nematic coatings*

**But colloids with Z = 2 appear above a thickness h* ≈ const. √(R a); R = sphere Radius a = microscopic length*

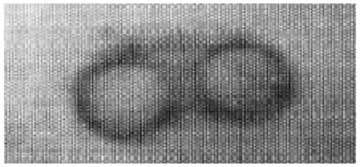


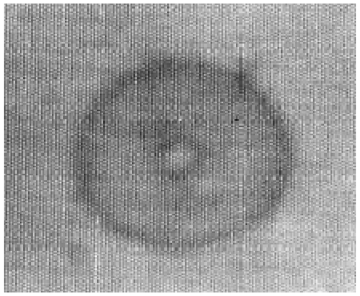


Curvature-induced defect unbinding on the torus

- Consider ***hexatic*** order on a torroidal template
- no ***topological*** necessity for defects in the ground state
- nevertheless, ***Gaussian curvature*** causes a defect-unbinding transition for $M < M_c$, for "fat" torii and moderate vesicle sizes….

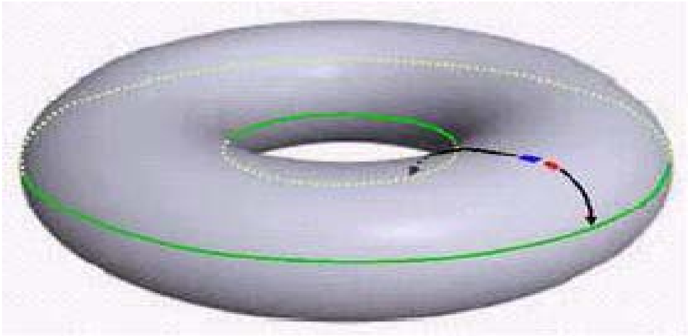
M. Mutz and D. Bensimon, Phys. Rev. A43, 4525 (1991)





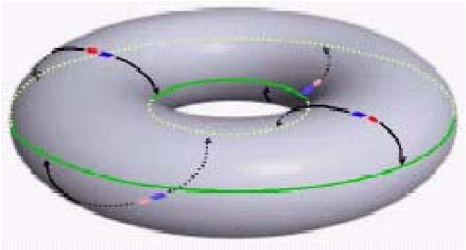
$$M = \frac{8\pi^2}{\sqrt{3}} \frac{R_1 R_2}{a_0^2} =$$ number of microscopic degrees of freedom

$$M_c \approx 4.6r\left(\frac{r+1}{r-1}\right)^{12}, r = R_1/R_2,$$



$$M_c = 10^{10}, r = \sqrt{2},$$

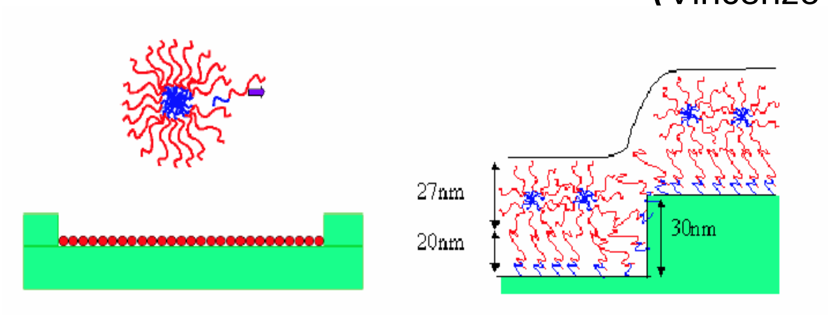
Clifford torus



[M. Bowick, A. Travessett and drn, Phys. Rev.E(in press)]

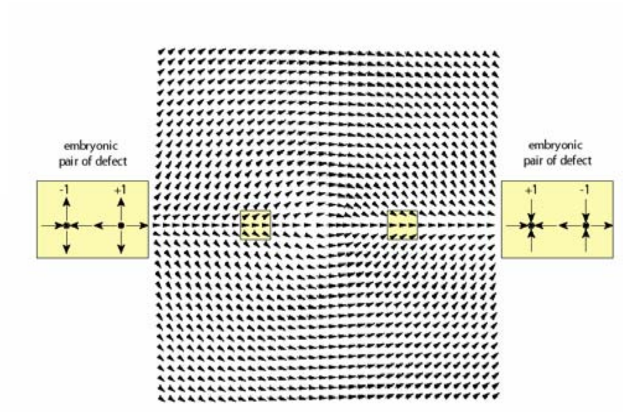
Defect generation and deconfinement on corrugated topographies

(Vincenzo Vitelli and drn)



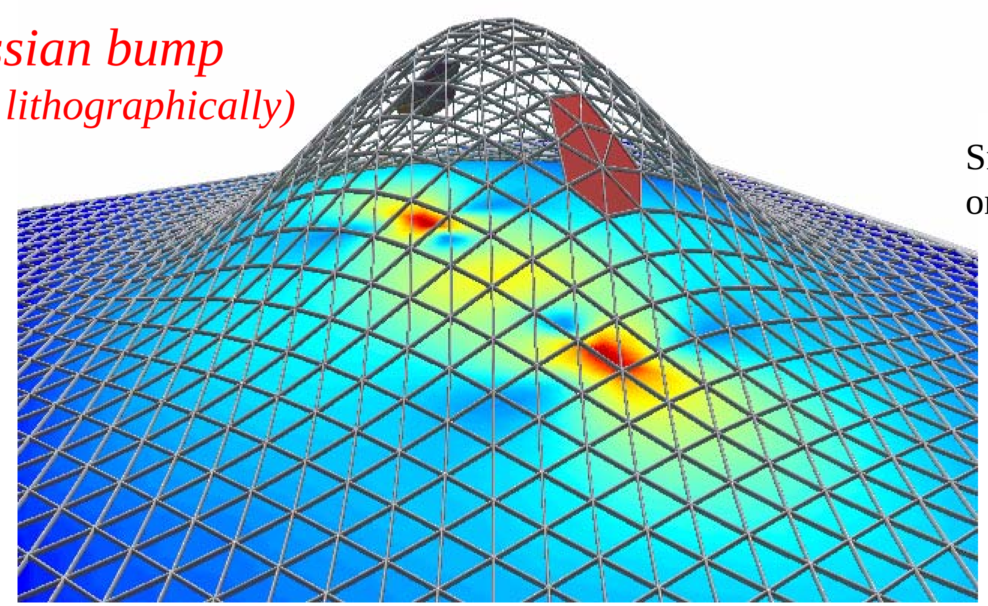
Equilibrium hexatic phases formed by templating large ordered arrays of block copolymer spherical domains on silicon substrates (Segalman et al. Macromolecules, **36**, 3272, 2002)

Dislocations can be generated thermally *OR* by increasing the curvature of the substrate ….



Smooth ground state texture for an XY model on the bump.

A Gaussian bump
(prepare lithographically)



Experiments by Rachel Segalman, Alex Hexamer and Ed Kramer, UCSB