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 virus buckling

Grain boundary scars and colloids on water droplets

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

--Experiments on colloids on water droplets (A. Bausch et. al.)

--Grain boundaries can terminate inside curved media….

Liquid crystal textures on curved surfaces

--Hexatics draped over a Gaussian bump

--Curvature-induced defect unbinding on a torus

--Colloids with a valence

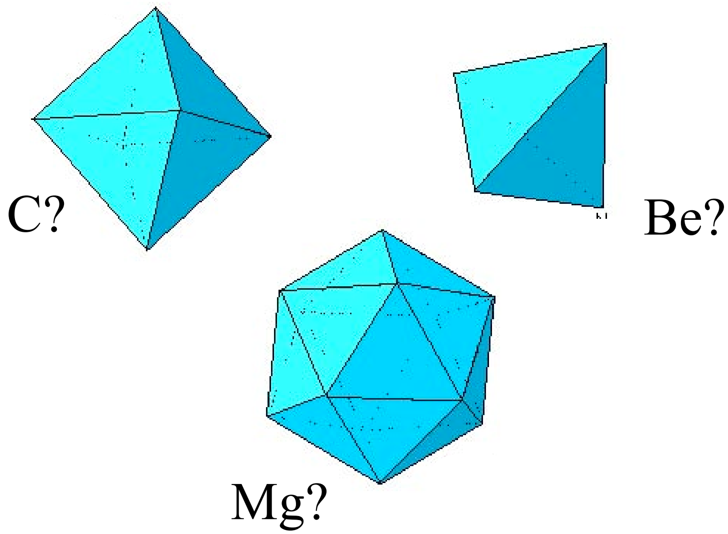
M. Rubinstein
S. Sachdev
S. Seung

J. Lidmar
L. Mirny

M. Bowick
A. Travesset
V. Vitelli

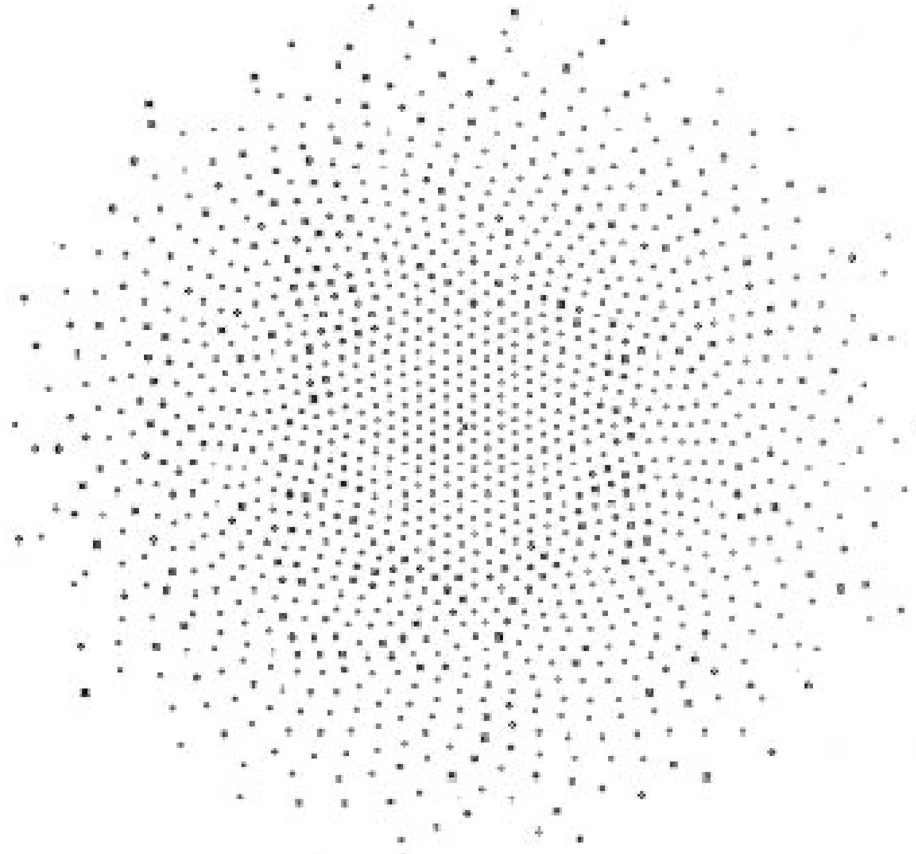
The Thomson Problem

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



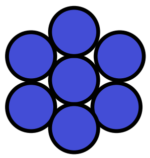
"The analytical and geometrical difficulties …of corpuscles…arranged in shells are much greater… and I have not as yet succeeded in getting a general solution." J.J. Thomson

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



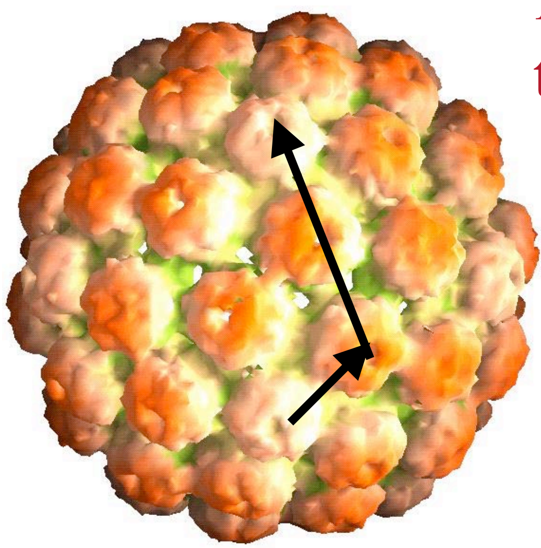
nucleation and growth on a sphere: R/a = 10; 1314 particles
M. Rubinstein and drn $(N_5 - N_7 = 12)$

Repulsive Particles on a Curved Surface: Structure and Defects



- Flat surface: Triangular lattice tiles the plane

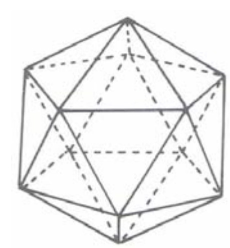
- Ordering on a sphere: ‘geometric frustration’ forces at least twelve 5-fold disclinations into the ground state…

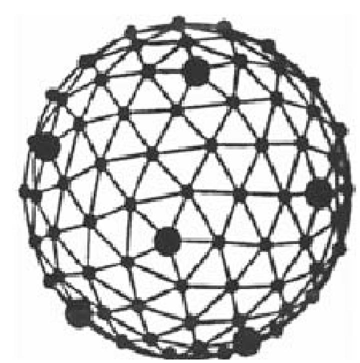


Simian virus SV40

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

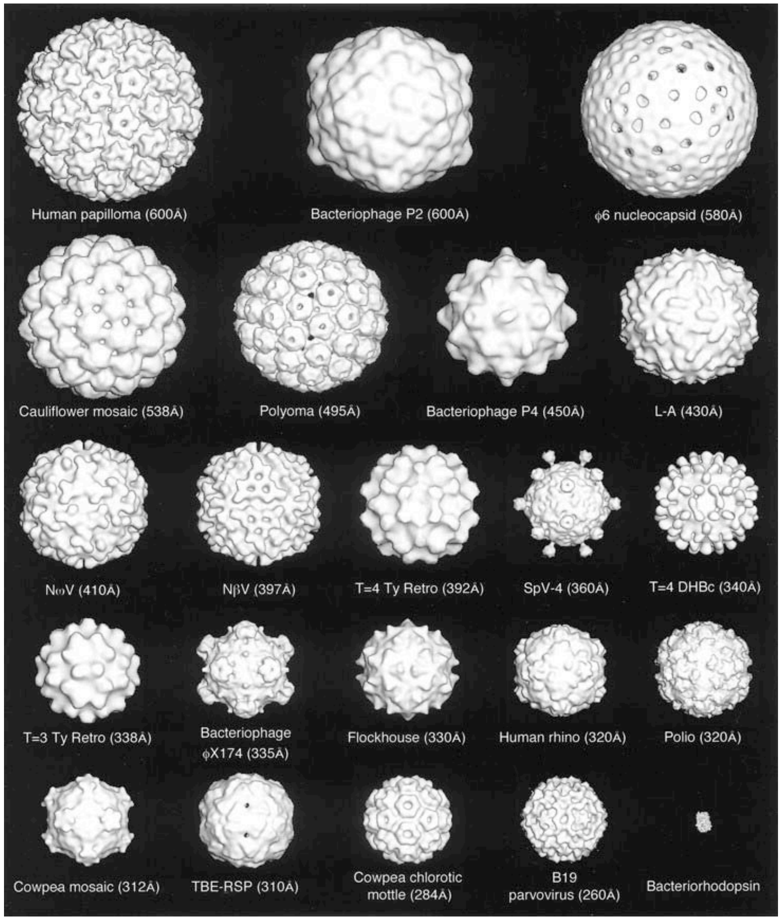
D. Caspar & A. Klug,
Cold Spring Harbor Symp.
on Quant. Biology **27, 1 (1962)**

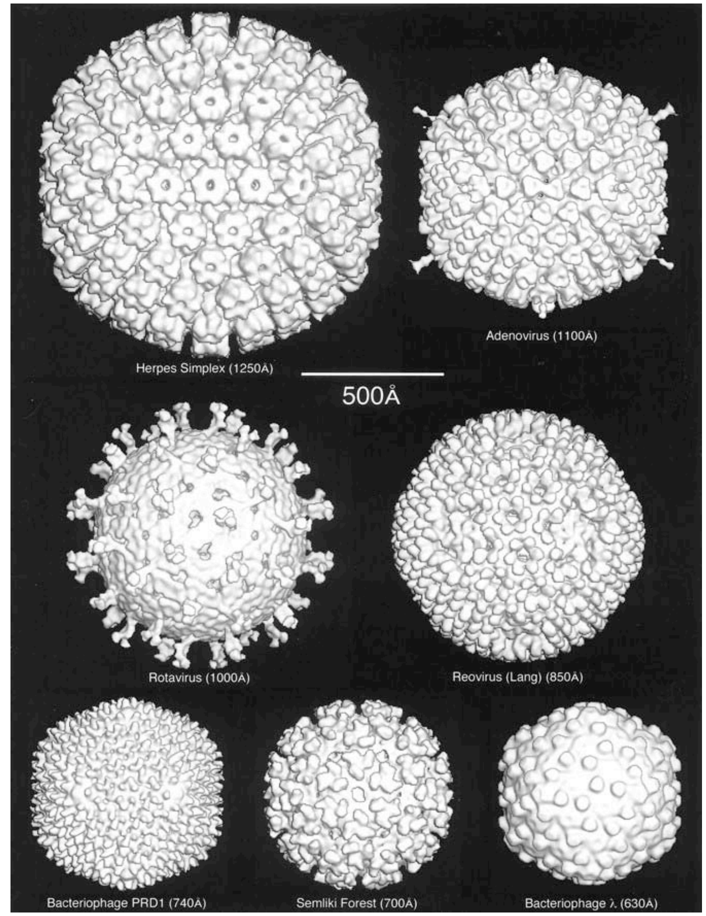




A gallery of viruses…

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

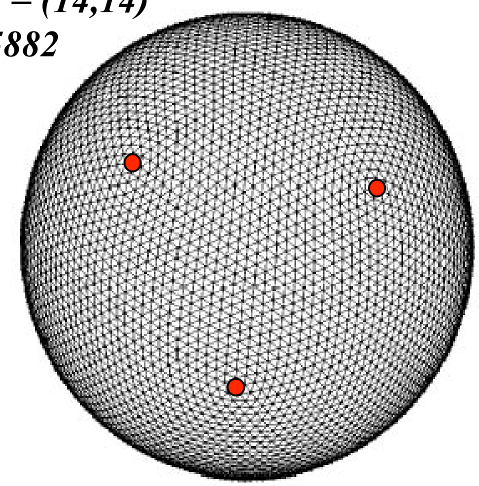


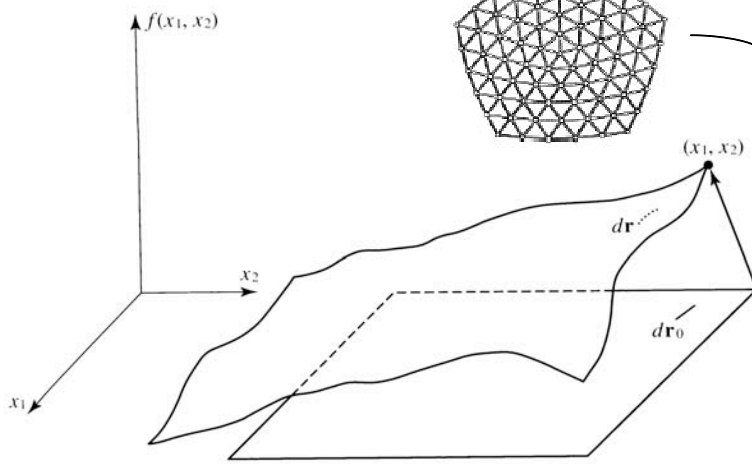


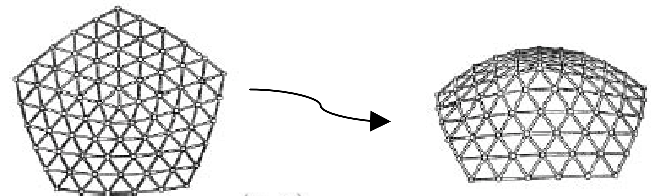
- The small viruses are round and large ones are facetted…

Strain relaxation via disclination buckling in large viruses…

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



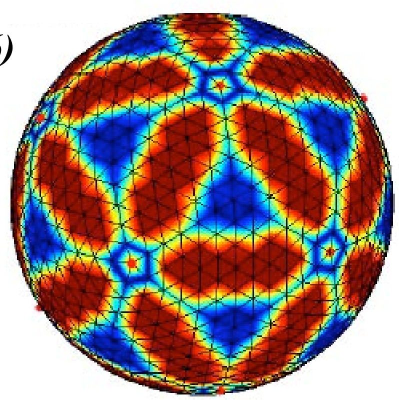




von Karman equations

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

Strain energy



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

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

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

Theory of Virus Shapes

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

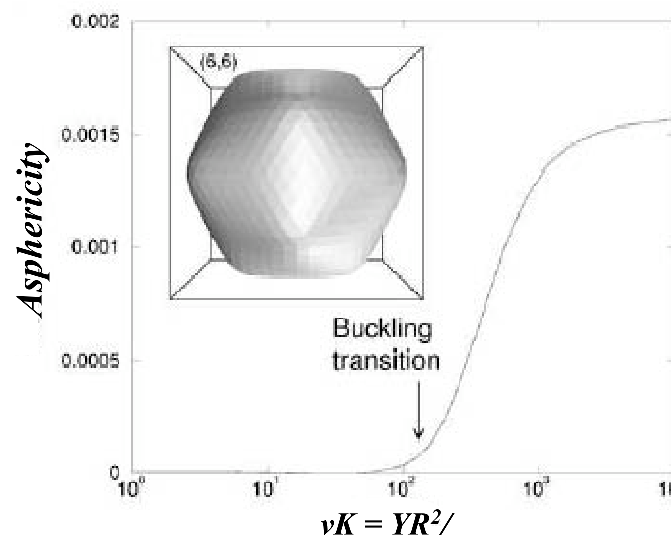
✱*Shape depends only on the 'von-Karman number' $vK = YR^2/$*

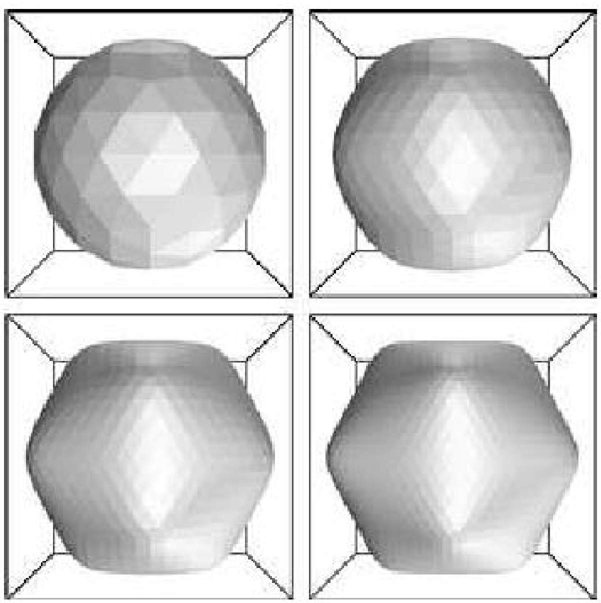
= bending rigidity of shell

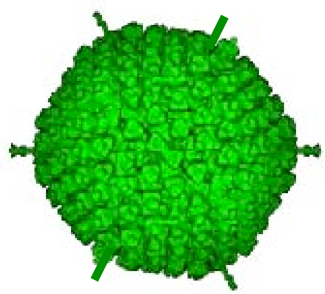
Y = Young's modulus of shell

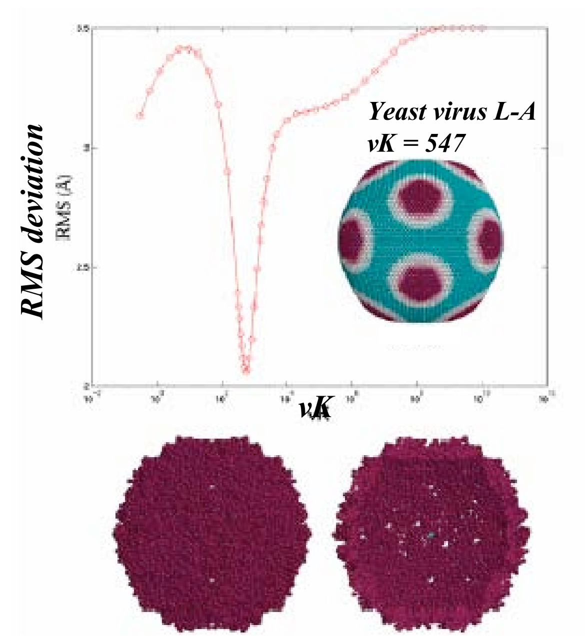
R = mean virus radius

✱*$(vK)_c$= 154 in flat space….*

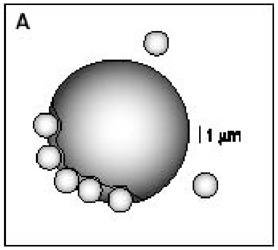


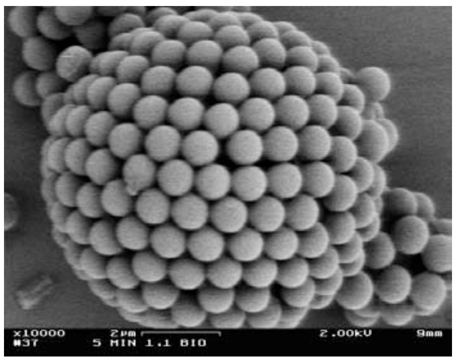






Spherical crystallography of 'colloidosomes'



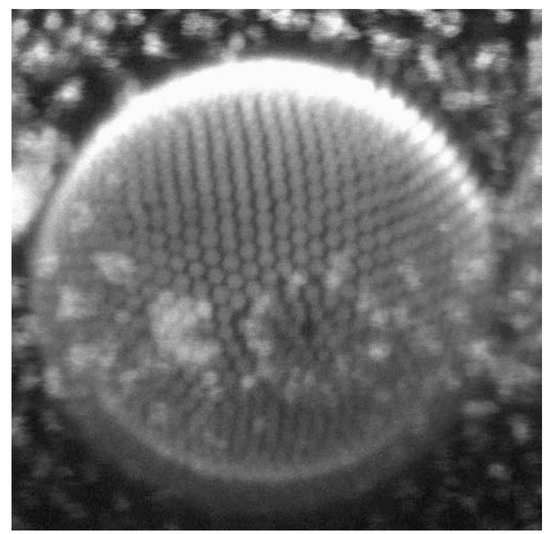


"Colloidosome" = colloids of radius ***a*** coating water droplet (radius ***R***) -- Weitz Laboratory

- ✱ 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….

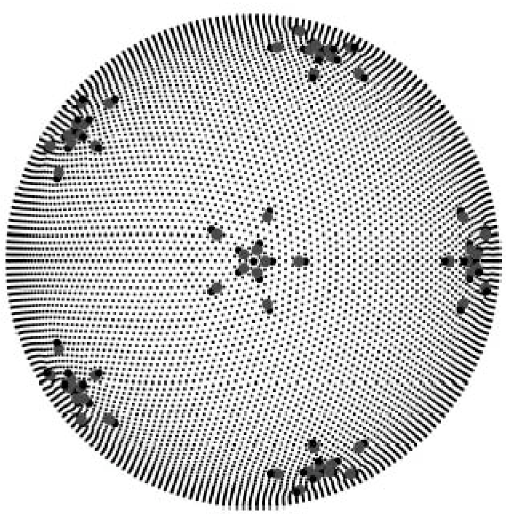
Ordering on a sphere ➔ a minimum of 12 5-fold disclinations, as in soccer balls and fullerenes -- what happens for $R/a >> 1$?

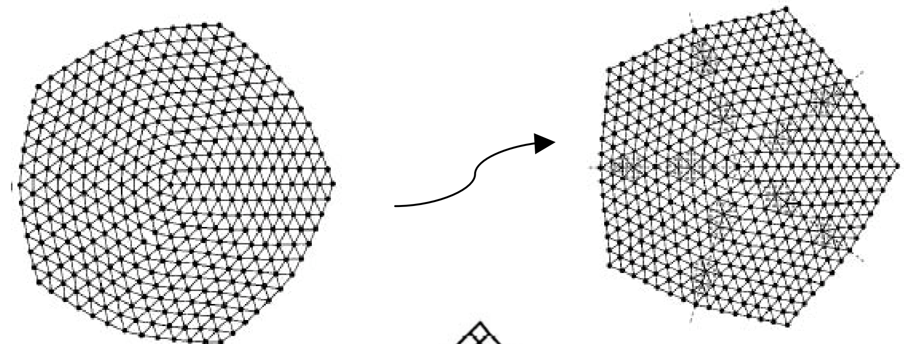


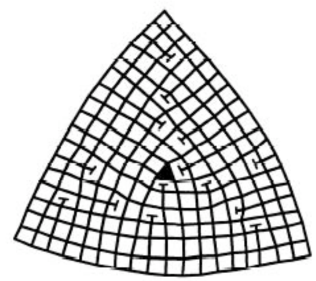
Confocal image: P. Lipowsky, & A. Bausch

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 (1988)

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

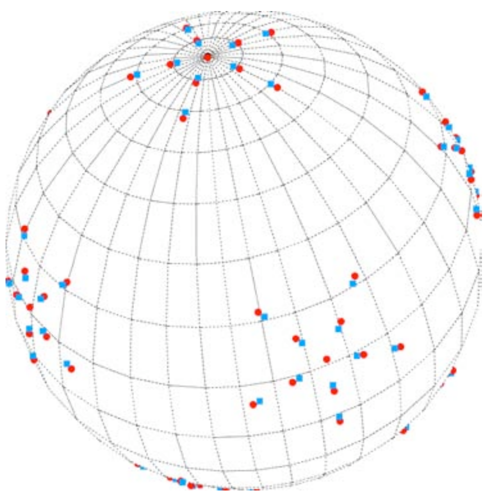
M. J. Bowick, A. Travesset and drn, Phys. Rev. B**62**, 8738 (2000)

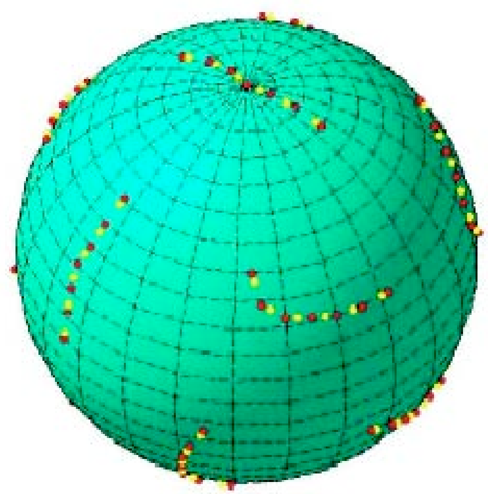
Continuum elastic theory of defects on spheres *(Bowick, Travesset and drn)*

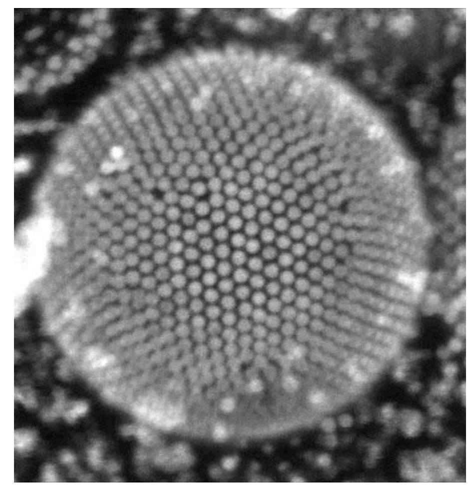
● **Finding the ground state of ~26,000 particles on a sphere is replaced by minimizing the energy of only ~ 250 interacting disclinations, representing points of local 5- and 7-fold symmetry.**

Dislocation = 5-7 pair =

Grain boundary = 5-7 5-7 5-7 …
= …



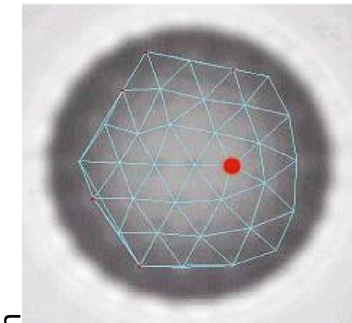


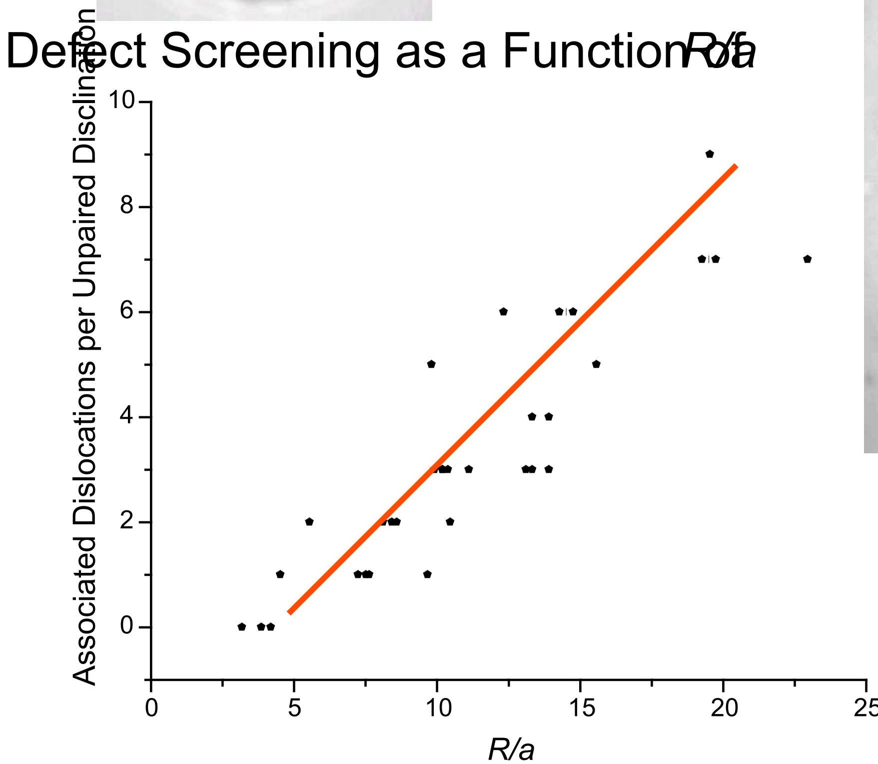


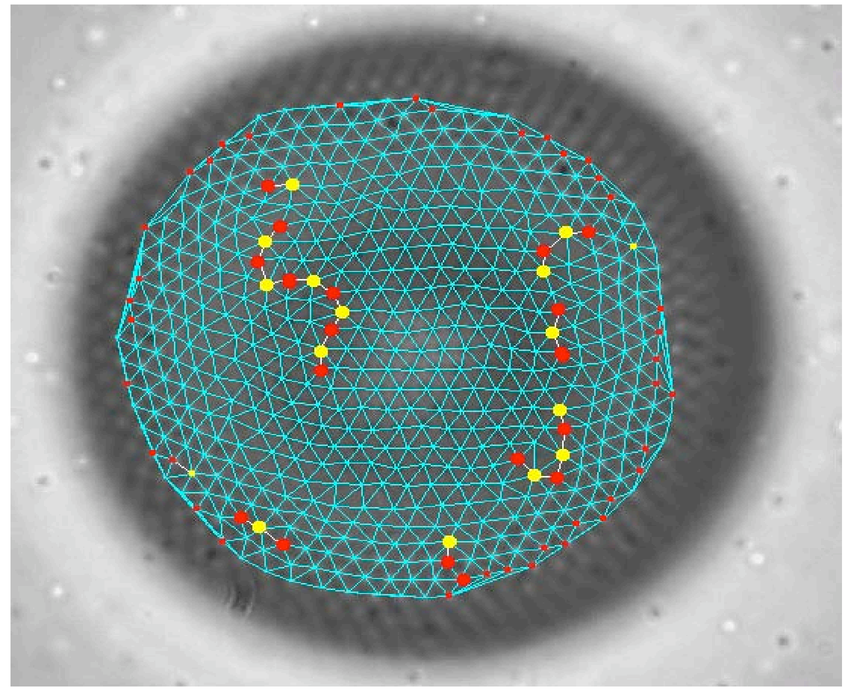
*What happens for real **colloidosomes**?*
(silanized silica beads)

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

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





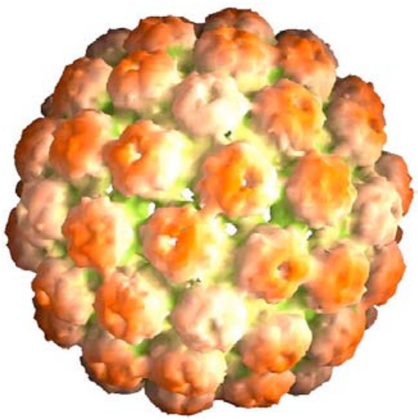


$(R/a)_c$ 5, determined by dislocation core energy

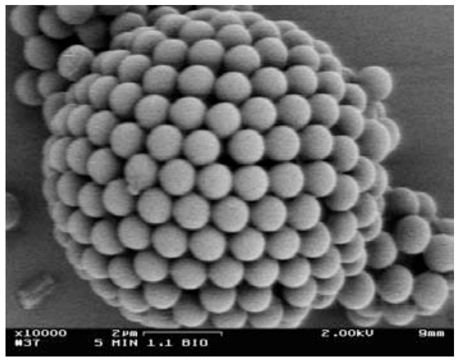
The Thomson Problem and Spherical Crystallography

David R. Nelson, Harvard University

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



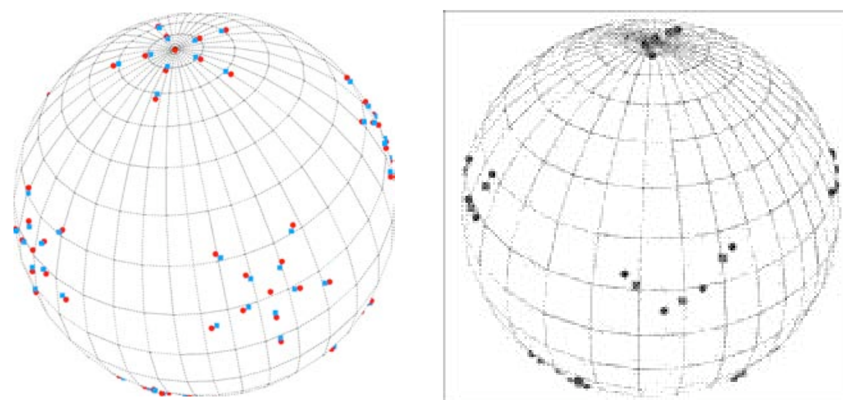
Simian virus SV40



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

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

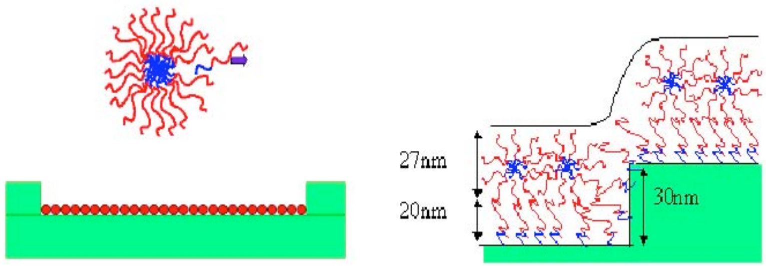
- **Continuum elastic theory (with M. Bowick and A. Travesset) shows that the 5-fold disclinations become unstable to unusual *finite length* grain boundaries (strings of dislocations) for R/a >> 1.**
- **Finding the ground state of ~26,000 particles on a sphere is replaced by minimizing the energy of 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.**



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

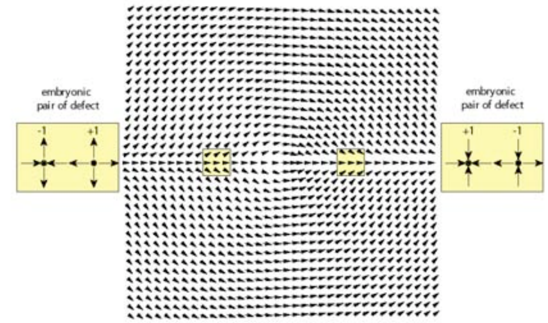
Defect generation and deconfinement on corrugated topographies

Vincenzo Vitelli and drn (see also S. Sachdev….)



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

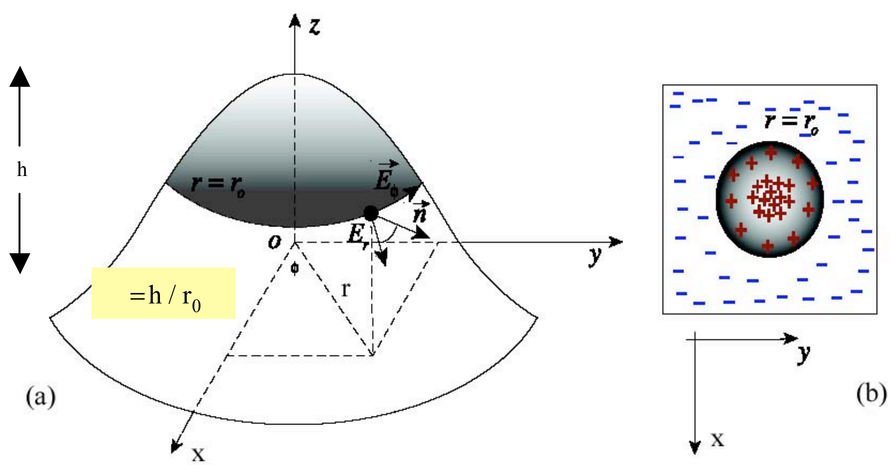
Disclinations can be generated thermally *OR* by increasing the curvature of the substrate ….

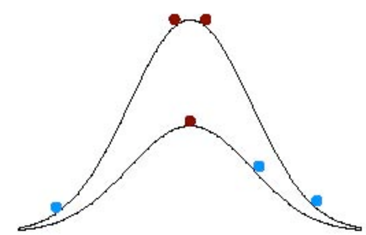


Smooth ground state texture for an XY model on the bump.

A Gaussian bump

(prepare lithographically)



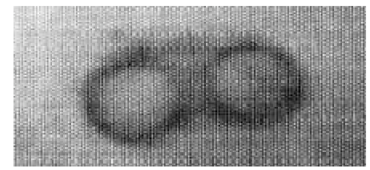


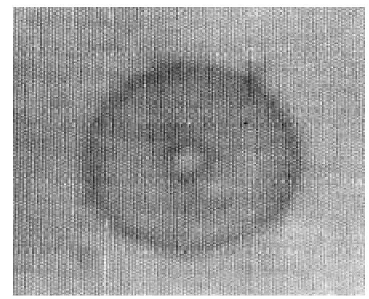
As the aspect ratio of the bump increases one or more defect dipoles are ripped apart by the spatially varying Gaussian curvature ….

Curvature-induced defect unbinding on the torus

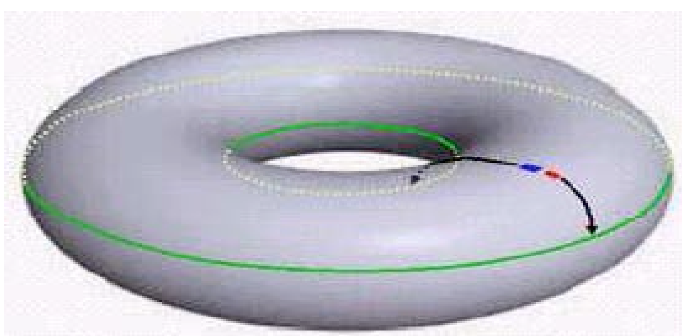
- Consider ***hexatic*** order on a torroidal template
- no ***topological*** necessity for defects in the ground state
- nevertheless, ***Gaussian curvature*** causes a defect-unbinding transition for $M < M_c$, for “fat” torii and moderate vesicle sizes….

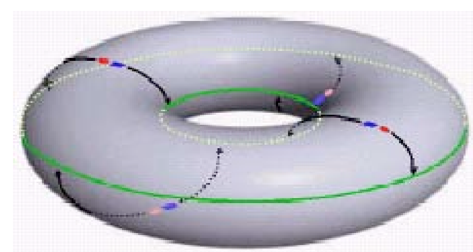
M. Mutz and D. Bensimon, Phys. Rev. A43, 4525 (1991)





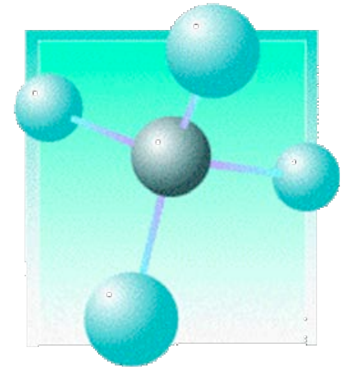
number of microscopic degreesof freedom





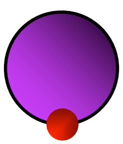
[M. Bowick, A. Travessett and drn, Phys. Rev.E(in press)]

Wanted: unique micron scale connections!

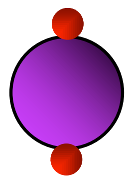


- Link micron particles as in organic chemistry
- Limited, controlled analogue of chemical valence
- Stereospecific geometry
- Building blocks for self-assembly

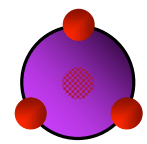
***N*=1**
a boojum defect?

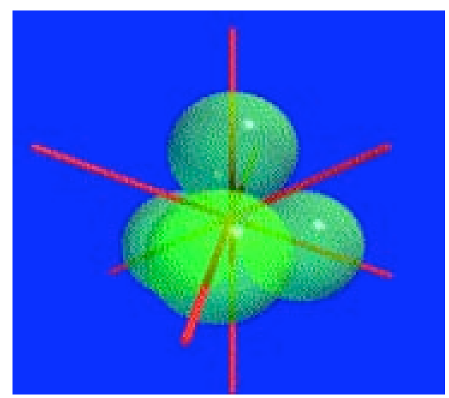


***N*=2**
a vector field on a sphere?



***N*=4**
2D nematics on a sphere?

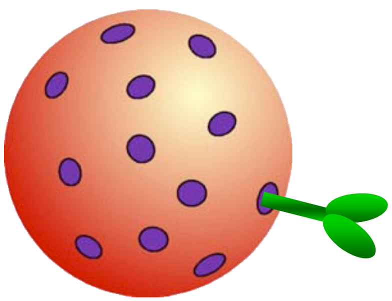




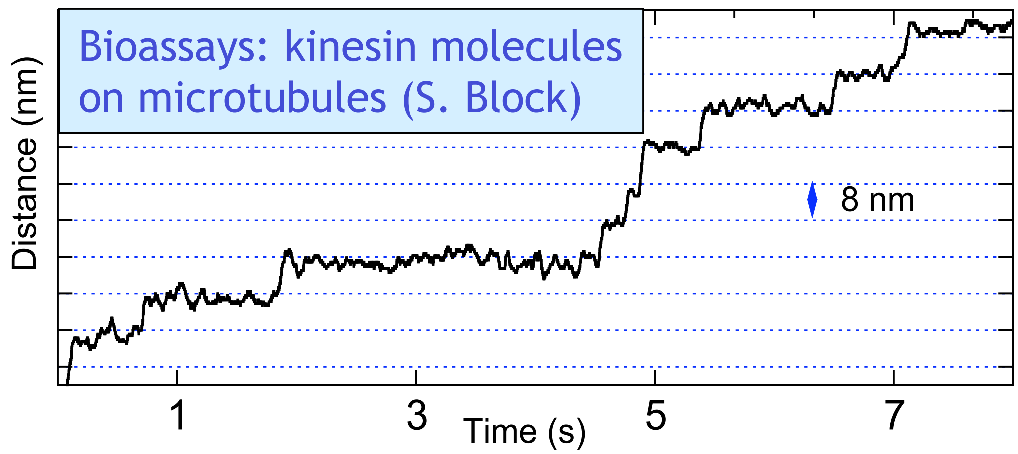
Wanted: Colloids with a valence

The numbers are small (good), but statistically variable (bad)

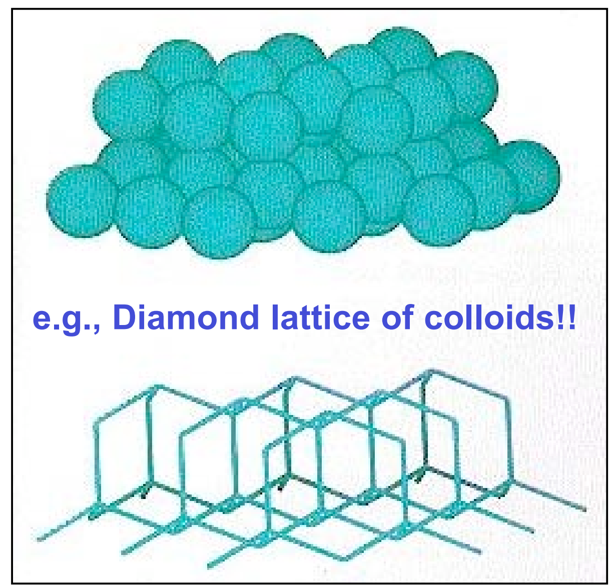
$$P(n,\langle x\rangle)=\frac{e^{\langle x\rangle}\langle x\rangle^{n}}{n!}$$



Current recipe:
Lots of 0's, a few 1's,
but many fewer 2's…



Monovalent, divalent, and *tetravalent* colloids needed……



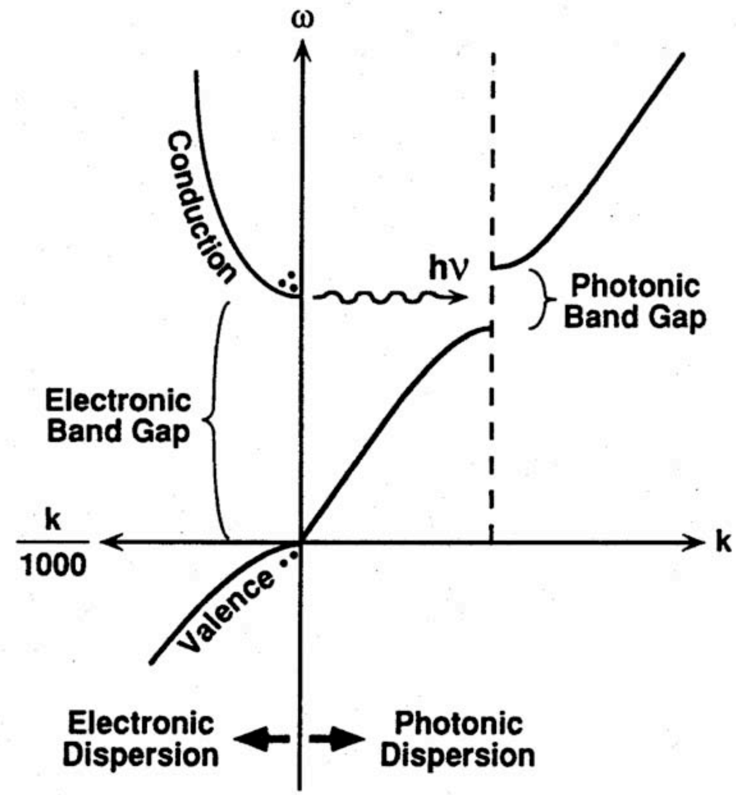
e.g., Diamond lattice of colloids!!

Photon & electronic band gaps

* Left side shows conduction and valence bands of and insulator or semiconductor

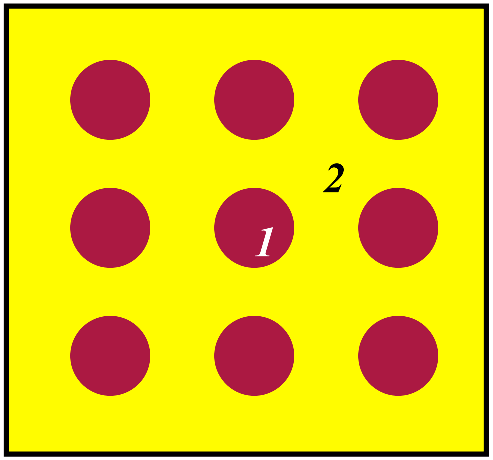
* Right side of the figure shows photonic band gap induced by periodic array of dielectric spheres (scale is 1000 times larger)

* Electron-hole recombination inhibited because photons have (almost!) no place to go!



Applications include more efficient semiconductor lasers and solar cells (due to reduced spontaneous emission),

Band gaps in periodic dielectric media



Dielectric constant = $_1$ inside spheres

Dielectric constant = $_2$ elsewhere

Solve Maxwell's equations for specified dielectric function _($\boldsymbol{r}$).....

$$\frac{1}{\_\,(\boldsymbol{r})} \qquad \boldsymbol{H}(\boldsymbol{r}) = \left(\frac{\ }{c}\right)^2 \boldsymbol{H}(\boldsymbol{r})$$

$$\boldsymbol{E}(\boldsymbol{r}) = \frac{ic}{\ \ (\boldsymbol{r})} \qquad \boldsymbol{H}(\boldsymbol{r})$$

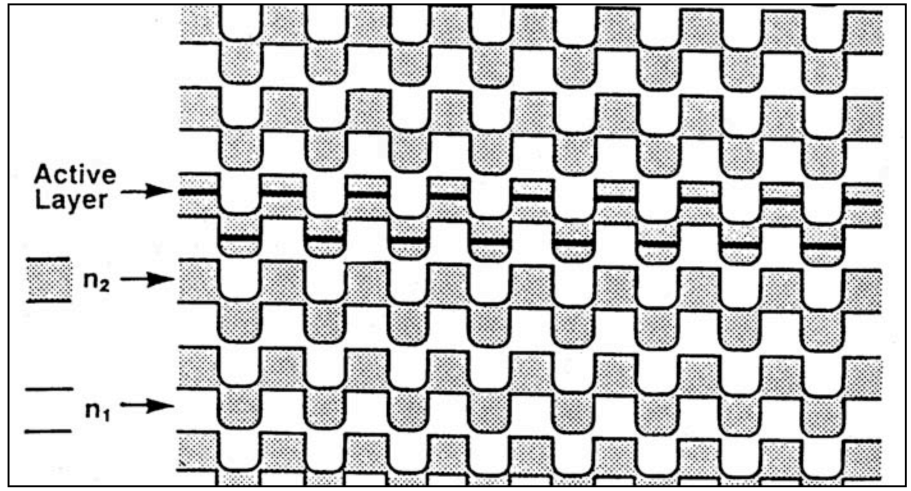
* Expand 1/ ($\boldsymbol{r}$) in Fourier modes of the reciprocal lattice

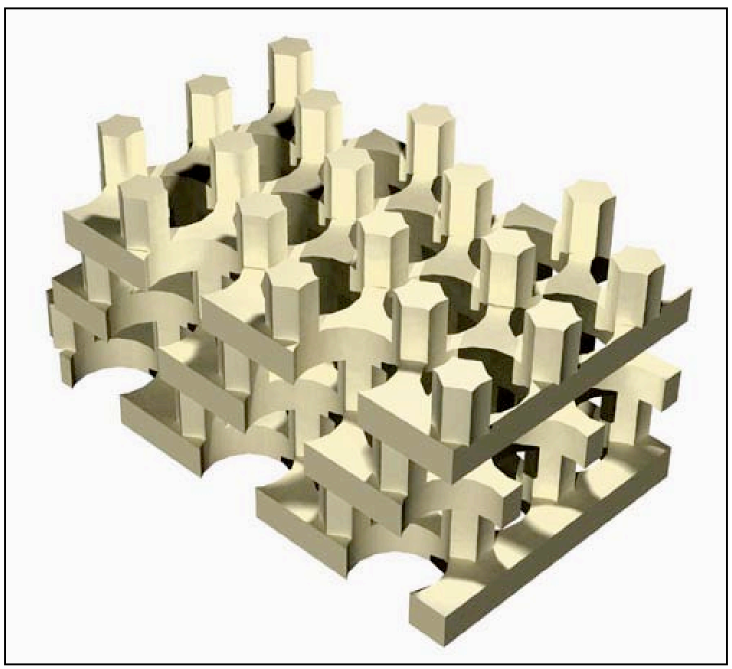
* Vary fill fraction and dielectric contrast $_1/\ _2$

* Compute eigenfrequencies; search for band gaps

Proposed structures with photonic bandgaps

E. Yablonovitch (1987)
MBE design for a GaAs
semiconductor laser





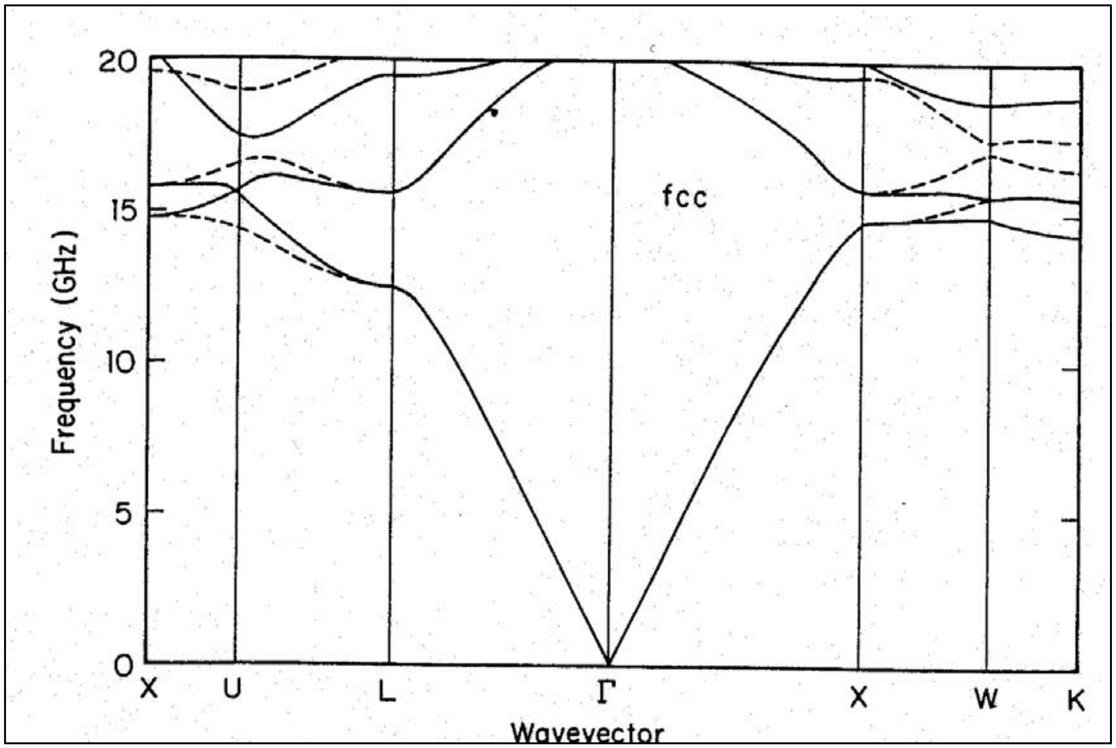
Joannopoulos, et. al. (2000)

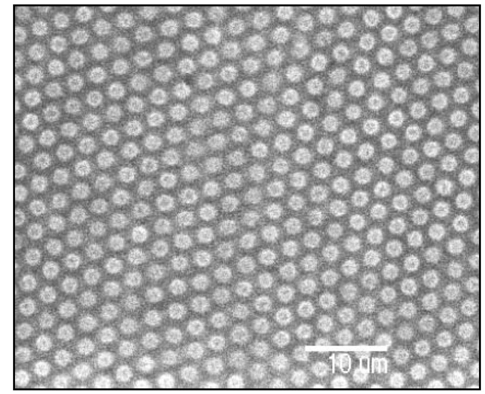
* Large, complete bandgap: over 21% of midgap frequency for Si/air (n_1/n_2 3.4)

* Extensive use of conventional lithographic techniques required

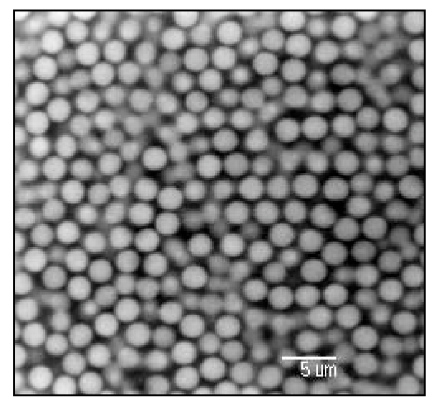
Photon band gaps in colloidal crystals…

In principle, self-assembly of colloids is cheaper and faster than lithography….





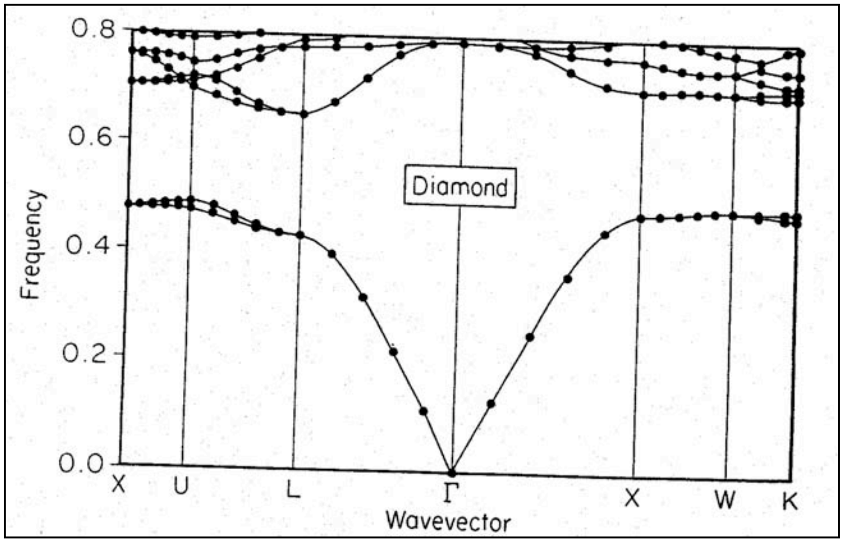
PMMA colloidal crystal
(fcc or random cp)



Colloidal glass

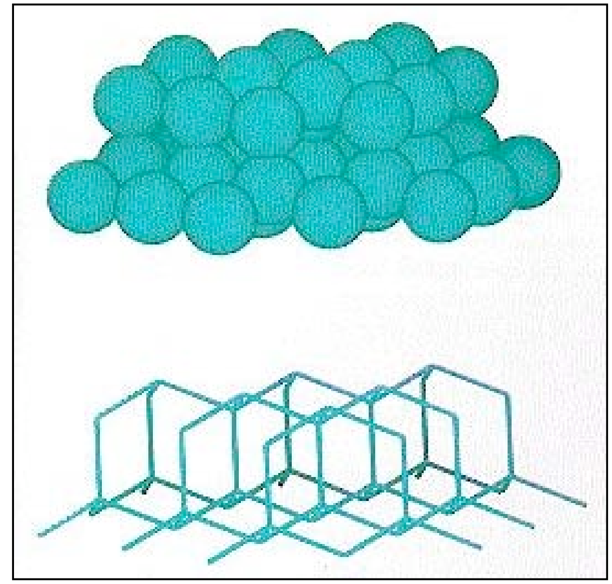
Unfortunately, a complete band gap in all directions is absent for fcc and other close packed structures…

Wanted: A *tetravalent* colloidal crystal!

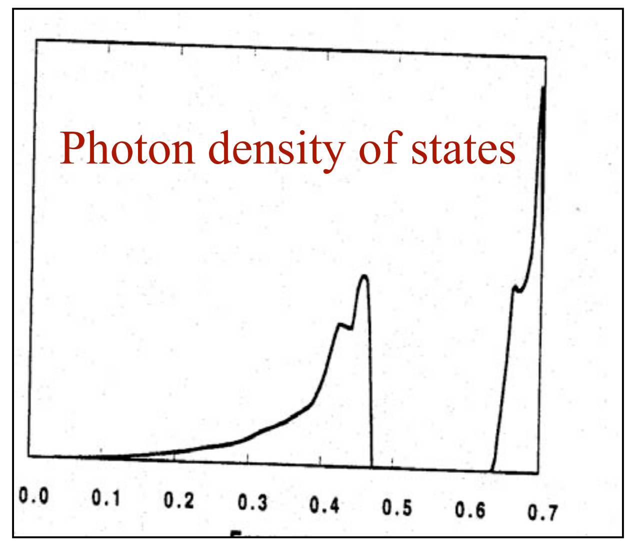


Mat.	**n**
Si	3.4
Ge	3.9
GaAs	3.6

Require
$n > 2$



* C. M. Soukoulis, et al.: Dielectric spheres in diamond lattice with $n =$ $=$ 3.6.
frequency axis scaling: $a/2$ c.
34% fraction. Gap (15% of midgap frequency.

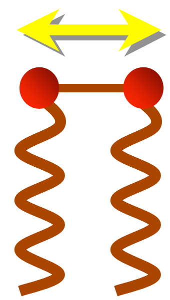


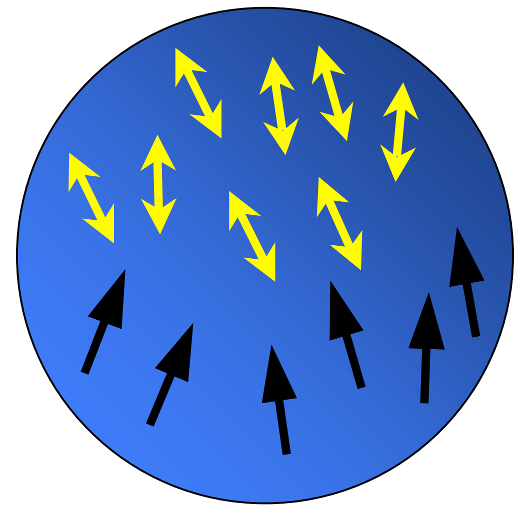
Frequency

Vector and nematic ordering on a sphere

Coat spheres with gemini lipids or triblock copolymers…

Like combing your hair…
leads to bald spots (defects):





$$\text{2D Liquid Crystals in flat space:}$$

$$E = \tfrac{1}{2} K \quad d^2\boldsymbol{r}\left[\quad \hat{\boldsymbol{n}}(\boldsymbol{r})\right]^2$$

$$K = \text{Frank constant}$$

$$\hat{\boldsymbol{n}}(\boldsymbol{r}) = \left[\cos \quad (\boldsymbol{r}), \sin \quad (\boldsymbol{r})\right]$$

$$T_n \qquad K$$

$$\circ \qquad (\boldsymbol{r})\, d\boldsymbol{l} = (2 \quad s)\, n$$

$$E_{\text{defect}} = n^2 s^2 \quad K \ln(R/a)$$

$$s = \text{min. defect 'charge'}$$

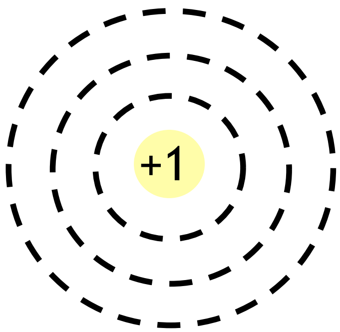
(analog of electron charge)

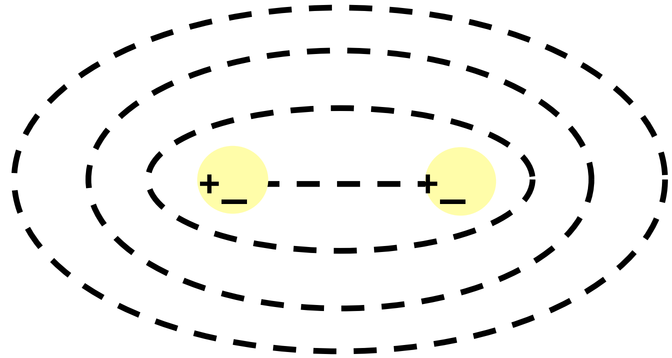
$$s = 1, \text{ vector}; \ s = \tfrac{1}{2}, \text{ nematic}$$

$n = \pm 1, \pm 2, \ldots$ (number of charges…)

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

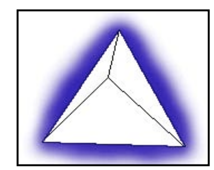
North Pole





Z = 2

Z = 4



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

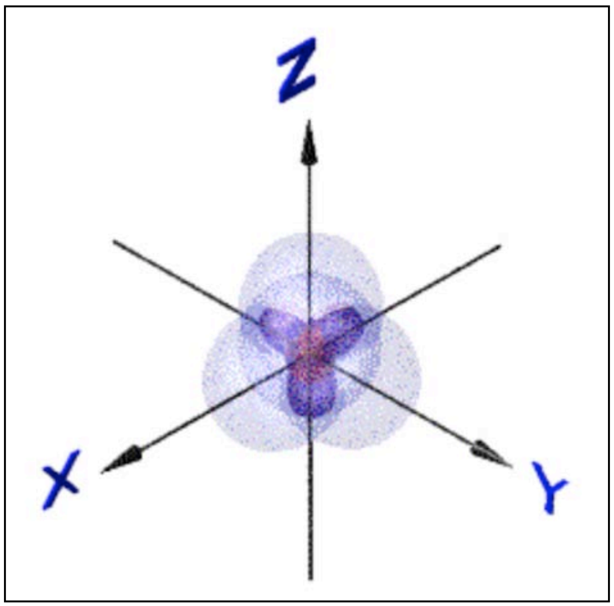
See T. C. Lubensky and J. Prost, J. Phys. II **2**, 371 (1992)

Long-range repulsion)

TETRAHEDRAL DEFECT ARRAY

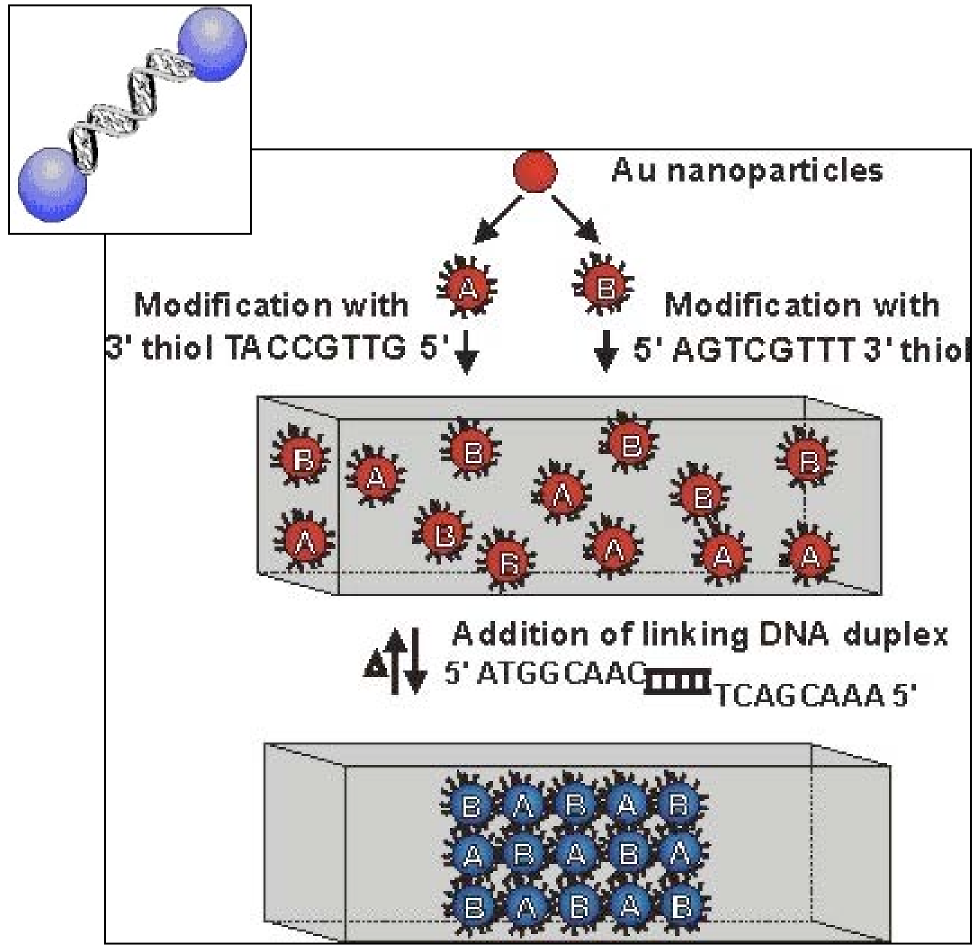
DNA-based control of colloidal connectivity?

• To make a tetravalent diamond lattice, we need to reproduce the quantum chemistry of **sp^3** hybridization on the micron scale of colloids.



Ångströms) microns…

The groups of Chad Mirkin (Northwestern) and Paul Alivisatos (Berkeley) have used DNA to link colloidal gold particles…

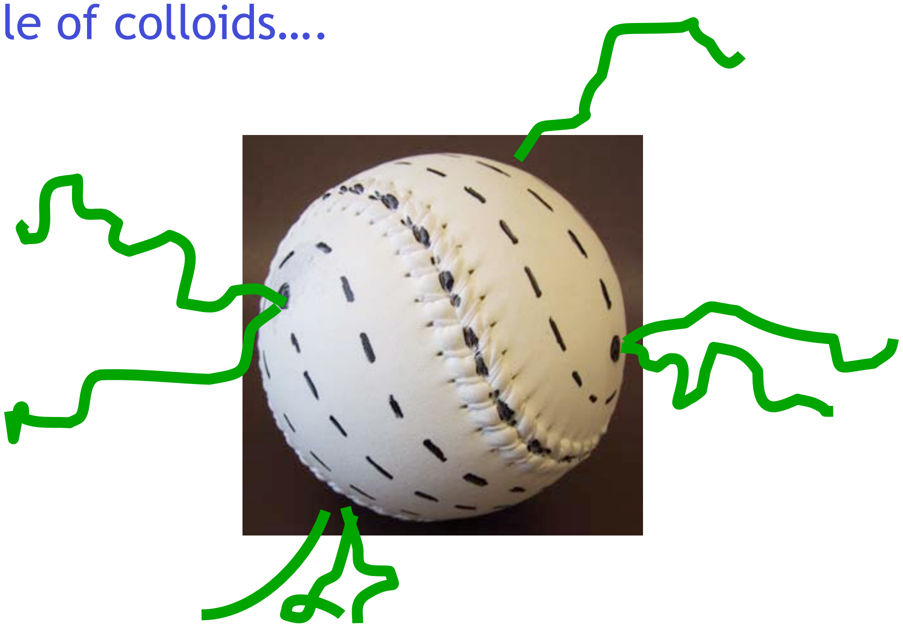


Linking colloids with a valence

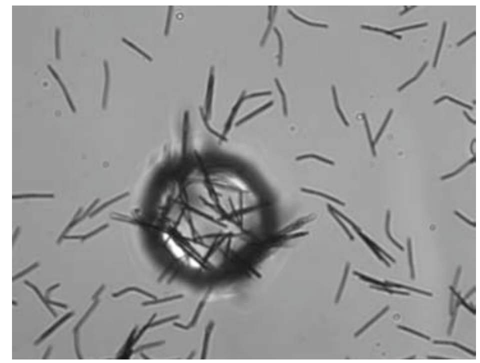
Possible nematogens include gemini lipids, (say, on an oil droplet), triblock copolymers, and CdSe nanocrystals.

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

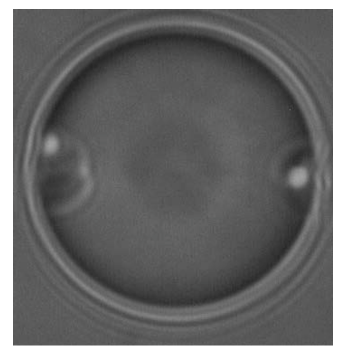
• may be possible to reproduce the quantum chemistry of **sp**^{3} hybridization on the micron scale of colloids….



The groups of Chad Mirkin (Northwestern) And Paul Alivisatos (Berkeley) have used DNA to link colloidal particles…



Weitz group



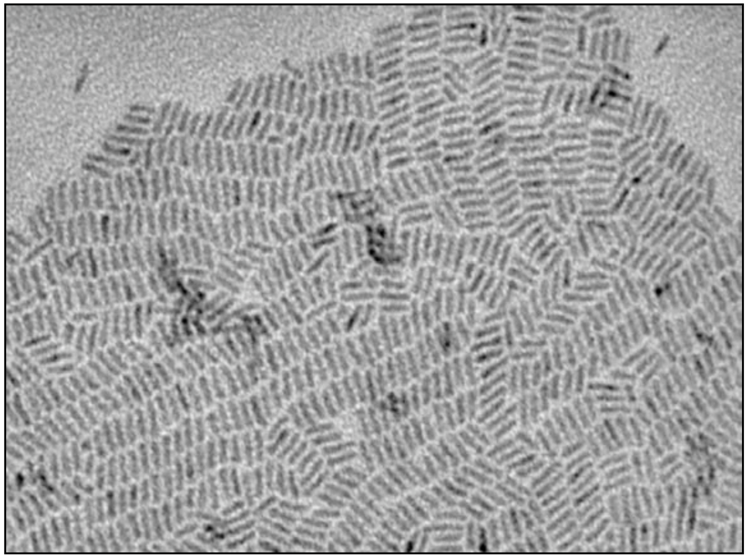
Fluoresent beads on nematic droplet colloidal analogue of sulfer…

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

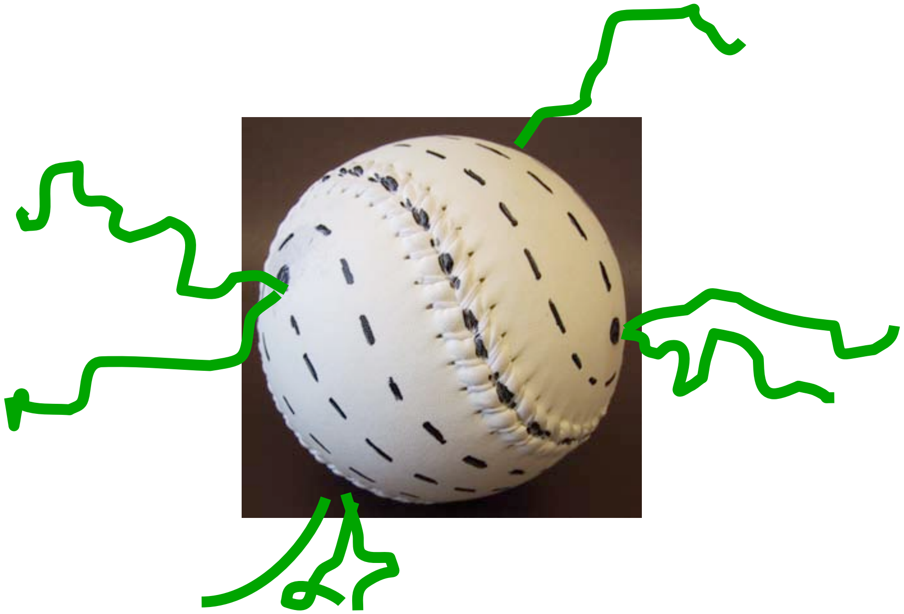
Implementation issues

• Good nematic surfactants needed. Possibilities include gemini lipids, (say, on an oil droplet), triblock copolymers, and nanocrystals.

• The four unique "bald spots" on a nematic-coated sphere can be used as a mask for depositing, say, gold-thiol linker to DNA.



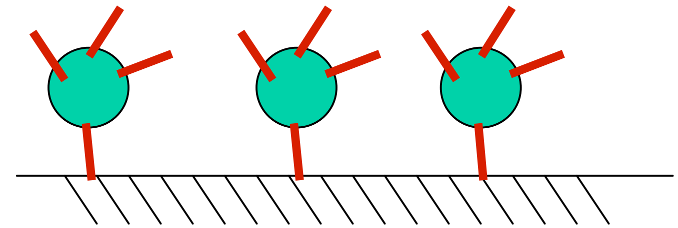
Dried film of 5 nm x 25 nm CdSe nanorods. P. Alivisatos lab



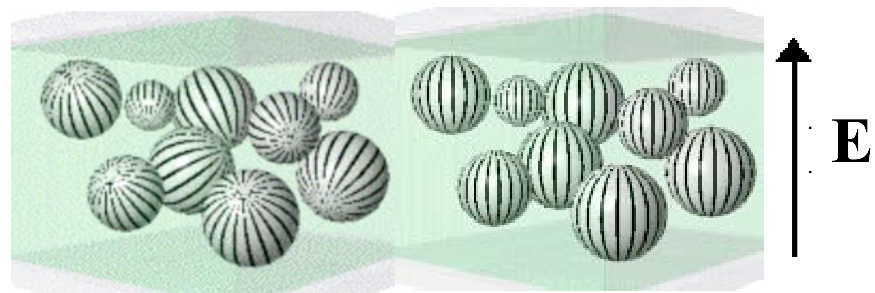
• Alternatively, DNA linkers mixed with nematic surfactants will segregate at tetrahedral defect sites.

Future directions

- Link to substrate) **“sp^2”** hybridization.



- **Vector** fields on surfaces imply two-fold valence; see also nematic droplets in a polymer matrix (PDLC’s)

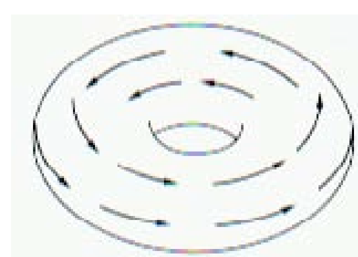


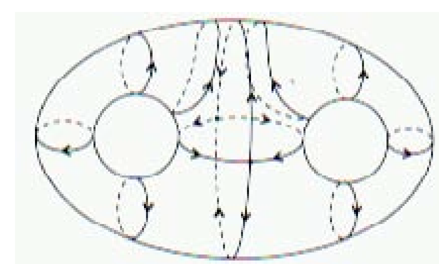
$$E = \tfrac{1}{2} \; d^2 r\, K_1 \big(\quad \boldsymbol{n}(\boldsymbol{r}) \big)^2 +$$

$$\tfrac{1}{2} \; d^2 r\, K_2 \big(\quad \boldsymbol{n}(\boldsymbol{r}) \big)^2$$

- Validity of the one Frank constant approximation?

- Other shapes? Torus, oblate and/or prolate ellipsoids, etc…





A use for photonic band gap materials

- **IR Camouflage Paint:** Low infrared emissivity
  → high reflectivity through Kirchoff's Law.
  But also seek no radar cross-section, unlike metal!

Photon emissivity is:

$$P_e(T,(\ )= A((\ )\ \frac{h(\ ^3/c^2}{\exp(h(\ /k_B T)\quad 1}$$

Infrared image

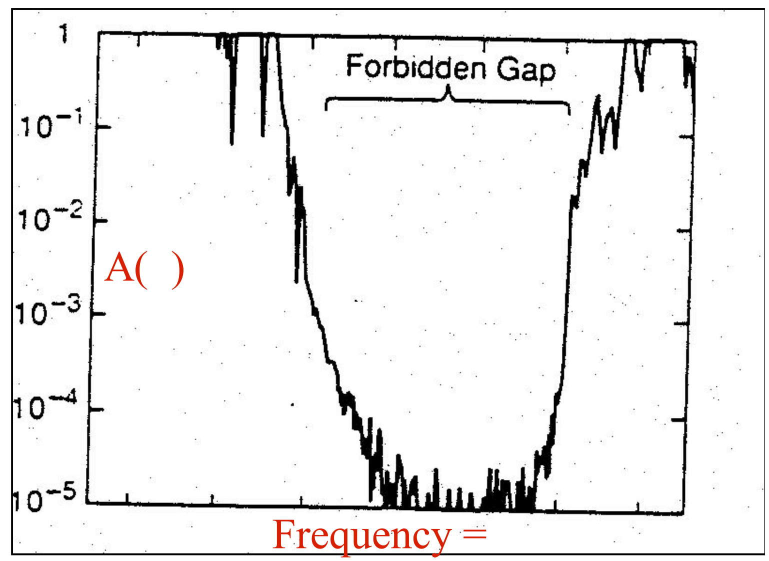
For metals (but high radar cross-section!):

$$\text{Absorption} = A(\ ) = 1 \quad R(\ ) \quad 2\sqrt{\ \ /\ \ }$$

For a successful photonic band gap material with low absorption:

$$A(\ ) \quad 10^{\ 5},\ \text{for}\ 0.7\propto \qquad\qquad 1.0\propto$$

Many other uses! Make microlasers, channel light tightly, etc.



Yablonovitch et. al. , microwaves