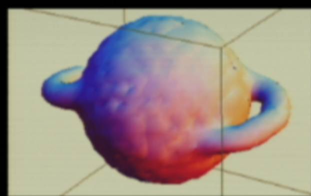
Title: Building Colloidal Crystals in Anisotropic Media

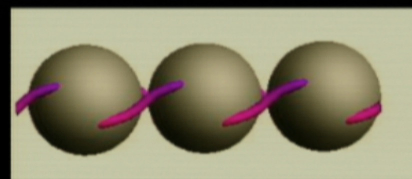
Date: Dec 05, 2013 10:30 AM

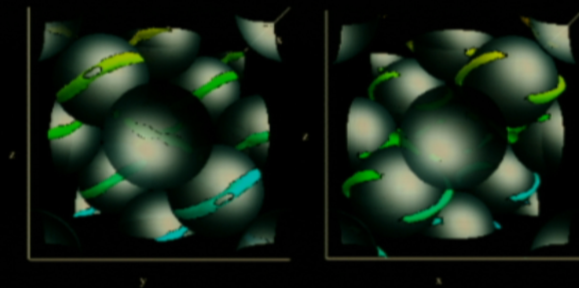
URL: http://pirsa.org/13120011

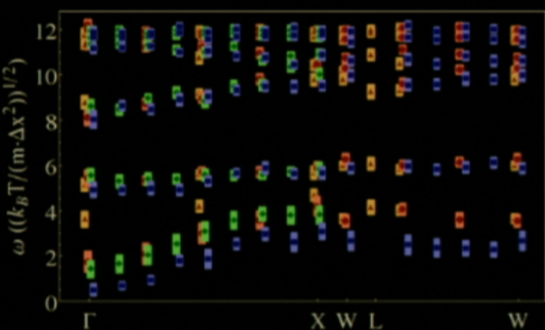
Abstract: Colloids in a liquid crystal matrix exhibit very anisotropic interactions. Further, these interactions can be altered by both properties of the colloid and of the liquid crystal. This gives a potential for creating specific colloidal aggregates and crystals by manipulating the interactions between colloids. However, modelling these interacting colloids in a liquid crystal is very challenging. We use a hybrid particle-lattice Boltzmann scheme that incorporates hydrodynamic forces and forces from the liquid crystal field. I will discuss configurations that we have studied,
including chains and a potentially stable colloidal crystal with a diamond lattice structure.

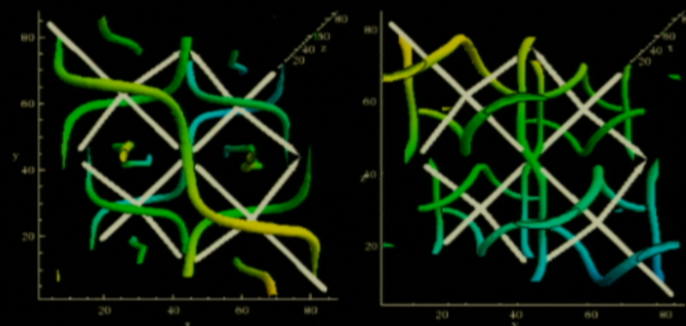
BUILDING COLLOIDAL CRYSTALS IN ANISOTROPIC MEDIA







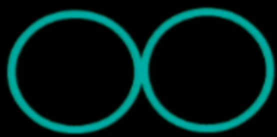




Colin Denniston,
F. Mackay, S. Ollila, C. Smith
University of Western Ontario

Colloidal Interactions for Spherically Symmetric Particles

- Excluded volume (hard sphere)



- Electrostatic (Coulomb)

- van der Waals (short-range dipole/dispersion interactions)

Colloidal Interactions for Spherically Symmetric Particles

- Excluded volume (hard sphere)

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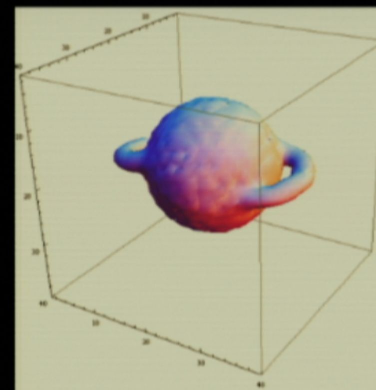
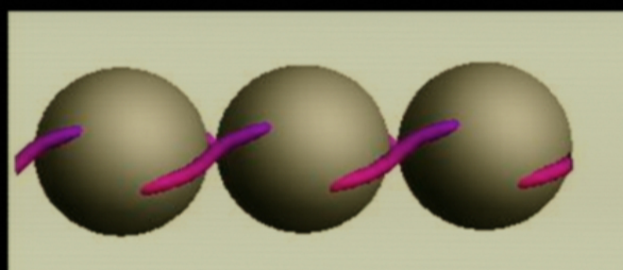
- van der Waals (short-range dipole/dispersion interactions)

…lead to fcc (hcp in microgravity) crystals at sufficient density, for the same reason that hard spheres and Group I elements (valence e in s-orbital) form these crystals: The interactions are spherically symmetric.

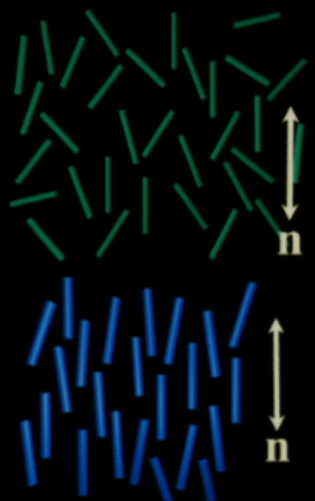
Outline

- Modeling
- Colloids in a Liquid Crystal
- Bonded Colloids
- Colloidal Crystals





Describing nematics

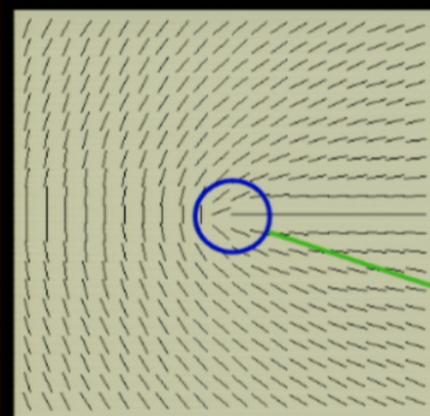


Weakly Ordered

Strongly Ordered

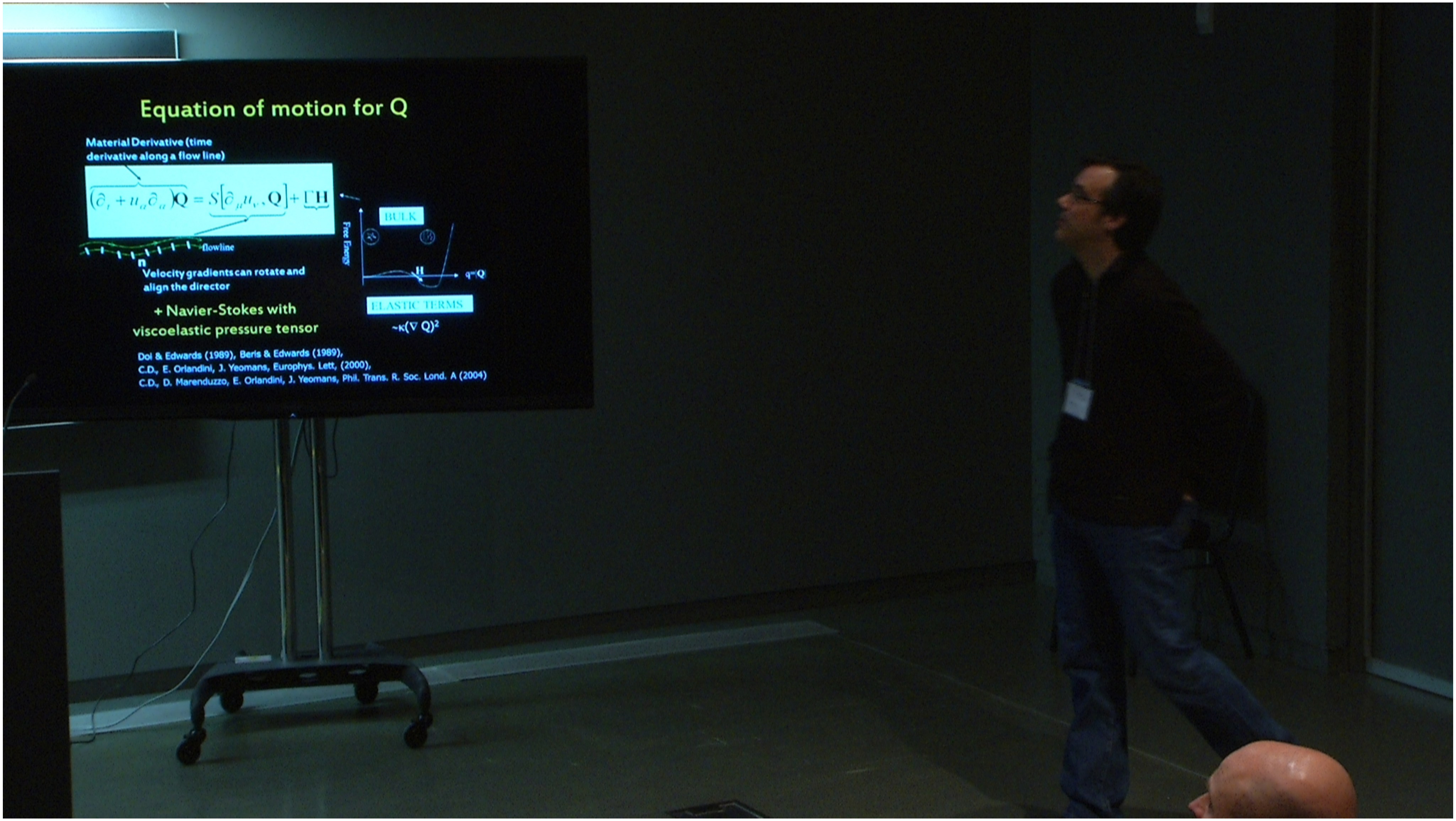
q : *scalar* order parameter $0 < q < 1$

Defects:



Biaxial Core:
two directors
n_1, n_2

- Tensor order parameter:
  $Q_{\alpha\beta} = \langle m_\alpha m_\beta - {}^{1}/_{3}\delta_{\alpha\beta} \rangle$


Equation of motion for Q
Material Derivative (time derivative along a flow line)
$(\partial_t + u_\alpha \partial_\alpha) Q = S[\partial_\mu u_\nu, Q] + \Gamma H$
flowline
n
Velocity gradients can rotate and align the director
+ Navier-Stokes with viscoelastic pressure tensor
Free Energy
BULK
ELASTIC TERMS
$\sim\kappa(\nabla Q)^2$
Doi & Edwards (1989), Beris & Edwards (1989),
C.D., E. Orlandini, J. Yeomans, Europhys. Lett, (2000),
C.D., D. Marenduzzo, E. Orlandini, J. Yeomans, Phil. Trans. R. Soc. Lond. A (2004)

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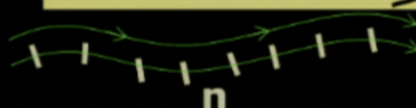

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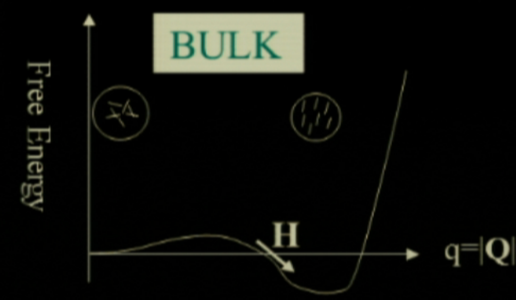

+ Navier-Stokes with viscoelastic pressure tensor

ELASTIC TERMS

$\sim\kappa(\nabla Q)^2$

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Continuity equation

$$(\partial_t + \partial_\alpha u_\alpha)\rho = 0$$

Navier-Stokes equation

$$\rho(\partial_t + u_\alpha \partial_\alpha) u_\beta = \partial_\alpha \tau_{\beta\alpha} - \partial_\alpha P_{\beta\alpha} + \eta \partial_\alpha (\partial_\alpha u_\beta + \partial_\beta u_\alpha)$$

Symmetric pressure tensor:

$$P_{\alpha\beta} = p_0 \delta_{\alpha\beta} - \sigma_{\alpha\beta}(Q, \nabla Q, H)$$

Anti-symmetric stress tensor:

$$\tau_{\alpha\beta} = [\mathbf{Q}\cdot\mathbf{H} - \mathbf{H}\cdot\mathbf{Q}]_{\alpha\beta}$$

Free Energy

$$\Im_B = \int d^3r \left\{ \frac{a}{2} Q_{\alpha\beta}^2 - \frac{b}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{c}{4} (Q_{\alpha\beta}^2)^2 \right\}$$

$$\Im_E = \int d^3r \{ L_1 (\partial_\alpha Q_{\beta\gamma})^2 + L_2 (\partial_\alpha Q_{\alpha\beta})(\partial_\gamma Q_{\beta\gamma}) \}$$

$$F_{surface} = \int \frac{1}{2} \alpha_s \left(Q_{\alpha\beta} - Q_{\alpha\beta}^0 \right)^2 dS$$

Molecular Field:

$$\mathbf{H} = -\left\{ \frac{\delta \Im}{\delta \mathbf{Q}} - \frac{\mathbf{I}}{3} Tr \frac{\delta \Im}{\delta \mathbf{Q}} \right\}$$

LC stress tensor:

$$-\sigma_{\alpha\beta} = \xi H_{\alpha\gamma}(Q_{\gamma\beta} + \tfrac{1}{3}\delta_{\gamma\beta}) + \xi(Q_{\alpha\gamma} + \tfrac{1}{3}\delta_{\alpha\gamma}) H_{\gamma\beta} - 2\xi(Q_{\alpha\beta} + \tfrac{1}{3}\delta_{\alpha\beta}) Q_{\gamma\varepsilon} H_{\gamma\varepsilon}$$

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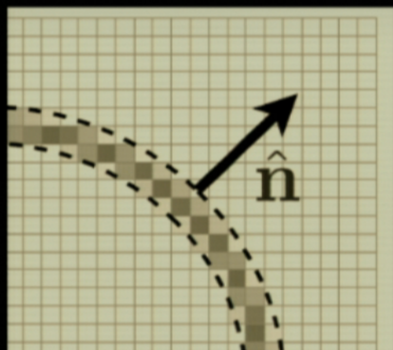
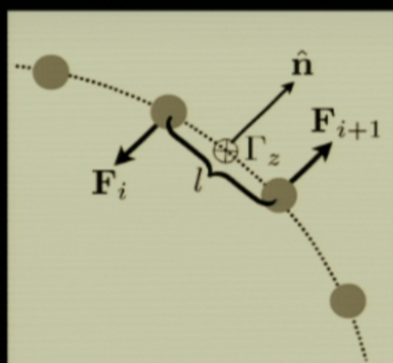
Putting colloids in a LC simulation



$$dF_\alpha = n_\beta \sigma_{\alpha\beta} dS.$$

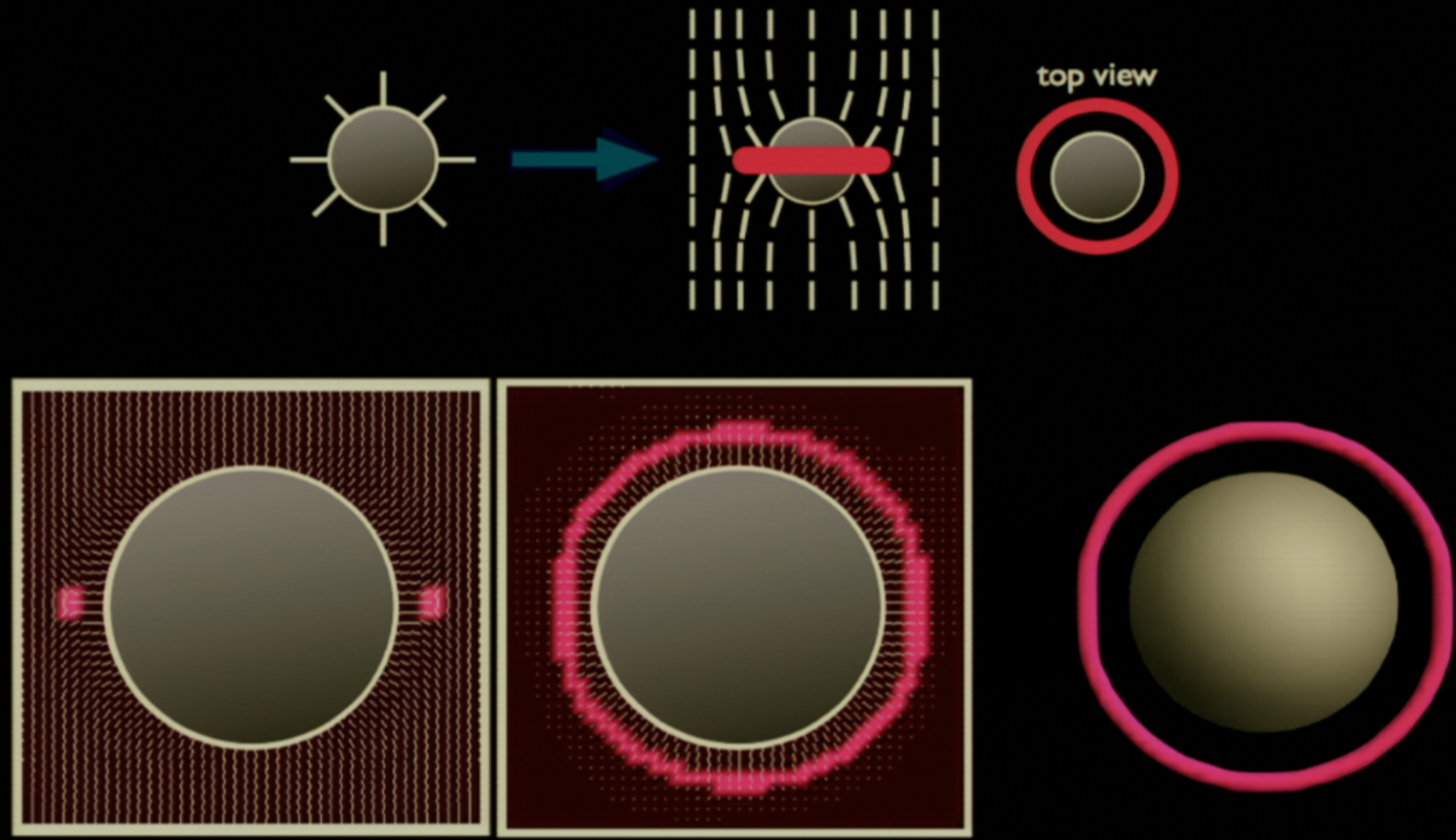
Symmetric Stress terms from LC only. Evaluate just outside surface.



$$\Gamma_\alpha = 2\tau_{\beta\gamma}^{applied} \Delta V.$$

Antisymmetric stress from LC surface energy

Example Results For a Saturn Ring Defect

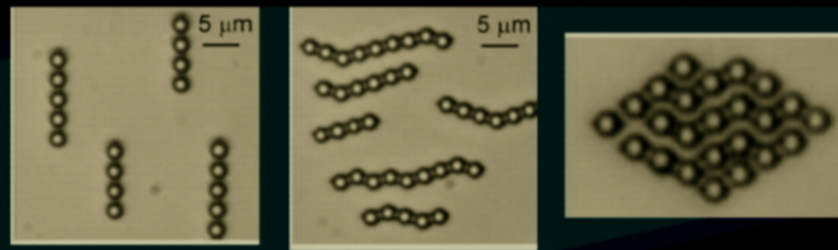


plots of the director, and the maximum eigenvalue

contour plot of the
maximum eigenvalue

These can self-assemble, typically into chains:

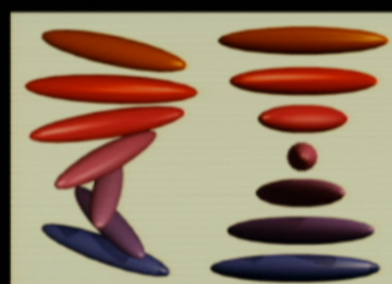
e.g.

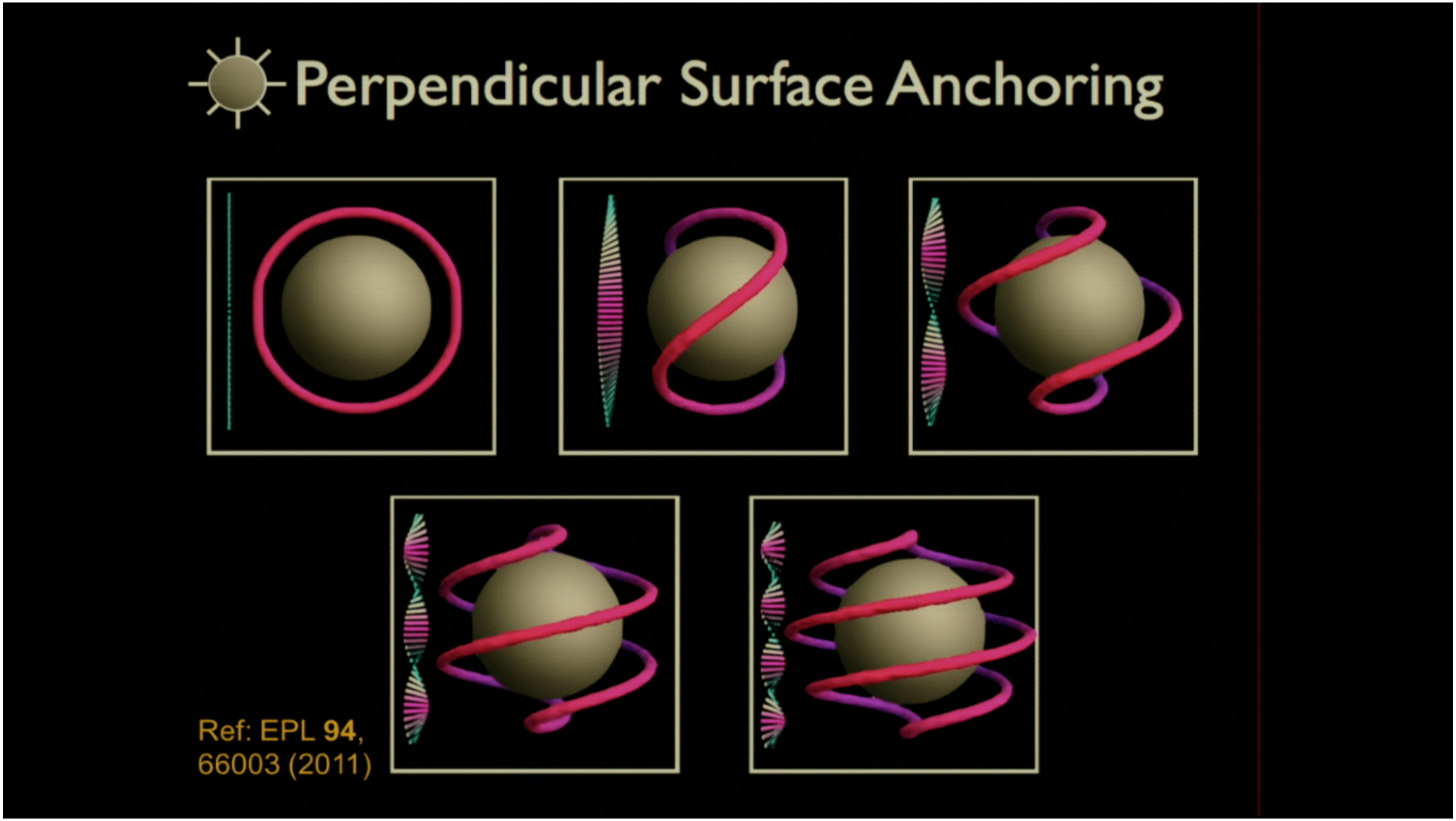


Muševič, I.; Škarabot, M.; Tkalec, U.; Ravnik, M.; Žumer, S., Science, 313, 954(2006)

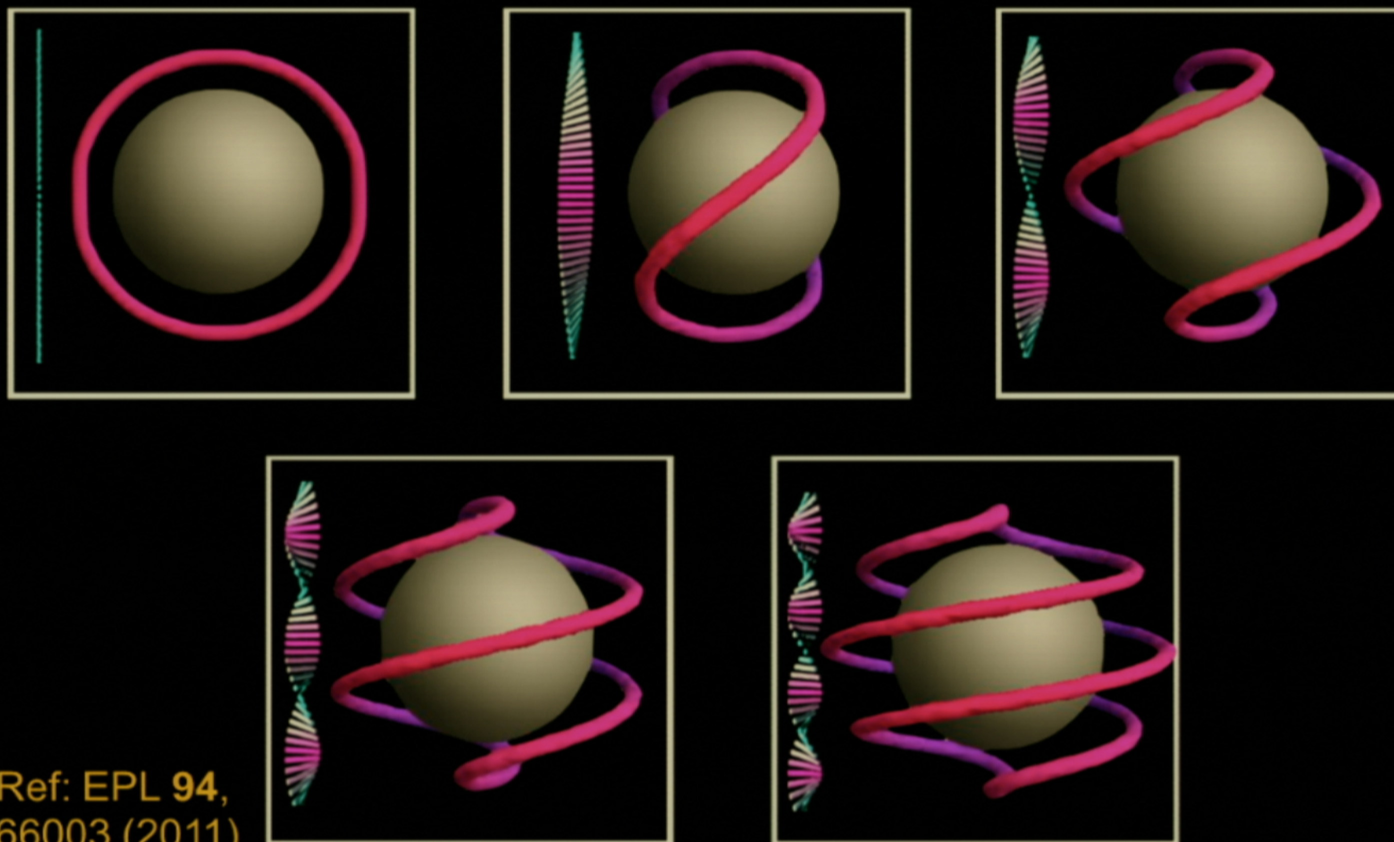
These were studied fairly extensively in last decade by Poulin, Weitz, Lubensky, Zumer, Musevic, and others.

- **OUR WORK:** investigate the possible structures formed by colloidal particles in a cholesteric liquid crystal.




Perpendicular Surface Anchoring
Ref: EPL **94**, 66003 (2011)

Perpendicular Surface Anchoring



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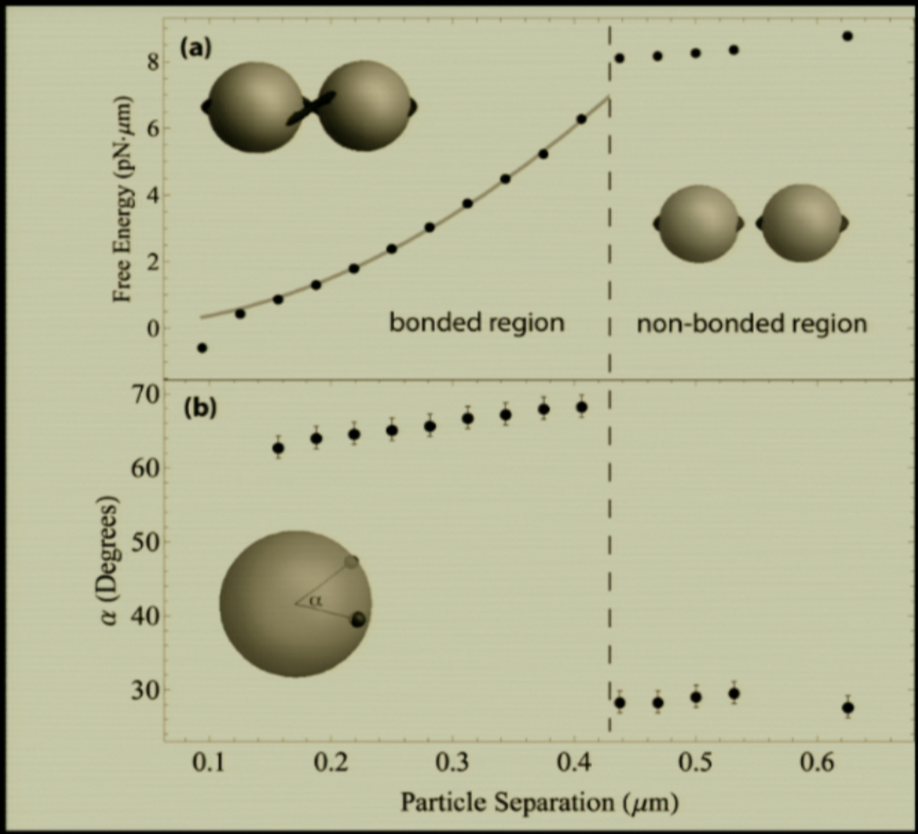
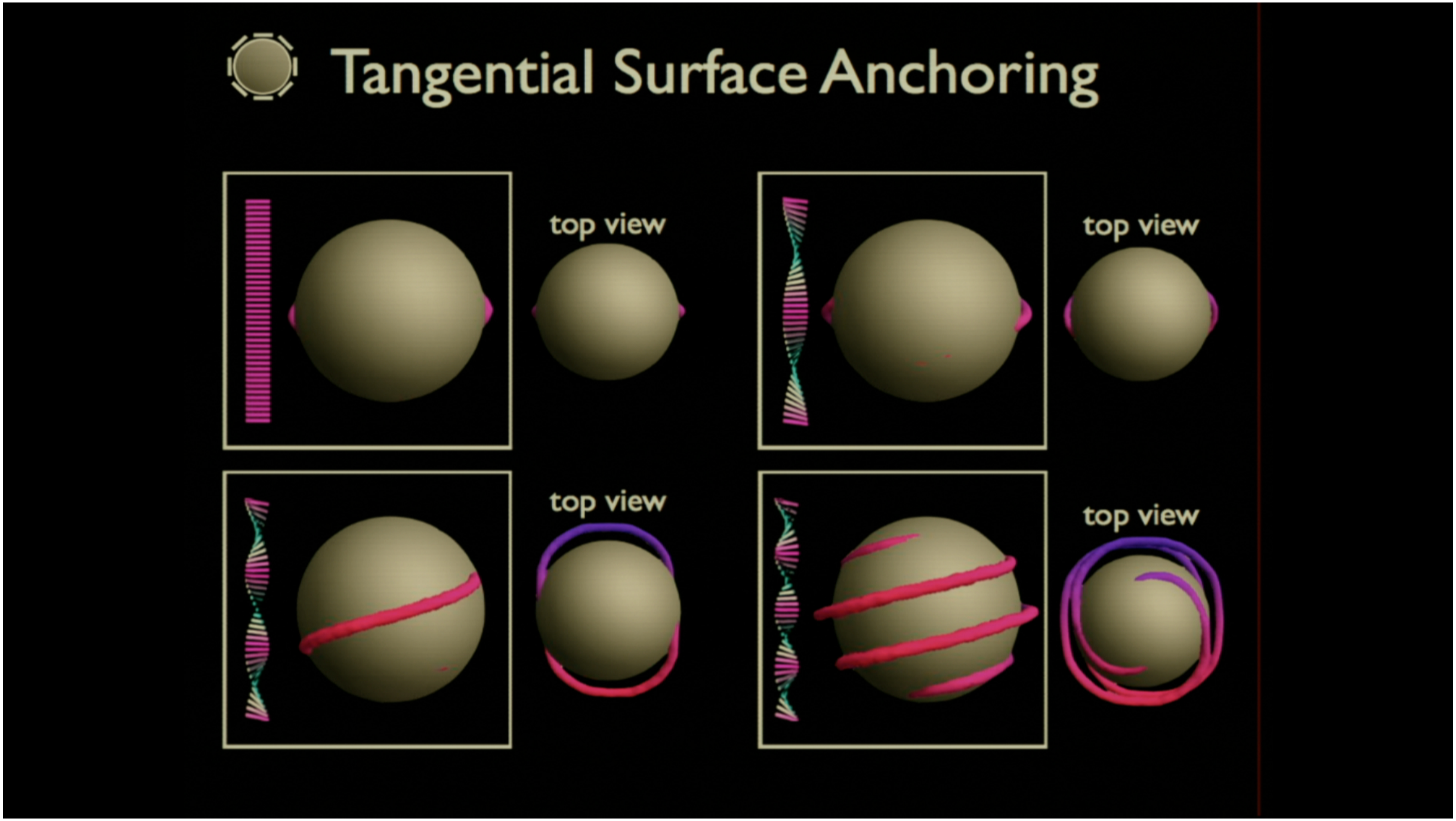
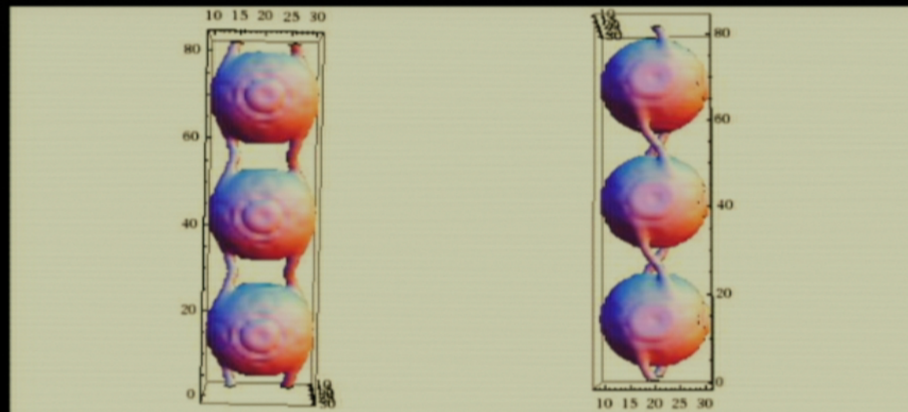
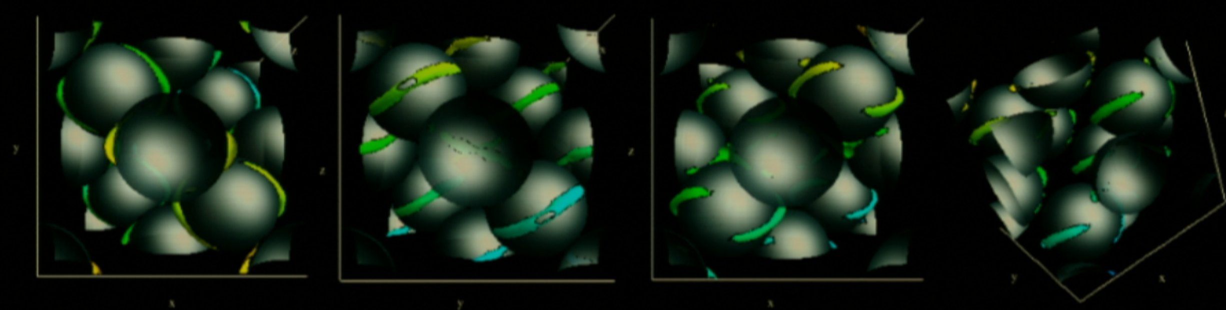

(a)
Free Energy (pN·μm)
bonded region
non-bonded region
(b)
α (Degrees)
α
Particle Separation (μm)


Tangential Surface Anchoring
top view
top view
top view
top view

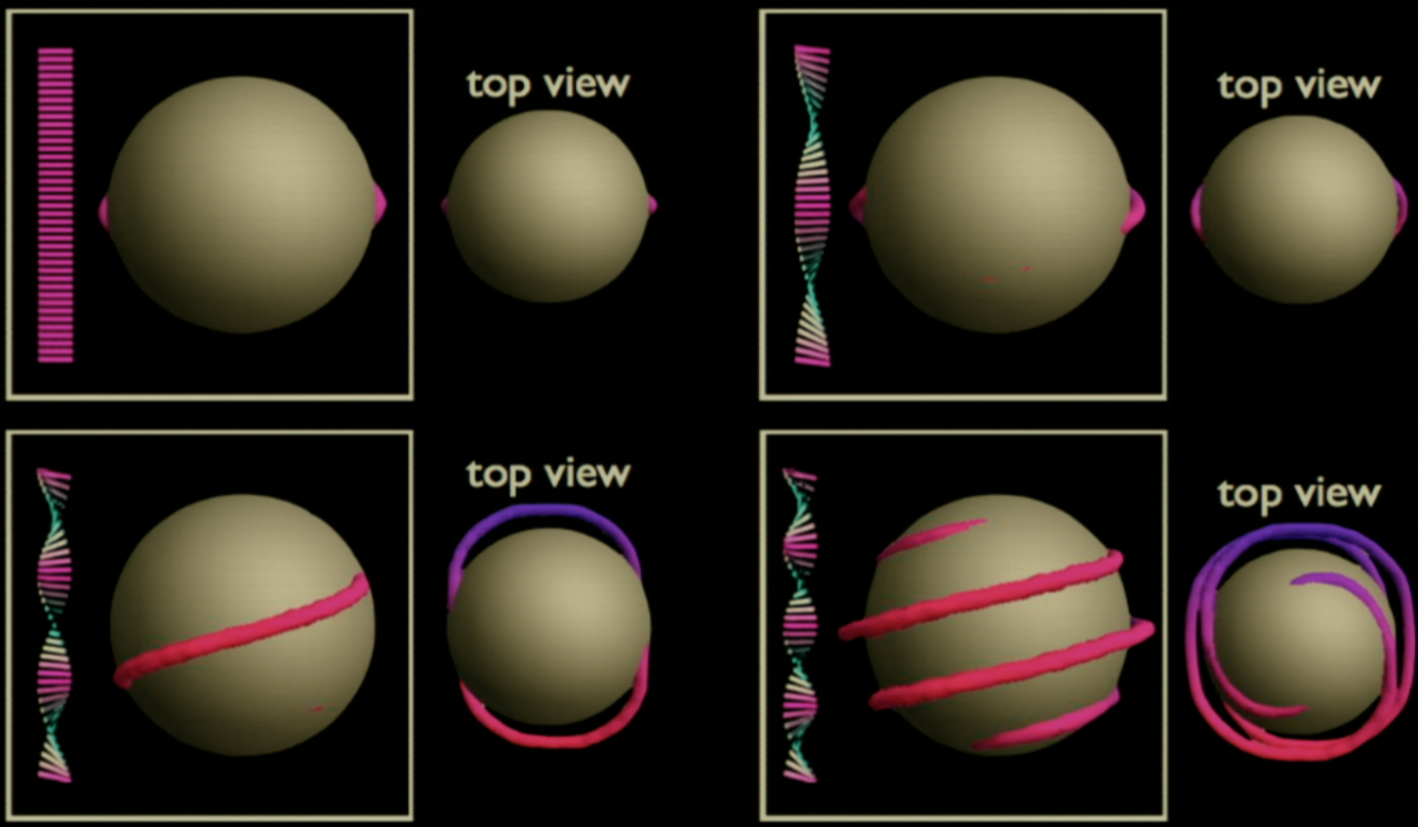
1D structures: Chain (polymer analogue)



3D structures: Diamond Lattice



Tangential Surface Anchoring



Lattice Structures for ⊥ anchoring

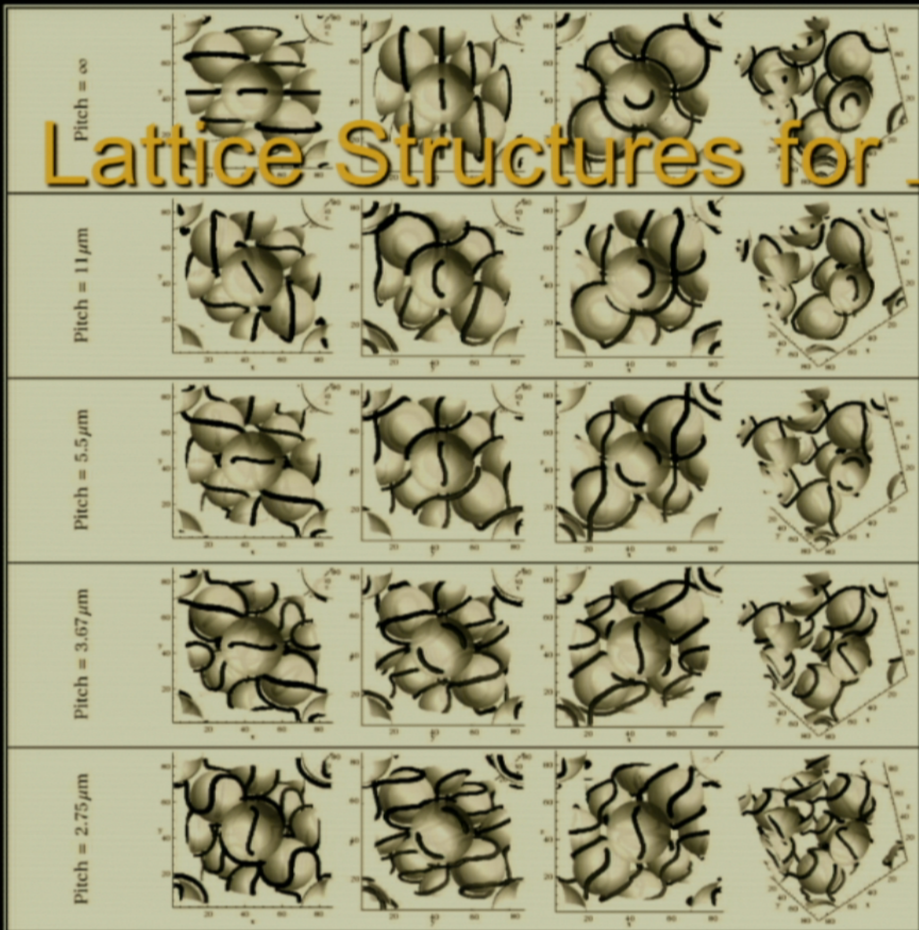
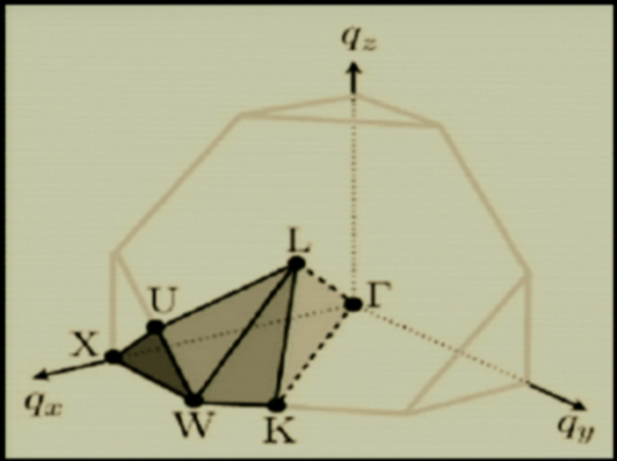
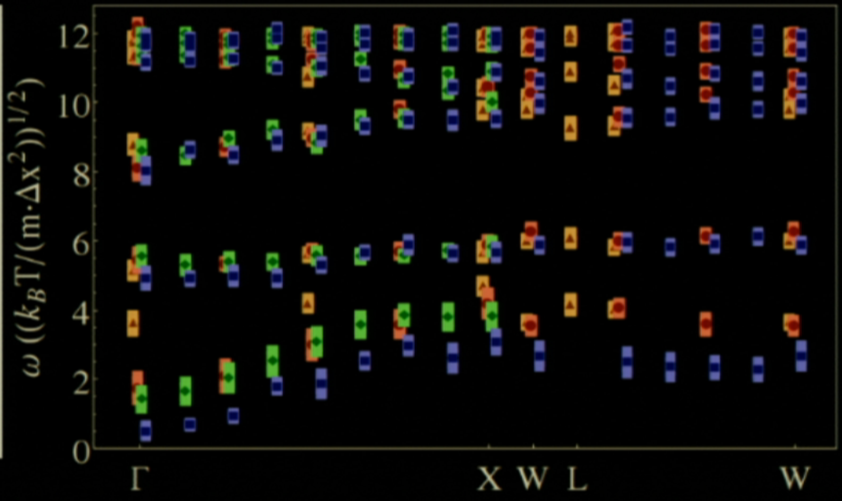


Figure 3 Various views of the defect structure around particles in a diamond lattice, as a function of the pitch of the cholesteric (corresponds to 0,1,2,3 and 4 twists in the system).

Is it stable?

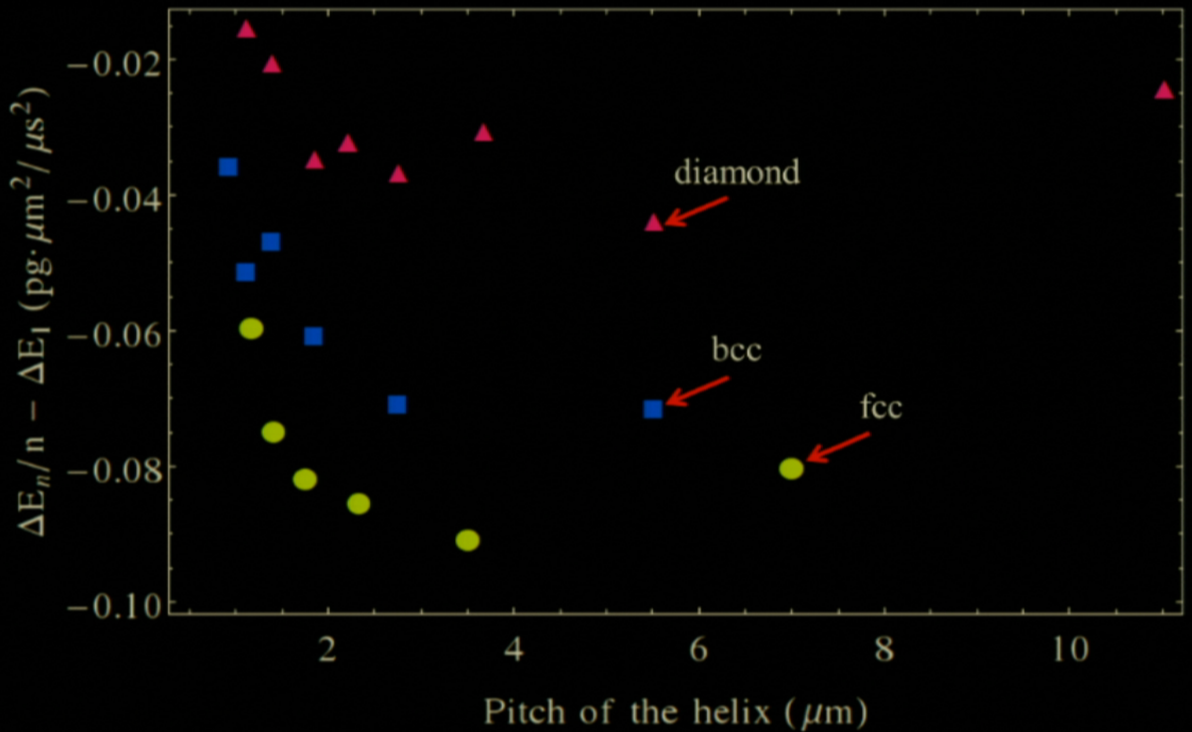
Add thermal noise and look at phonon spectrum (2nd derivative test for minima)





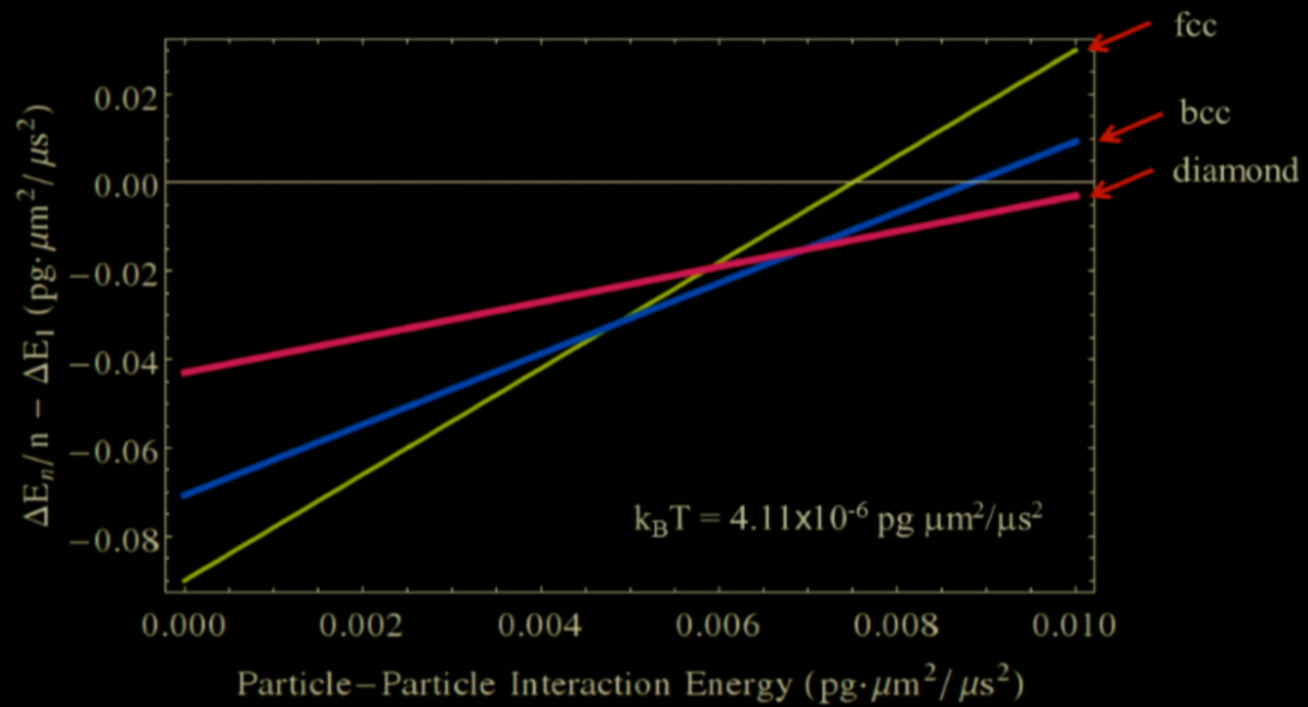
Number of unit cells
Orange:2x2x2, red:4x2x1,
green:8x1x1, blue:8x2x2

Other Lattices LC energy:



Further Stabilize diamond lattice?

-with short-range repulsive interaction between beads included



Summary & Conclusions

- Spheres in liquid crystals are accompanied by defects which can lead to non-trivial interactions
- Spheres in a cholesteric can give a "tetravalent" bonding structure, but it is phase locked to the background
- Homeotropic anchoring can lead to a stable diamond colloidal lattice