I Geometrically Frustrated Assembly (GFA)

Outline of lectures:

1) What is GFA? Illustrative view
2) Continuum theory / gradient ground-state order
3) Consequences of GFA (self limitation)
4) "Frustration escape"
5) Discrete models of GFA

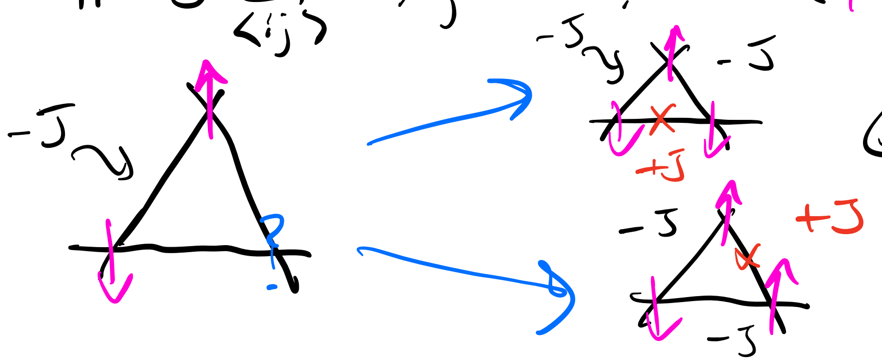
(if time)

Defining terms:

geometric frustration – obstruction of uniform, locally-favored (i.e. interactions) by non-local geometric constraints

Ex. Ising anti-ferromagnet, triangular lattice

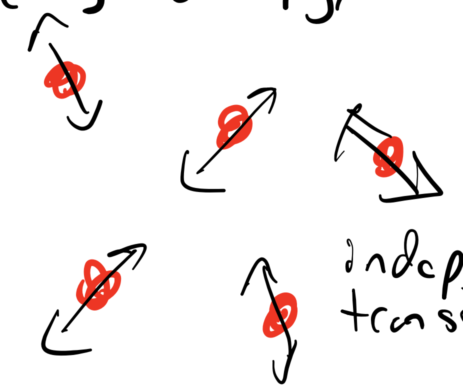
$$H = J \sum_{\langle ij \rangle} s_i s_j \qquad s_i = \pm 1 \quad (\uparrow \downarrow)$$



closed loops (odd #) obstructs uniform $-J$

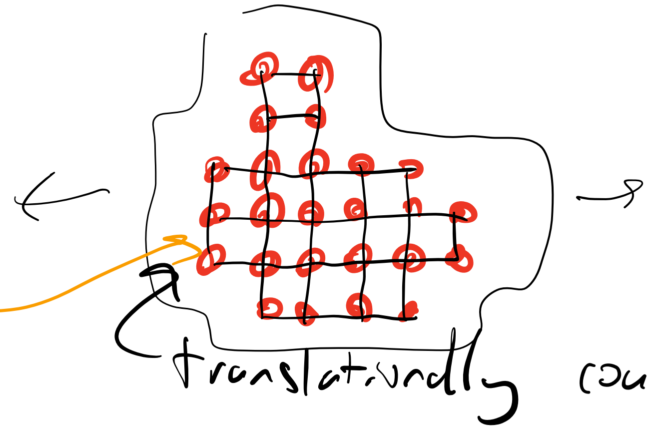
self-assembly - spontaneous (thermodynamic) formation of collective, multi-unit structure

free particles
(high entropy/low cohesion)



independent translation

aggregate
(low entropy/high cohesion)

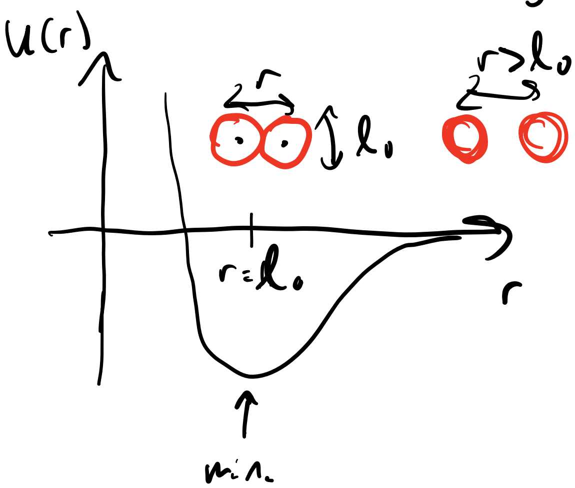


translationally coupled

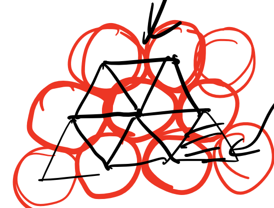
Network (graph of interactions)

1) emergent (not apriori fixed)
2) geometrically embedded

Ex. Short-range, isotropic attractions in 2D



all neighbors have $r=\ell_0$



repeating local motif

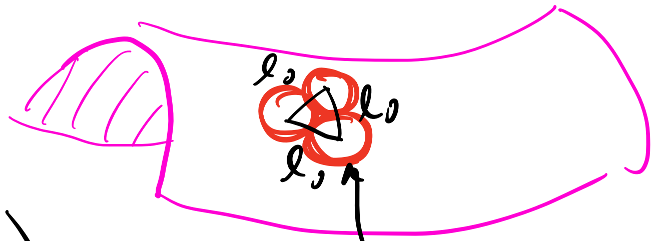
equilateral triangles tiles 2D plane

=> groundstate = uniform triangular lattice (e.g. crystal)

What about non-Euclidean surface?

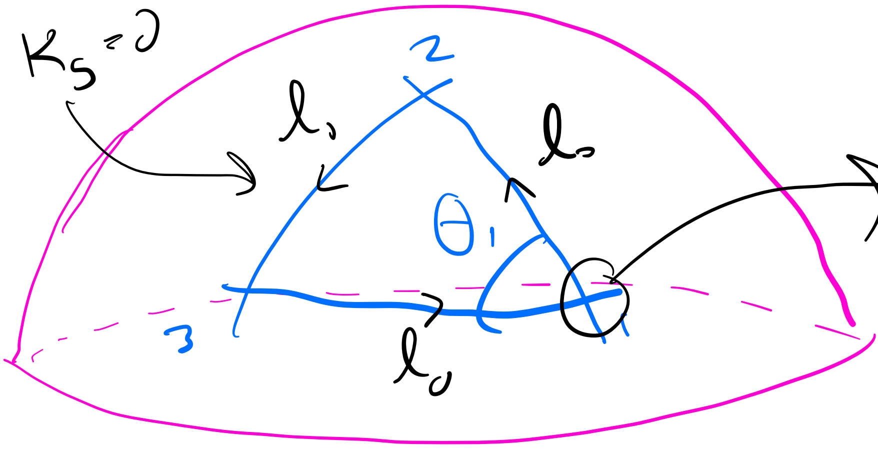
$K_G = \kappa_1 \kappa_2 \neq 0$

$K_G < 0$



can this continue?

$K_G > 0$
(e.g. spherical cap)



$$\oint_{\text{corner}_i} dl\, K_g = \pi - \theta_i$$

internal angle

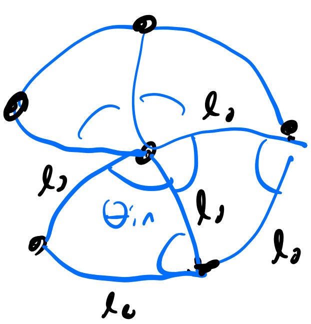
Gauss Bonnet: $\displaystyle\int_{\text{patch}} dA\, K_G + \oint_{\text{boundary}} dl\, K_g = 2\pi$

$$\Rightarrow \sum_{i=1}^{n} \theta_i = (n-2)\pi + \int dA\, K_G$$

geodesic triangle $\rightarrow 3\theta_{in}$, $\quad (n-2)\pi \rightarrow \pi$

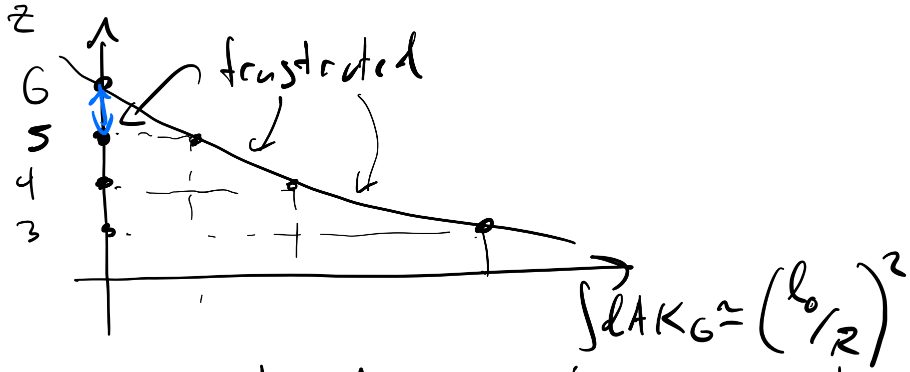
$$\theta_{in} = \frac{\pi}{3} + \int dA\, K_G \quad > \frac{\pi}{3} \text{ for } K_G > 0$$

$\sim l_0^2 K_G = (l_0/R)^2$ sphere



Z = # fitting particles around center (particle)

$$= \frac{2\pi}{\theta_{in}} = \frac{6}{1 + \int dA\, K_G}$$



Commensurate for special values (deltahedra):

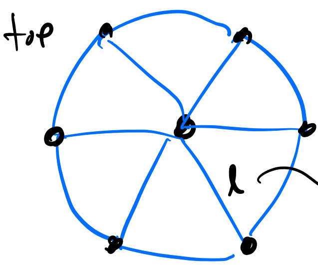
$z = 5$ (icosahedron) $\rightsquigarrow$ $3\theta_{in} - \pi = \int dA\, K_G$

$3\left(\frac{2\pi}{5}\right) - \pi = \frac{\pi}{5}$

$z = 4$ (octahedron)

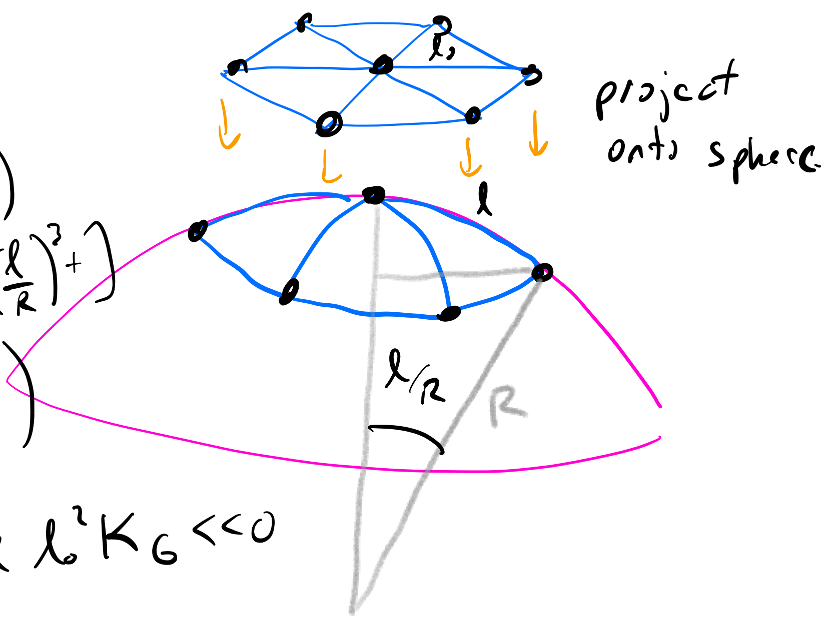
$z = 3$ (tetrahedron)

What happens for $\ell_0 \ll R$?



$z = 6$ is "closest" packing

$\ell = ?$ Estimate



$$\ell_0 = R \sin\left(\ell/R\right)$$
$$\approx R\left[\frac{\ell}{R} - \frac{1}{3!}\left(\frac{\ell}{R}\right)^3 + \right]$$
$$\approx \ell\left(1 - \frac{1}{6}\left(\frac{\ell_0}{R}\right)^2\right)$$

Misfit $\dfrac{\ell - \ell_0}{\ell_0} \propto \ell_0^2 K_G \ll 0$

→ elastic strain of interaction

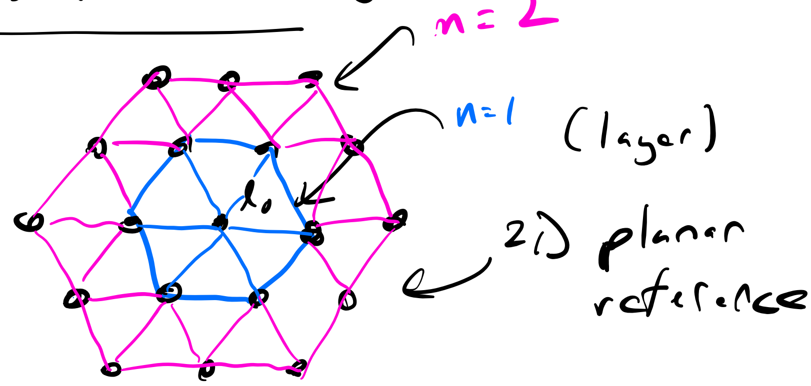
→ $z = 6$ still favored.

This is GFA limit. When misfit is small enough on local scale ℓ_0, but not necessarily for $r \gg \ell_0$.

We will show misfit grows with size

Example to try:

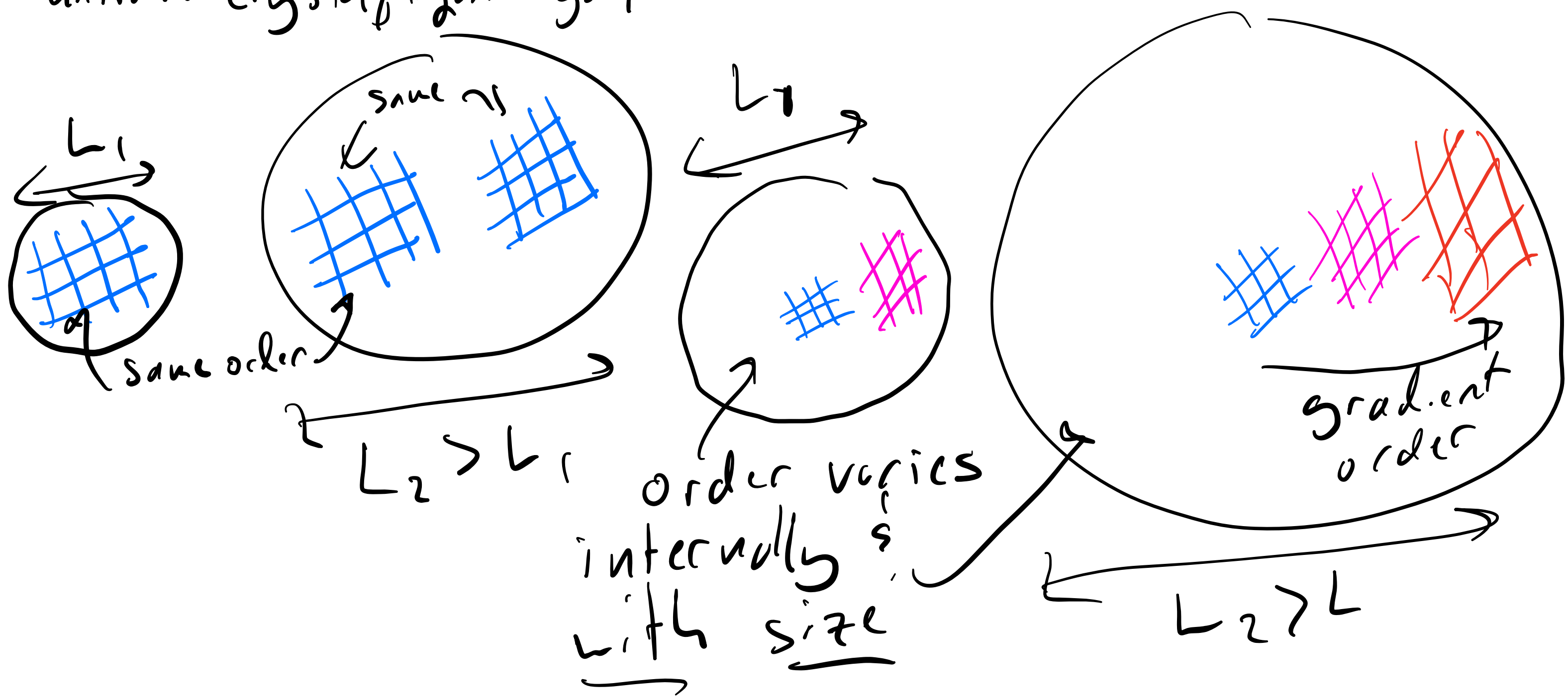
estimate $\ell(n)$ from spherical projection (assume $l_0/R \ll 1$)



GFA falls outside of standard paradigm

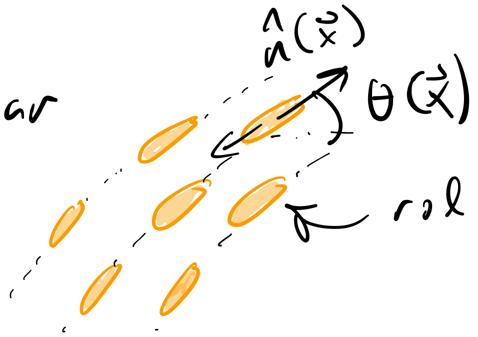
"Standard CM"
uniform crystal/liquid crystal

GFA (small frustration)



2nd illustration: 2D nematic liquid crystal

A) Planar



$$\hat{n} = \cos\theta(\vec{x})\,\hat{x} + \sin\theta(\vec{x})\,\hat{y}$$

Frank Free energy (distortions):

$$F = \frac{1}{2}\int dA \left[K_1 (\nabla_\perp \cdot \hat{n})^2 + K_3 (\nabla_\perp \times \hat{n})^2 \right]$$

$$\nabla_\perp \cdot \hat{n} = \partial_x n_x + \partial_y n_y \quad \text{"splay"}$$

$$\nabla_\perp \times \hat{n} = \partial_x n_y - \partial_y n_x \quad \text{"bend"}$$

What is ground state?

$\theta(\vec{x}) = \text{const.}$ (uniform, $F = 0$)

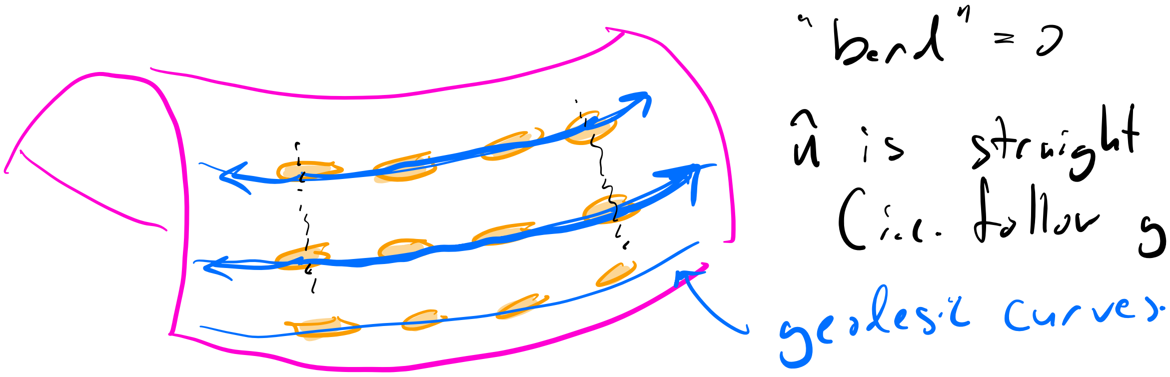
"splay" = "bend" = 0 everywhere.

B) 2D nematic on curved surface (tangential order)

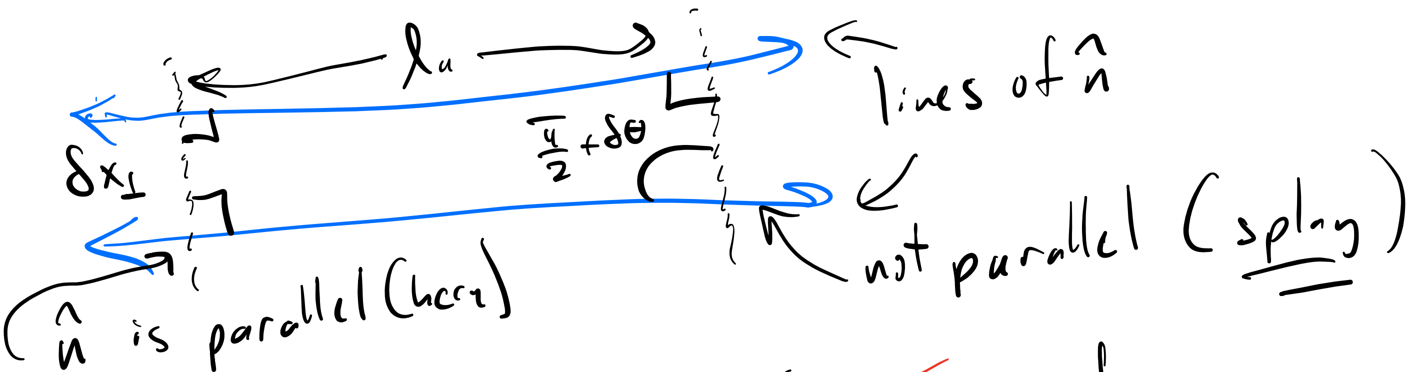
Consider $K_3 \to$ large

"bend" = 0

$\hat{n}$ is straight (i.e. follow geodesics)



Consider the quadralateral polygon.



$$\sum_i \theta_i = \underbrace{\cancel{4\times\frac{\pi}{2}}}_{=2\pi} + \delta\theta = \underbrace{\cancel{(4-2)\pi}}_{=2\pi} + \int dA\, K_G$$

$$\boxed{\delta x_\perp l_u K_G \simeq \delta\theta}$$

$$\text{"splay"} \simeq \left|\frac{\delta\hat{n}}{\delta x_\perp}\right| \simeq \frac{\delta\theta}{\delta x_\perp} \simeq l_u K_G$$

in general for GFA $\quad$ "strain" $\simeq l_u^{\,n} \times |\text{frustration}|$

$n = 1$ or 2

$\Rightarrow$ Strain gradients in ground state order grow with size & frustration.

Slides: More GFA examples &

Canonical models of 3D frustration

- polytetrahedral order
- double-twist in chiral LC