“Chiral” Phase Transitions and Elasticity in Frustrated Polyelectrolyte Bundles

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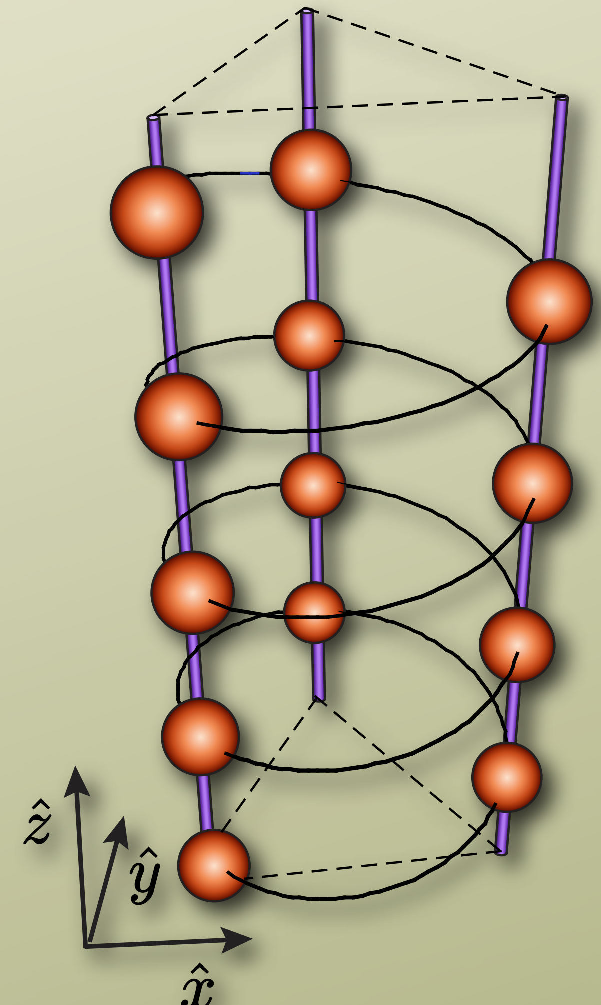
preprint available at *cond-mat/0601462*



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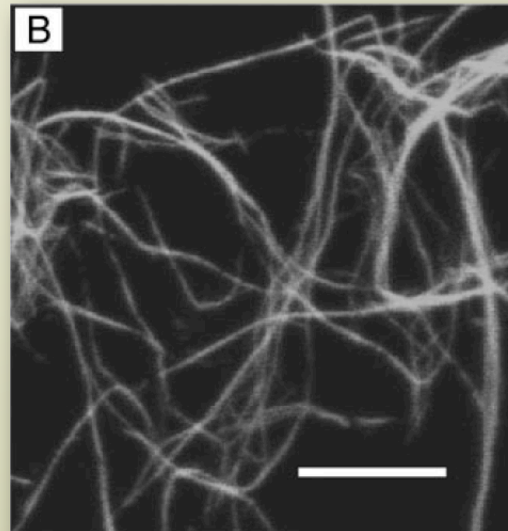
NSF DMR04-04507

Bundling of Bio-Macromolecules *in vitro*

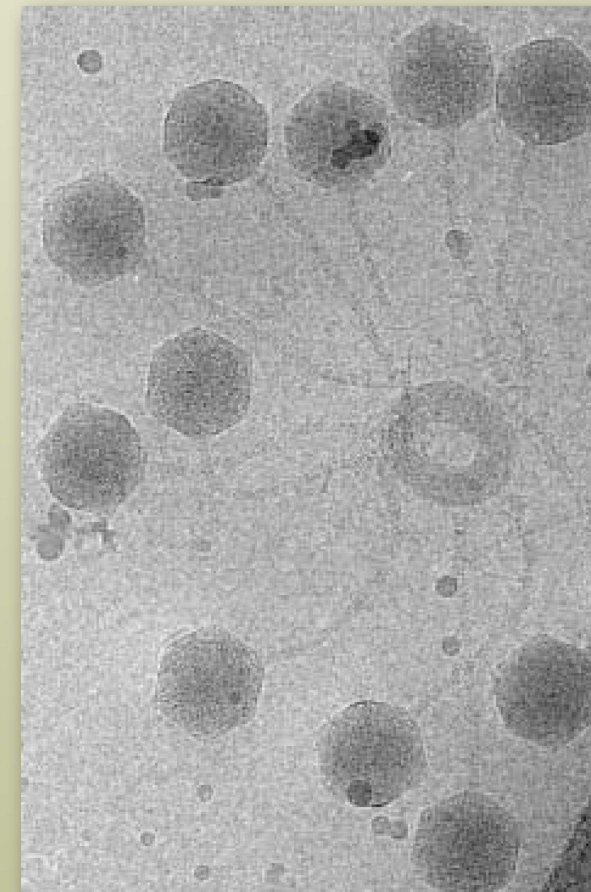
aqueous solution
(buffer & salt)
+
stiff, charged polymers
(low concentration)
+
*poly*valent counterions
(low concentration)

= spontaneous bundle condensation

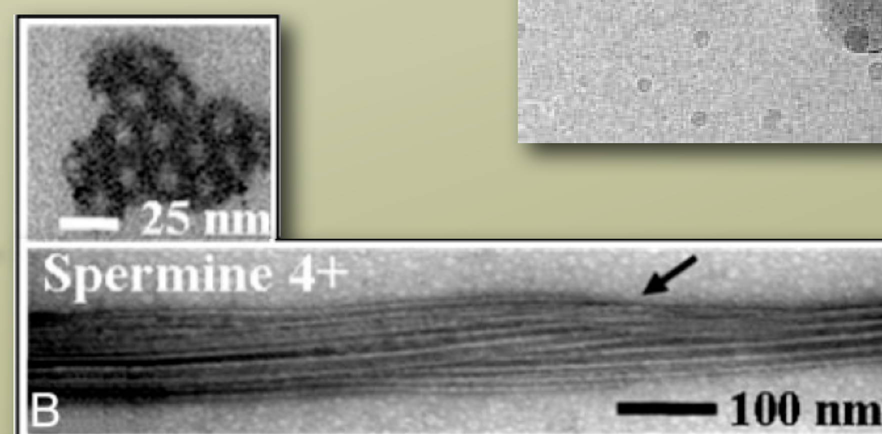
actin filaments



DNA



microtubules



Angelini, Liang, Wriggers & Wong, *PNAS* (2003).
Lambert, Letellier, Gelbart & Rigaud, *PNAS* (2001).
Needleman, Ojeda-Lopez, Raviv, Miller, Wilson & Safinya, *PNAS* (2004).

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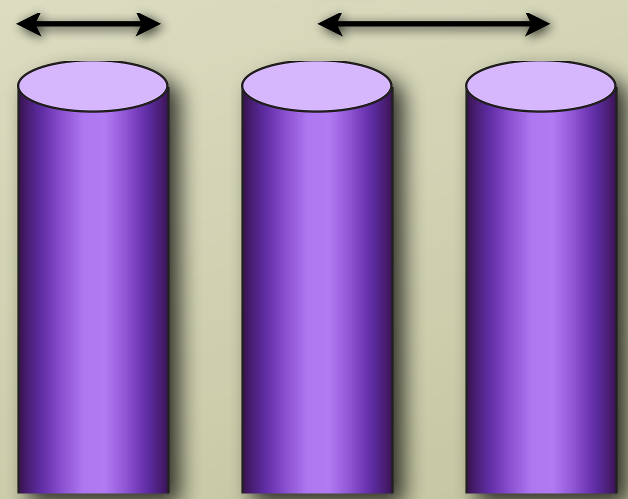
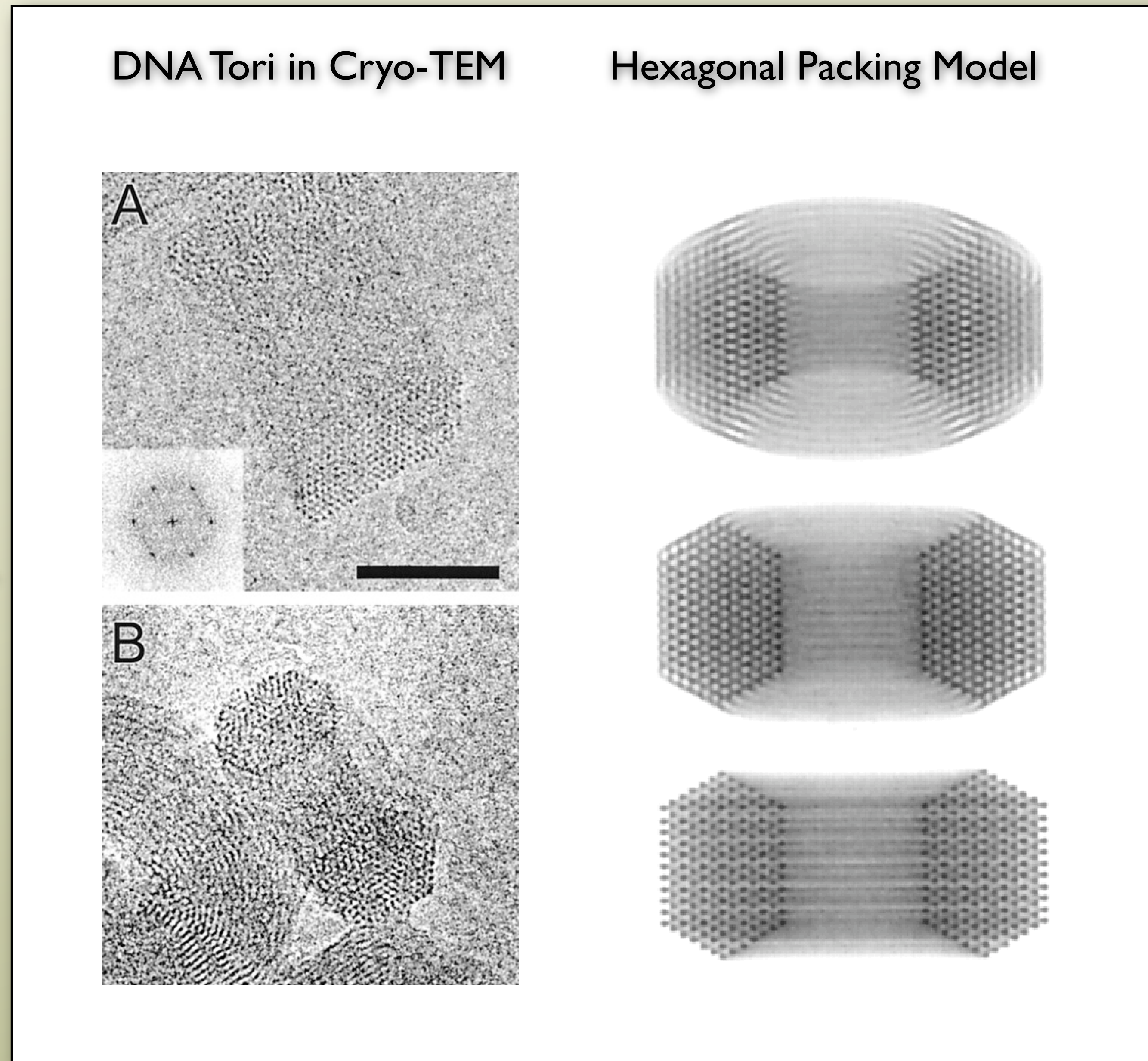
Condensed Polyelectrolyte Structure

Aggregates are hexagonal packing of rod-like macromolecules

DNA bundles:

$D = 20\text{Å}$ $\quad R_{nn} \approx 20 - 40\text{Å}$





Hud & Downing, *PNAS* (2001).

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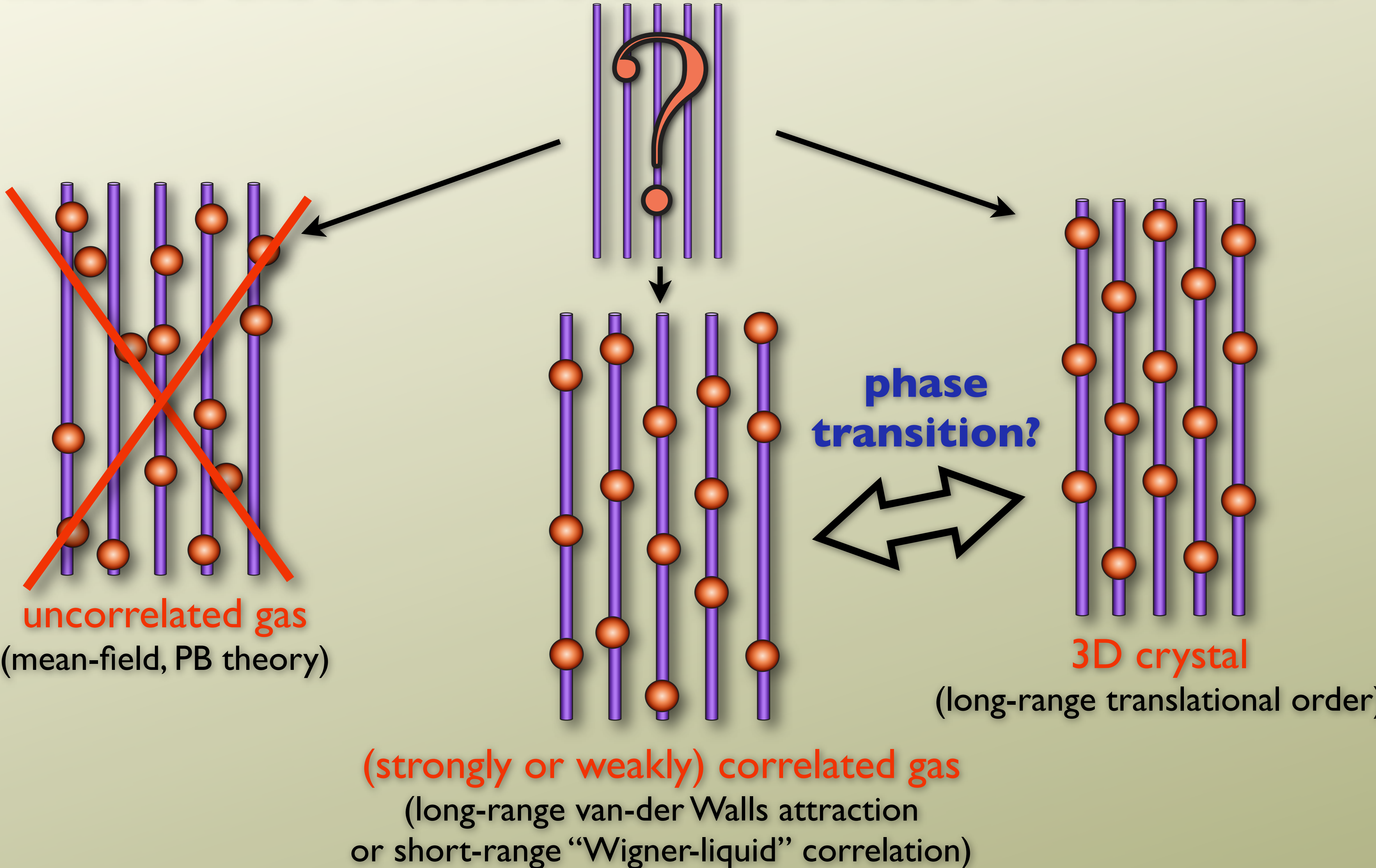
What is the structure of condensed counterions?



Bloomfield, *Bio. Poly.* (1997); Grosberg, Nguyen &Shklovskii , *RMP* (2002); Levin, *RPP* (2002).

Outline

-Counterion fluctuations near phase transition:

- -Longitudinal phonons of Wigner solid
- -Rod-rod interactions

-"Spin" Hamiltonian for counterion fluctuations in bundle

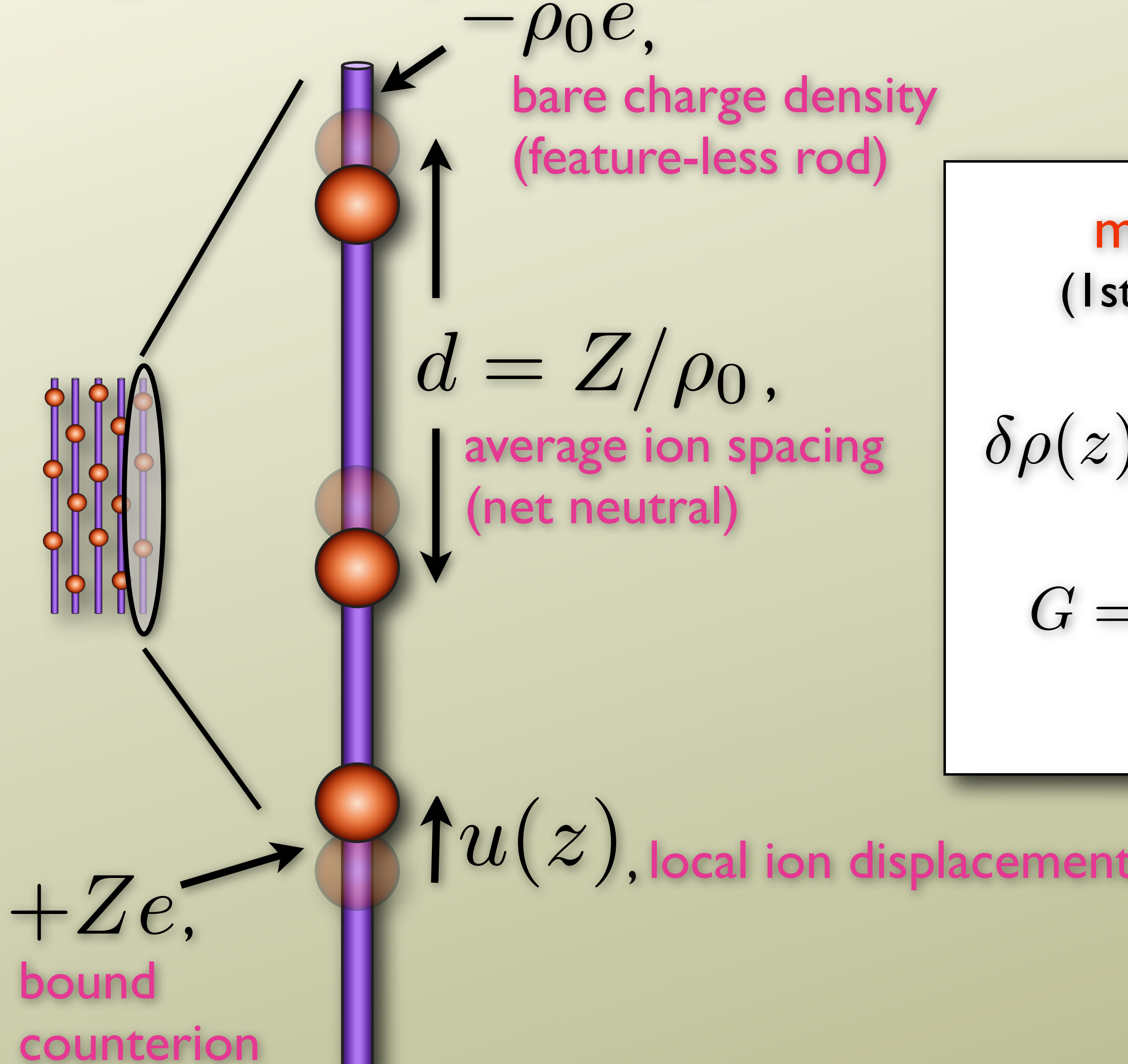
-Freezing transition:

- -Mapping to insulating-to-superconducting transition in d=2 arrays of Josephson junctions at T=0
- -Current response of Josephson array vs. elastic response of polyelectrolye bundle

-Effect of polyelectrolyte structure:

- -Excluded volume effects of core
- -Chirality, molecular pitch, and vortex ground states

Phonon Fluctuations of One-Dimensional Wigner "Crystal" (primitive model)



modulated charge density
(1st Fourier mode approximation)

$$\delta\rho(z) \simeq \frac{2Z}{d}\cos\Big(G(z-u(z))\Big)$$

$$G = \frac{2\pi}{d}$$, reciprocal lattice vector

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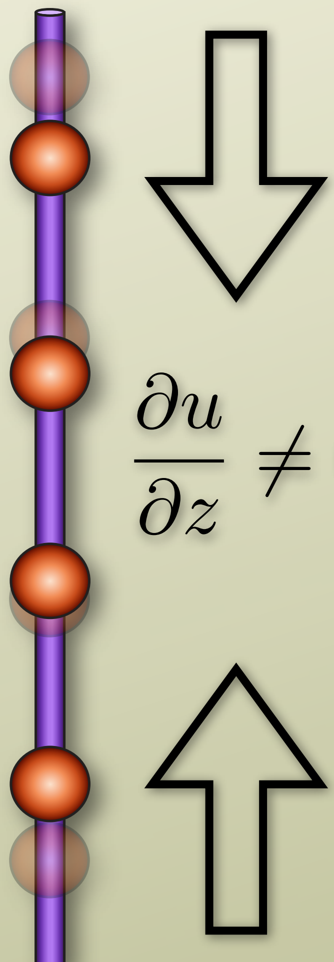
1D Phonon Fluctuations of Single Rod Destroy Long-Range Order of “Crystal”

longitudinal fluctuation



$$\frac{\partial u}{\partial z} \neq 0$$

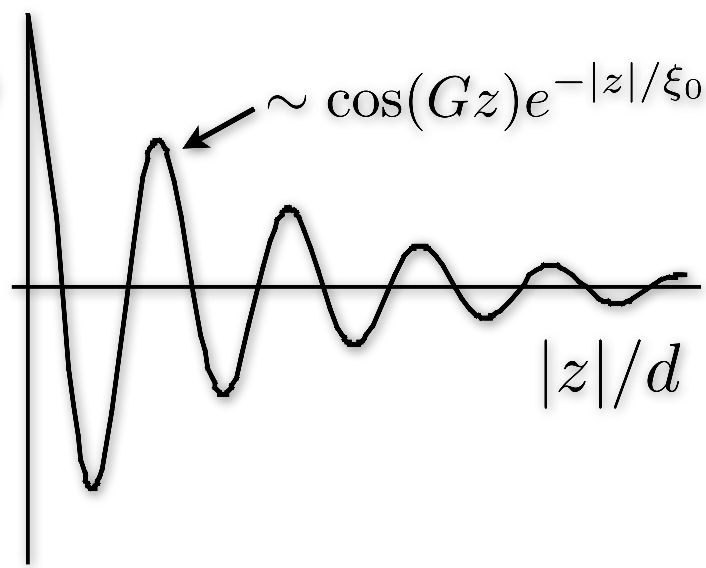
compressibility of 1D charge “crystal”

long-wavelength fluctuation

$$H_{rod}[u(z)] = \frac{CG^2}{2} \int_0^L dz \left(\frac{\partial u}{\partial z}\right)^2; \quad CG^2 \sim \frac{(Ze)^2}{d^2}$$

liquid-like charge correlations

$$\langle \delta\rho(z) \rangle \sim e^{-L/\xi_0} \to 0, \quad \xi_0 = 2\beta C$$



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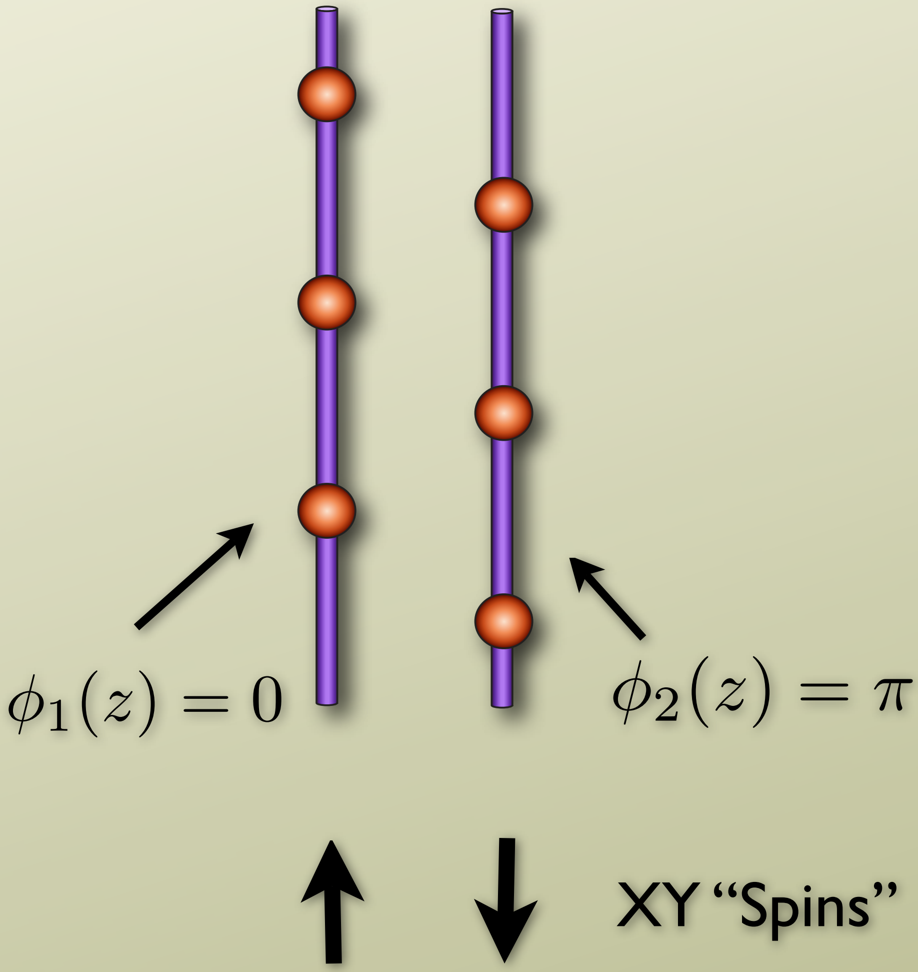
Ion Fluctuations and XY Spins

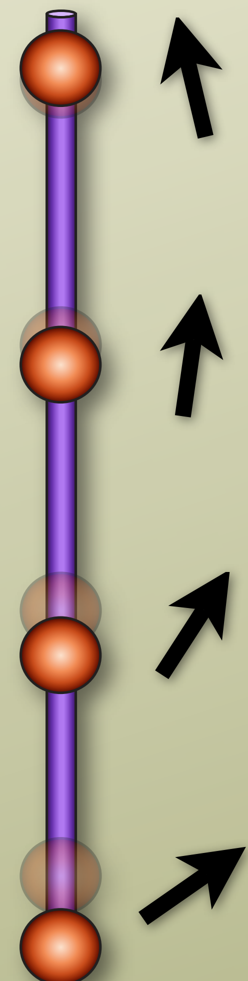
rod (or "spin") phase

$$\phi_i(z) = G u_i(z)$$



Periodicity of 1D Lattice:

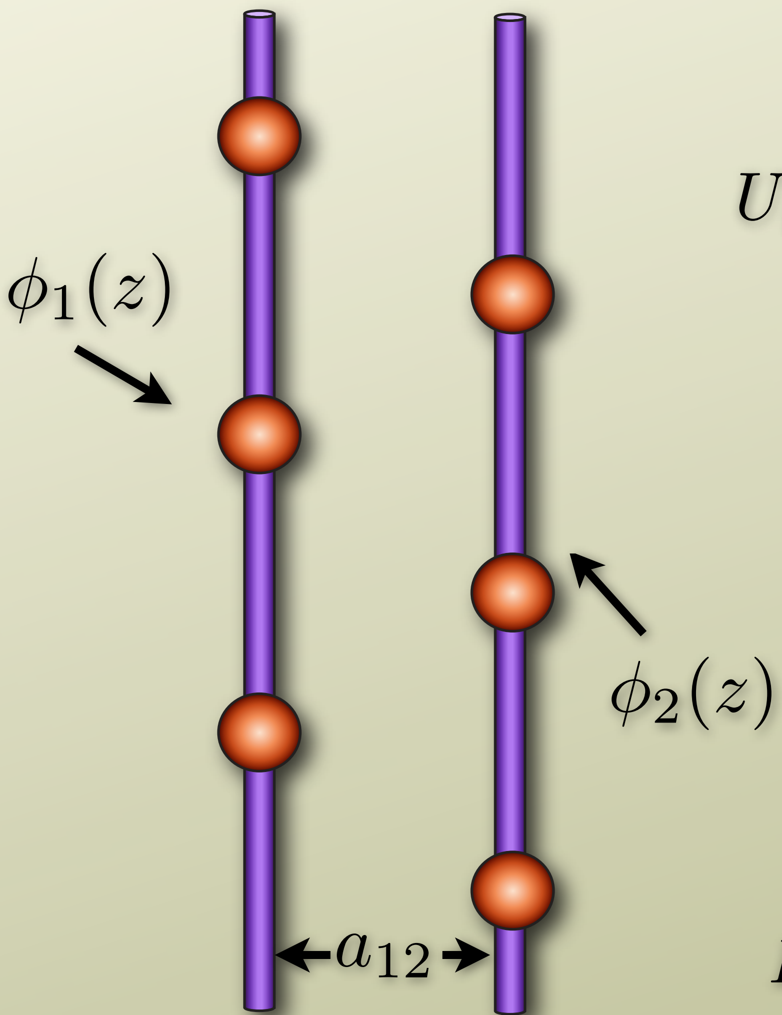
$u(z) \rightarrow u(z) + d$ (or $\phi(z) \rightarrow \phi(z) + 2\pi$)



longitudinal phonon = phase or "spin" gradient

$$\frac{\partial \phi}{\partial z} \neq 0$$

Rod-Rod Interactions and XY Anti-Ferromagnet



(screened) Coulomb interaction

$$U_{int} = \int dz_1 dz_2 \; \delta\rho_1(z_1) V(|\mathbf{r}_1 - \mathbf{r}_2|) \delta\rho_1(z_2)$$

$$\simeq -E_{12} \int dz \cos\Big(\phi_1(z) - \phi_2(z) - \pi\Big)$$

electrostatics favors “anti-alignment” of rod phases (charge staggering)

$$E_{12} \propto \frac{(Ze)^2}{d^2} K_0(Ga_{12}),$$ effective coupling strength (short-ranged interactions)

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“Spin” Model of Frustrated Hexagonal Bundle

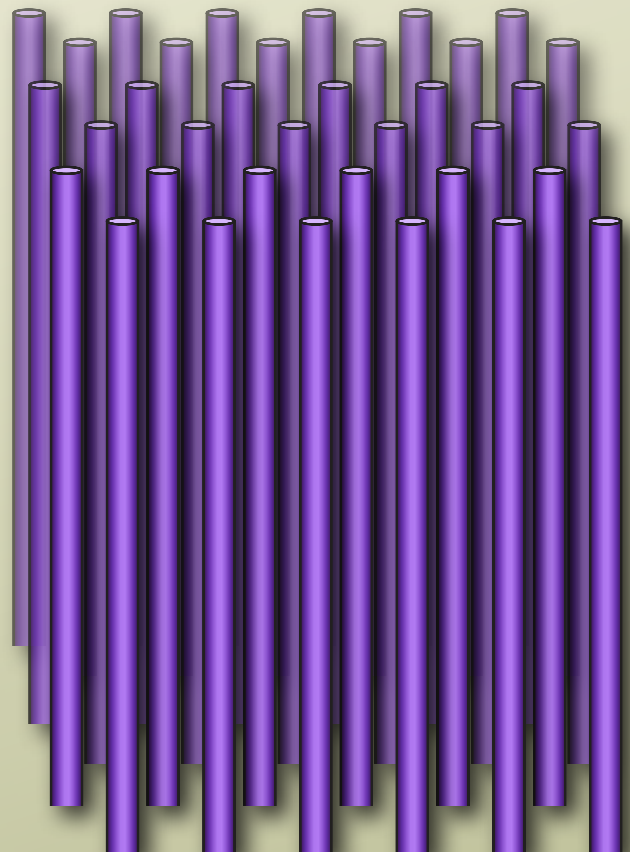
longitudinal fluctuations

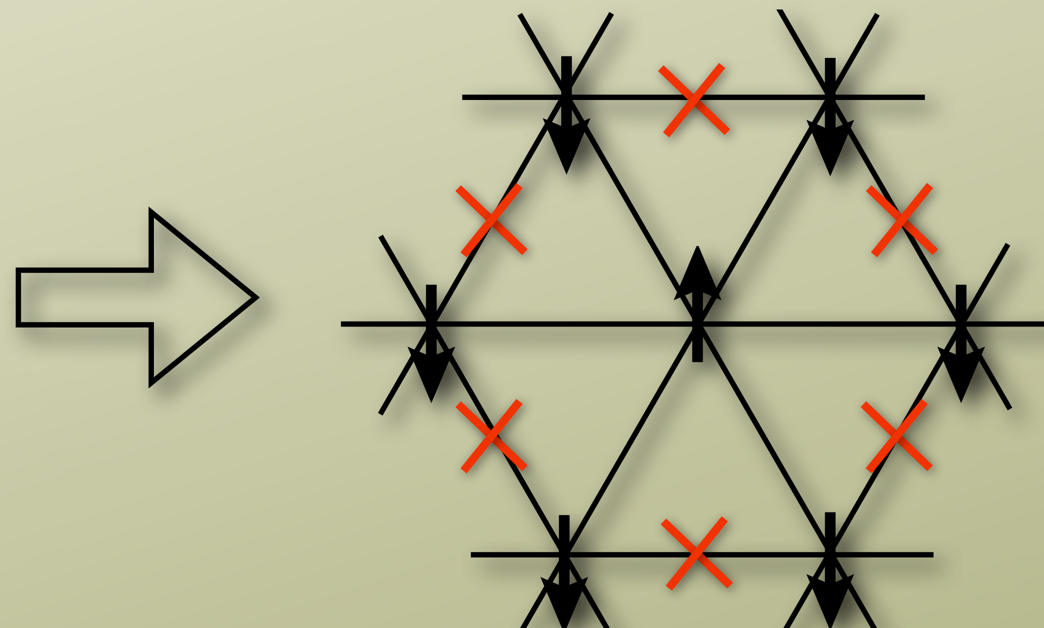
nearest-neighbor interaction

$A_{ij} = \pi$

$$H[\phi_i(z)] = \int_0^L dz \Big\{ \sum_i \frac{C}{2}\Big(\frac{\partial \phi_i}{\partial z}\Big)^2 - E_{ij} \sum_{\langle ij \rangle} \cos\big(\phi_i(z) - \phi_j(z) - A_{ij}\big) \Big\}$$

$$\phi_i(z) = G u_i(z)$$





triangular lattice is frustrated!

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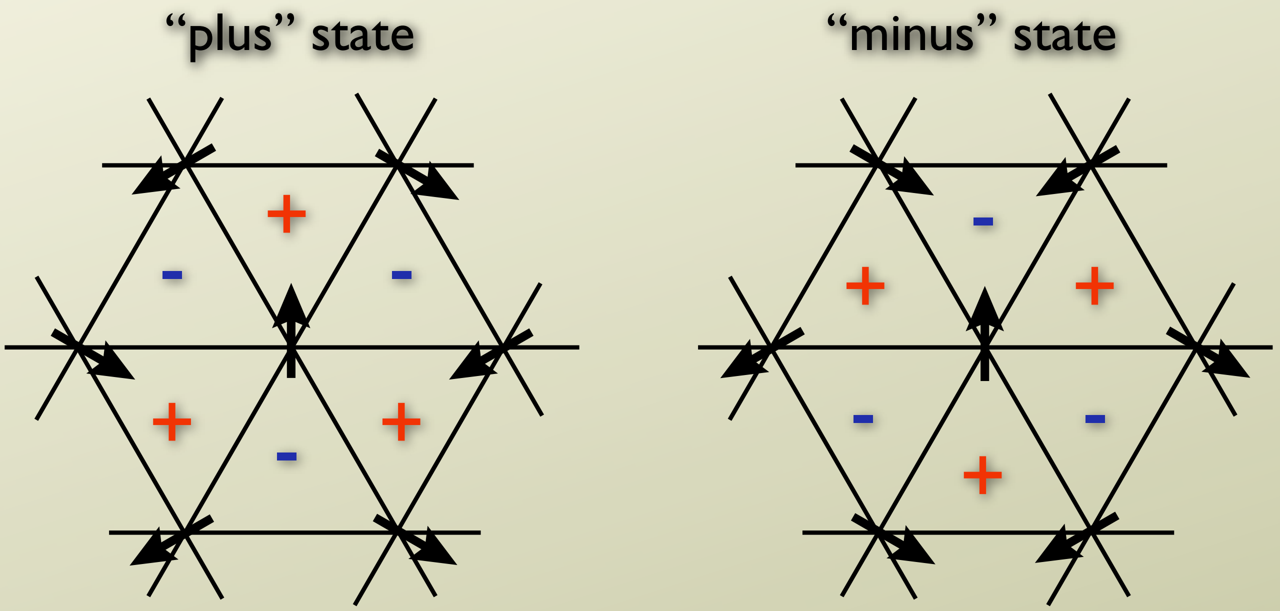
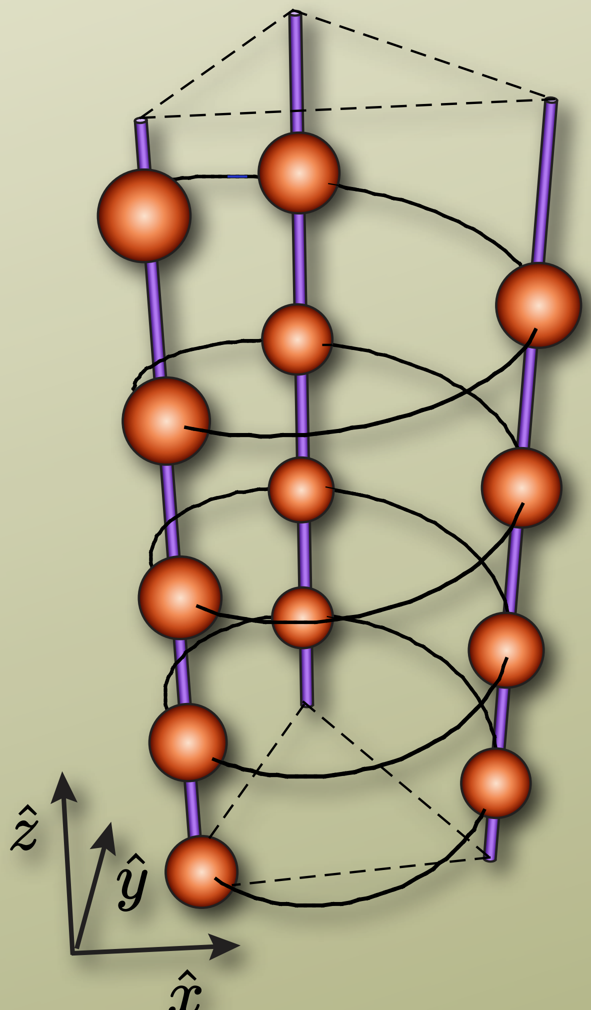
Charge Ordered Ground States are Locally "Chiral"

2 degenerate ground states



helical winding around plaquette



Charge ordering breaks discrete as well as continuous symmetry, U(1) x Z_2 order parameter

Kawamura, *J. Phys.: C. M.* (1998).

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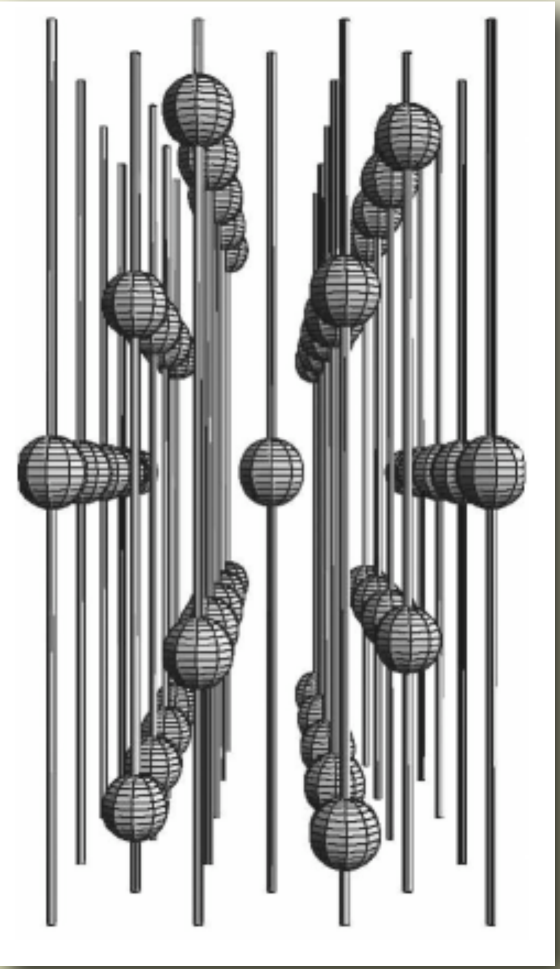
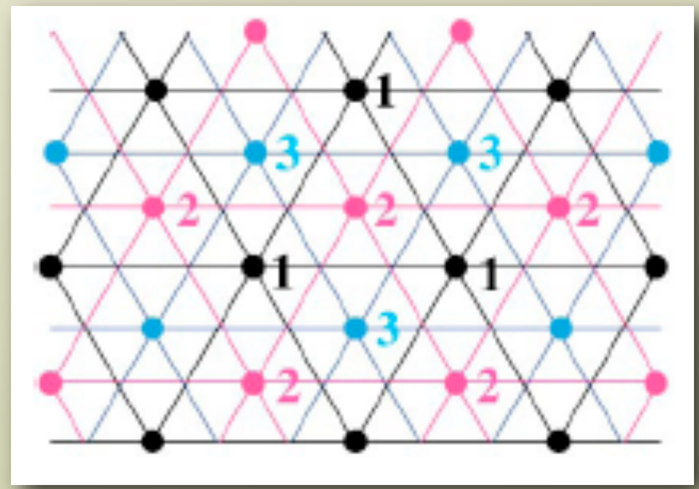
Counterion ground states are FCC-like (BCT) stacking of hexagonal arrays

bundle side view



bundle top view



2 discrete ground states correspond to ABCABC or ACBACB stacking (not 3D chiral)

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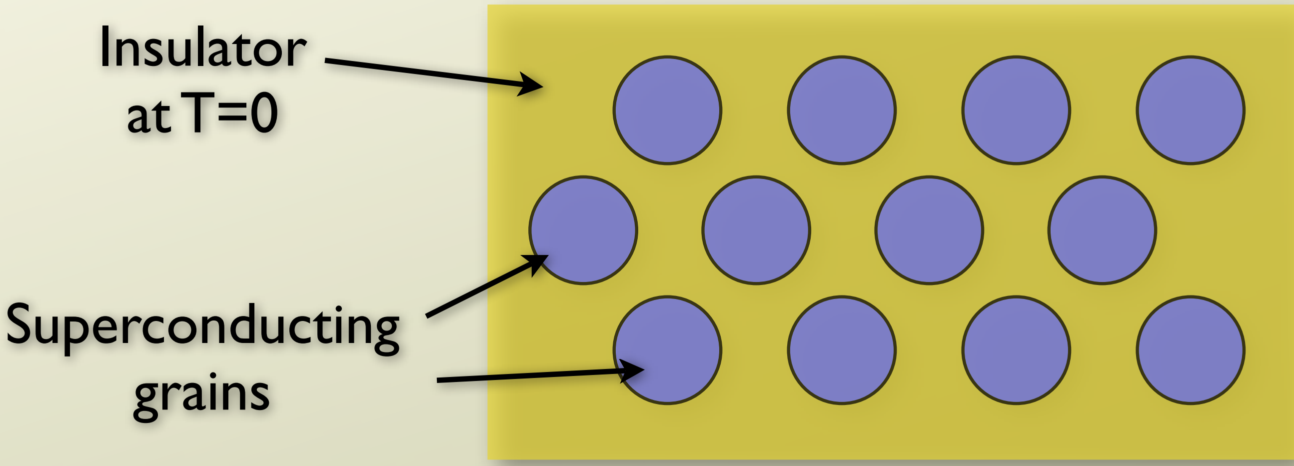
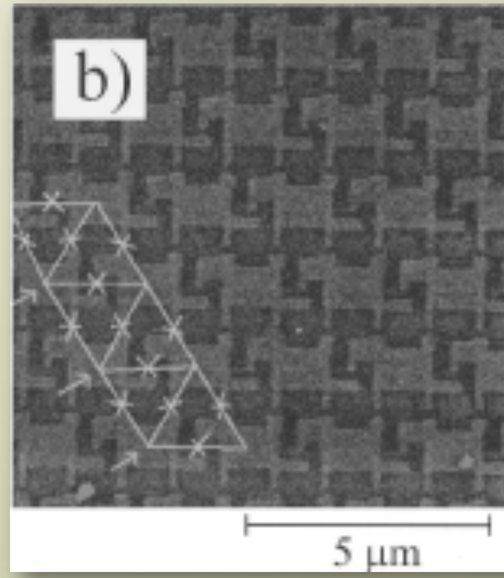
Rudnick & Jasnow, *PRE* (2003).

Mapping to Frustrated 2D Josephson-Junction Array at T=0

array top view



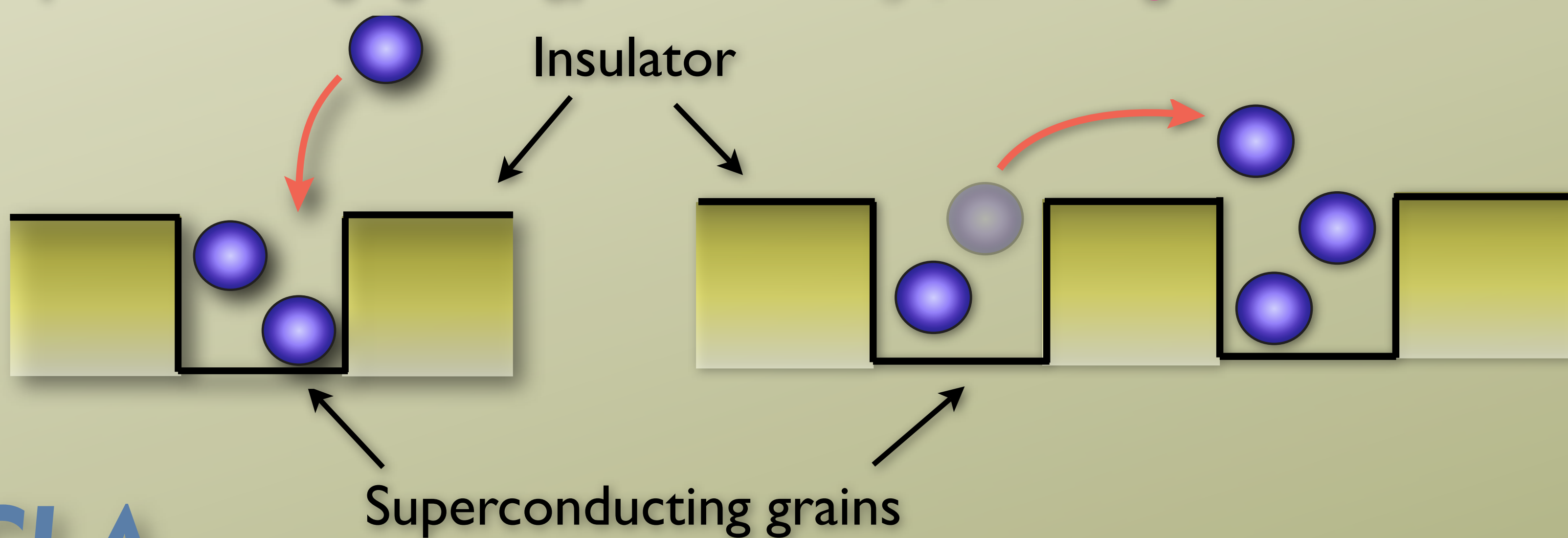


van der Zant, *et al. PRB* (1996).

array side view

E_C, capacitive charging energy

E_J, tunneling matrix element



H, applied field

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Array Action vs. Bundle Free Energy

Finite-T Path-Integral Representation:

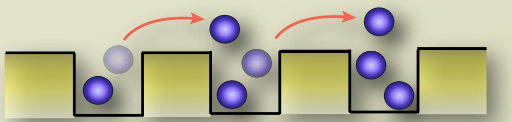
applied vector potential

$$A_{ij} = \frac{2\pi}{\Phi_0}\int_i^j d\mathbf{x}\cdot\mathbf{a}$$

Classical action

τ, imaginary time

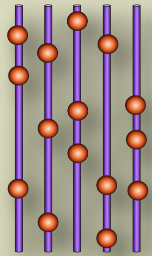
$$\mathcal{S}[\phi_i(\tau)] = \int_0^{\hbar\beta} d\tau \left\{ \sum_i \frac{1}{2E_C}\left(\frac{\partial\phi_i}{\partial\tau}\right)^2 - E_J \sum_{\langle ij\rangle} \cos\left(\phi_i(\tau) - \phi_j(\tau) - A_{ij}\right) \right\}$$



ϕ_i , superconducting phase

$n_i = -i\dfrac{\partial}{\partial\phi_i}$, number operator

Doniach, *PRB* (1981).



longitudinal fluctuations

nearest-neighbor interaction

$A_{ij} = \pi$

$$H[\phi_i(z)] = \int_0^L dz \left\{ \sum_i \frac{C}{2}\left(\frac{\partial\phi_i}{\partial z}\right)^2 - E_{ij} \sum_{\langle ij\rangle} \cos\left(\phi_i(z) - \phi_j(z) - A_{ij}\right) \right\}$$

ϕ_i , longitudinal ion displacement

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Phase Behavior Frustrated ($A_{ij} = \pi$) Systems

d=2 triangular JJ array

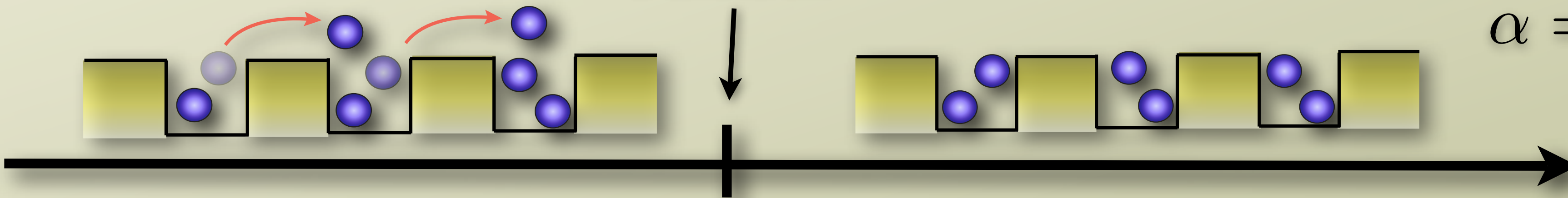
Superconducting

$$\rho_s = \langle \psi_i^2 \rangle \neq 0$$

Insulating

$$\rho_s = 0$$

continuous transition



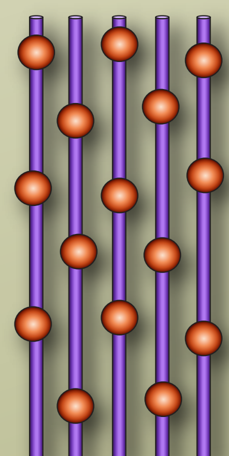
$$\alpha = \frac{E_C}{E_J}$$

$$\alpha_c = 6$$

d=3 hexagonal PE bundle

Charge Solid

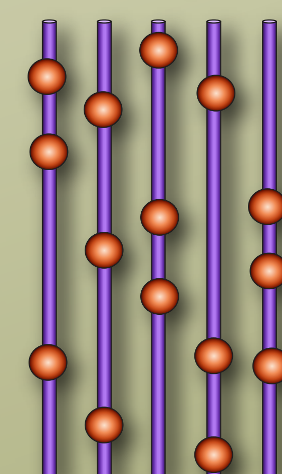
$$\langle \delta\rho_i(z) \rangle \neq 0$$



Charge Liquid

$$\alpha = (\beta^2 C E_{ij})^{-1}$$

$$\langle \delta\rho_i(z) \rangle = 0$$



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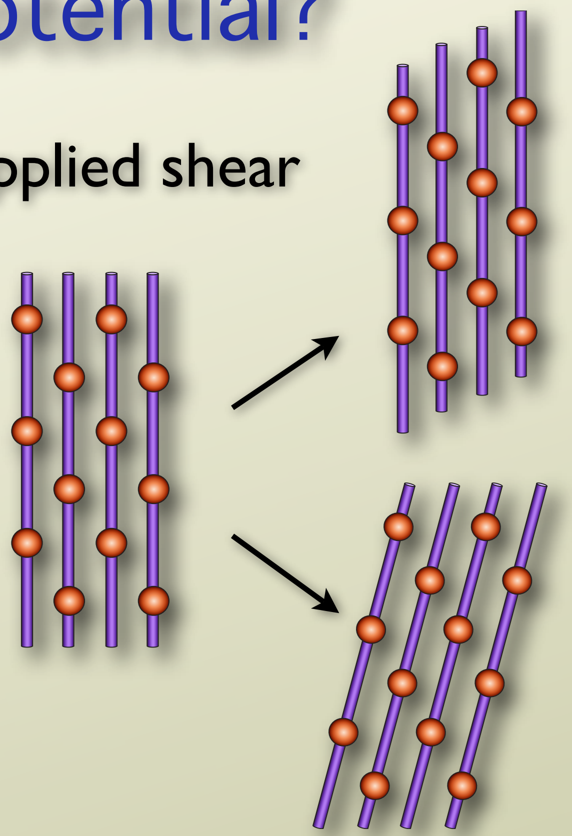
Granato & Kosterlitz *PRL* (1990).

What plays the role of the applied vector potential?

applied shear



nearest-neighbor interactions

$$-\int dz E_{ij} \sum_{\langle ij \rangle} \cos\left(\phi_i(z) - \phi_j(z) - A_{ij}\right)$$

$$A_{ij} \to \pi + 2G \int_i^j dx_i \epsilon_{zi}$$

$$\epsilon_{ij} = \frac{1}{2}\left(\partial_i u_j + \partial_j u_i\right)$$, strain tensor

Current response of JJ Array

Elastic response (to shear) of PE Bundle

$$j_x(\omega) = C_{xx}(w) a_x(\omega) \longrightarrow \sigma_{xz}(q_z) = C_{xzxz}(q_z)\epsilon_{xz}(q_z)$$

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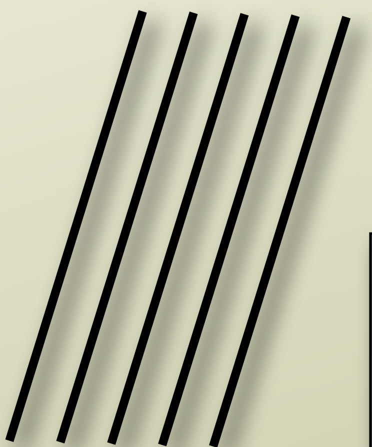
Current (Elastic) Response in SC (Solid) vs. Ins. (Liquid) Phases

superconducting — uniform shear

$$j_x = \rho_s a_x \longrightarrow \sigma_{xz} = \mu \epsilon_{xz}$$

dielectric — bending

$$j_x = \omega^2 \epsilon a_x \longrightarrow \sigma_{xz} = q_z^2 K \epsilon_{xz}$$



Continuum Elasticity

$$F = \frac{1}{2} \int d^3x d^3x' \epsilon_{ij}(x) C_{ijkl}(x, x') \epsilon_{kl}(x')$$

$$\sigma_{ij}(x) = \frac{\delta F}{\delta \epsilon_{ij}(x)} = \int d^3x' C_{ijkl}(x, x') \epsilon_{kl}(x')$$

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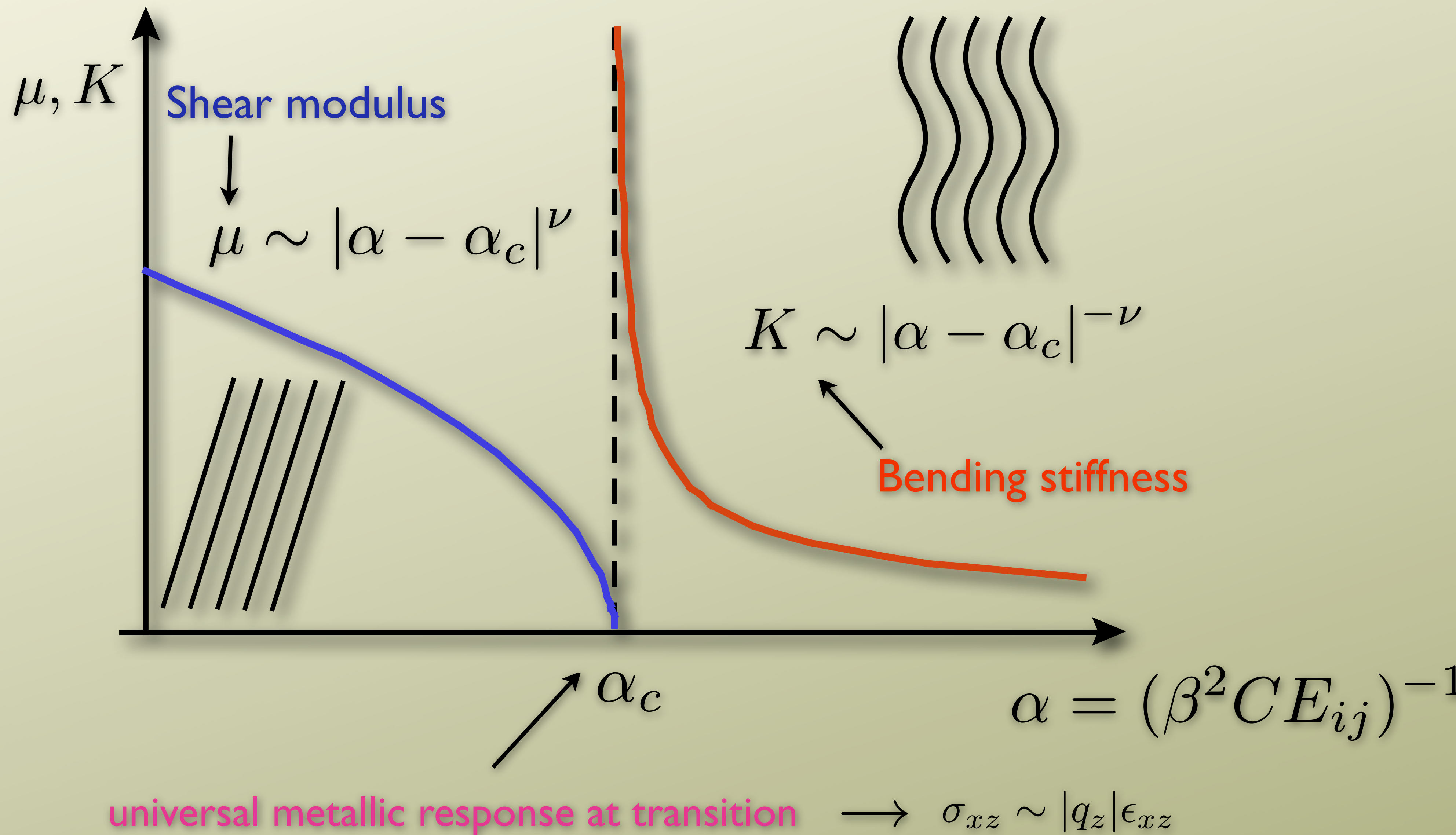
Charge ordering leads to anomalous growth in shear response



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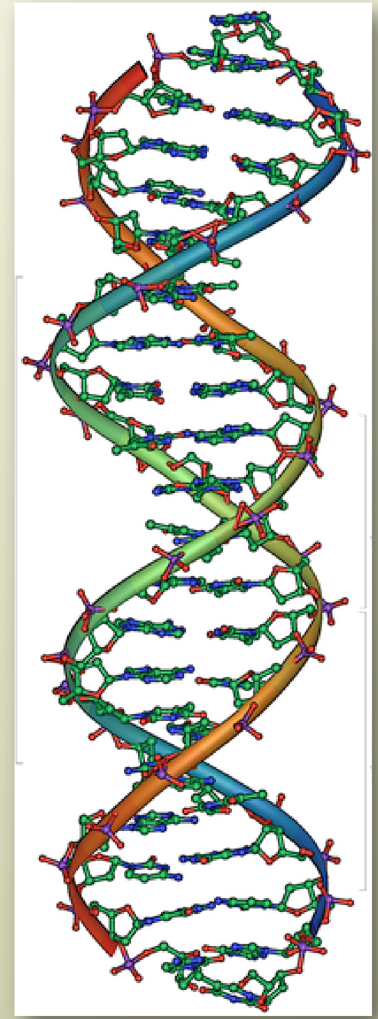
Fisher, Grinstein & Girvin *PRL* (1990).

Influence of Molecular Structure on Ground States?

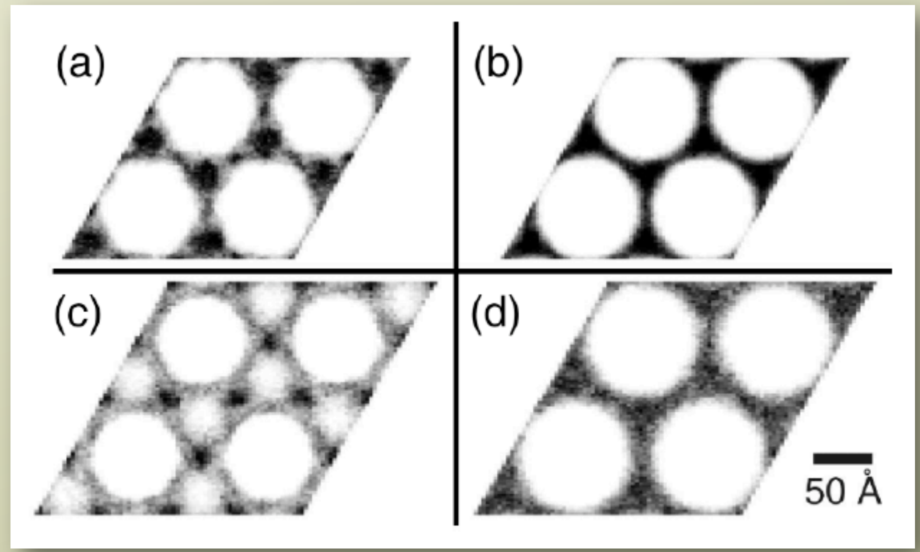
DNA is not featureless
(spiral charge distribution)

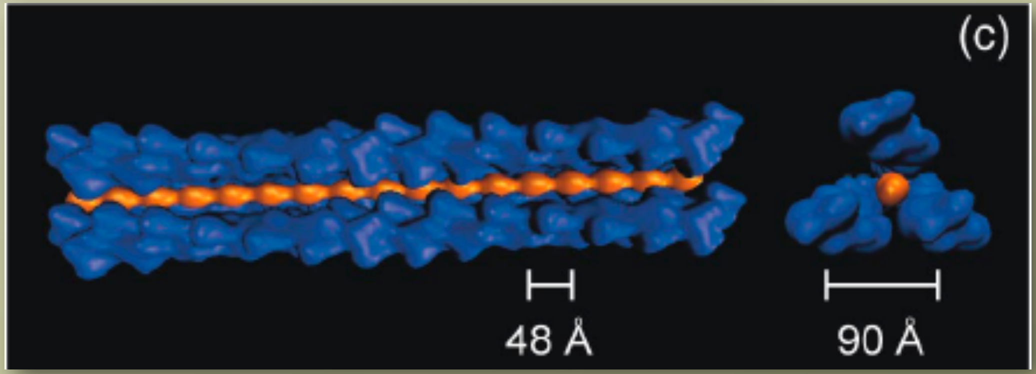


$$p = 10\text{bp}$$
$$= 3.4\text{nm}$$

http://en.wikipedia.org/wiki/DNA/

Steric effects exclude ions
from PE core volume





Sanders, Guaqueta, Angelina, Lee,
Slimmer, Luijten & Wong *PRL* (2005).

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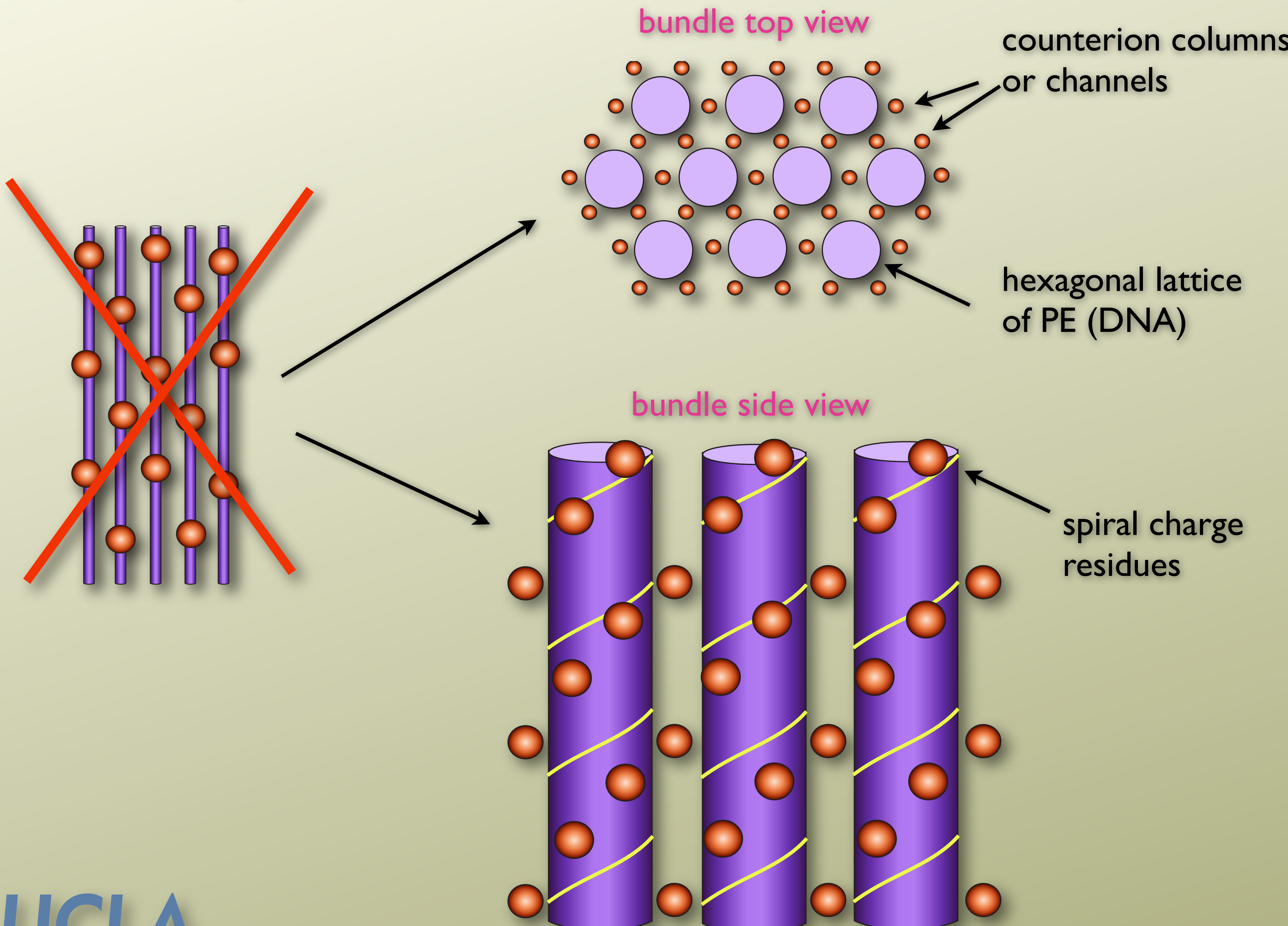
Microscopic chiral model with excluded volume



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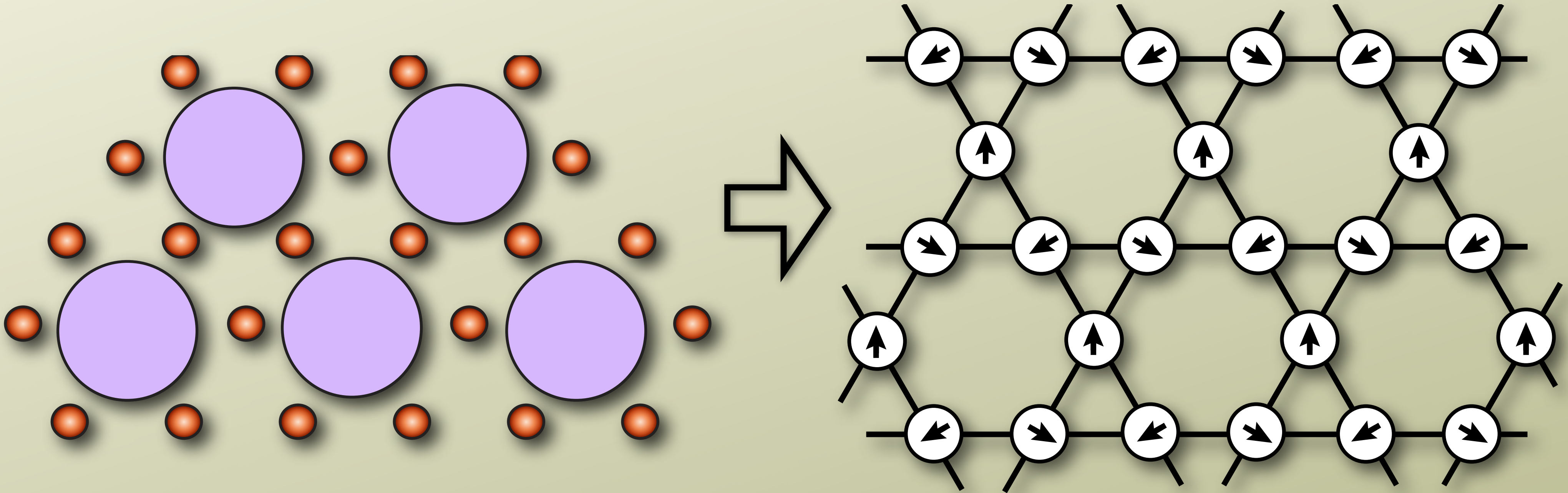
Counterion Fluctuations: XY (anti-ferromagnetic) spins on kagome lattice



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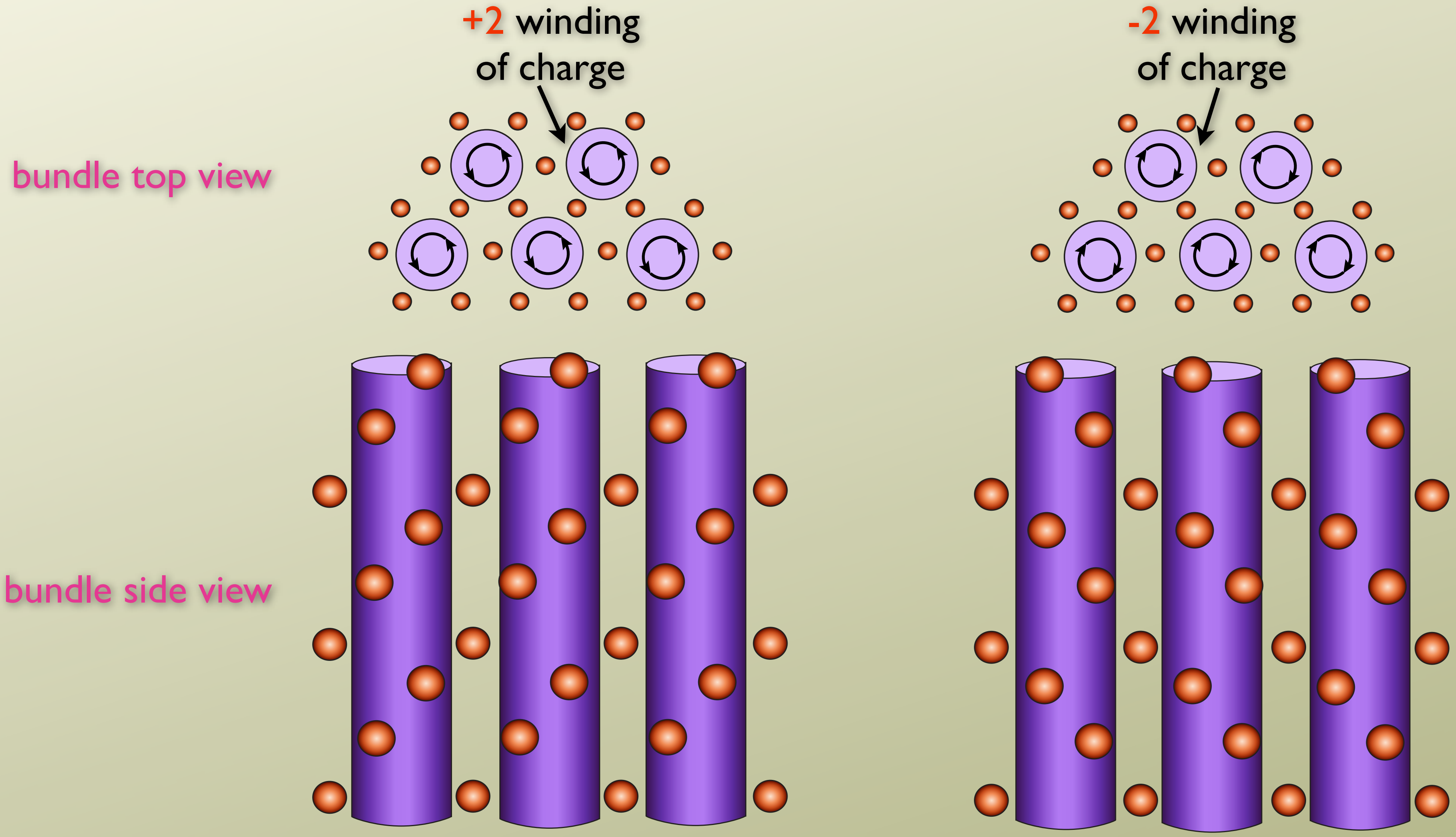
Kagome model eithout chirality: 2 degenerate, **chiral** ground states (w/ nnn. interactions)



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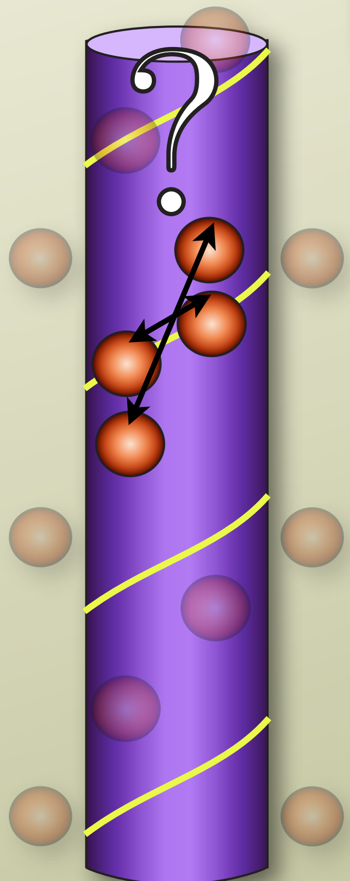
Korshunov *PRB* (2002).

Can helical pitch lift chiral degeneracy?

Simplest model for chiral interaction with PE:
neighboring columns have preferred phase difference, $\phi_i - \phi_j = \frac{\pi}{3}\left(\frac{d}{p}\right) \neq \pi$

d, charge spacing along columns
p, pitch of PE charge distribution



chiral nearest-neighbor interactions

$$-\sum_{\langle ij \rangle} E^* \cos\left(\phi_i - \phi_j - \frac{\pi}{3}\left(\frac{d}{p}\right)\right)$$

$$+$$

AF nearest-neighbor (direct) interactions

$$-\sum_{\langle ij \rangle} E_{nn} \cos\left(\phi_i - \phi_j - \pi\right)$$

effective chiral nn interactions

$$= -\sum_{\langle ij \rangle} E^*_{nn} \cos\left(\phi_i - \phi_j - (\pi + f)\right)$$

$f \rightarrow 0$, no chirality

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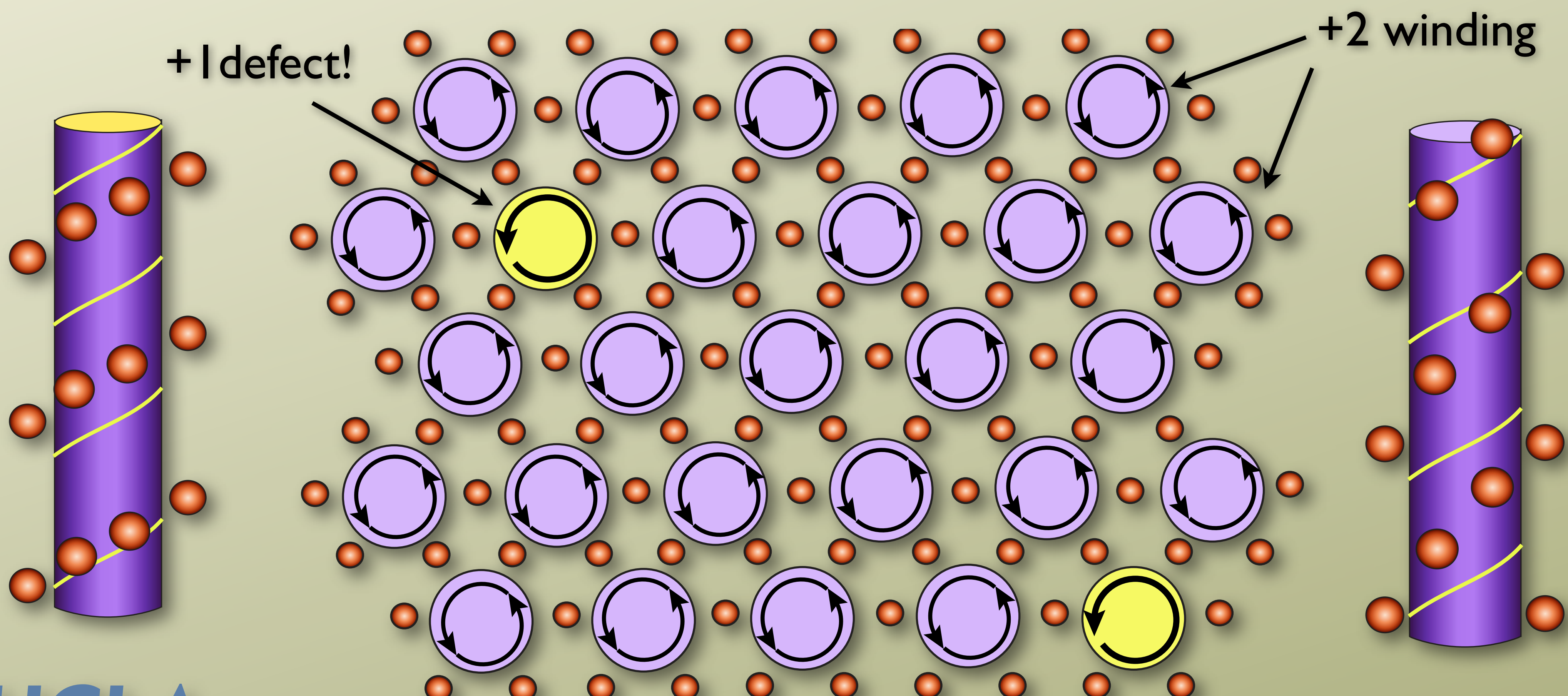
Incommensurability forces screw defects (vortices) into ground state!

Molecular pitch wants phase to wind around $\times \frac{3f}{\pi}$ ....

...but charge neutrality requires integer winding! (-1, 0, +1, etc.)



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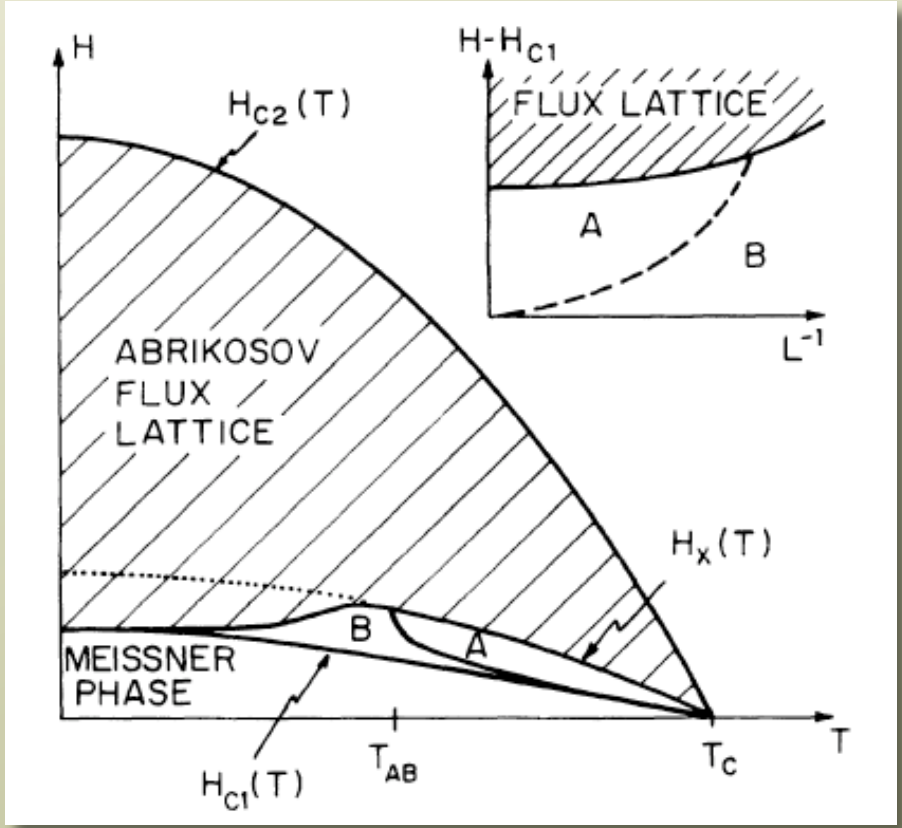
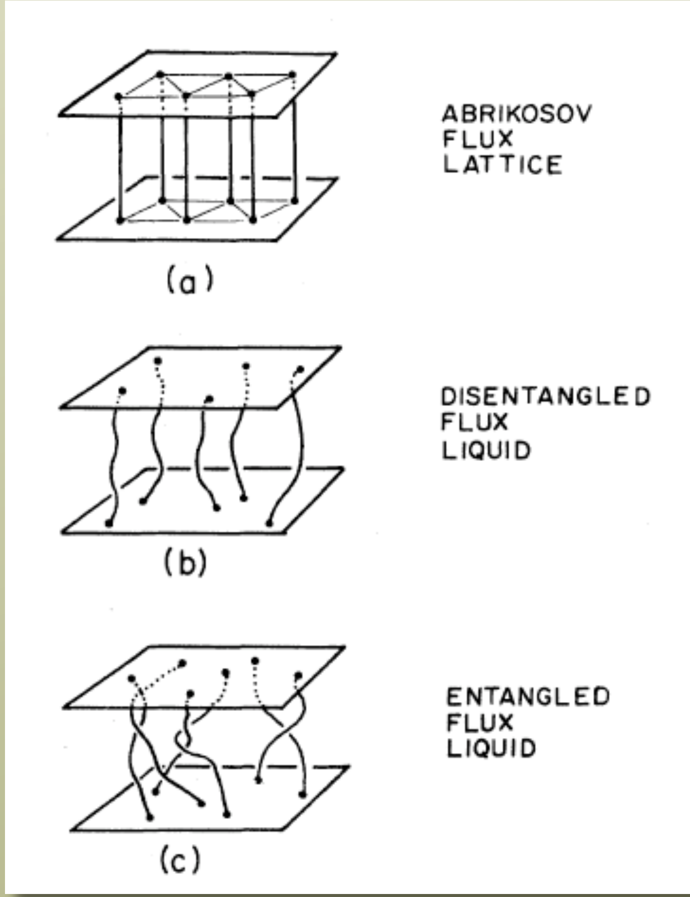
Chiral PE Bundles & Vortices in Type II Superconductors (New Phases!)

1) defect density ~ f like applied magnetic field, H

2) Elastic twist of PE can screen long-range effects of defects, $\lambda \sim \sqrt{\frac{K_{tw}}{E_{nn}}}$





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Nelson *PRL* (1988).

Summary

-Charge freezing transition in same universality class as Ins. to SC quantum phase transition

-Phase transition leads to anomalous elastic properties of bundle

-Molecular chirality may induce defect-rich ground states

Outlook

-Elastic properties of flux liquid phases

-Gauge fluctuations due to polymer bending modes

-Simulation (where is phase transition?), M. Stevens, Sandia

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preprint available at *cond-mat/0601462*