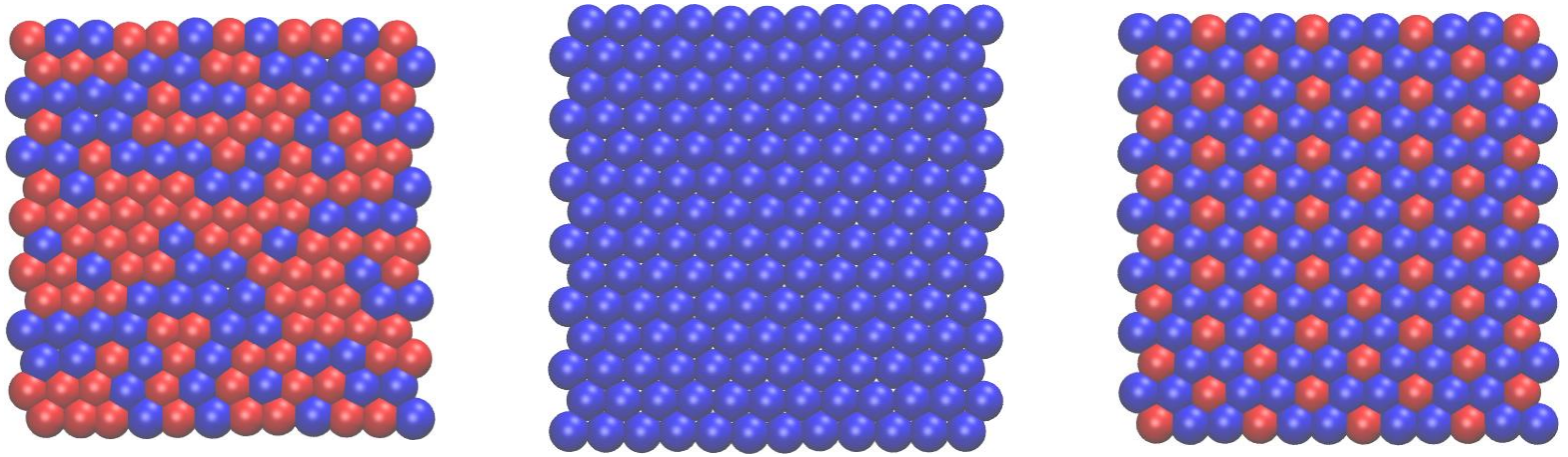
Mean-field critical behavior and dynamics of a model lattice-mismatched solid



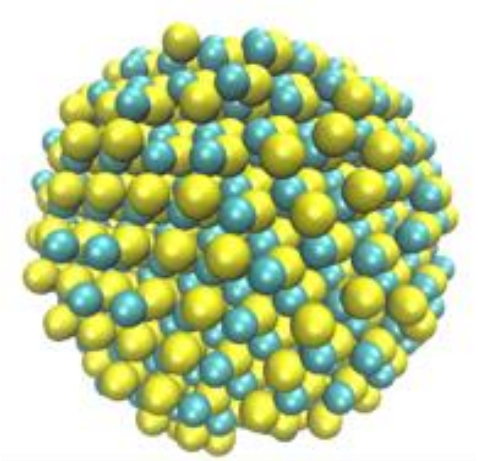
Layne Frechette

Northern California Theoretical Chemistry Meeting

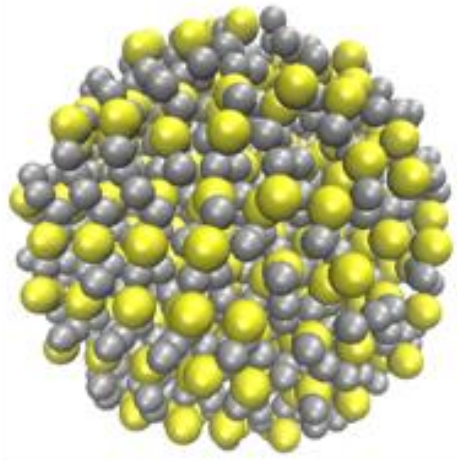
May 19th, 2019

ESI Erwin Schrödinger International Institute for Mathematics and Physics

Cation exchange produces patterned nanocrystal heterostructures



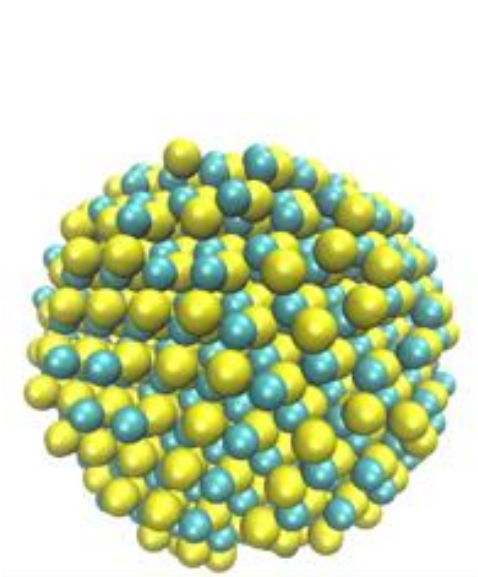
Ag-rich solution



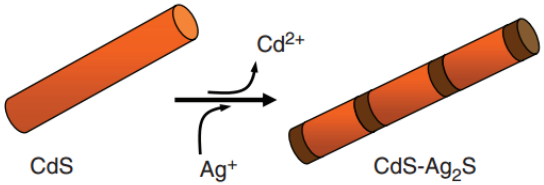
CdS

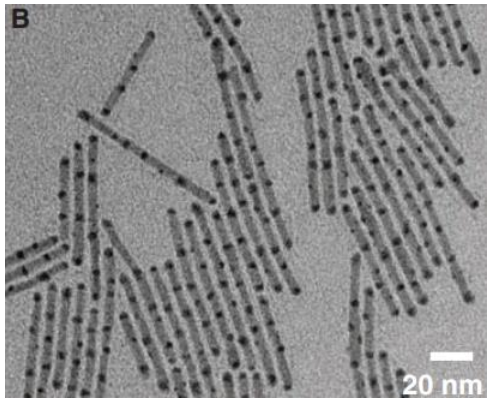
Ag_2S

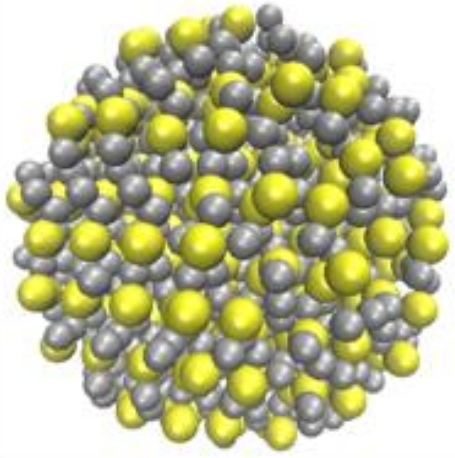
Cation exchange produces patterned nanocrystal heterostructures



CdS



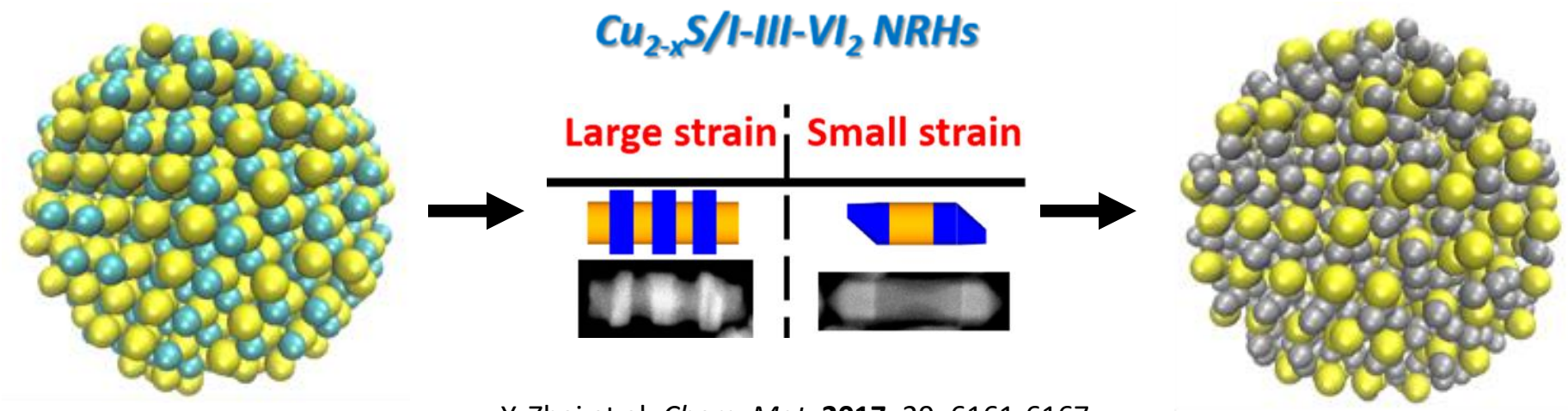




Ag_2S

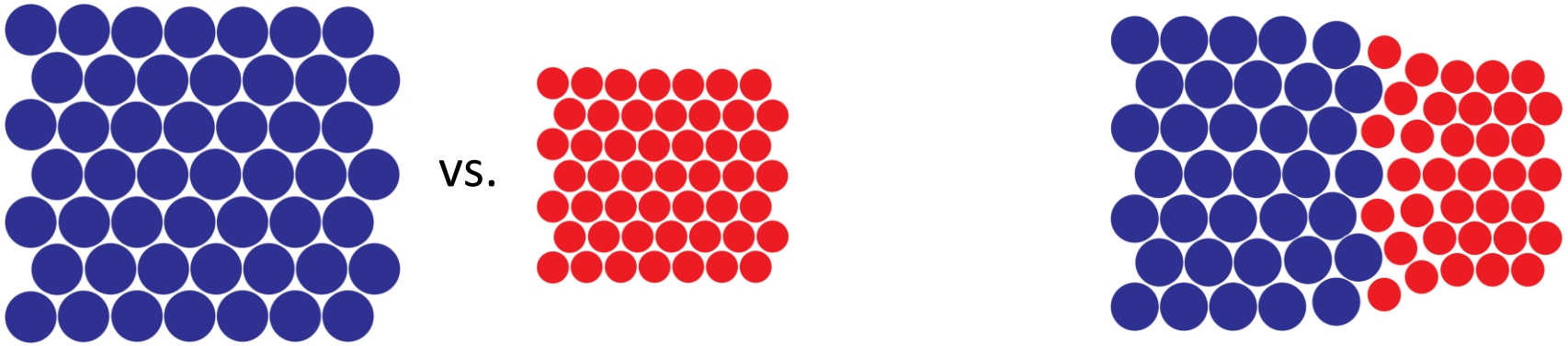
R.D. Robinson et al. *Science* **2007**, 317, 355-358.

Elastic strain plays an important role

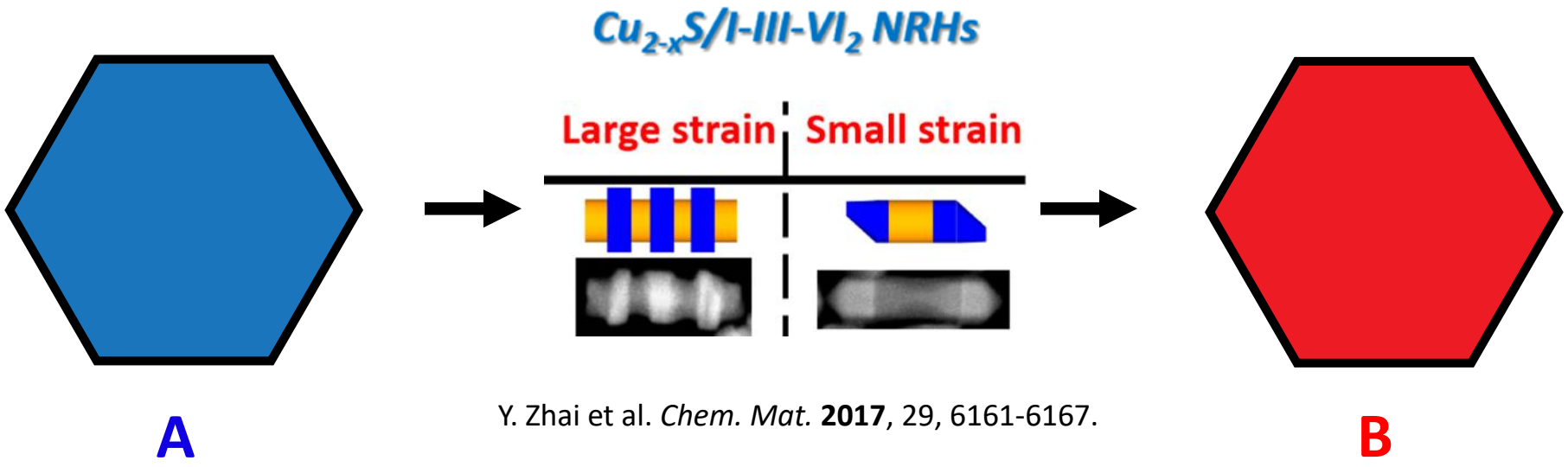


Y. Zhai et al. *Chem. Mat.* **2017**, 29, 6161-6167.

CdS **Ag_2S**



Elastic strain plays an important role



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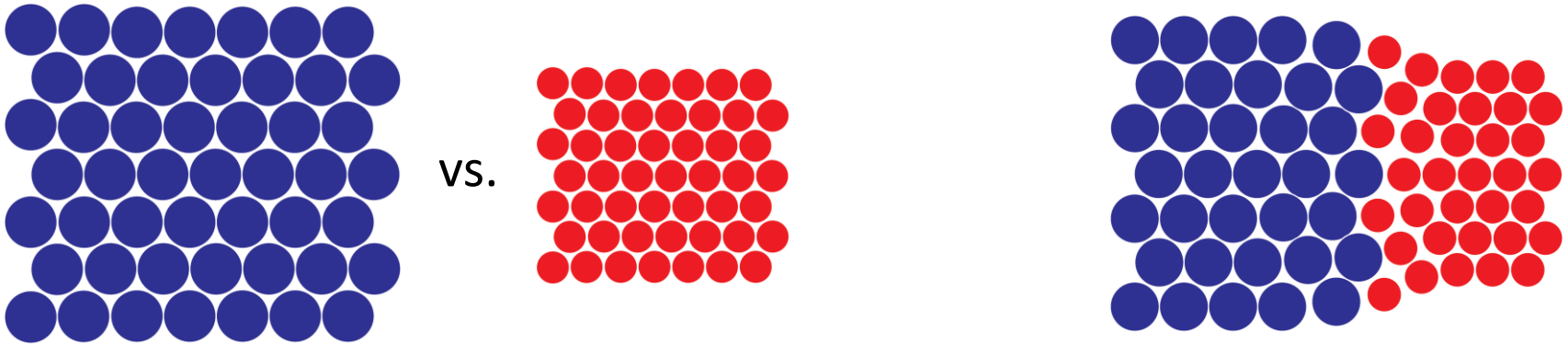
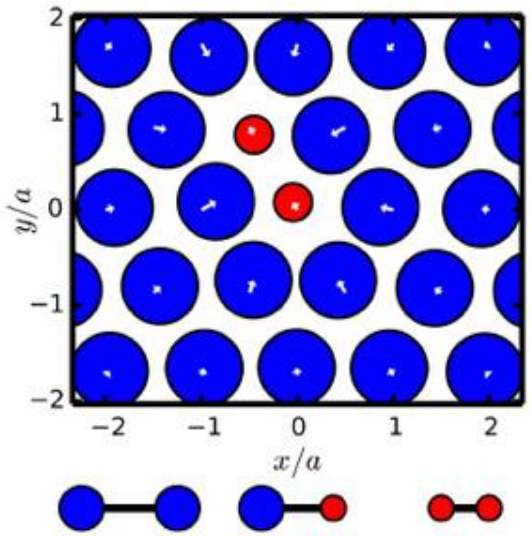
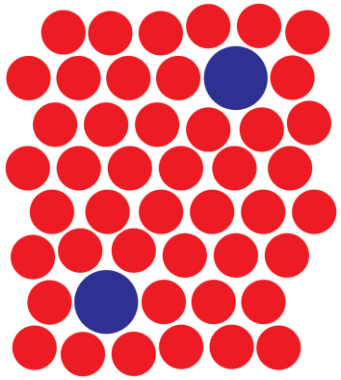


A simple model describes elastic coupling to compositional heterogeneity





Atom at each lattice site $\boldsymbol{r}$ has an identity

$$\sigma_{\mathbf{r}} = +1 \quad (A) \quad \text{or} \quad \sigma_{\mathbf{r}} = -1 \quad (B)$$

and a displacement $\boldsymbol{u_r}$ away from its ideal lattice position.

Locally preferred bond length

$$\ell(\mathbf{r}, \mathbf{r}') = \bar{\ell} + \frac{\Delta}{2}(\sigma_{\mathbf{r}} + \sigma'_{\mathbf{r}})$$

depends on atoms' identities.

Energy is quadratic in displacements:

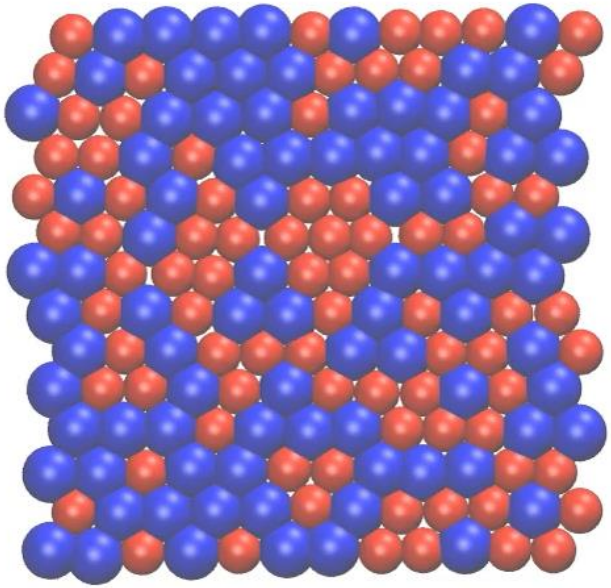
$$\mathcal{H} = \frac{K}{4} \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} \left[|(\mathbf{r} + \mathbf{u}_{\mathbf{r}}) - (\mathbf{r}' + \mathbf{u}_{\mathbf{r}'})| - \ell(\mathbf{r}, \mathbf{r}') \right]^2$$

At a given composition $c = (2N)^{-1} \sum_{\mathbf{r}} (1 + \sigma_{\mathbf{r}})$

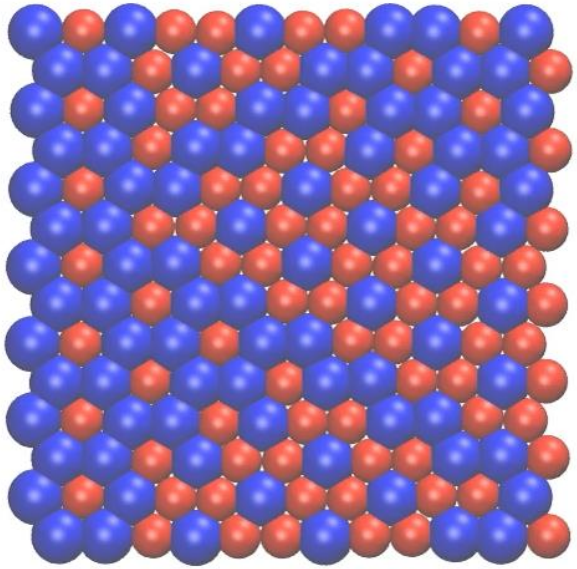
what patterns dominate at equilibrium?

Monte Carlo simulations reveal intriguing phase behavior

Sample equilibrium distribution $P[\{\sigma\},\{\mathbf{u}\}] \propto e^{-\beta\mathcal{H}}$ of atoms on a periodic, two-dimensional, triangular lattice.

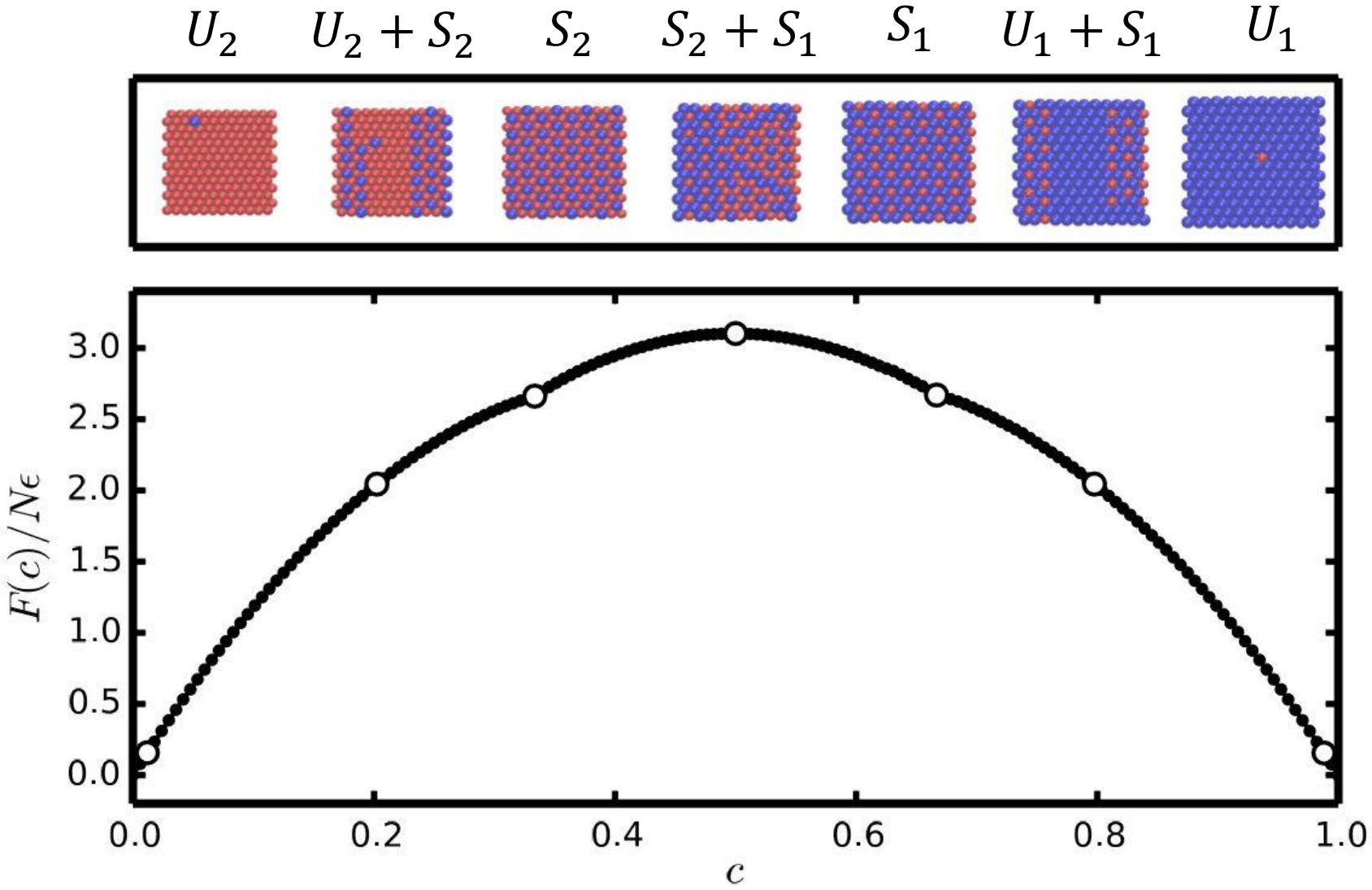


high T, c=1/2



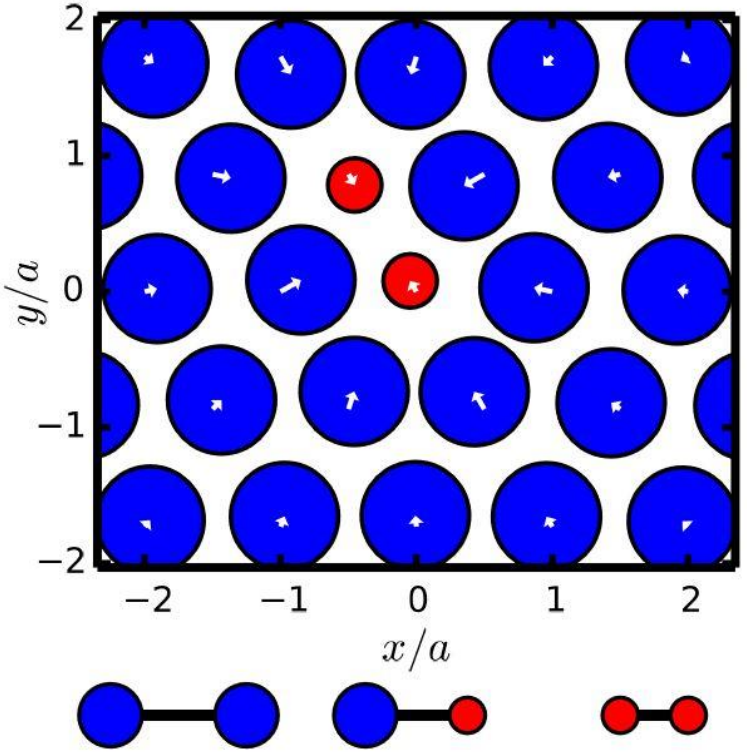
lower T, c=1/2

Monte Carlo simulations reveal intriguing phase behavior



Can a simple theory predict the phase diagram?

Constructing an effective Hamiltonian

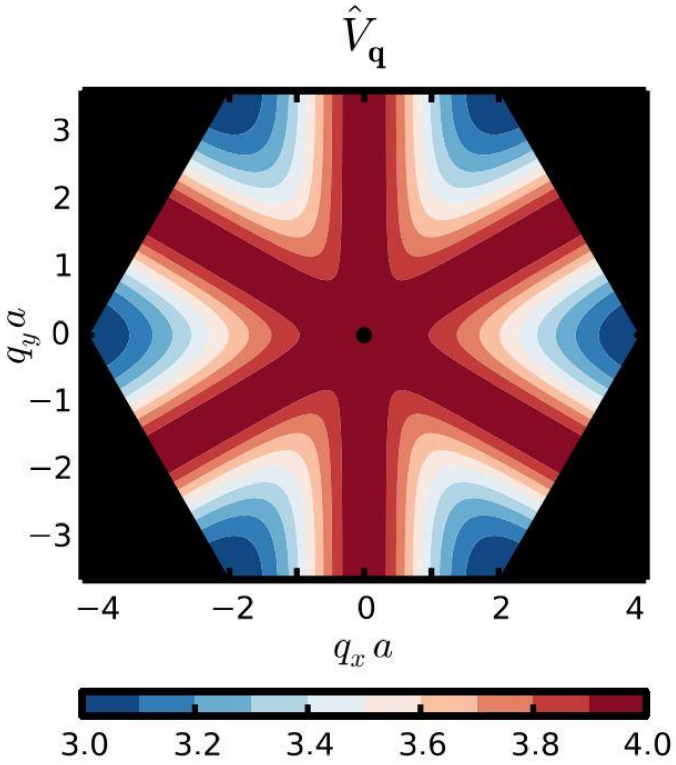


Life is easier if we write down an *effective*, spin-only Hamiltonian.

1) Go to Fourier Space:

$$\mathcal{H} = \frac{K}{2N} \sum_q \left[\hat{\mathbf{u}}_q \cdot \mathbf{F} \cdot \hat{\mathbf{u}}_{-q} + \Delta^2 \left(\sum_\alpha g_\alpha \right) \hat{\sigma}_q \hat{\sigma}_{-q} - \Delta \left(\mathbf{h} \cdot \hat{\mathbf{u}}_q \hat{\sigma}_{-q} - \mathbf{h} \cdot \hat{\mathbf{u}}_{-q} \hat{\sigma}_q \right) \right]$$

Constructing an effective Hamiltonian

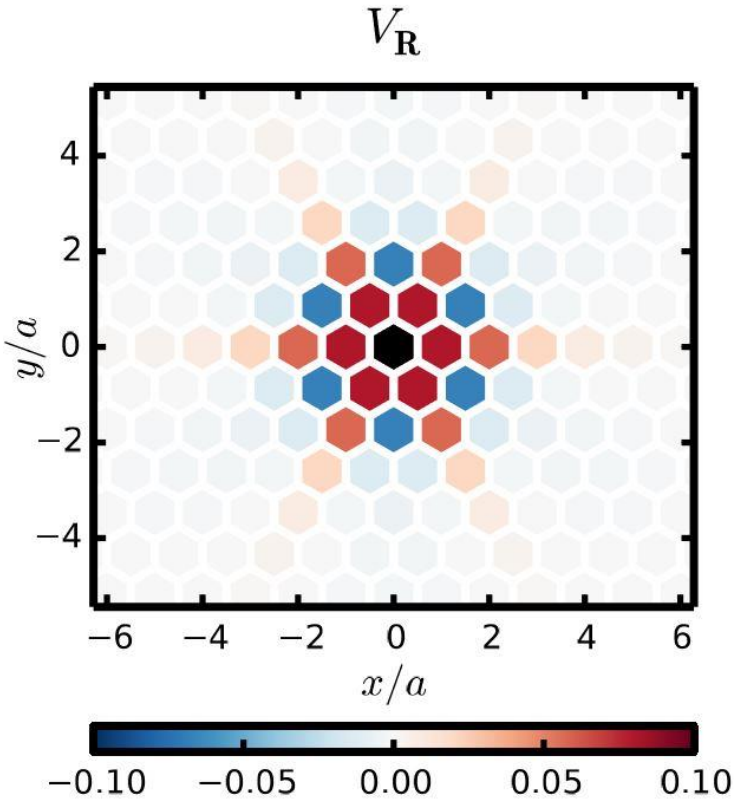


Life is easier if we write down an *effective*, spin-only Hamiltonian.

2) Integrate out displacement fluctuations:

$$e^{-\beta\mathcal{H}_{\rm eff}(\{\hat{\sigma}_q\})} = \int \prod_q d\hat{\mathbf{u}}_q e^{-\beta\mathcal{H}(\{\hat{\mathbf{u}}_q\},\{\hat{\sigma}_q\})} \implies \mathcal{H}_{\rm eff}(\{\hat{\sigma}_q\}) = \frac{1}{N}\sum_q |\hat{\sigma}_q|^2 \hat{V}_{\rm eff}(\mathbf{q})$$

Constructing an effective Hamiltonian



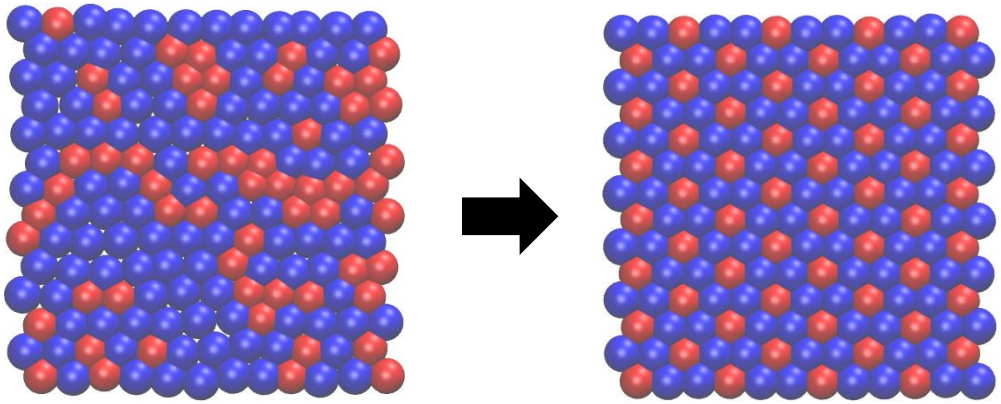
Life is easier if we write down an *effective*, spin-only Hamiltonian.

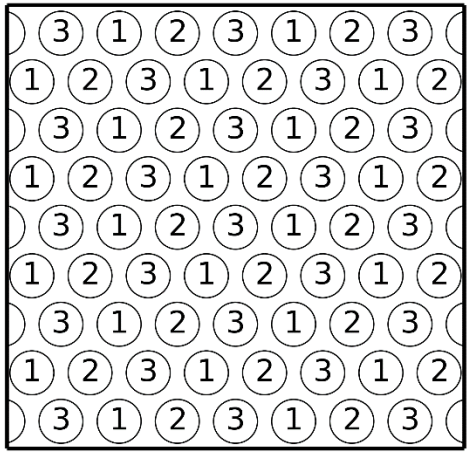
3) Transform back to real space:

$$\mathcal{H}_{\text{eff}}(\{\sigma_r\}) = \sum_{r,r'} V_{\text{eff}}(\mathbf{r}-\mathbf{r}')\sigma_r\sigma_{r'} \qquad V_{\text{eff}}(\mathbf{r}) = \frac{1}{N}\sum_{q} \hat{V}_{\text{eff}}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}$$

Mean Field Theory

Fix composition and predict sublattice ordering.





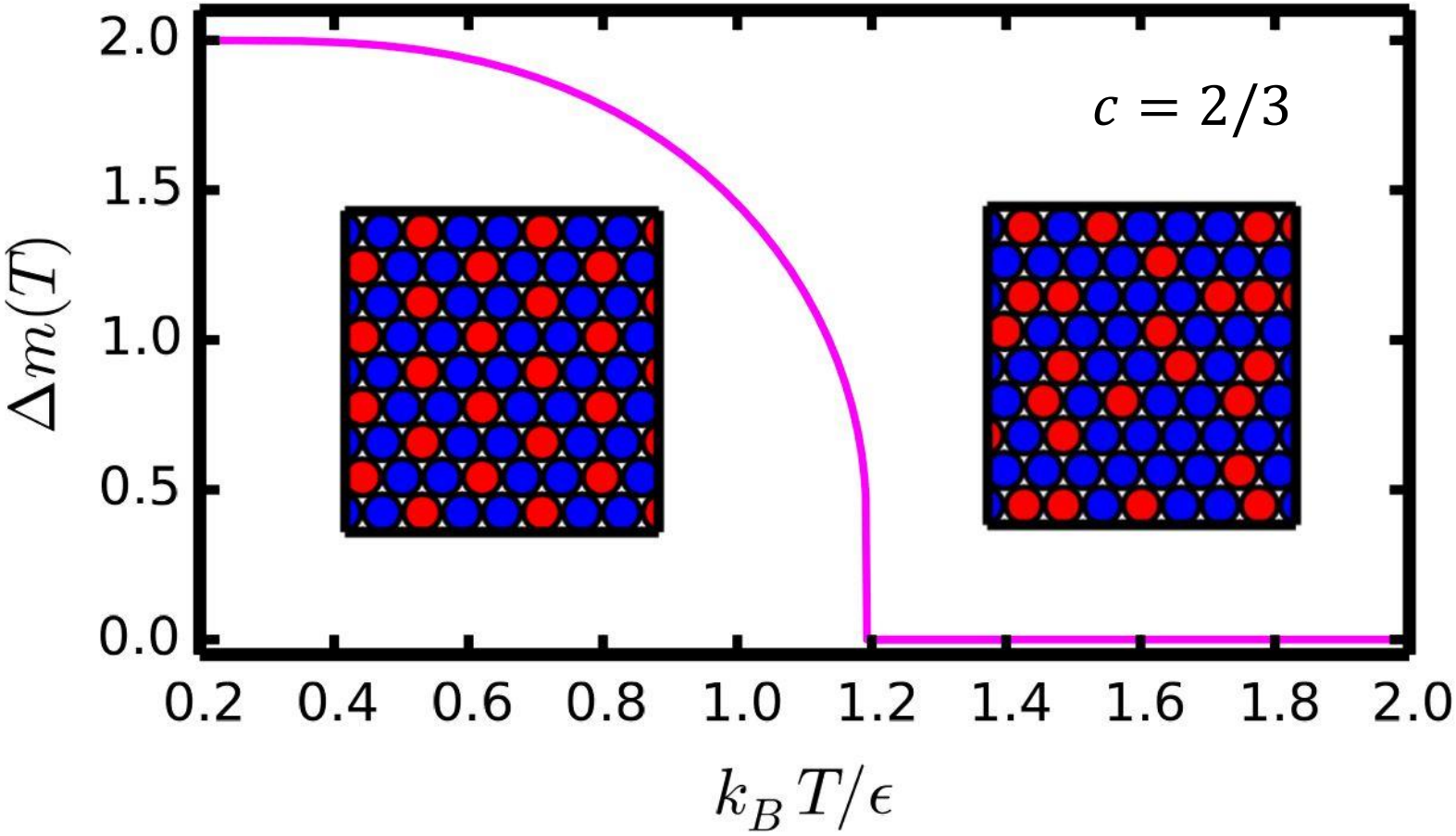
Sublattice $\alpha = 1,2,3$

Optimize parameters of an uncorrelated reference system,

$$\mathcal{H}_0 = -\sum_{\alpha} h_\alpha \sum_{r}{}^{(\alpha)}\sigma_r$$

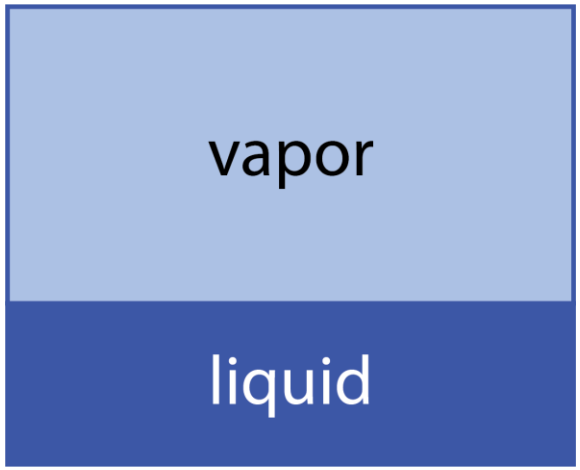
which yields self-consistent equations for sublattice compositions.

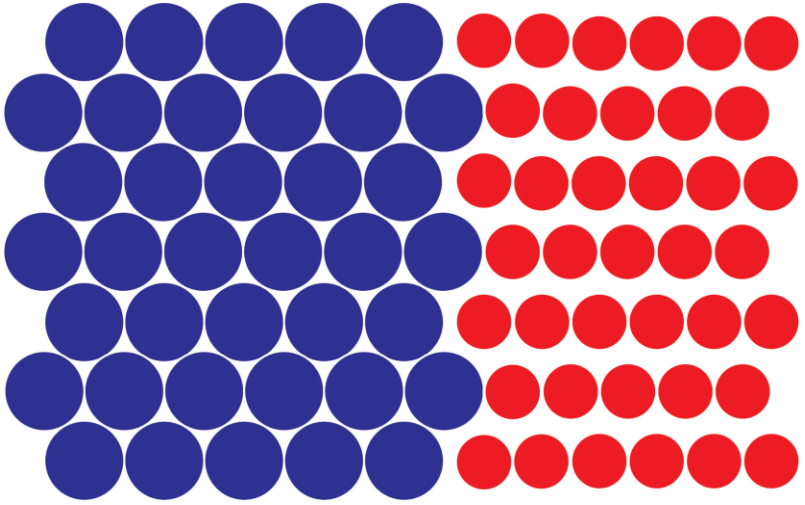
Mean field theory predicts superlattice transition



What about coexistence?

The free energy cost of elastic coexistence is extensive

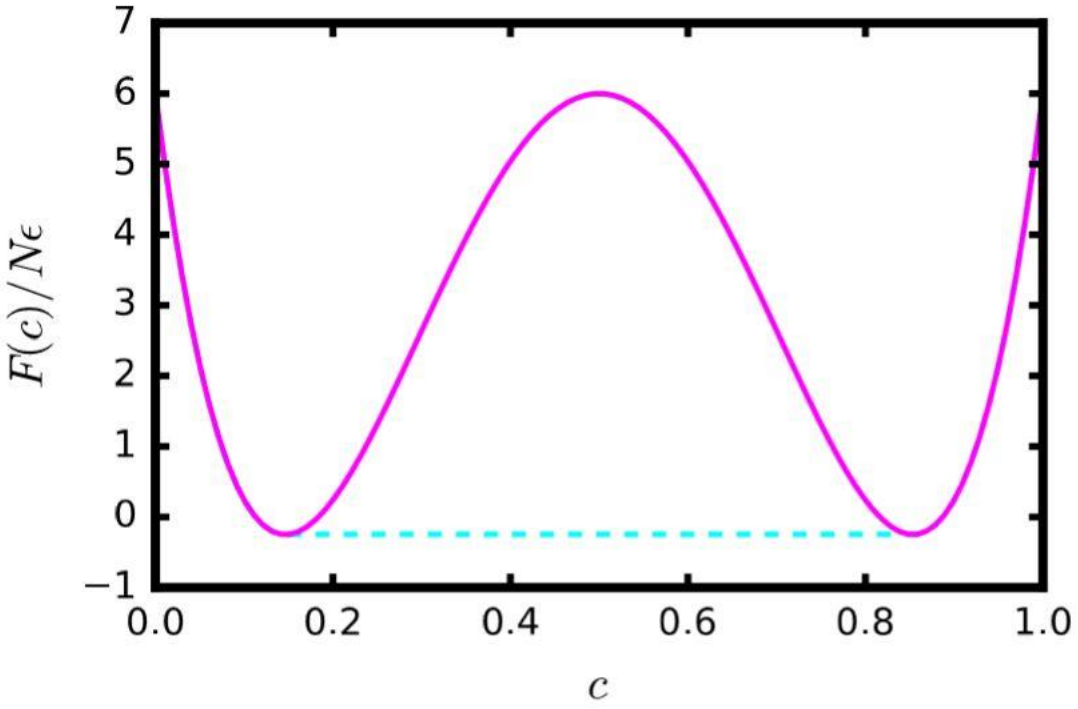




Free energy of coexistence is proportional to the **area** of the interface.

Neither bulk phase is content with lattice dimensions. Cost of coexistence is proportional to **volume**.

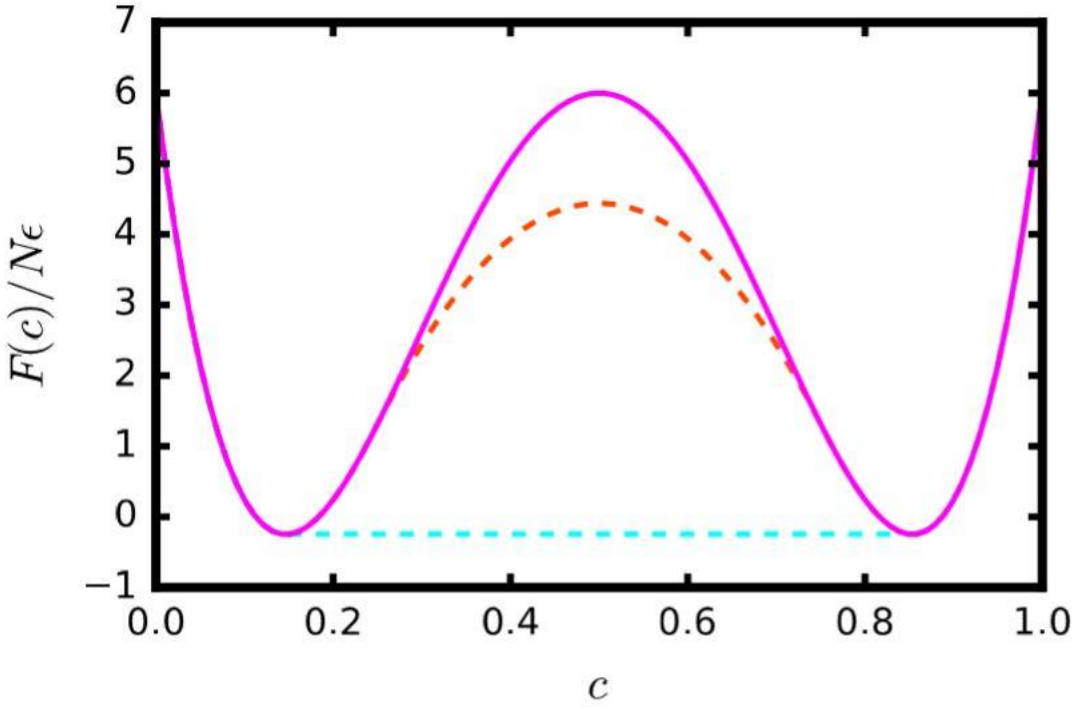
A graphical “quadratic construction” can account for elastic coexistence



$$\frac{F}{N} = f(c_1) - \frac{\Delta c_1}{\Delta c_2 - \Delta c_1}\left(f(\Delta c_2) - f(\Delta c_1)\right)$$

$$\Delta c_1 = c - c_1 \qquad \Delta c_2 = c - c_2$$

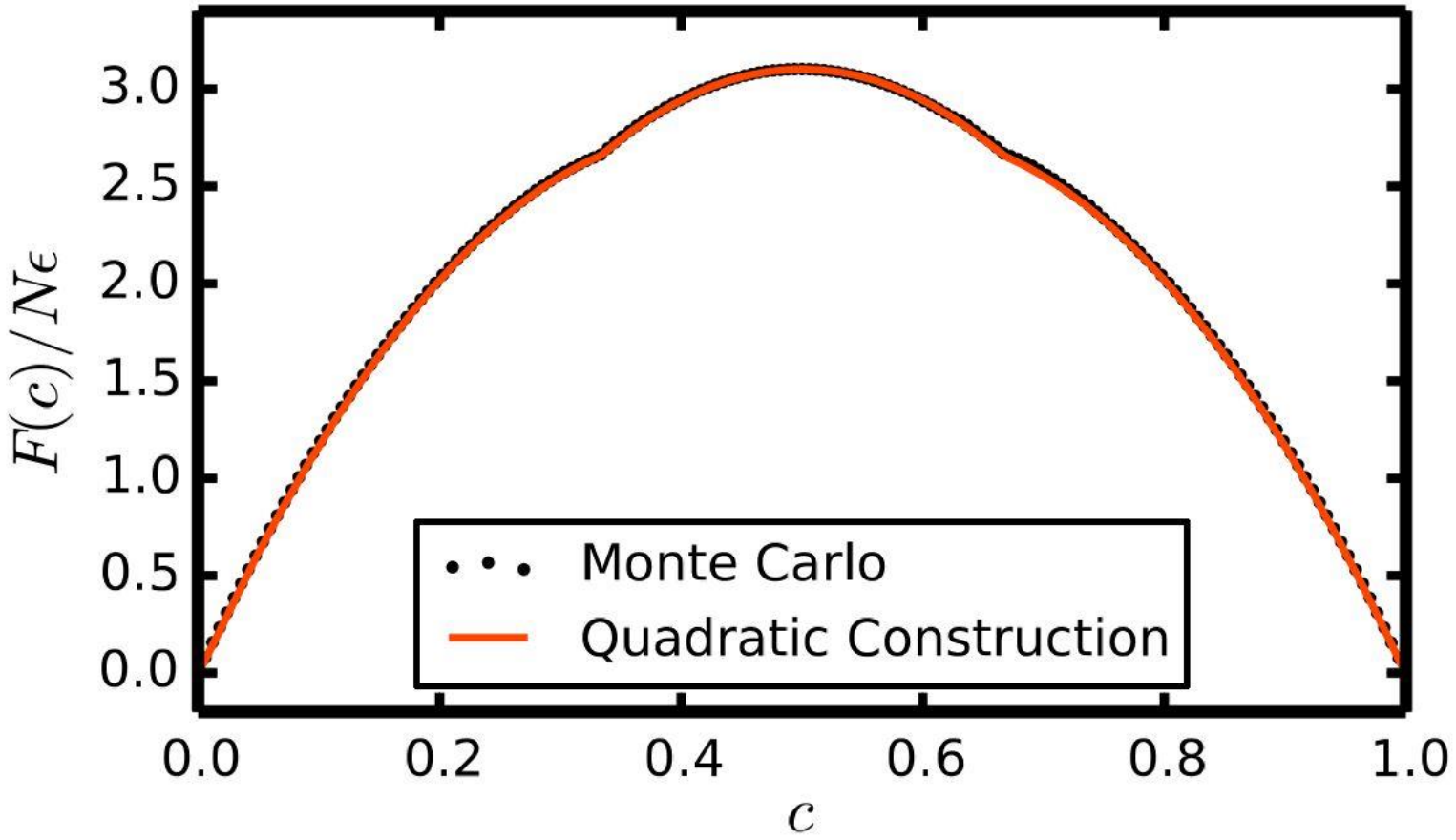
A graphical “quadratic construction” can account for elastic coexistence



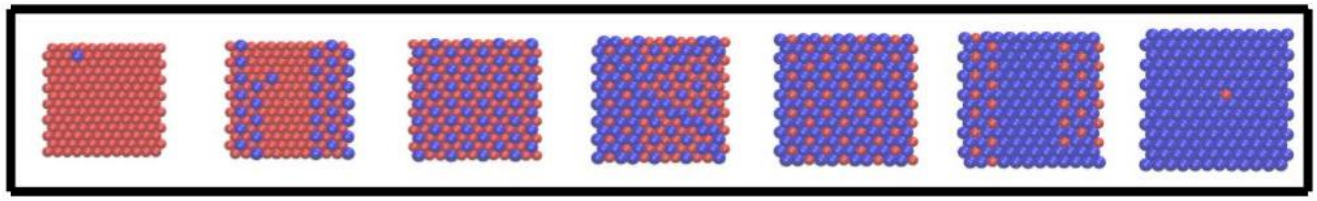
$$\frac{F}{N} = f(c_1) - \frac{\Delta c_1}{\Delta c_2 - \Delta c_1}\left(f(\Delta c_2) - f(\Delta c_1)\right) + \mathrm{Y}\Delta l^2 \Delta c_1 \Delta c_2$$

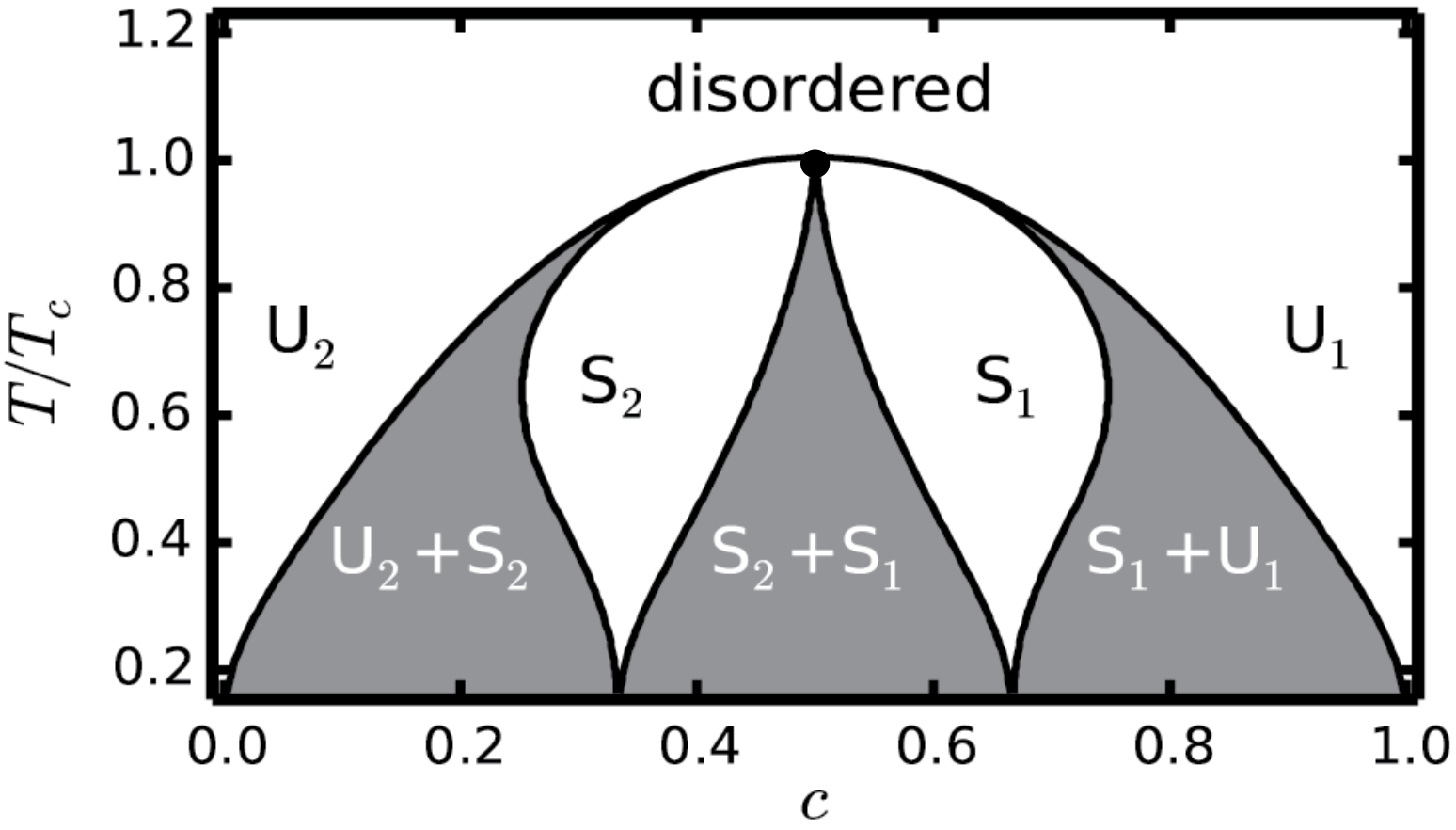
$$\Delta c_1 = c - c_1 \qquad \Delta c_2 = c - c_2$$

A graphical “quadratic construction” can account for elastic coexistence

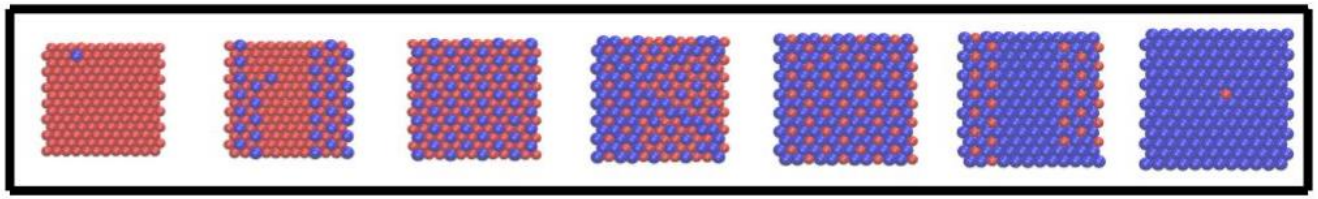


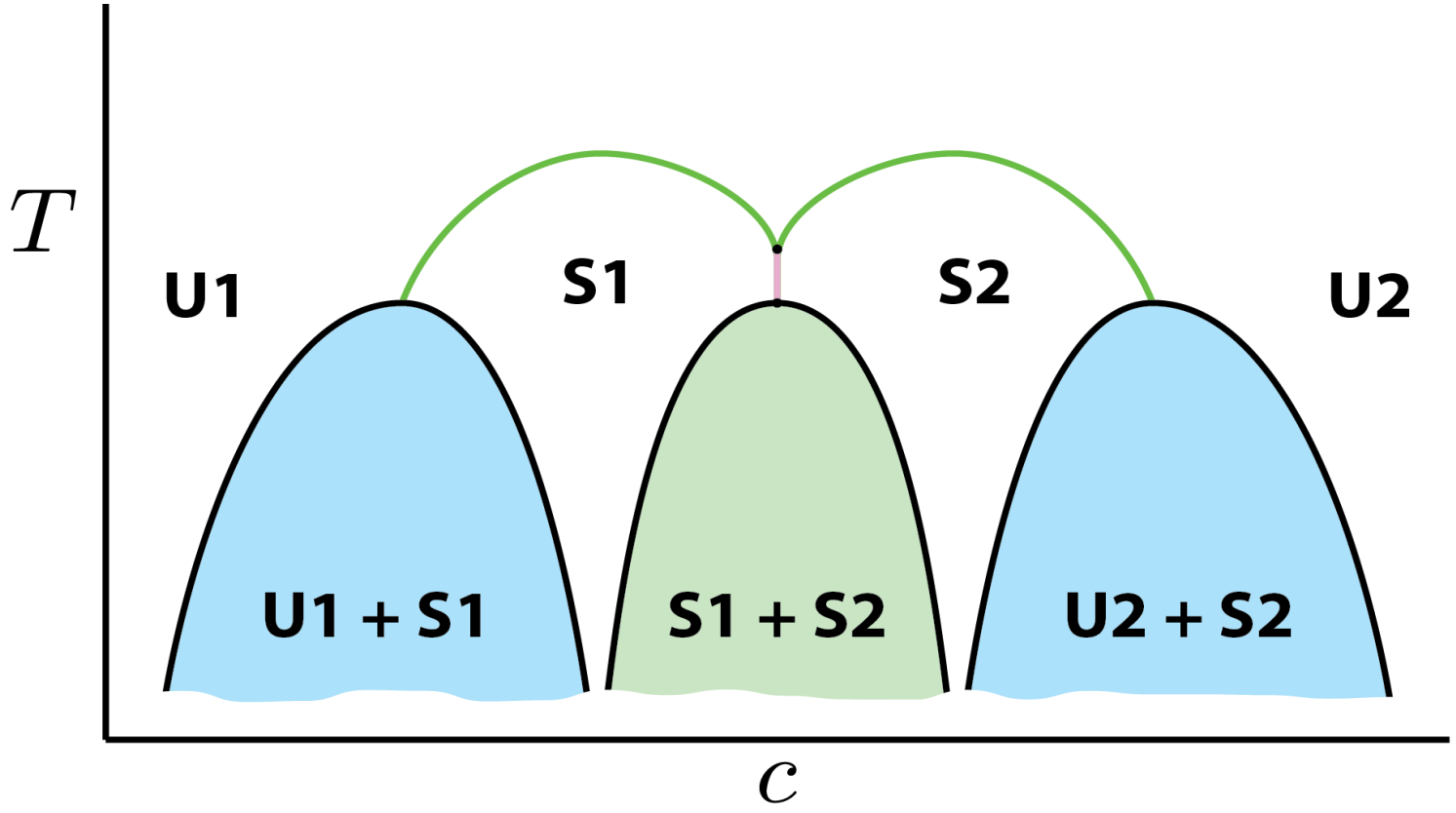
Phase diagram captures patterns observed in simulations





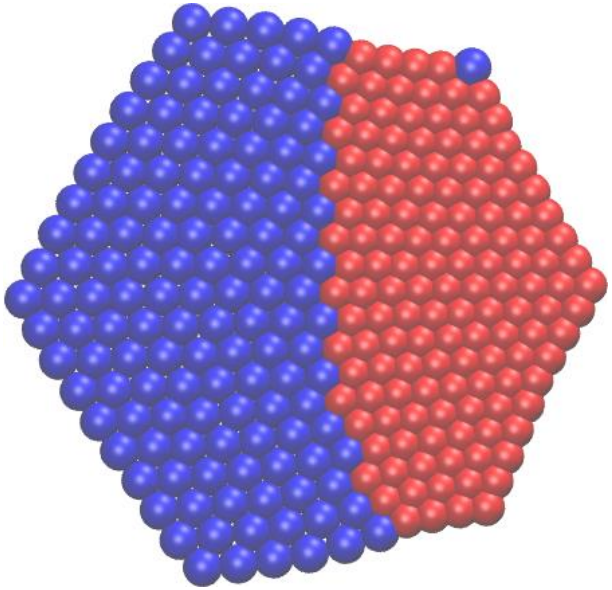
Monte Carlo phase diagram is more complex





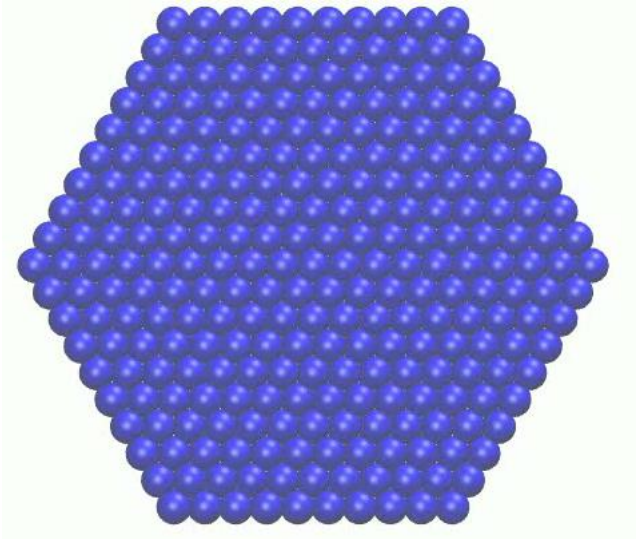
What about the nanocrystal?

Equilibrium:



Free surface
relieves strain.

Nonequilibrium:



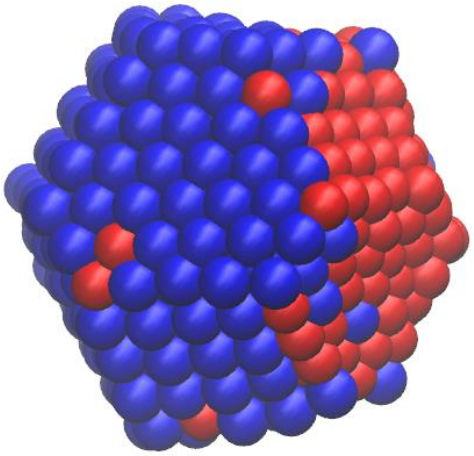
Surface exchange: k_{ex}
Bulk diffusion: k_{diff}

Conclusion

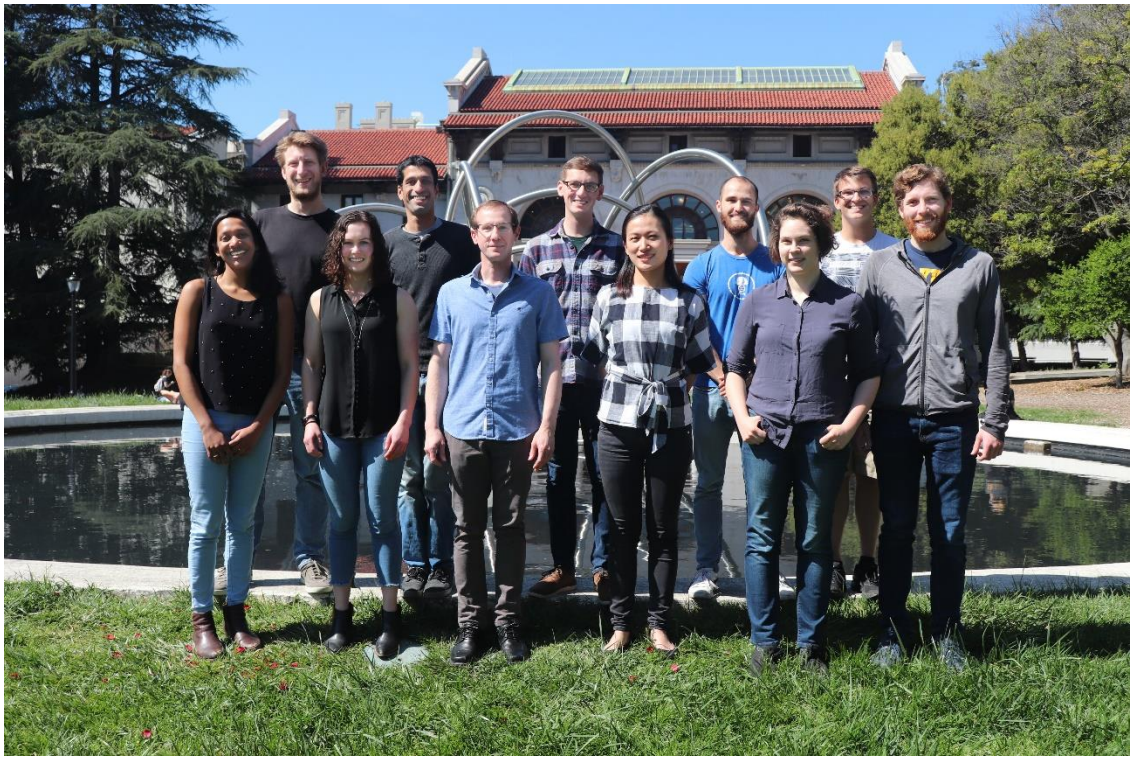
- Lattice mismatch induces rich phase behavior.
- A “quadratic construction” accounts for the extensive cost of elastic phase separation.
- Nanoscale ion exchange reactions are significantly influenced by both bulk phase behavior and kinetics.

Future Work:

- Thoroughly characterize kinetics.
- Explore the interplay between elastic interactions and local chemistry.
- Extend results to three dimensions.



Acknowledgements



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ESI Erwin Schrödinger International Institute for Mathematics and Physics

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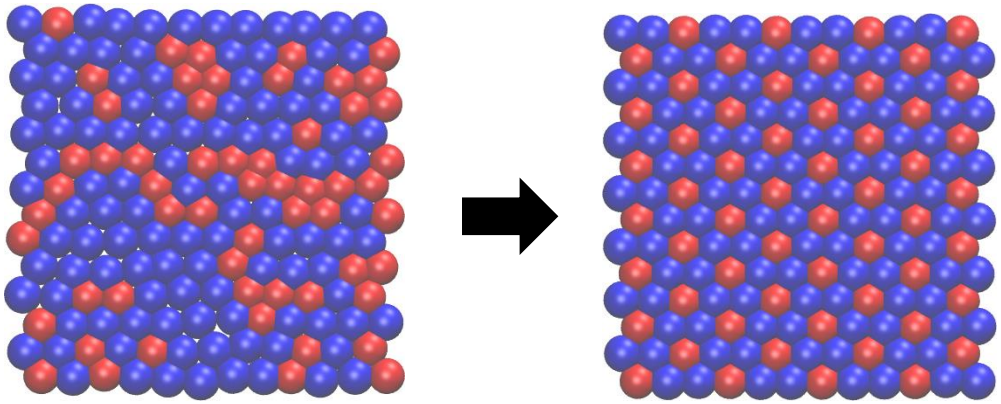
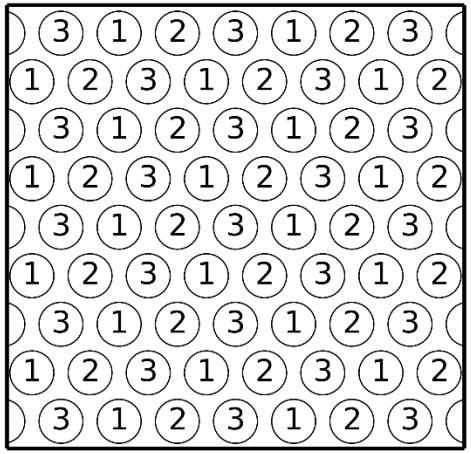
Mean Field Theory, Part II

Fix composition and predict sublattice ordering.





$$\mathcal{H} = \sum_{r,r' \neq r} \sigma_r V_{r-r'} \sigma_{r'}, \qquad \mathcal{H}_0 = -\sum_{\alpha} h_\alpha \sum_{r}^{(\alpha)} \sigma_r$$

Constraint: $$\bar{m} = 2c - 1 = \frac{1}{N} \sum_{r} \sigma_r$$

Mean Field Theory, Part II

Handle constraint with Lagrange multiplier μ:

$$Q_0 = e^{-\beta\mu N\bar{m}} \prod_{\alpha} \prod_{r}^{(\alpha)} 2\cosh\beta(\mu + h_\alpha)$$

$$m_\alpha = \tanh\beta(\mu + h_\alpha)$$

Apply variational procedure to obtain self-consistent equations for the sublattice magnetizations.

$$m_\alpha = \tanh\beta\left(\mu - \frac{2}{N_\alpha}\sum_{\gamma} m_\gamma J_{\alpha\gamma}\right)$$

$$\bar{m} = \sum_{\alpha} m_\alpha x_\alpha$$

Solve these equations numerically for a given composition and compute difference of sublattice magnetizations, $\Delta m = m_1 - m_2$.