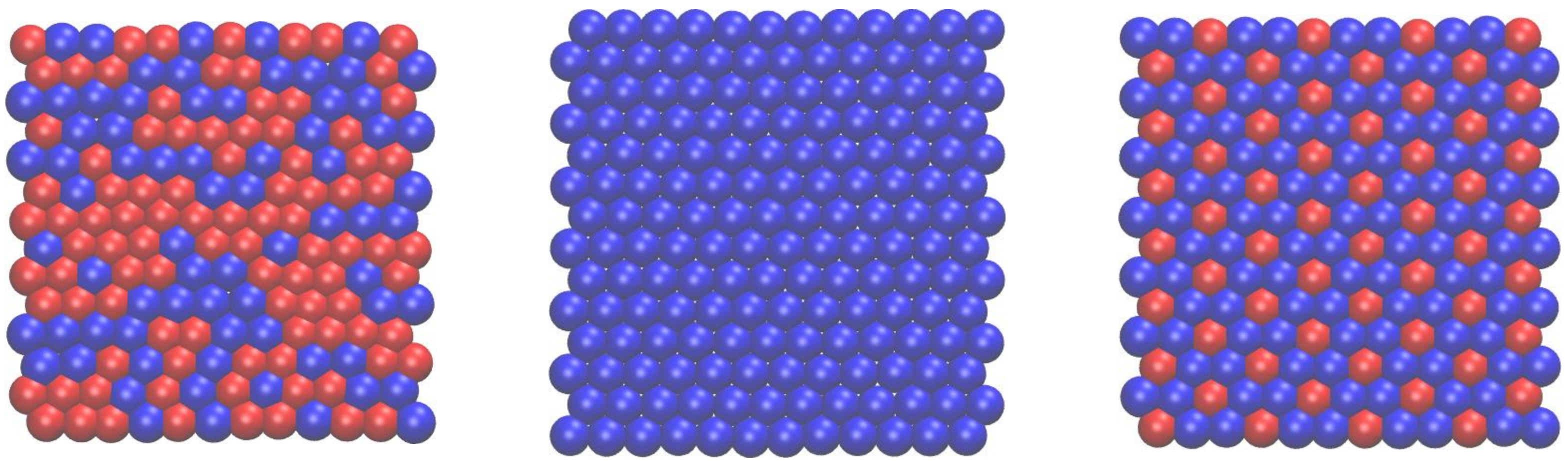
Modulated order and unconventional coexistence in a model of lattice-mismatched solids



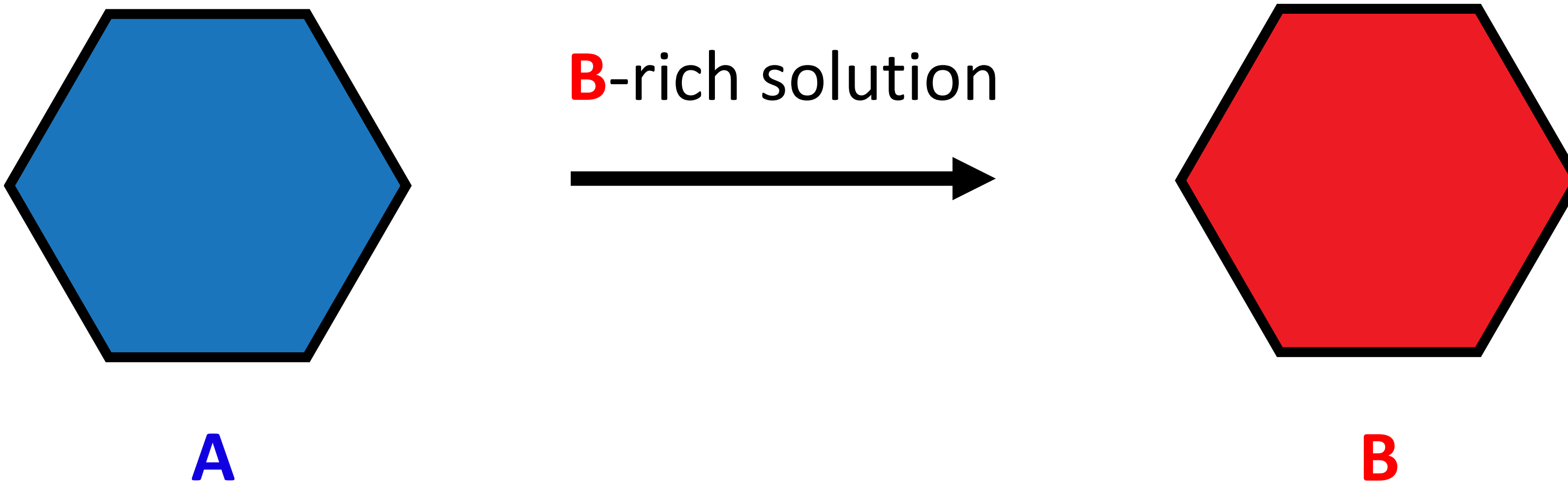
Layne Frechette

APS March Meeting

March 6th, 2019

Erwin Schrödinger International Institute for Mathematics and Physics

Cation exchange produces patterned nanocrystal heterostructures



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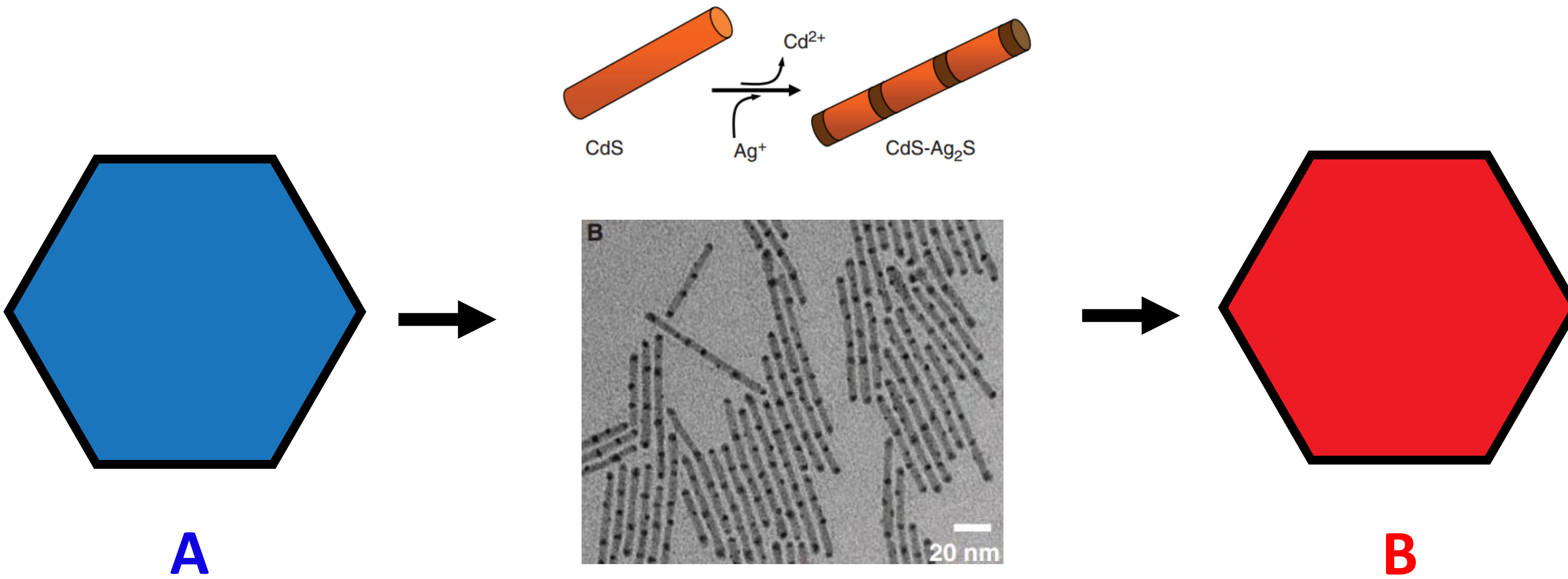
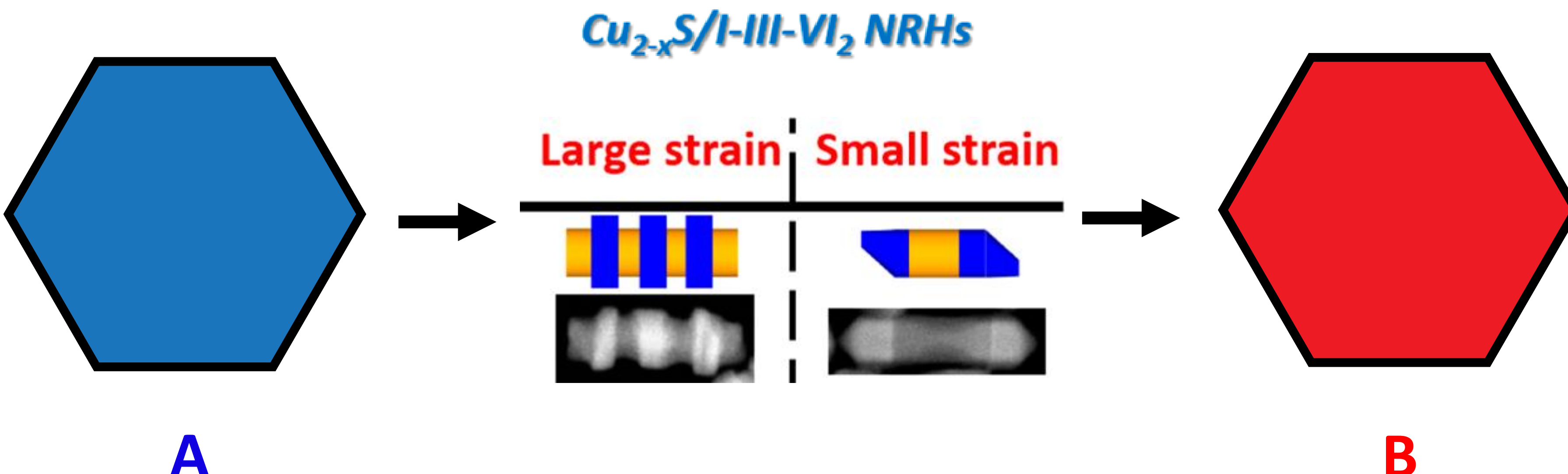


R.D. Robinson et al. *Science* **2007**, 317, 355-358.

Elastic strain plays an important role



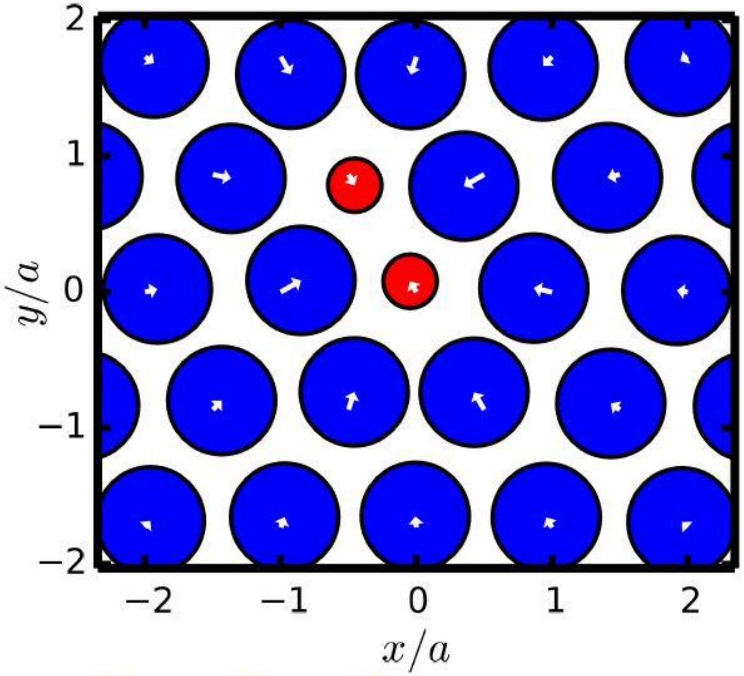
Y. Zhai et al. *Chem. Mat.* **2017**, 29, 6161-6167.

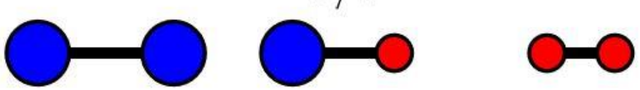
How does lattice mismatch mediate interactions between atoms?

Are these patterns metastable or at equilibrium?

A simple model describes mechanical and compositional fluctuations

$$\mathcal{H} = (K/2)\sum_{\mathbf{R},\hat{\alpha}} \left[|a\hat{\alpha} + \mathbf{u_R} - \mathbf{u}_{\mathbf{R}+a\hat{\alpha}}| - l(\sigma_\mathbf{R}, \sigma_{\mathbf{R}+a\hat{\alpha}}) \right]^2$$





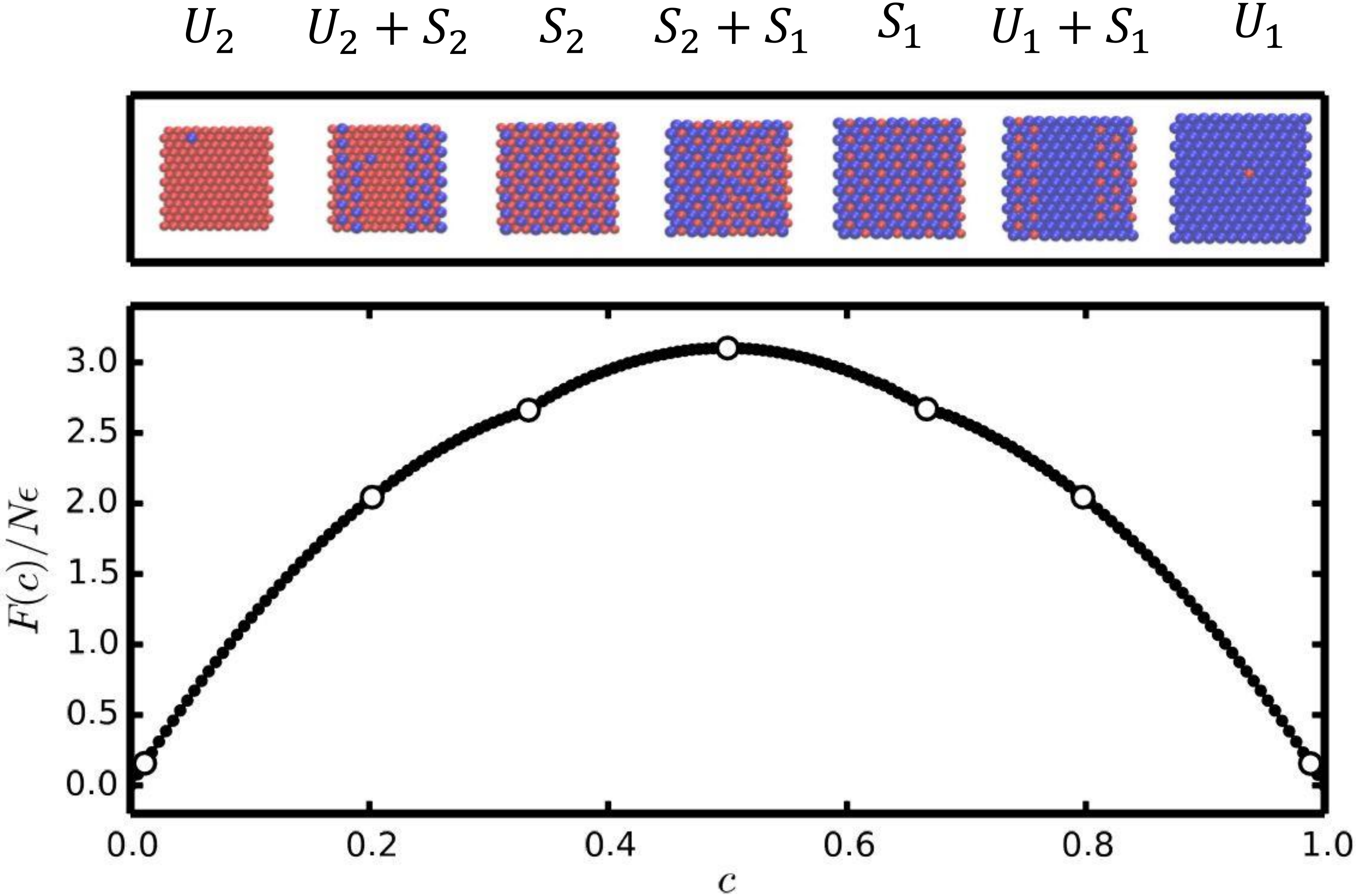
l_{AA} l_{AB} l_{BB}

Elastic strain is encoded in displacement field $\boldsymbol{u_R}$.

Bond length depends on atom type $\sigma_{\boldsymbol{R}}$, which couples strain to local composition.

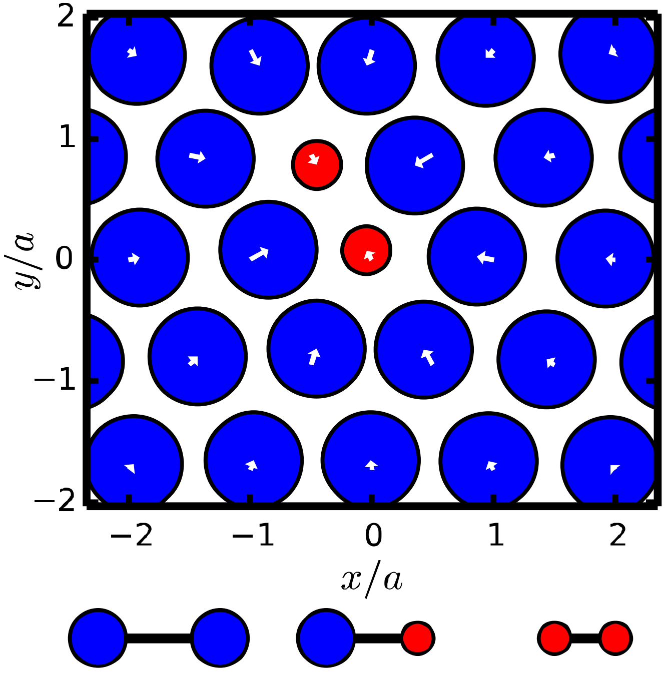
L.B. Frechette, C. Dellago, P.L. Geissler, in preparation.

Monte Carlo simulations reveal intriguing phase behavior

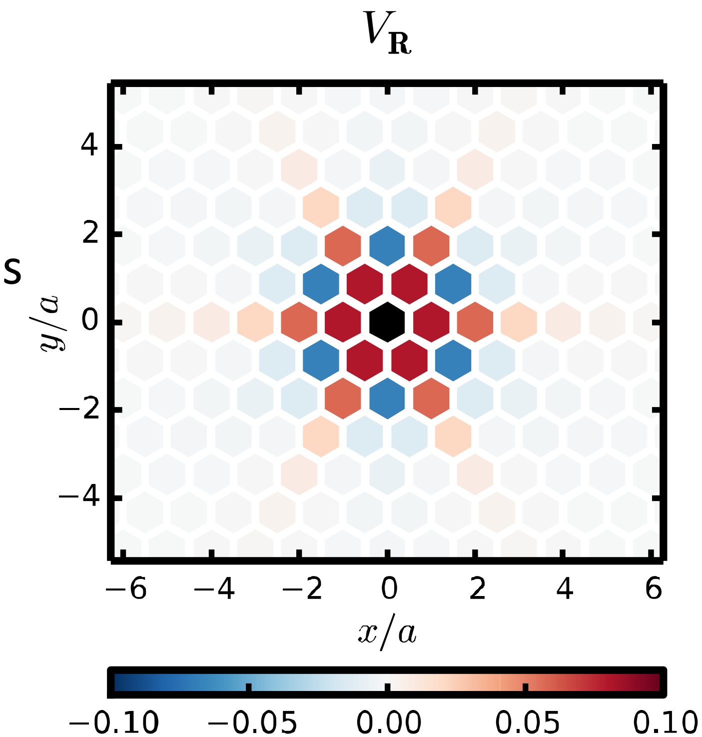


Strain energetics are captured by an effective potential

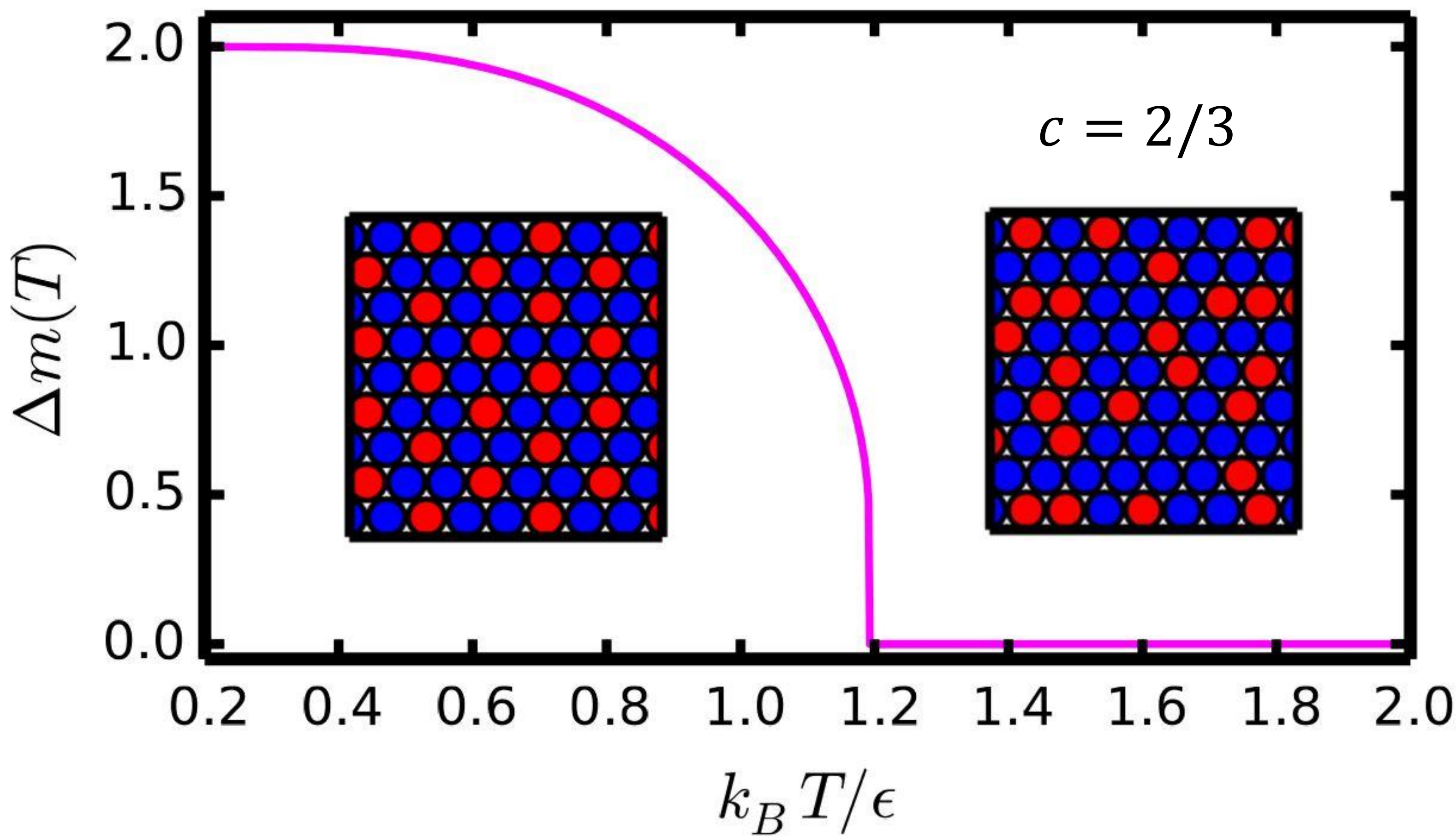
$$\mathcal{H}_{\text{eff}} = \sum_{\mathbf{R},\mathbf{R}'\neq\mathbf{R}} V_{\mathbf{R},\mathbf{R}'}\sigma_{\mathbf{R}}\sigma_{\mathbf{R}'}$$



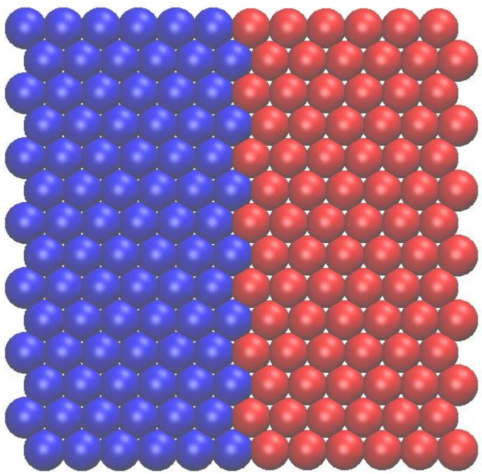
Integrate out elastic fluctuations



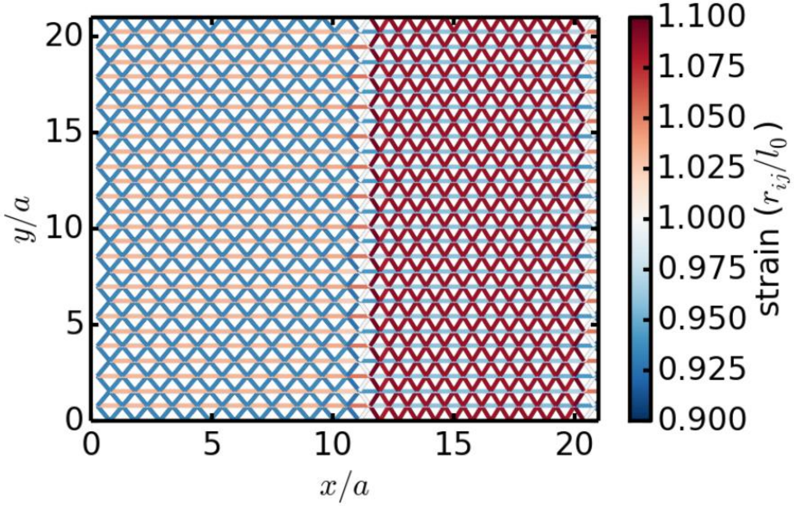
Mean field theory predicts superlattice transition

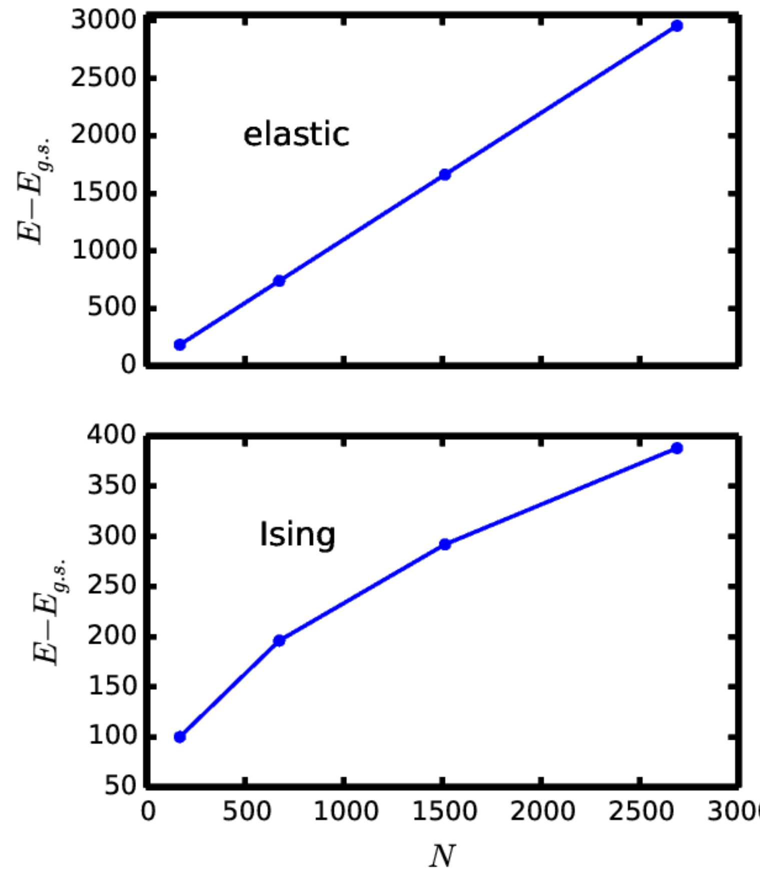


The free energy cost of elastic coexistence is extensive

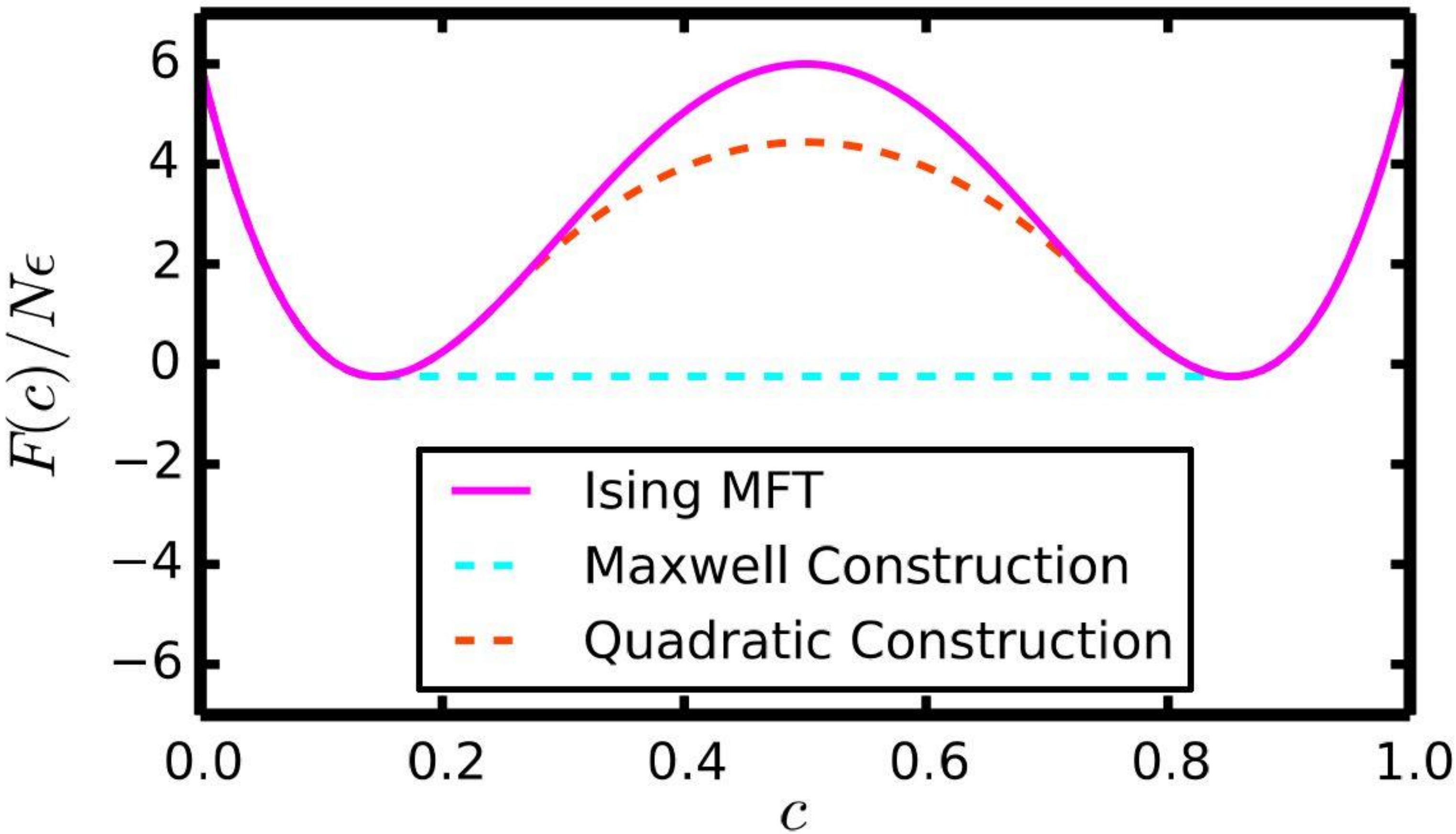


Cost of deforming domain to fit in box: $E = Y(L - L_0)^2$





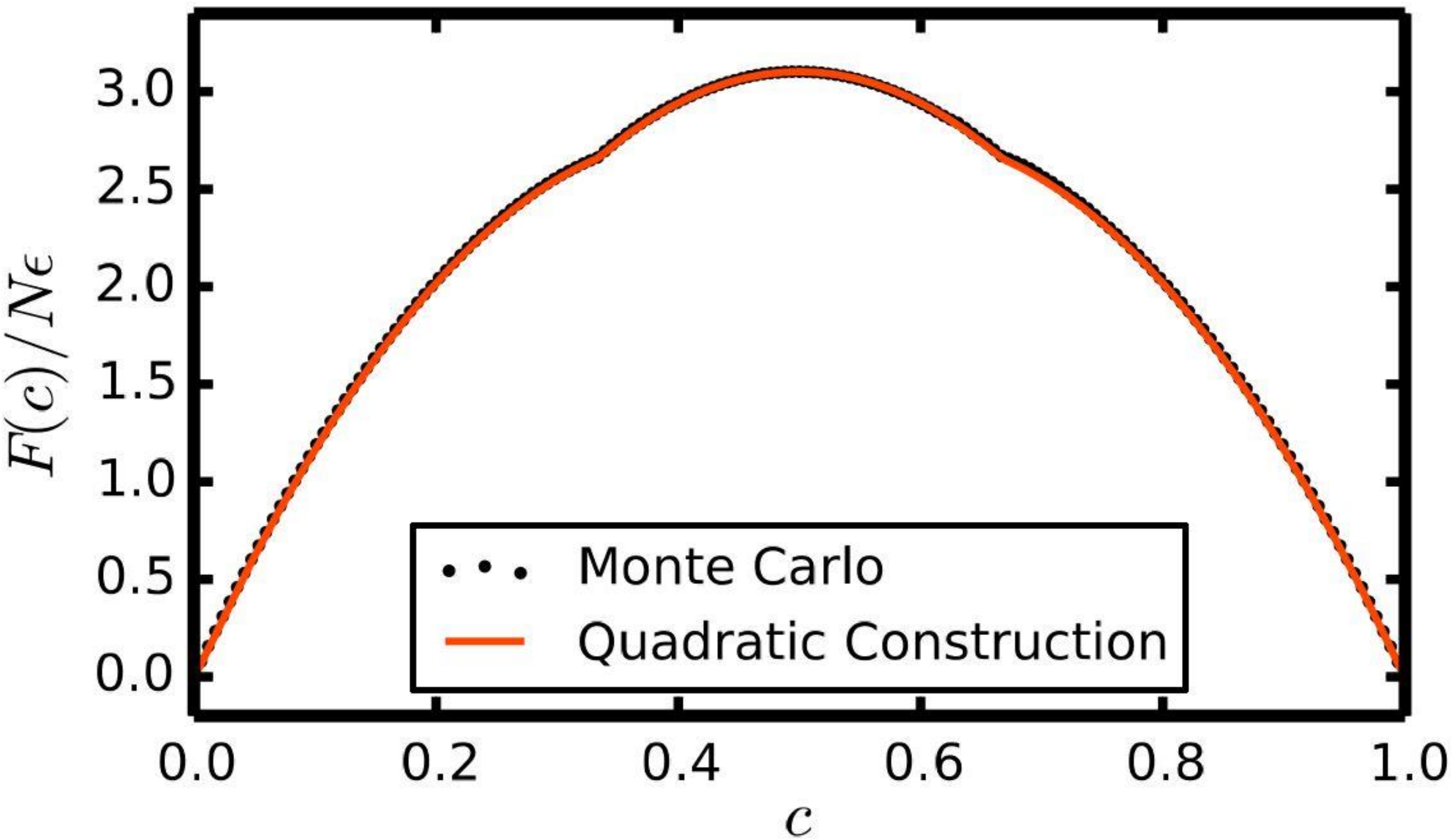
A graphical "quadratic" construction can account for elastic coexistence



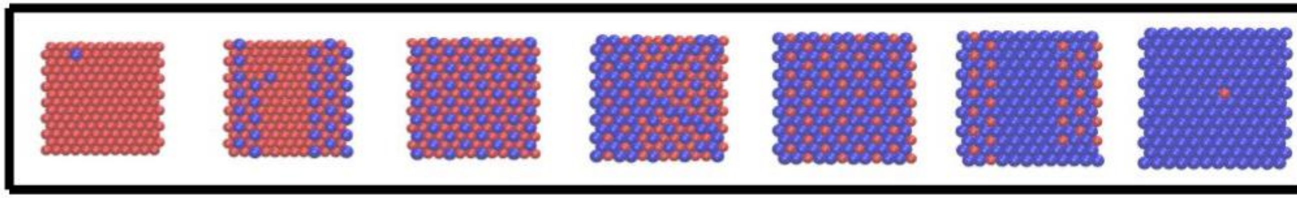
$$\frac{F}{N} = f(c_1) - \frac{\Delta c_1}{\Delta c_2 - \Delta c_1}\left(f(\Delta c_2) - f(\Delta c_1)\right) + Y \Delta l^2 \Delta c_1 \Delta c_2$$

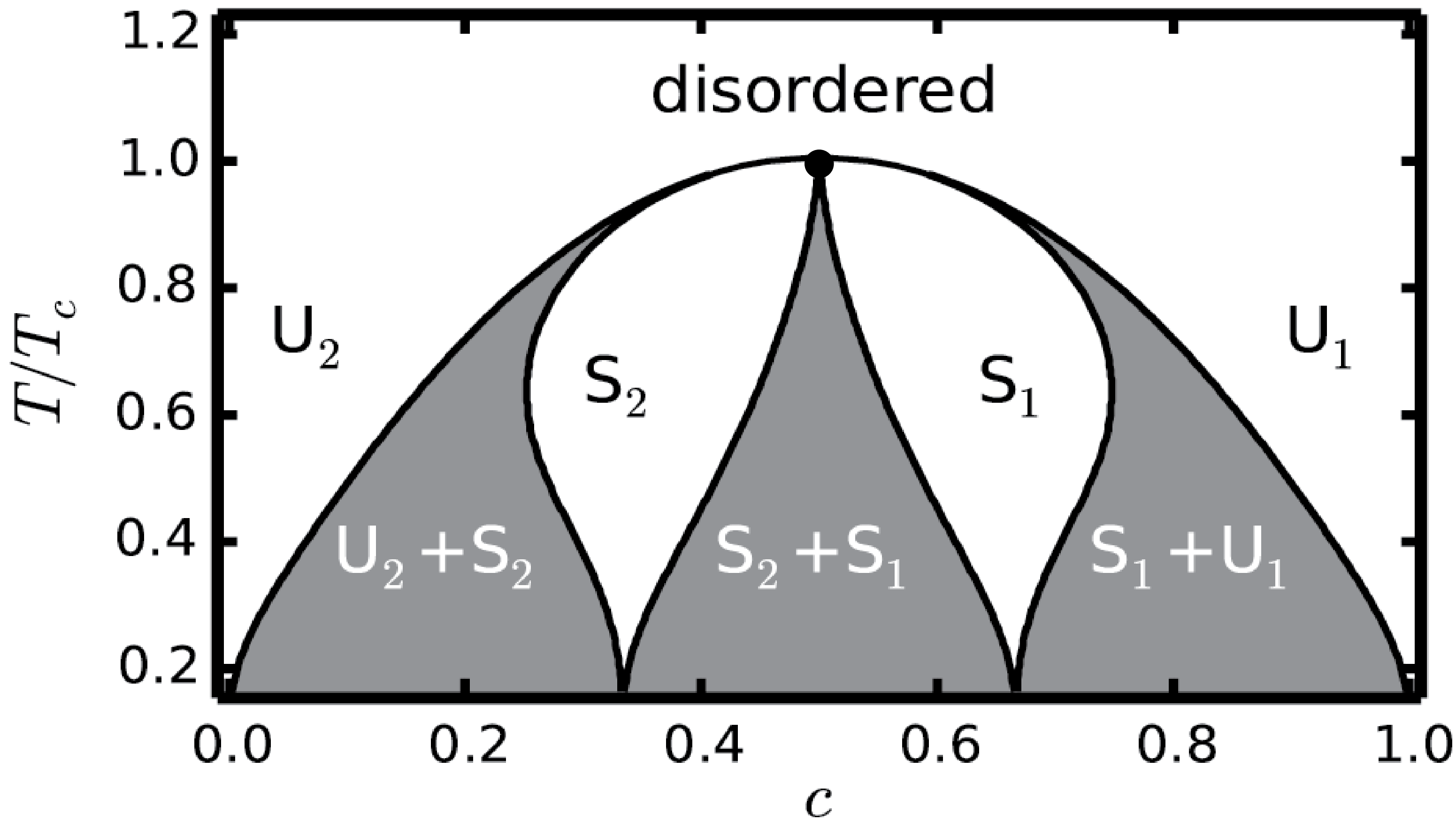
$\Delta c_1 = c^* - c_1$ $\Delta c_2 = c^* - c_2$

A graphical “quadratic” construction can account for elastic coexistence



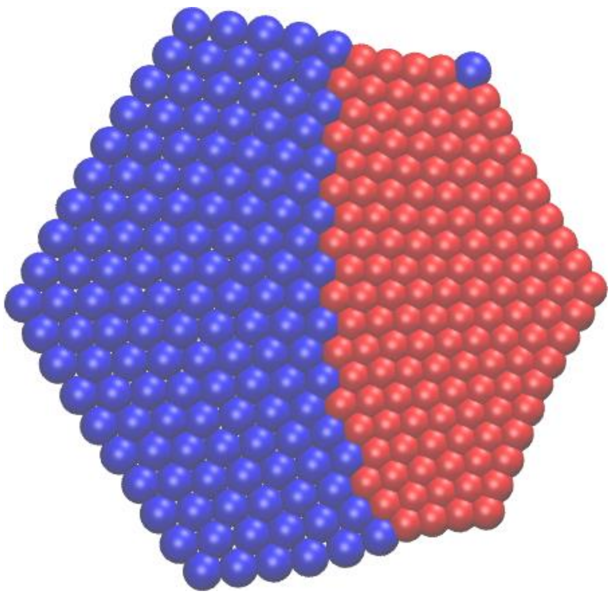
Phase diagram captures patterns observed in simulations





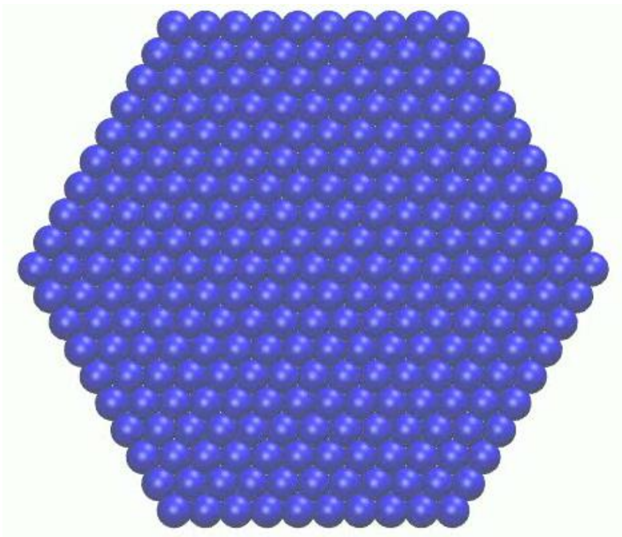
What about the nanocrystal?

Equilibrium:



Free surface
relieves strain.

Nonequilibrium:



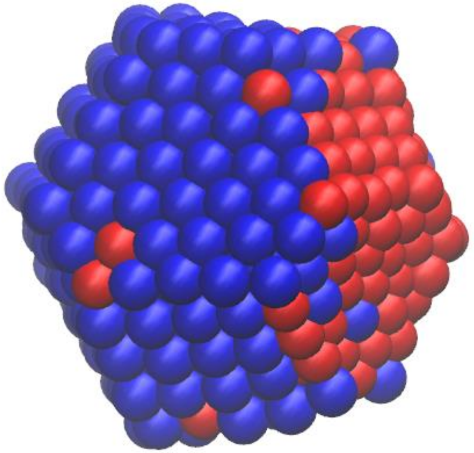
Surface exchange: k_{ex}
Bulk diffusion: k_{diff}

Conclusion

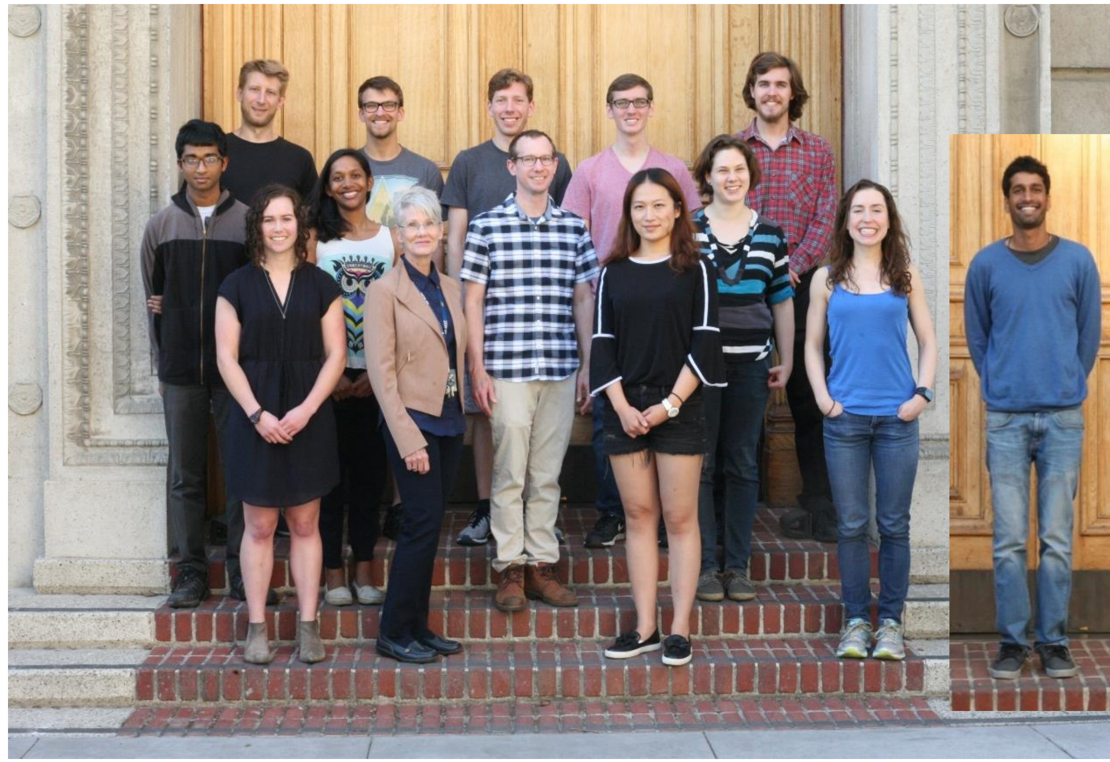
- Elastic interactions due to lattice mismatch induce rich phase behavior.
- A "quadratic construction" accounts for the extensive cost of elastic phase separation.
- Nanoscale ion exchange reactions are significantly influenced by both bulk phase behavior and kinetics.

Future Work:

- Characterize influence of factors like temperature on kinetics.
- Explore the interplay between elastic interactions and local chemistry.
- Extend results to three dimensions.



Acknowledgements



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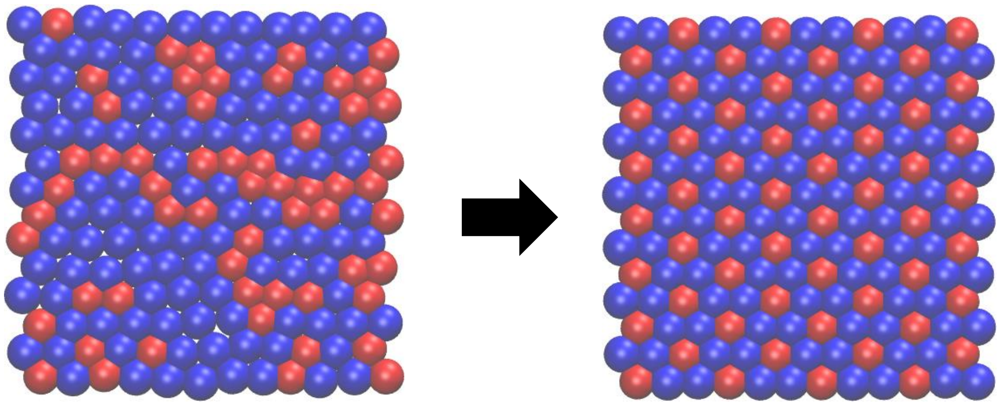
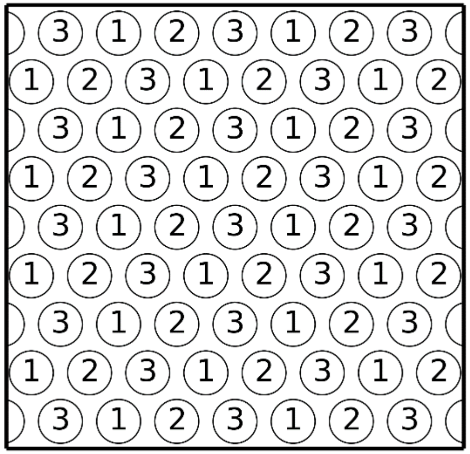
Mean Field Theory, Part II

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, $\Delta m = m_1 - m_2$.

Phase diagram captures patterns observed in simulations