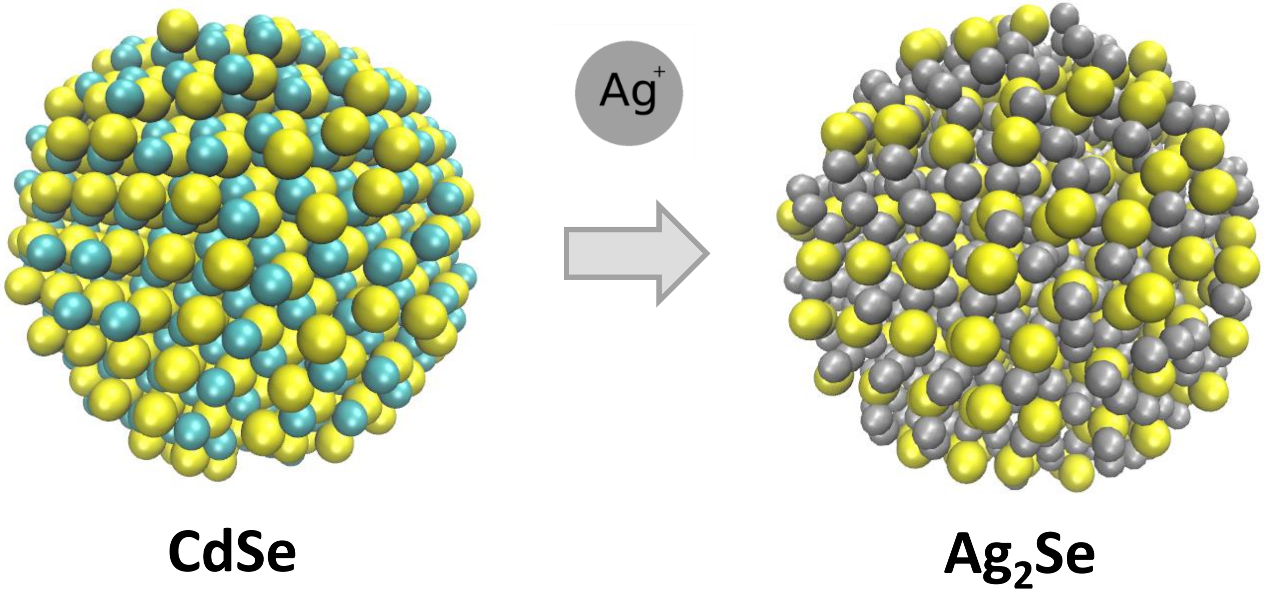
Exploring the phase behavior of an elastic Ising model for cation exchange

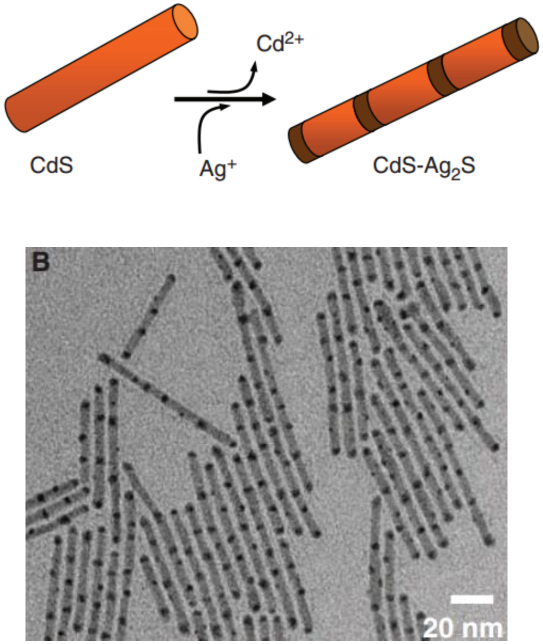


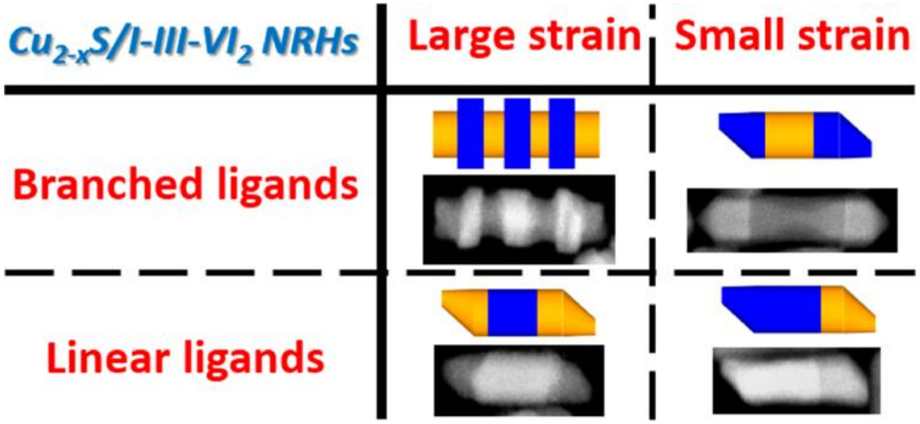
Layne Frechette

Pitzer Center Theoretical Chemistry Seminar

April 4th, 2018

Cation exchange produces a variety of nanocrystal heterostructures





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

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

What are the equilibrium phases of these nanocrystals?

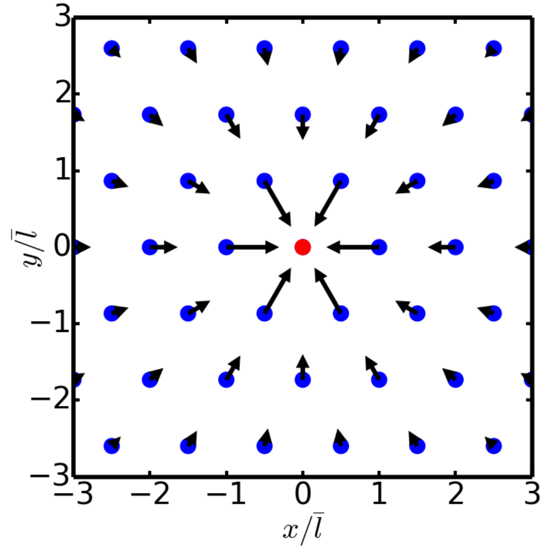
How does lattice mismatch mediate interactions between atoms?

Elastic Ising Model

$$\mathcal{H} = \frac{K}{2} \sum_{\langle i,j \rangle} (|\mathbf{r}_{ij}| - l_{ij})^2 \qquad l_{ij} = \begin{cases} l_{AA}, & \sigma_i = \sigma_j = 1 \\ l_{AB}, & \sigma_i \neq \sigma_j \\ l_{BB}, & \sigma_i = \sigma_j = -1 \end{cases}$$

Write in terms of displacement field:

$$\mathcal{H}(\{\mathbf{u}_r\}, \{\sigma_r\}) \approx \frac{K}{2} \sum_{r,\alpha} \left[\boldsymbol{\alpha} \cdot (\mathbf{u}_r - \mathbf{u}_{r+\alpha}) - \frac{\Delta}{2} (\delta\sigma_r + \delta\sigma_{r+\alpha}) \right]^2$$

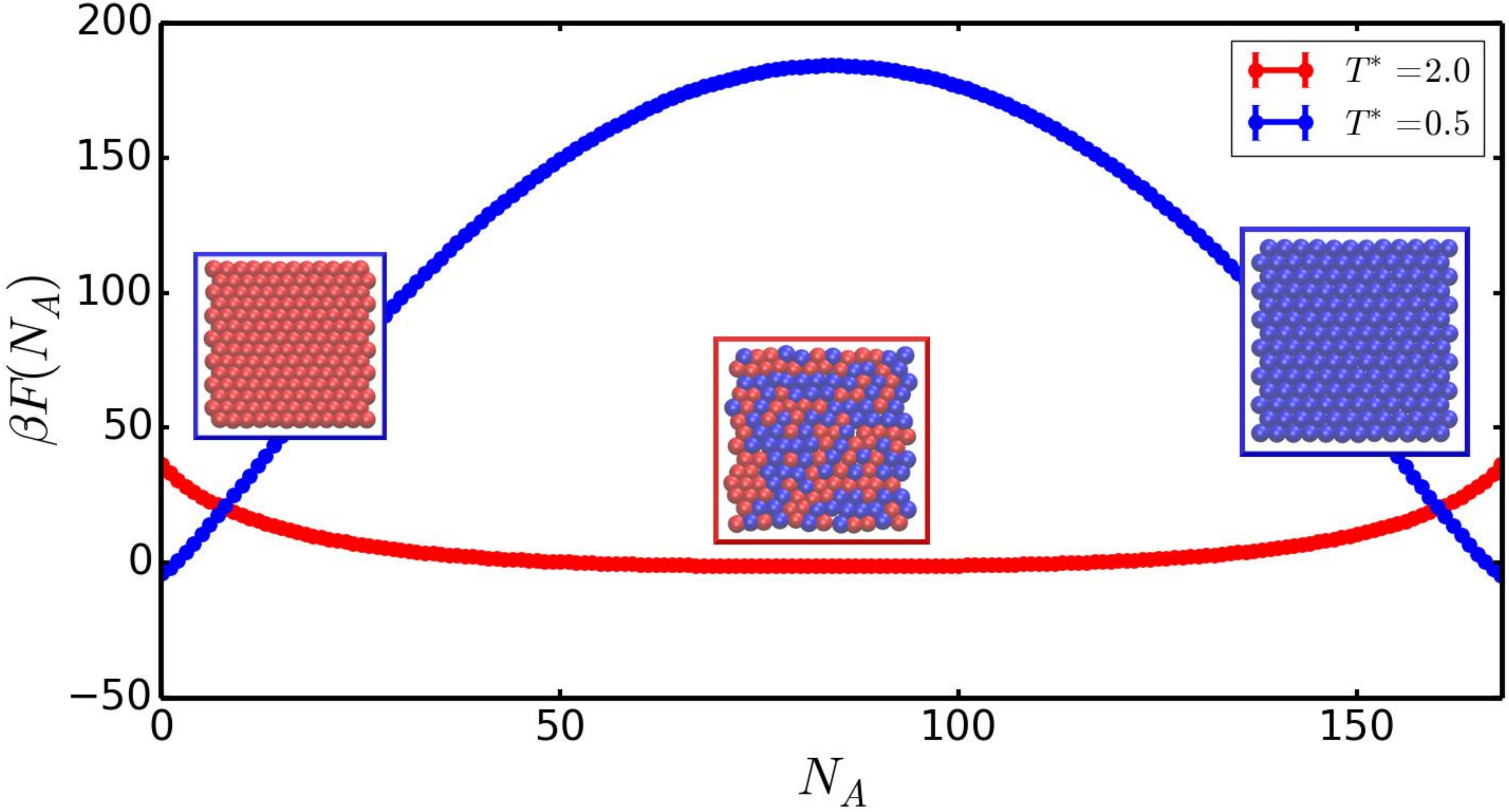


A, **B**

$$\delta\sigma_r = \sigma_r - \langle \sigma \rangle$$

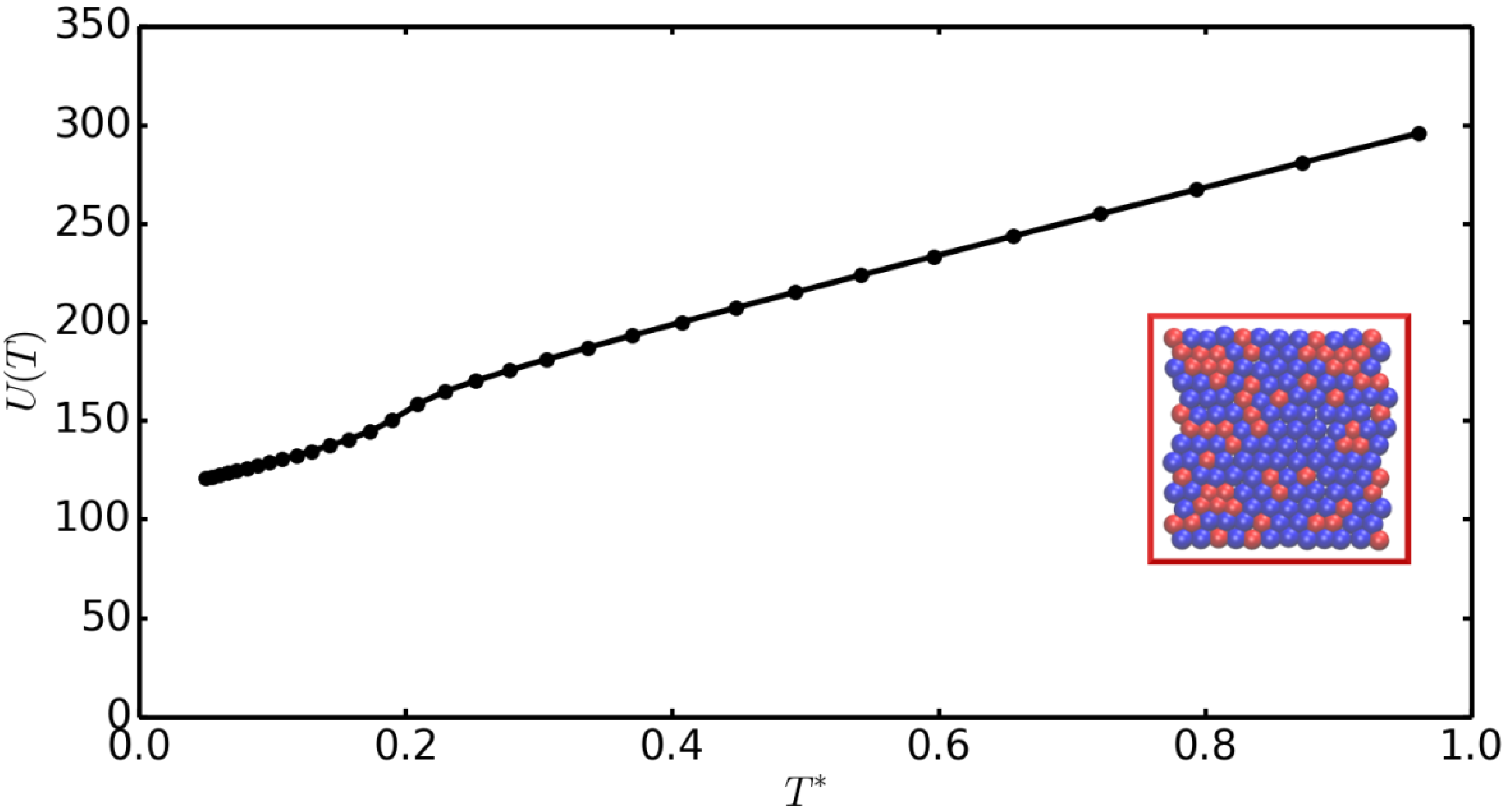
$$\Delta = (l_{AA} - l_{BB})/2$$

Bulk Phase Behavior



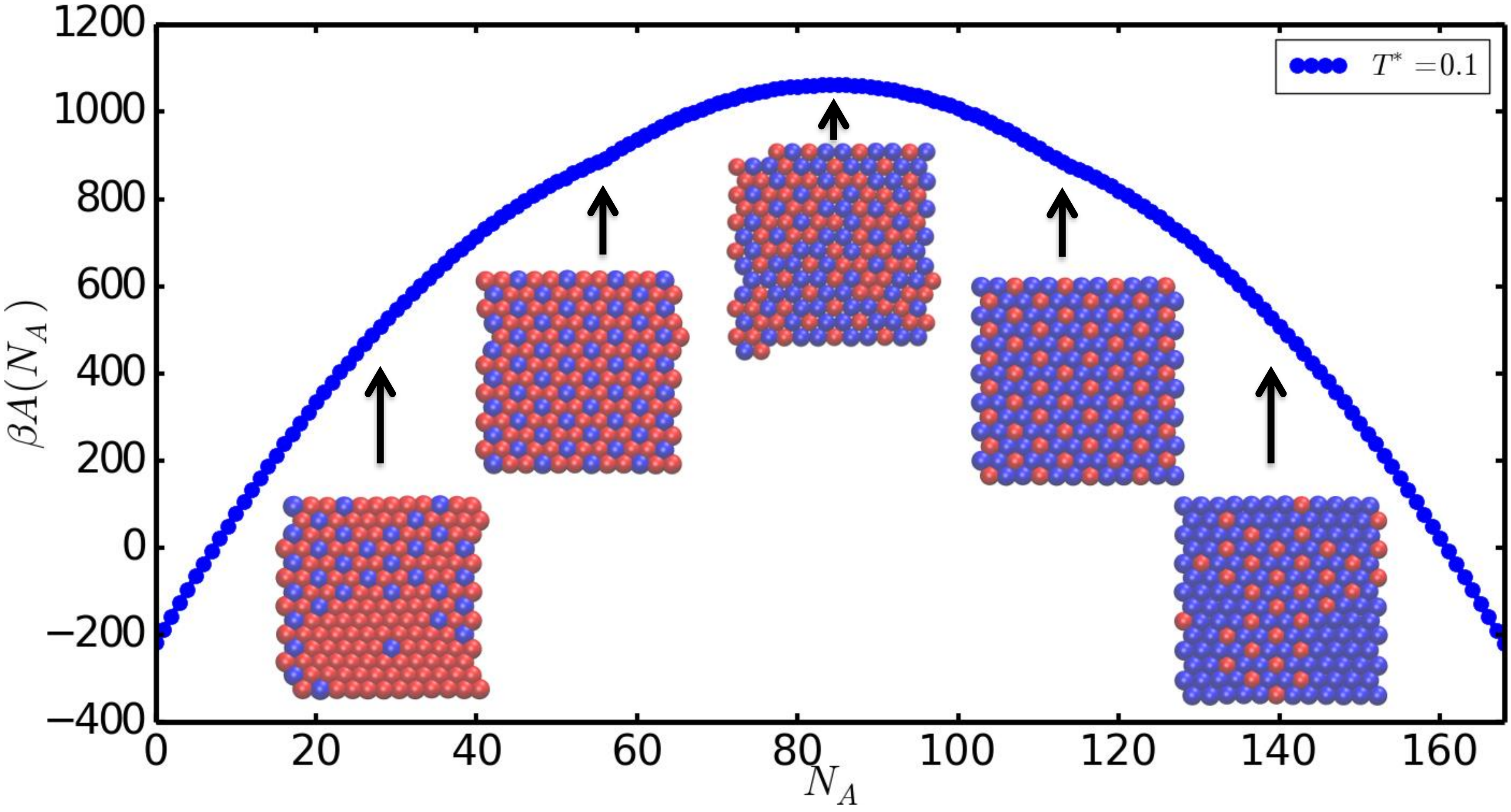
Intuition would suggest that the system phase separates at low temperature…

Does the system phase separate?



Rather than phase separating, the bulk system undergoes a transition to a “superlattice” phase.

Superlattice Configurations



Can we predict this phase behavior with a simple theory?

Microscopic explanation for frustrated phase separation

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

1) Go to Fourier Space:

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

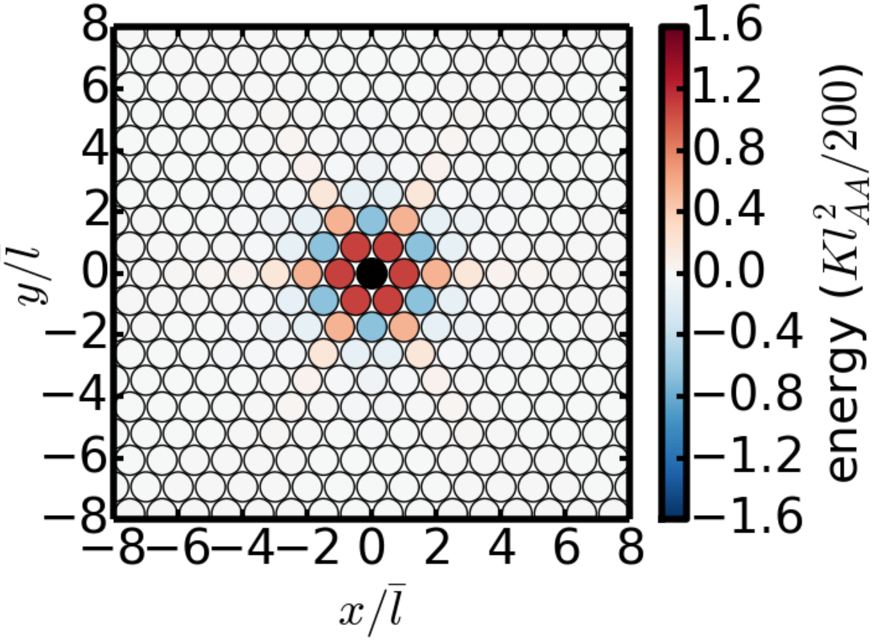
2) Integrate out displacement fluctuations:

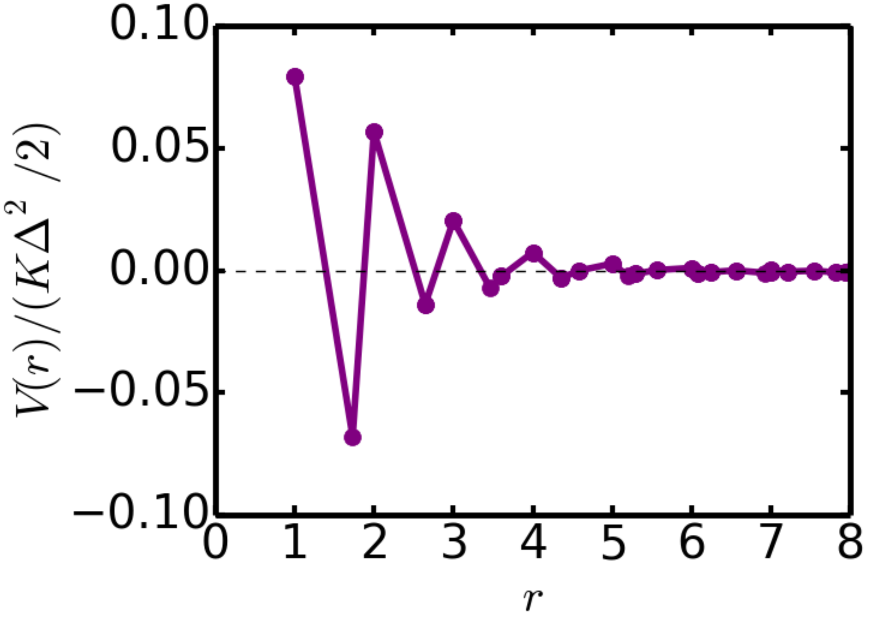
$$e^{-\beta\mathcal{H}_{\text{eff}}(\{\hat{\sigma}_q\})} = \int \prod_q d\hat{\mathbf{u}}_q e^{-\beta\mathcal{H}(\{\hat{\mathbf{u}}_q\},\{\hat{\sigma}_q\})} \implies \mathcal{H}_{\text{eff}}(\{\hat{\sigma}_q\}) = \frac{1}{N}\sum_q |\hat{\sigma}_q|^2 \hat{V}_{\text{eff}}(\mathbf{q})$$

3) Transform back to real space:

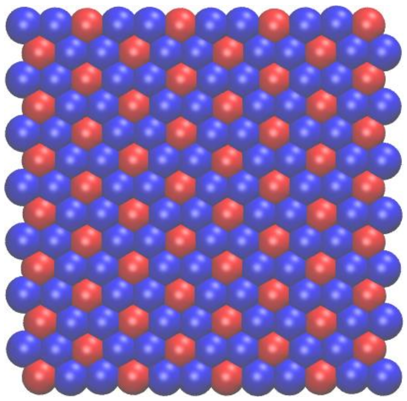
$$\mathcal{H}_{\text{eff}}(\{\sigma_r\}) = \sum_{r,r'} V_{\text{eff}}(\mathbf{r}-\mathbf{r}')\sigma_r\sigma_{r'} \qquad V_{\text{eff}}(\mathbf{r}) = \frac{1}{N}\sum_q \hat{V}_{\text{eff}}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}}$$

Effective potential for triangular lattice



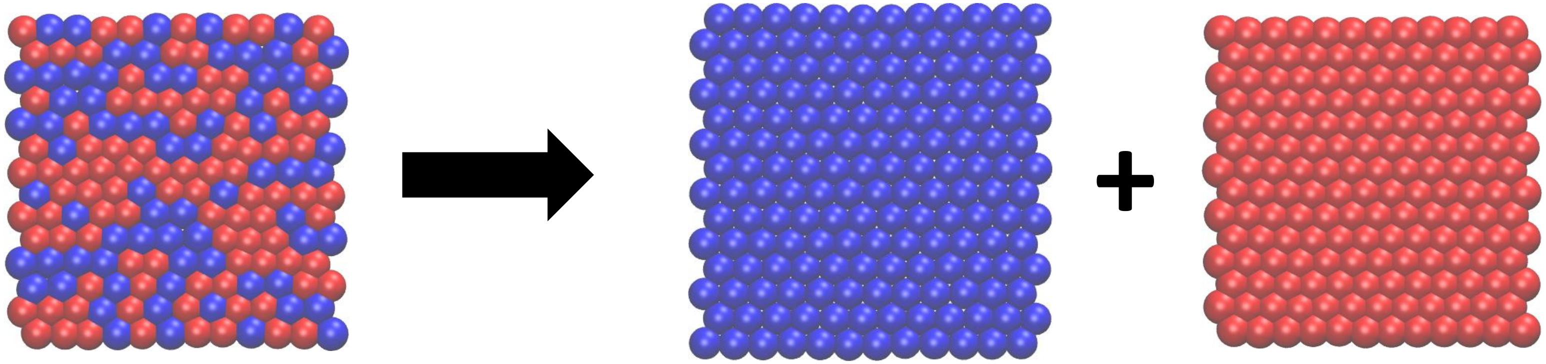


$$\mathcal{H}_{\mathrm{eff}} = \mathcal{H}_{\mathrm{eff}}(\{\sigma_r\}) = \sum_{r,r'} V_{\mathrm{eff}}(\mathbf{r} - \mathbf{r}')\sigma_r \sigma_{r'}$$



Mean Field Theory, Part I

Allow composition to fluctuate and predict its spontaneous symmetry breaking.



Variational MFT: Map many-body Hamiltonian to optimal one-body reference Hamiltonian.

$$\mathcal{H} = \sum_{r,r'} \sigma_r V_{r-r'} \sigma_{r'} \qquad \Longrightarrow \qquad \mathcal{H}_0 = -h_0 \sum_r \sigma_r$$

Obtain partition function and composition in reference system:

$$Q_0 = \left(2\cosh \beta h_0\right)^N , \qquad \langle \sigma_i \rangle_0 \equiv m = \tanh \beta h_0$$

Mean Field Theory, Part I

Get optimal reference field by minimizing reference free energy:

$$0 = \frac{\partial \log Q_{\text{est}}}{\partial \beta h_0}, \quad Q_{\text{est}} = Q_0 e^{-\beta \langle \Delta \mathcal{H} \rangle_0}$$

Need to evaluate average of Hamiltonian in the reference system. A nice property of the potential makes this easy.

$$\langle \mathcal{H} \rangle_0 = \sum_{r, r' \neq r} \langle \sigma_r \rangle_0 V_{r-r'} \langle \sigma_r' \rangle_0$$

$$\sum_r V_{r-r'} = 0 \implies \sum_{r \neq r'} V_{r-r'} = -V_0$$

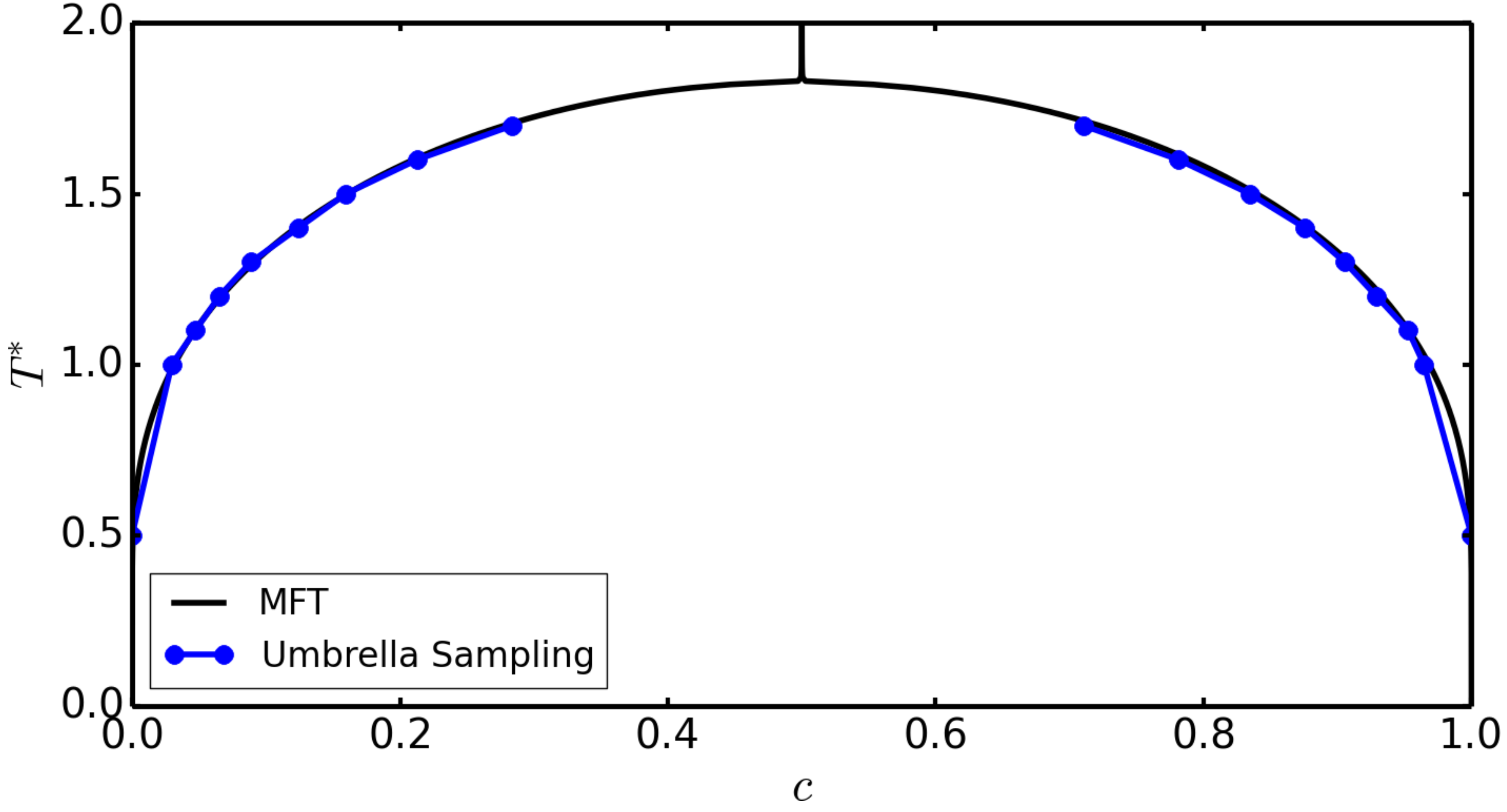
Resulting reference field can be used to obtain self-consistent equation for magnetization and hence critical temperature.

$$h_0 = 2V_0 m \implies m = \tanh 2\beta V_0 m, \quad k_B T_c = 2V_0$$

Mean Field Theory, Part I

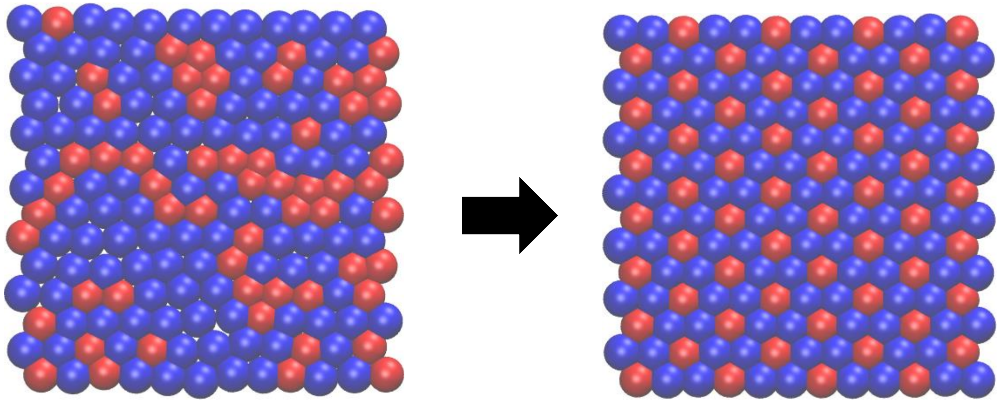
These results *quantitatively* agree with simulation!
Why? The effective potential is very long-ranged.

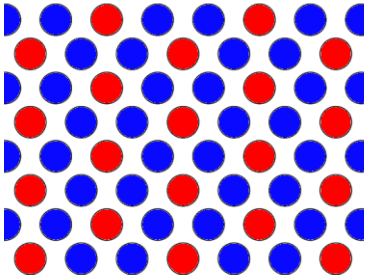
$$k_B T_c = 2V_0 \approx 1.825$$



Mean Field Theory, Part II

Fix composition and predict sublattice ordering.





Sublattice 1 $x_1 = N_1/N$

Sublattice 2 $x_2 = N_2/N$

$$\mathcal{H} = \sum_{r,r' \neq r} \sigma_r V_{r-r'} \sigma_{r'}, \quad \mathcal{H}_0 = -h_1 \sum\nolimits_r^{(1)} \sigma_r - h_2 \sum\nolimits_r^{(2)} \sigma_r$$

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

Mean Field Theory, Part II

Constraint makes canonical ensemble awkward, so switch to grand canonical ensemble.

$$\Xi_0 = \prod_r^{(1)} 2\cosh\beta(\mu + h_1) \prod_r^{(2)} 2\cosh\beta(\mu + h_2)$$

$$m_j = \tanh\beta(\mu + h_j) \qquad Q_0 = e^{-\beta\mu N\bar{m}}\Xi_0$$

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

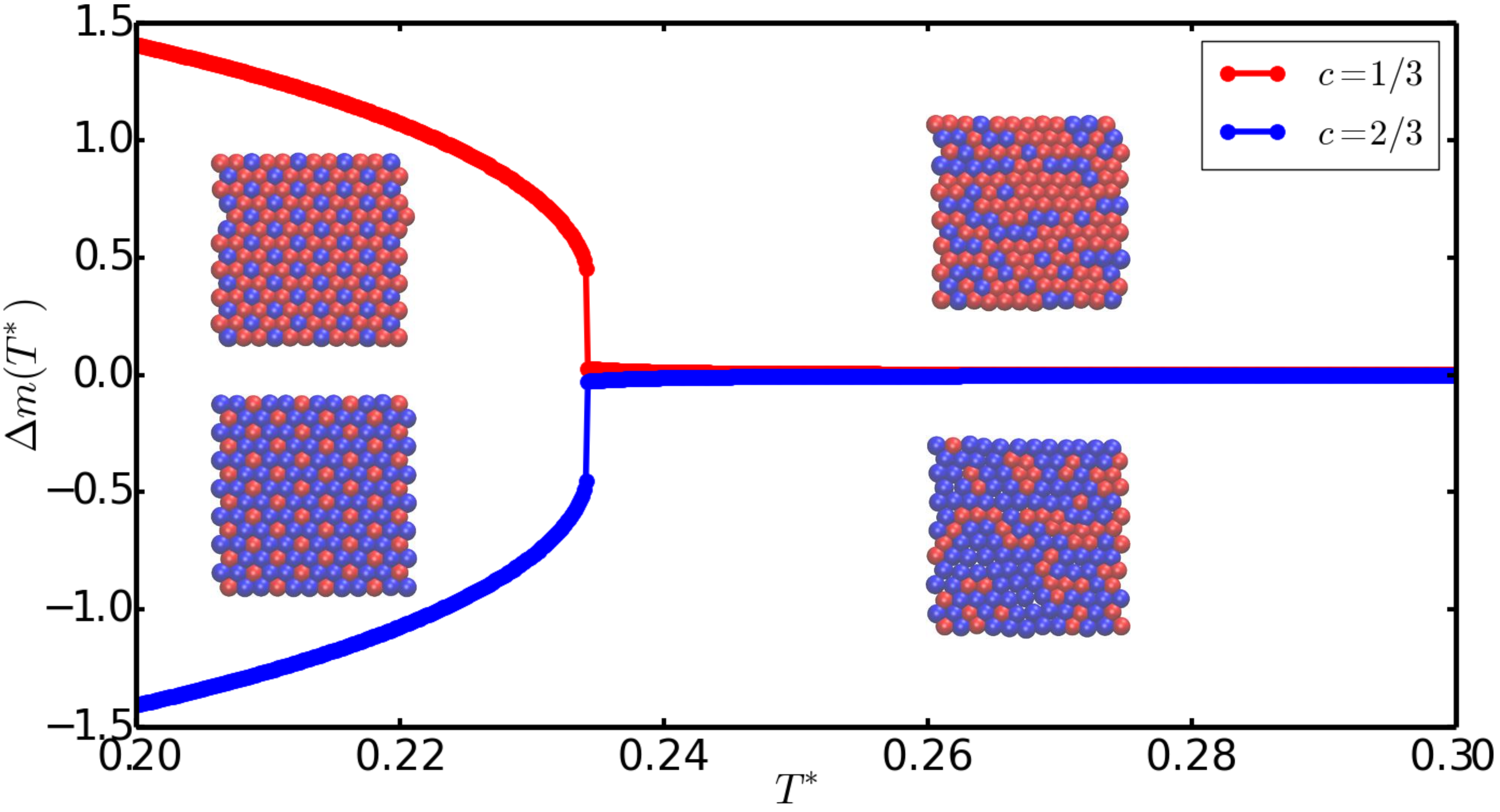
$$m_1 = \tanh\beta(\mu - 2J_{11}m_1 - 2J_{12}m_2/x_1)$$

$$m_2 = \tanh\beta(\mu - 2J_{22}m_2 - 2J_{12}m_1/x_2)$$

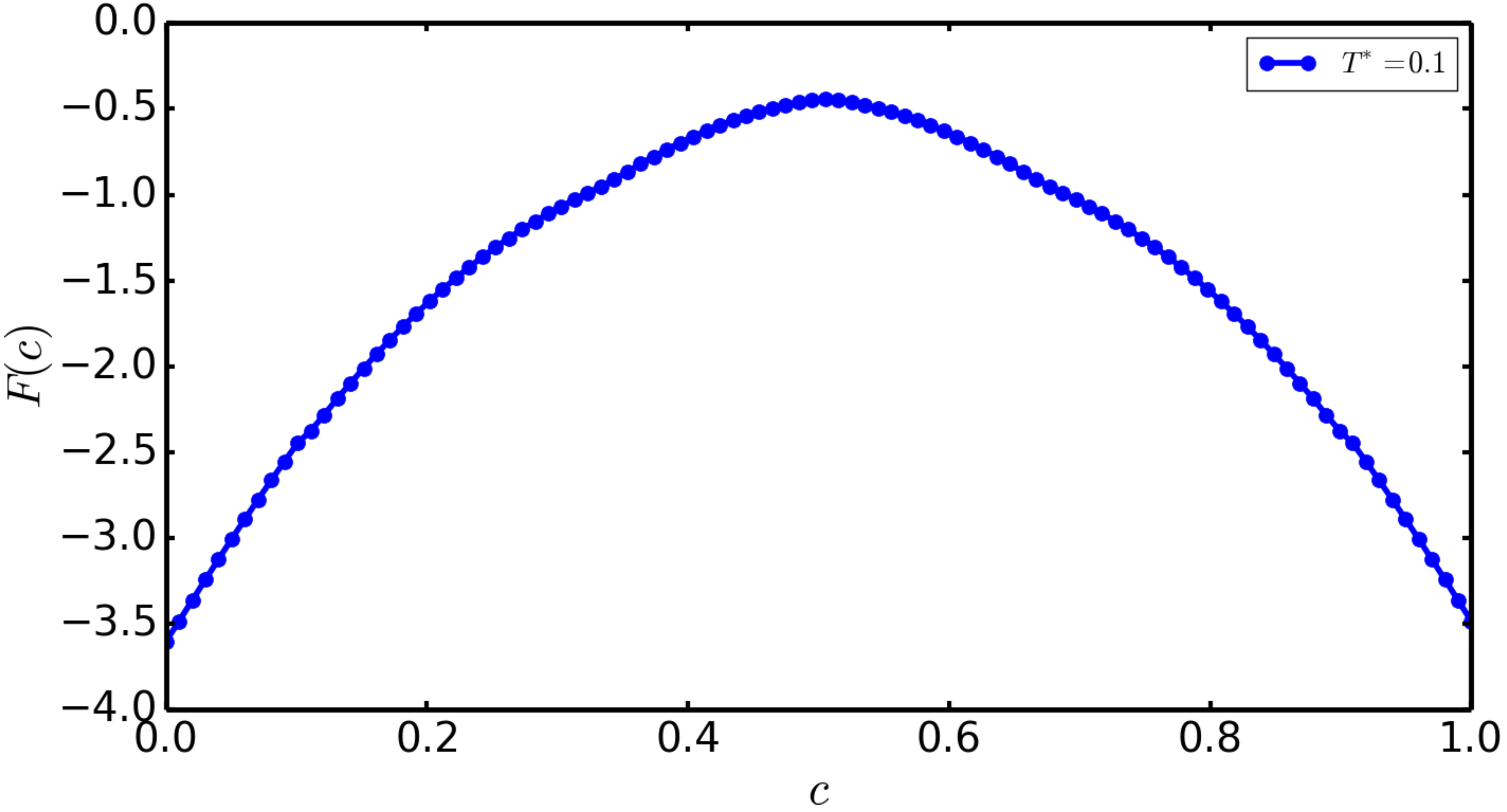
$$\bar{m} = x_1 m_1 + x_2 m_2$$

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

Mean Field Theory, Part II

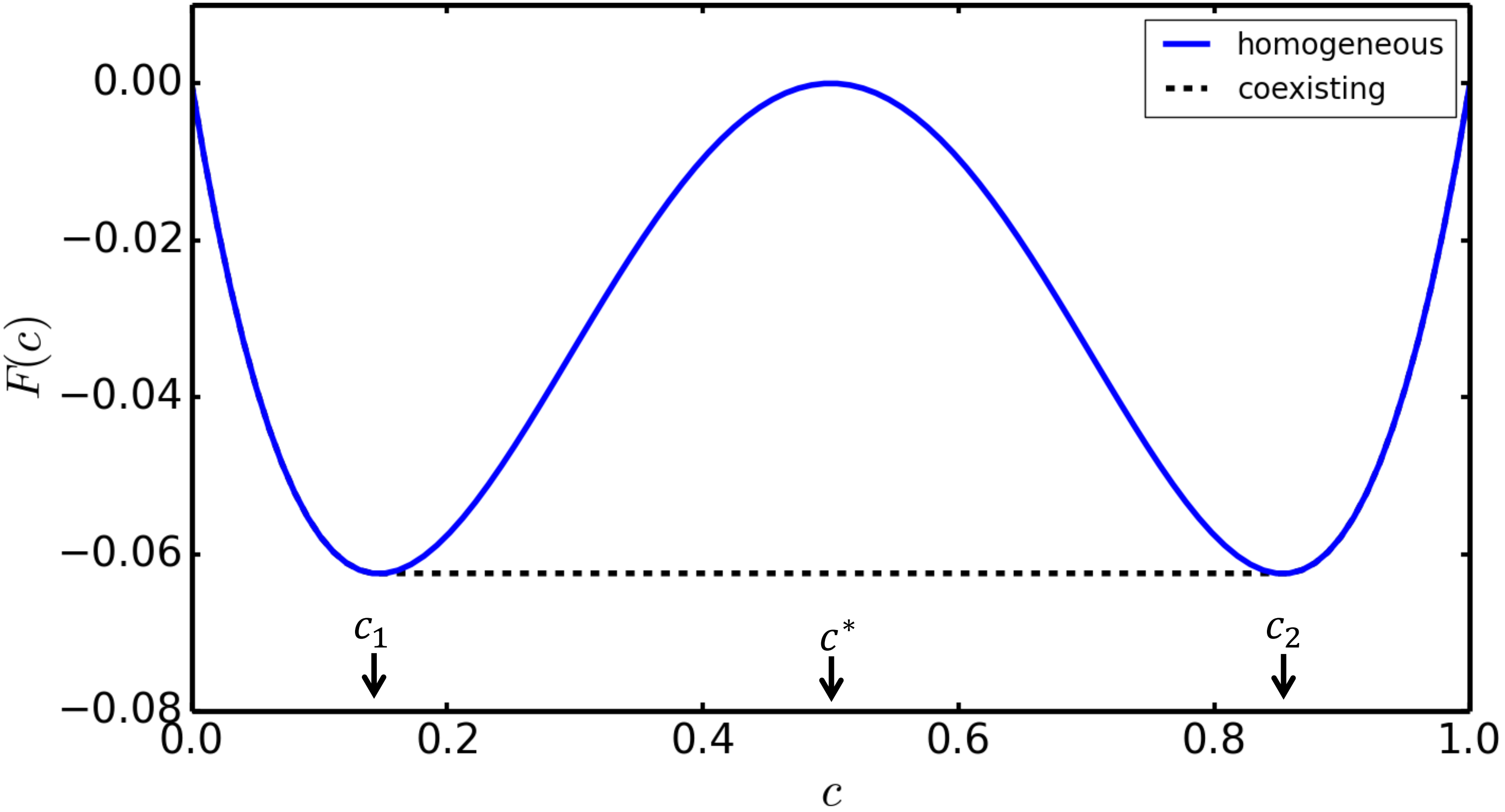


Mean Field Theory, Part II



Mean field theory only knows about homogeneous phases, so how do we predict coexistence?

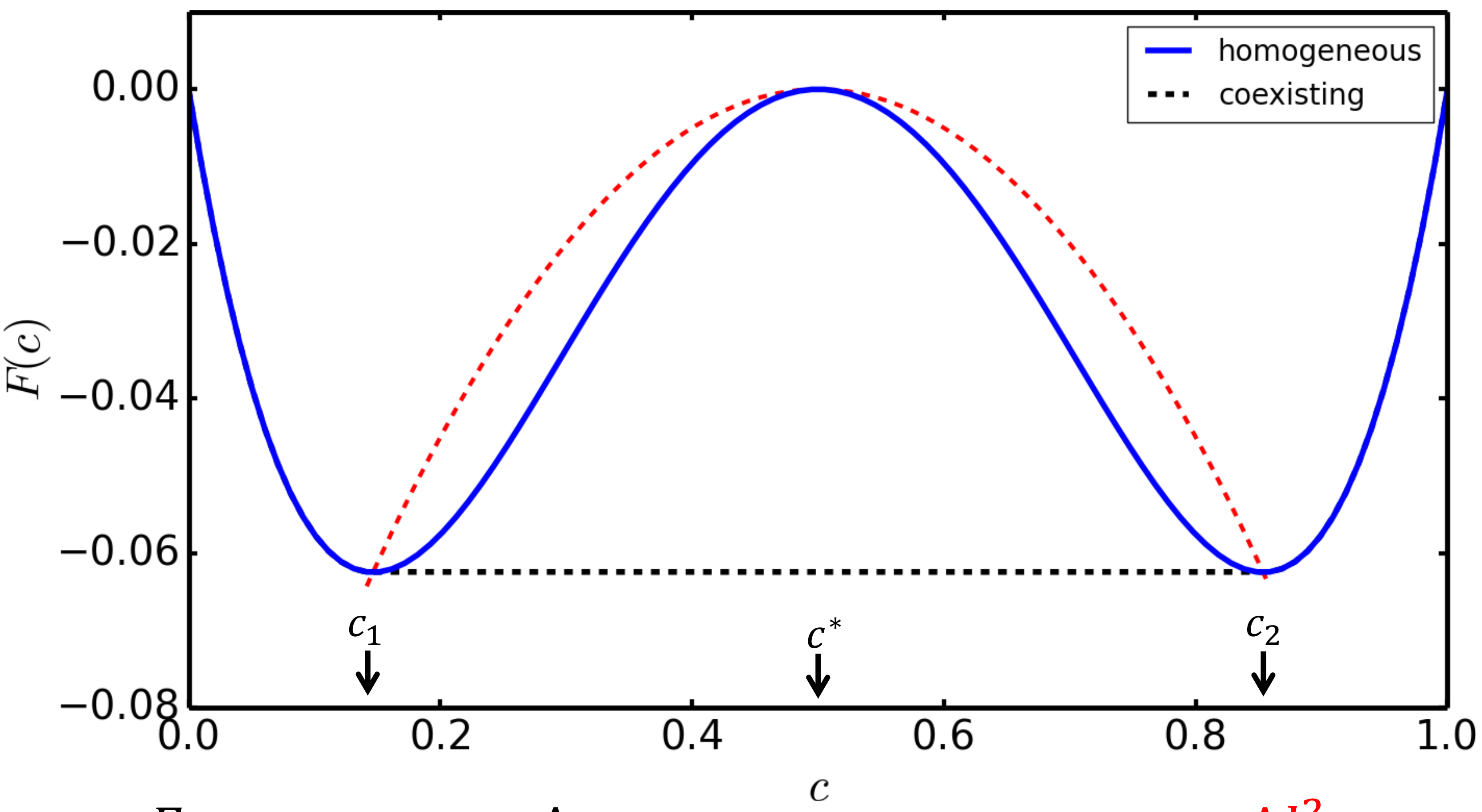
Predicting coexistence with a double tangent construction



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

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

Predicting coexistence with a double tangent construction



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

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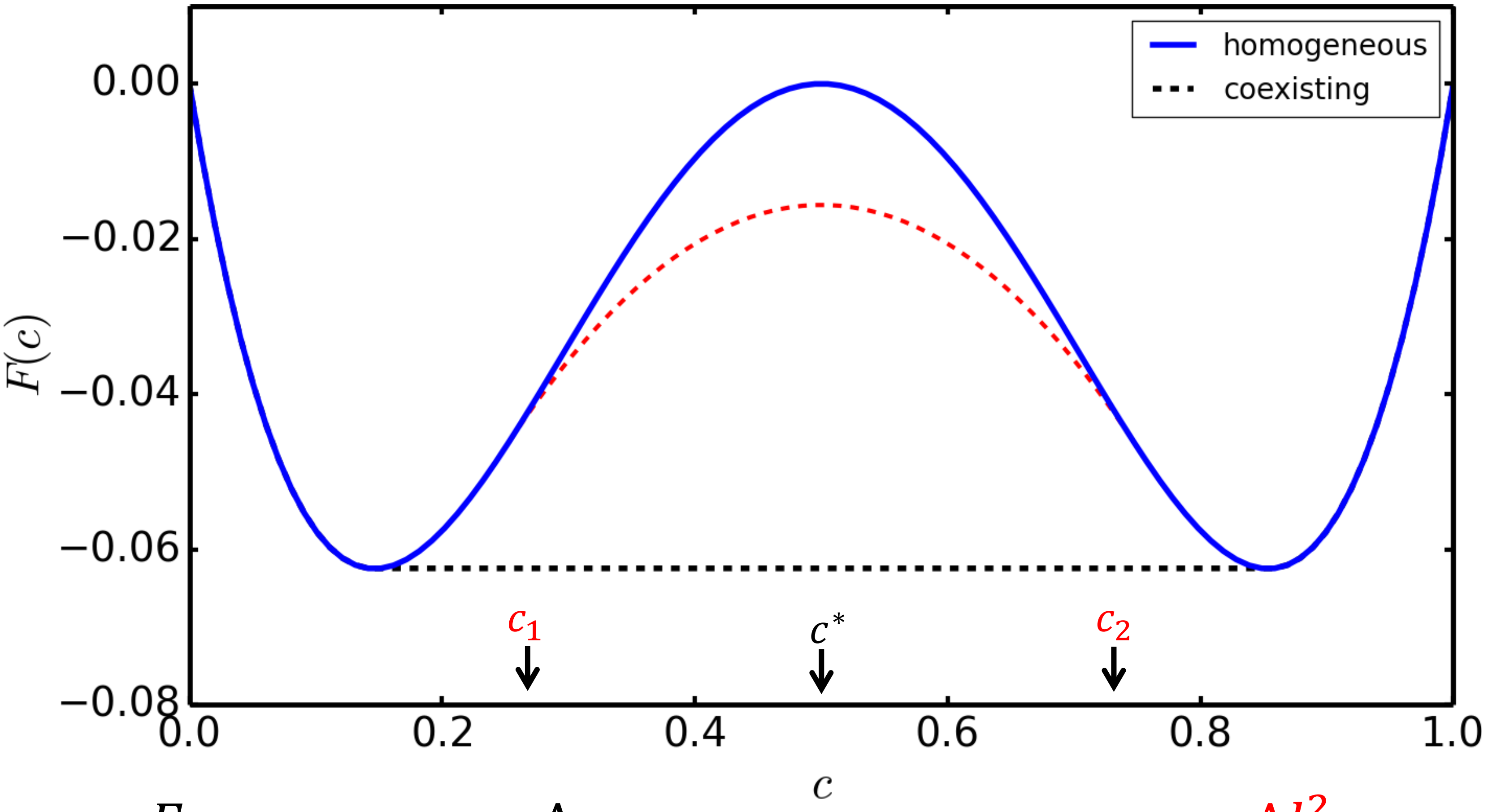
Predicting coexistence with a double tangent construction



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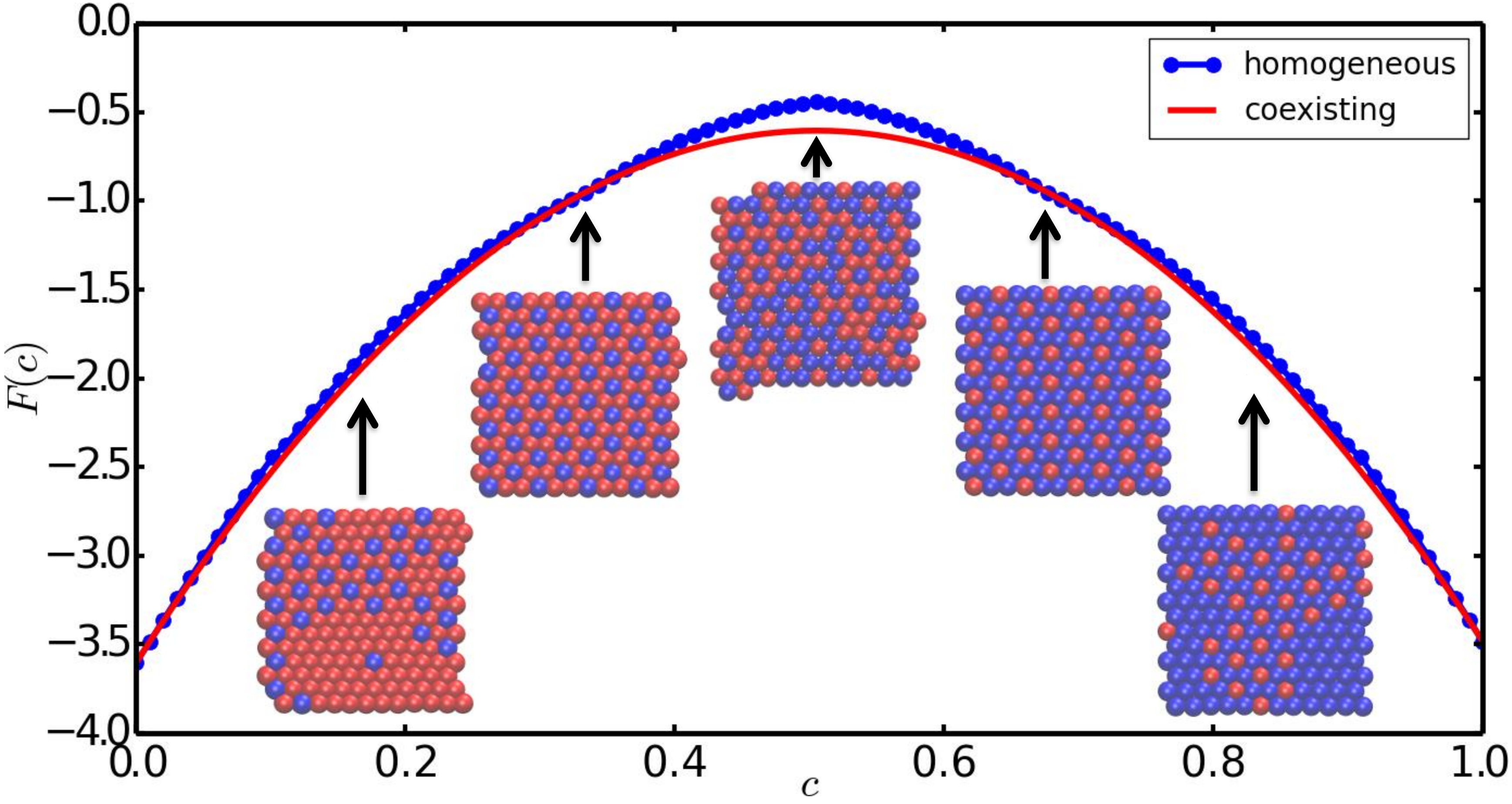
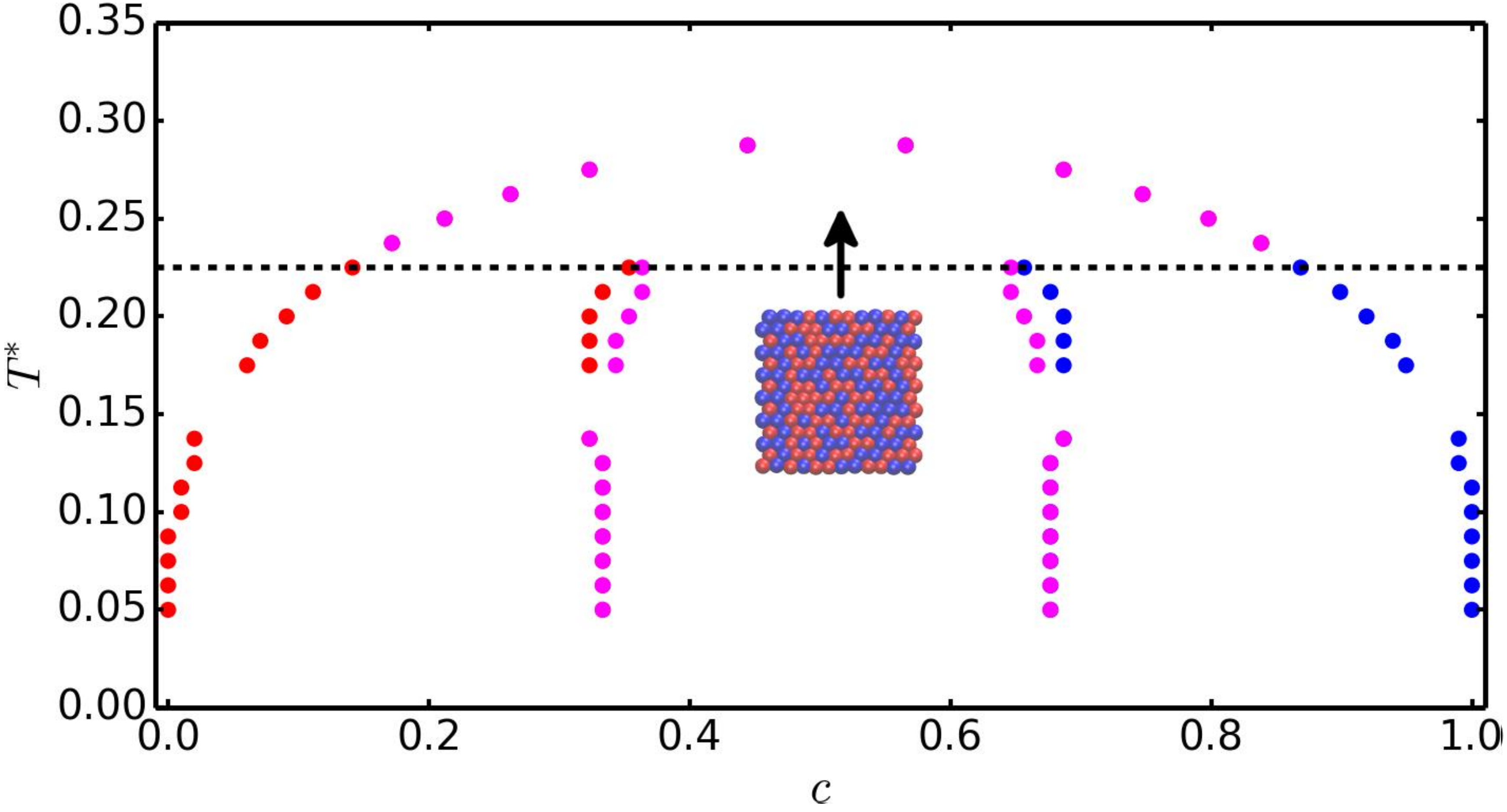
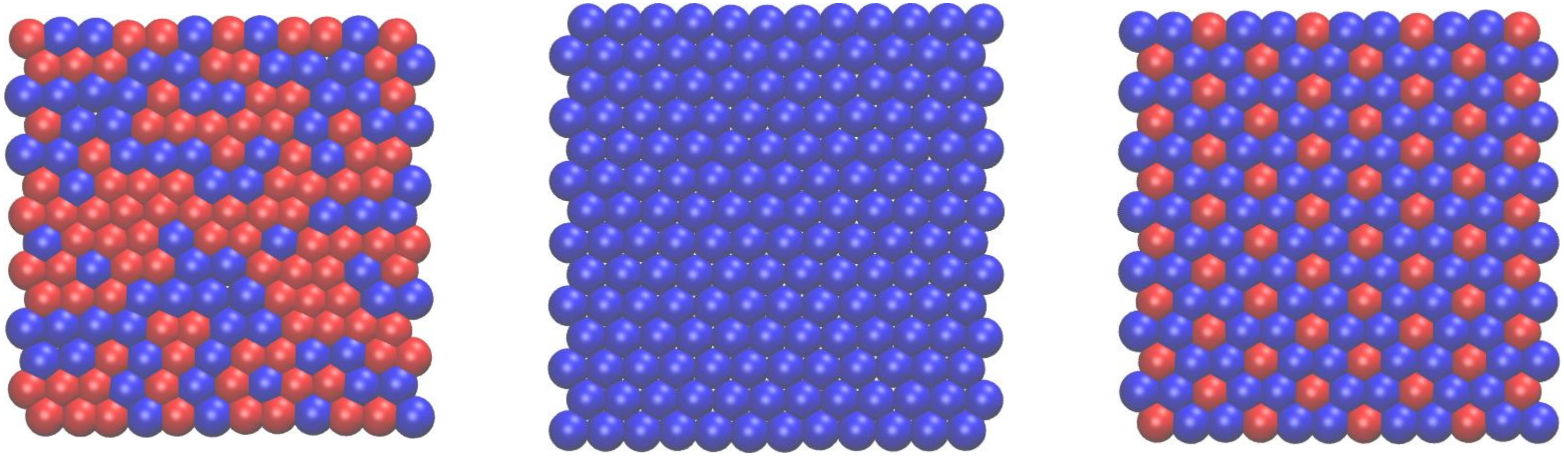
Predicting coexistence with a double tangent construction



Superlattice Phase Diagram

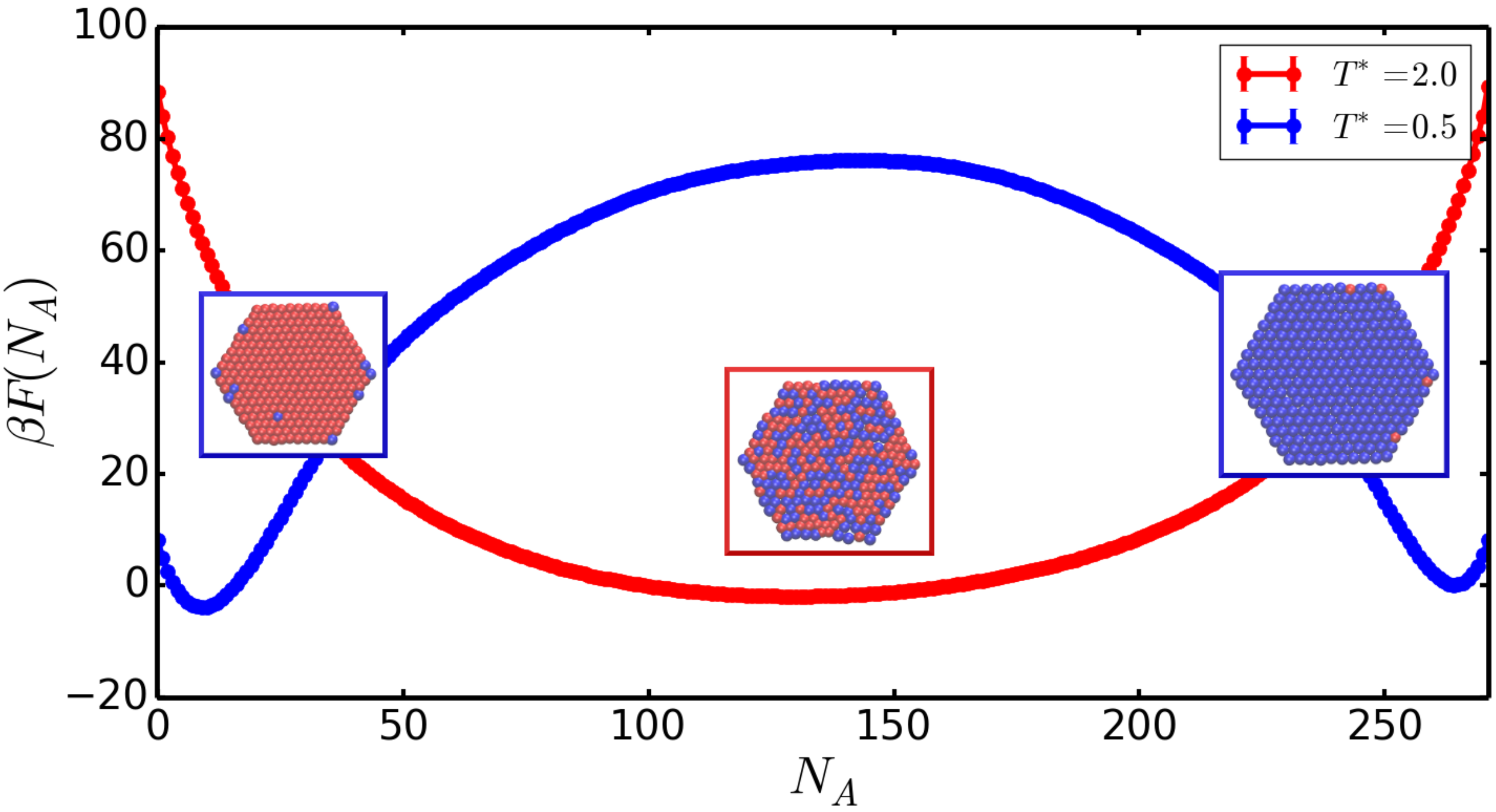


Summary of bulk phase behavior

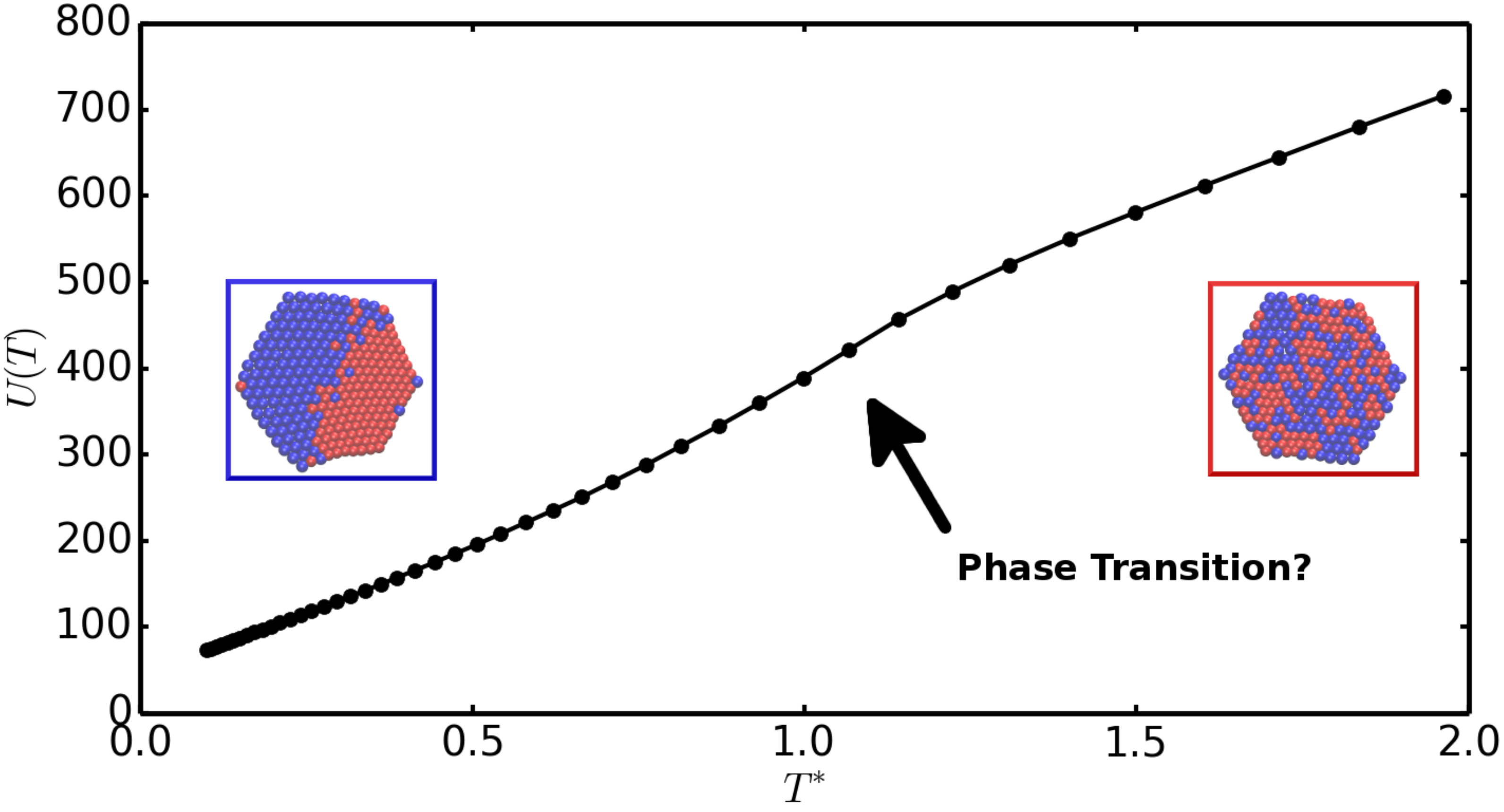


- Lattice mismatch induces long-ranged interactions.
- The long-ranged interactions result in interesting phases.
- Transitions between these bulk phases are accurately described by mean field theory.
- What about the nanocrystal?

Nanocrystal Phase Behavior



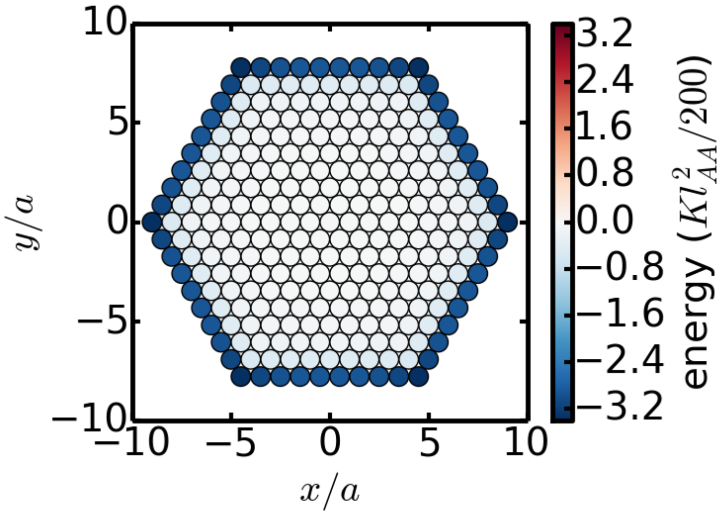
Nanocrystal Phase Separates!



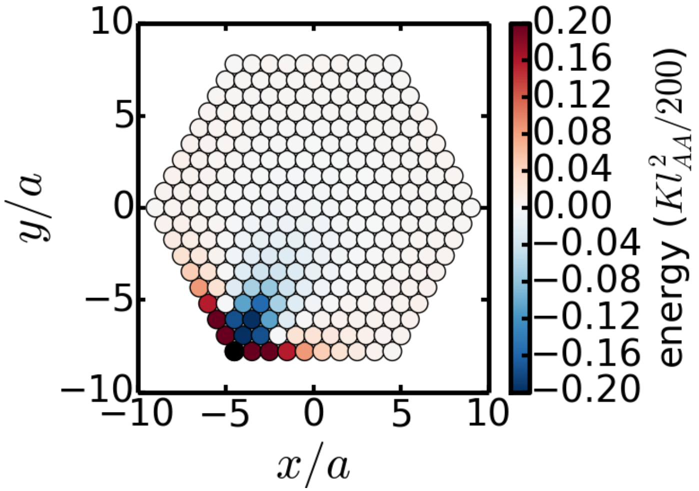
Why is it different from bulk?

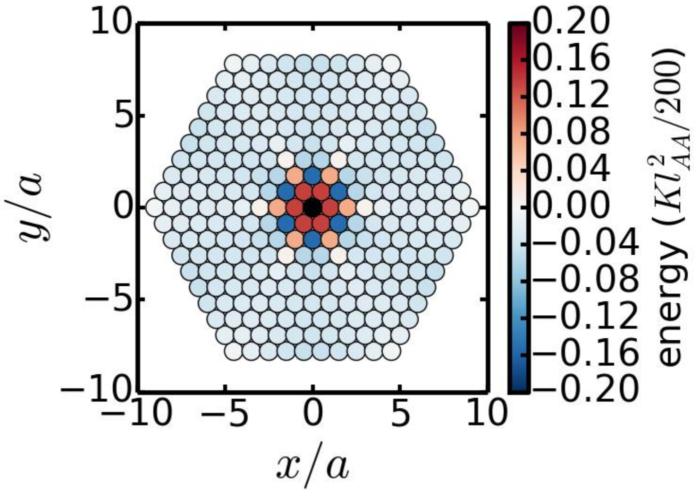
Why does the nanocrystal phase separate?

An impurity creates less strain at the surface than in bulk, so it is energetically favorable for it to be located at the surface.

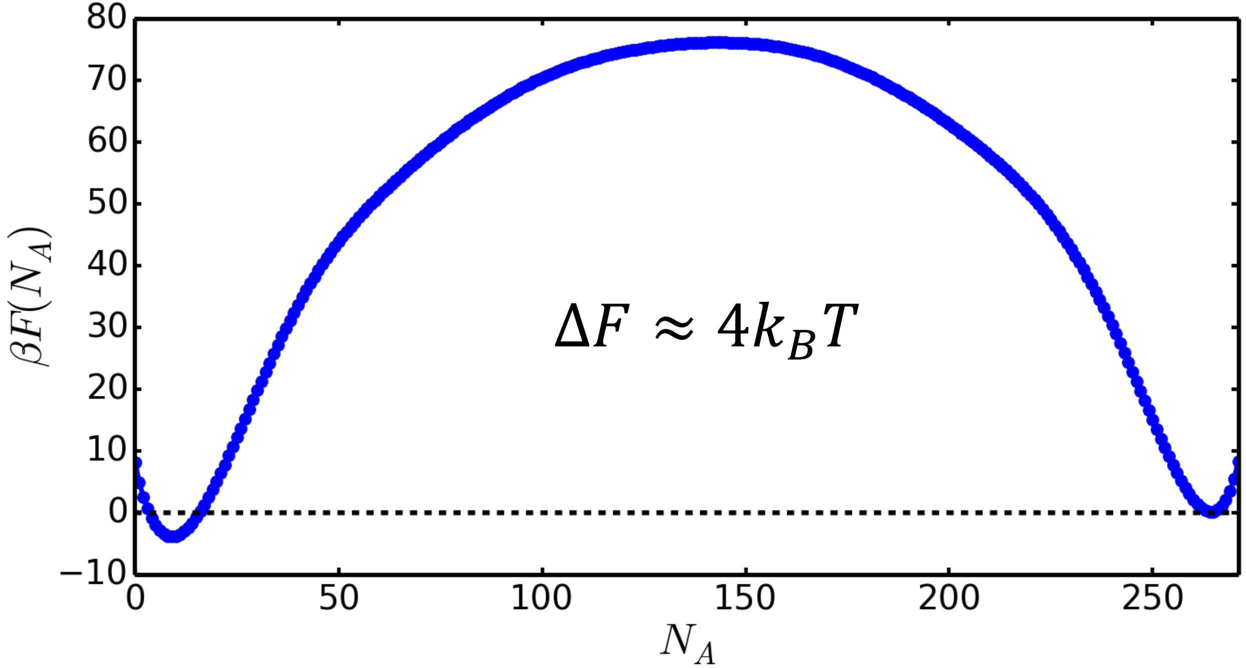


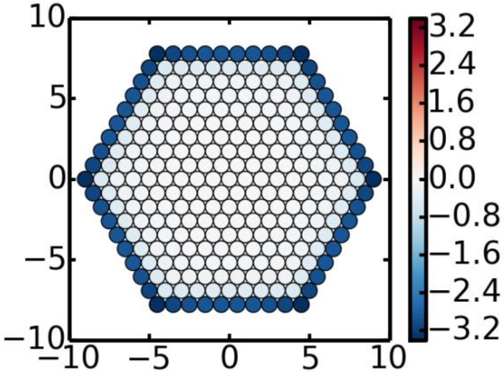
Why doesn't this lead to a core-shell structure? Presence of an impurity affects the energy of putting in an additional impurity.





Why is the nanocrystal free energy profile asymmetric?





A lattice, **B** impurity

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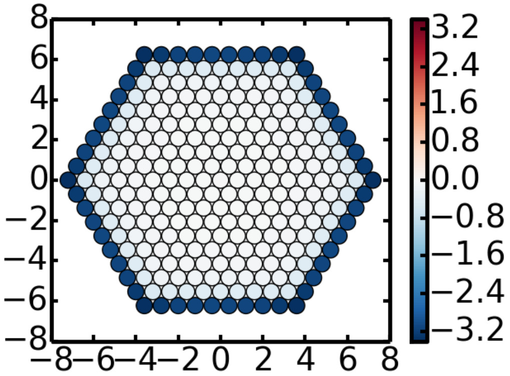
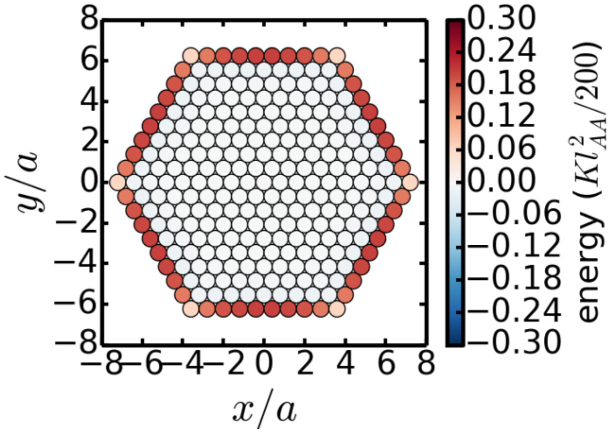
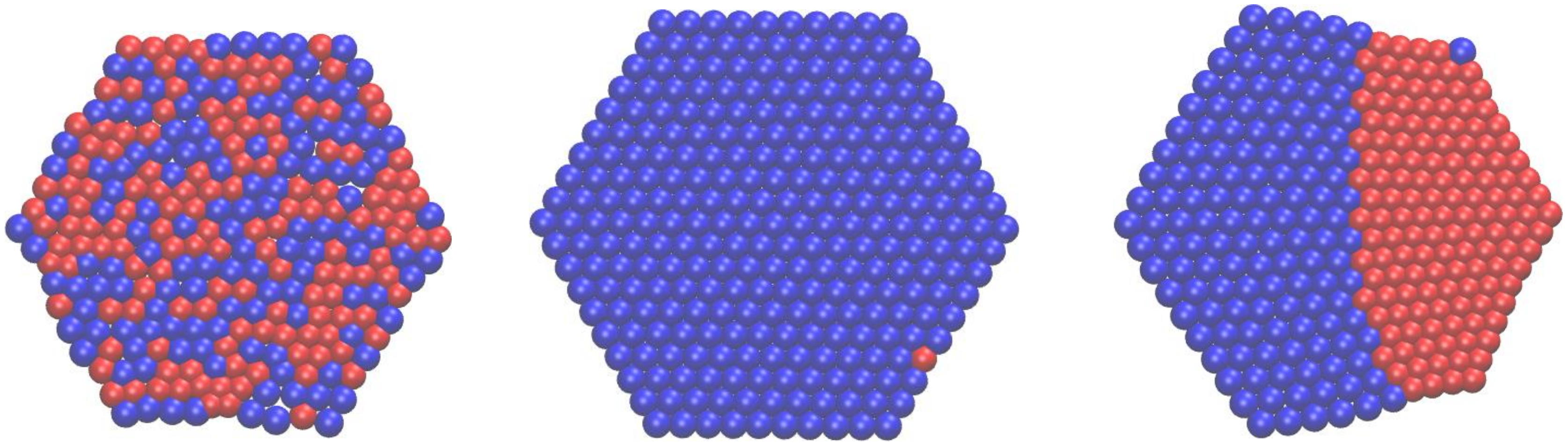


B lattice, **A** impurity

=



Summary of nanocrystal phase behavior

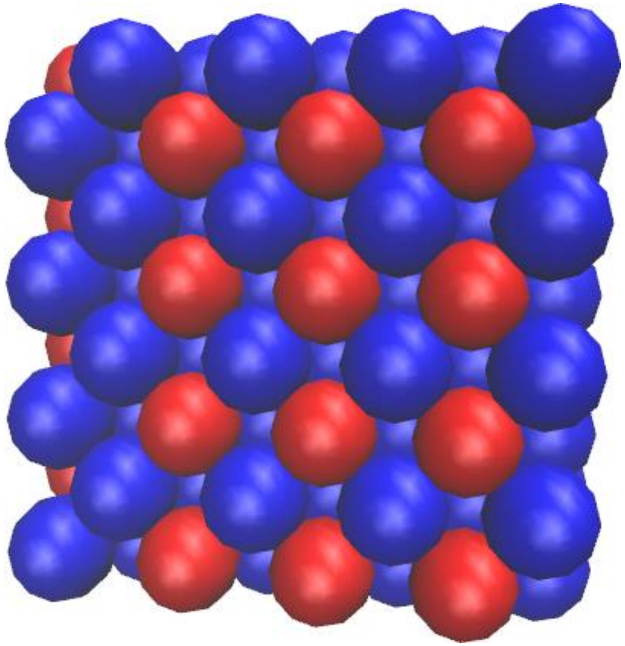


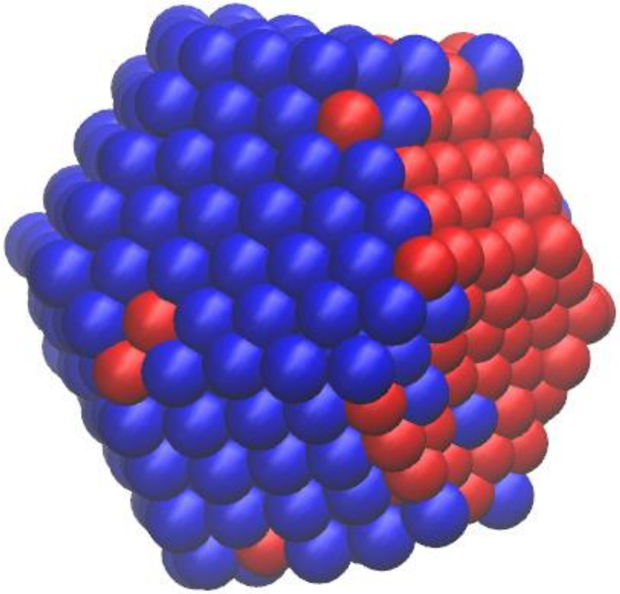
- Unlike bulk, the nanocrystal phase separates.
- This is due to strain relief at the free surface.
- The presence of the surface also makes **B**-rich nanocrystals slightly favored over **A**-rich nanocrystals.

Extensions of the model

Ways to add realism to the model:

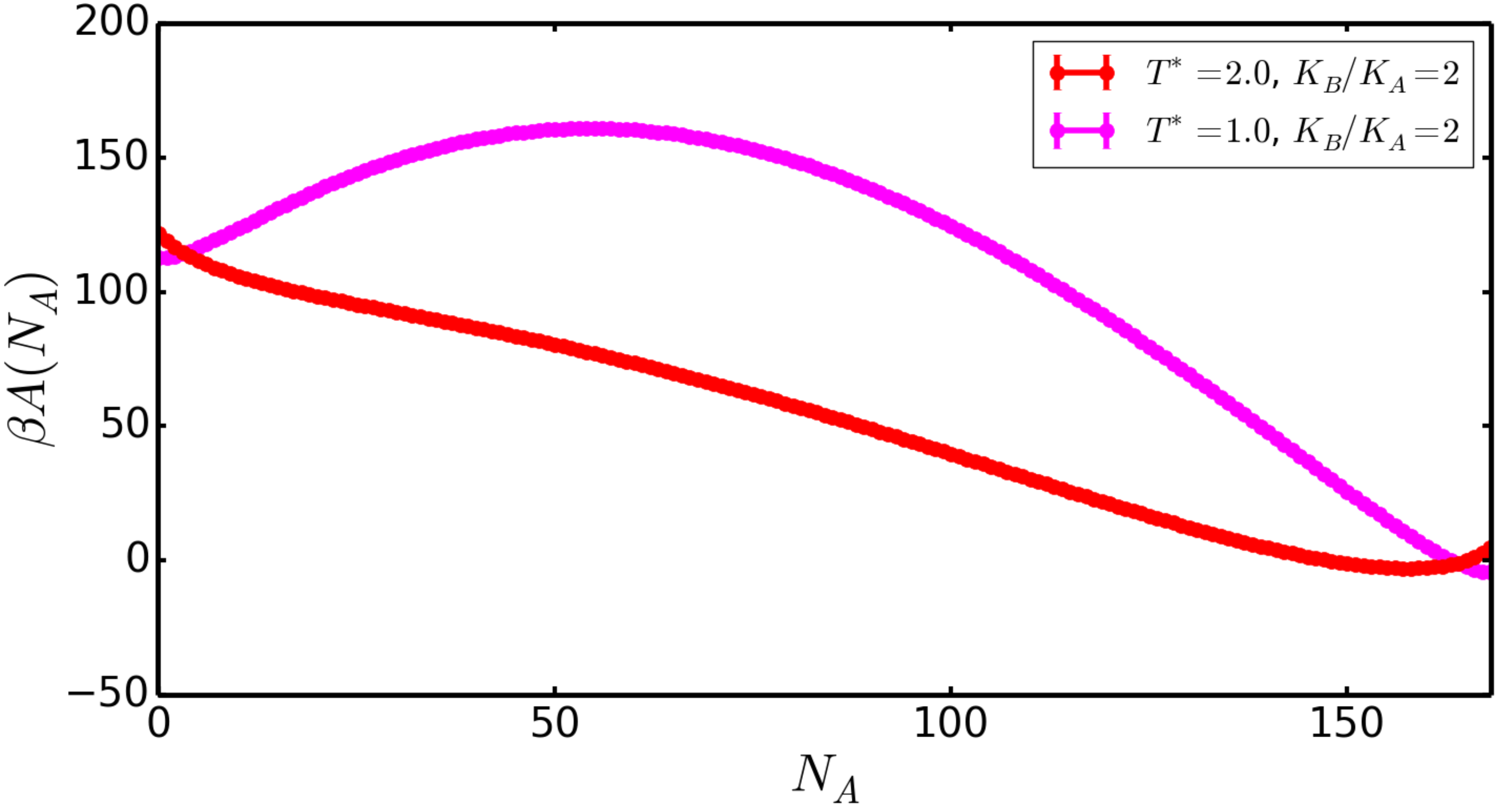
- Extend from 2d to 3d.
- Make spring constants spin-dependent.
- Allow bonds to break and form.





Making spring constants spin-dependent

$$K = K(\sigma_i, \sigma_j) = \sqrt{K(\sigma_i, \sigma_i) K(\sigma_j, \sigma_j)}$$

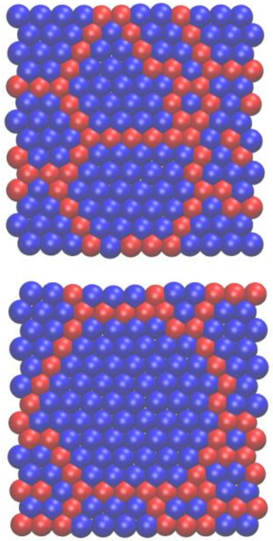


Free energy difference between pure phases is entirely due to the difference in their *vibrational entropy*: $\Delta S \propto N \log \frac{K_B}{K_A}$.

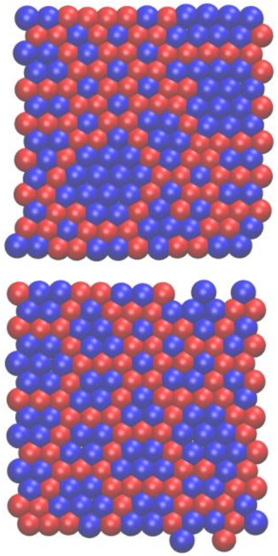
Making spring constants spin-dependent

K_B/K_A = 2

$c = 2/3$



$c = 1/2$



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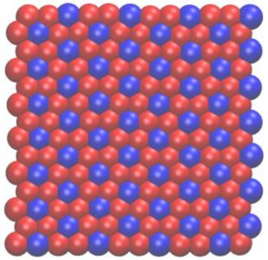

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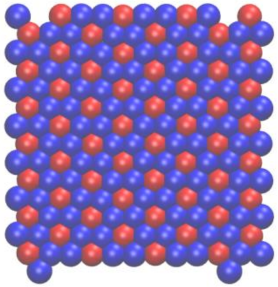

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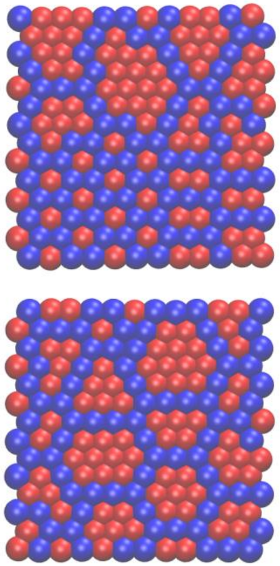

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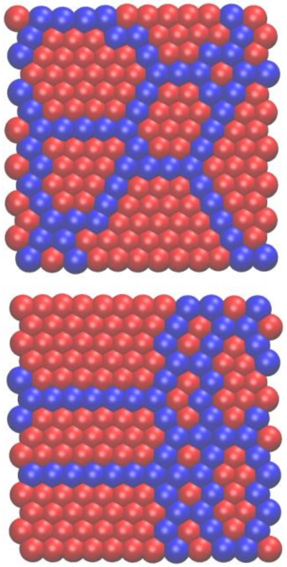
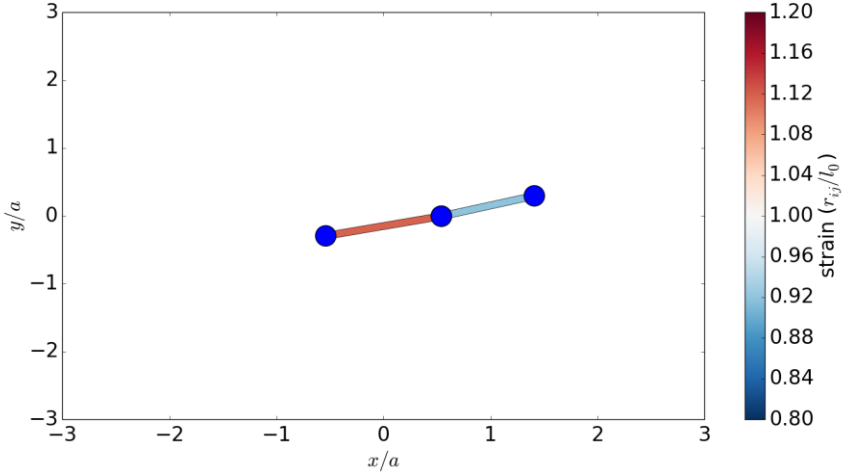
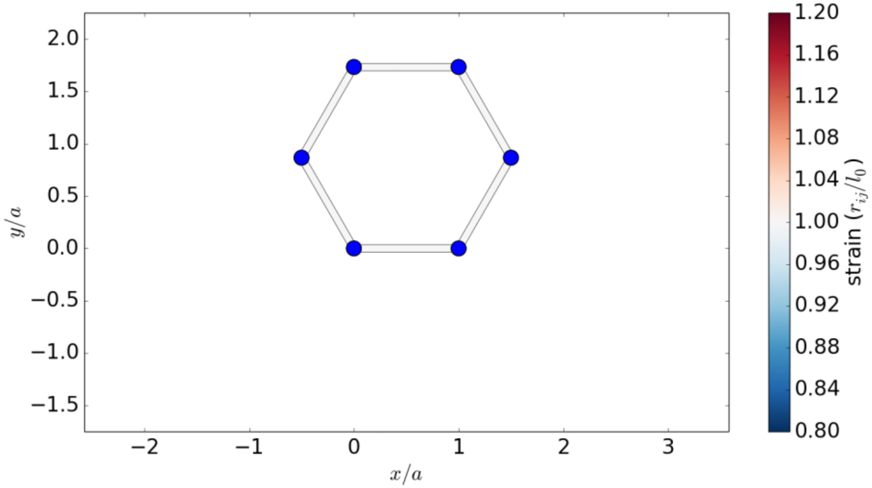


Allowing bonds to break and form





Introduce a coordination energy that biases the atoms to have n^* bonds:

$$E_b(n) = -\epsilon + \delta|n - n^*|$$

Attempt bond-making and bond-breaking moves in a way that satisfies detailed balance:

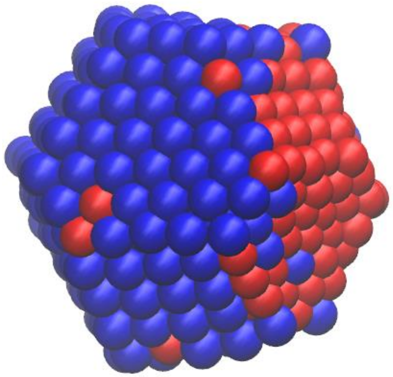
$$P_{\text{break}}(C \to C') = \min\left[1, \frac{n_b(C)}{n_u(C')} e^{-\beta\Delta E}\right]$$

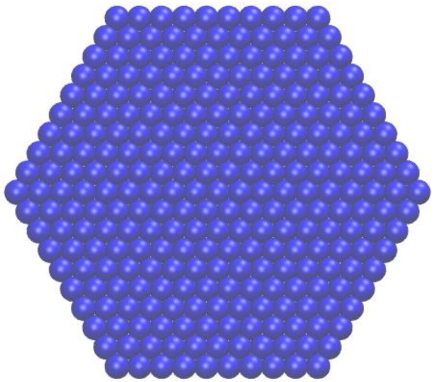
$$P_{\text{make}}(C \to C') = \min\left[1, \frac{n_u(C)}{n_b(C')} e^{-\beta\Delta E}\right]$$

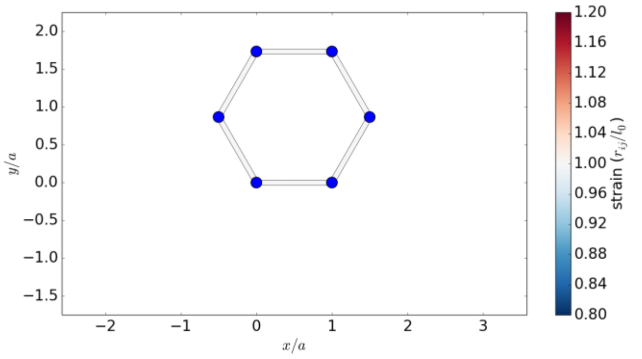
Conclusion and future directions

We have shown that elastic interactions due to lattice mismatch give rise to interesting equilibrium phase behavior, and that this behavior is quite sensitive to boundary conditions. There is still much work to be done:

- Complete study of 3d behavior.
- Study spin-dependent spring constant behavior.
- Allow bonds to break and form.
- Explore dynamics of ion exchange.







Acknowledgements

Phillip Geissler
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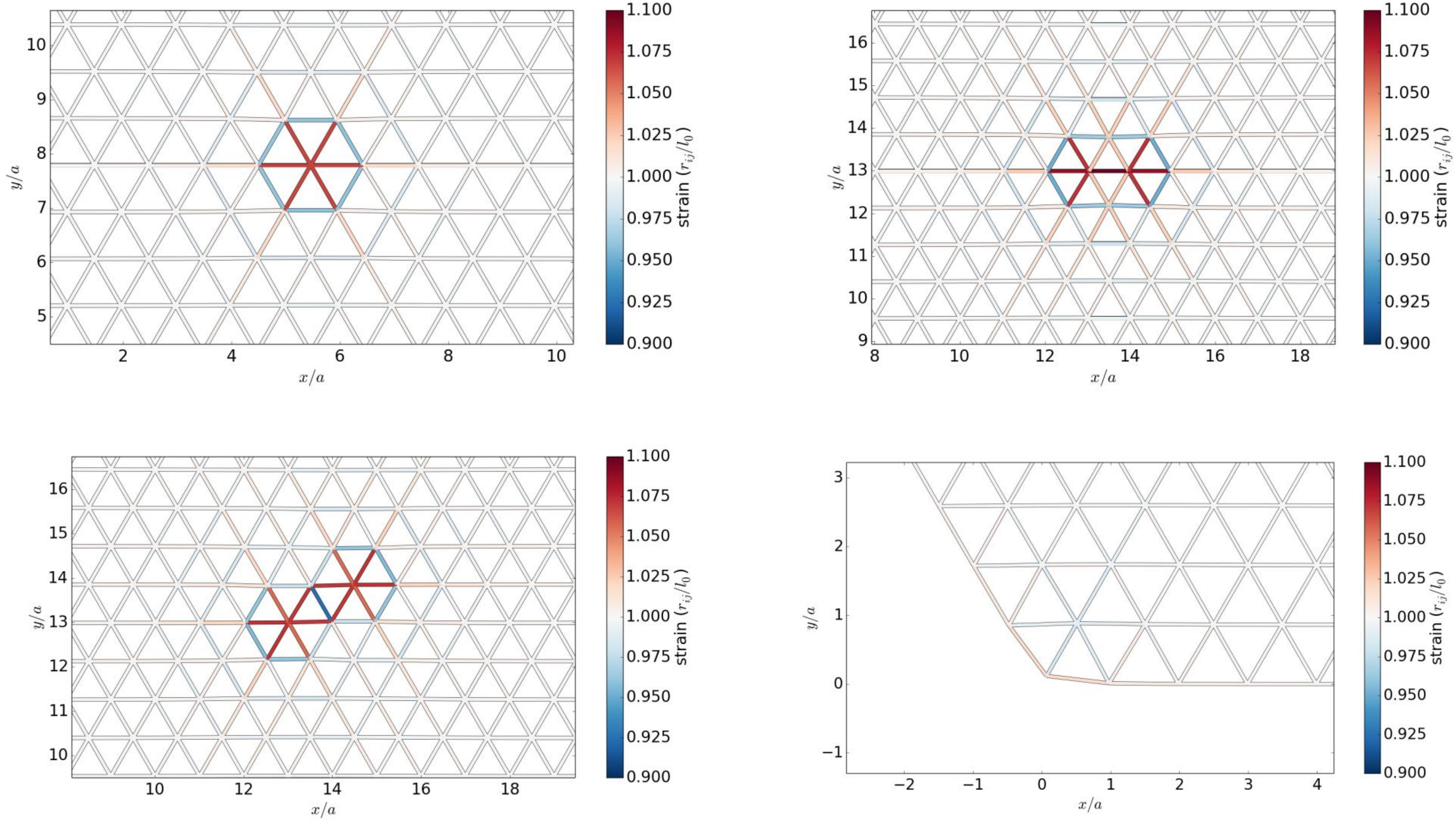
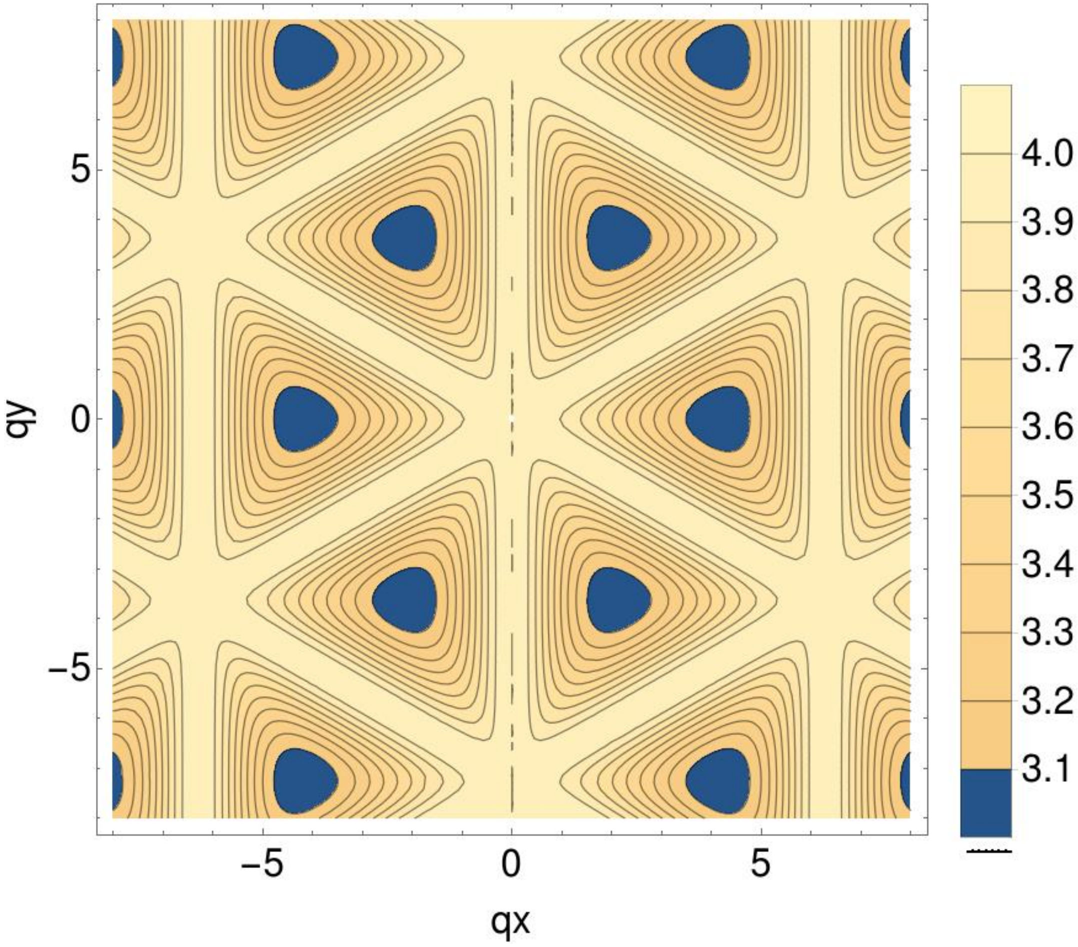
David Limmer

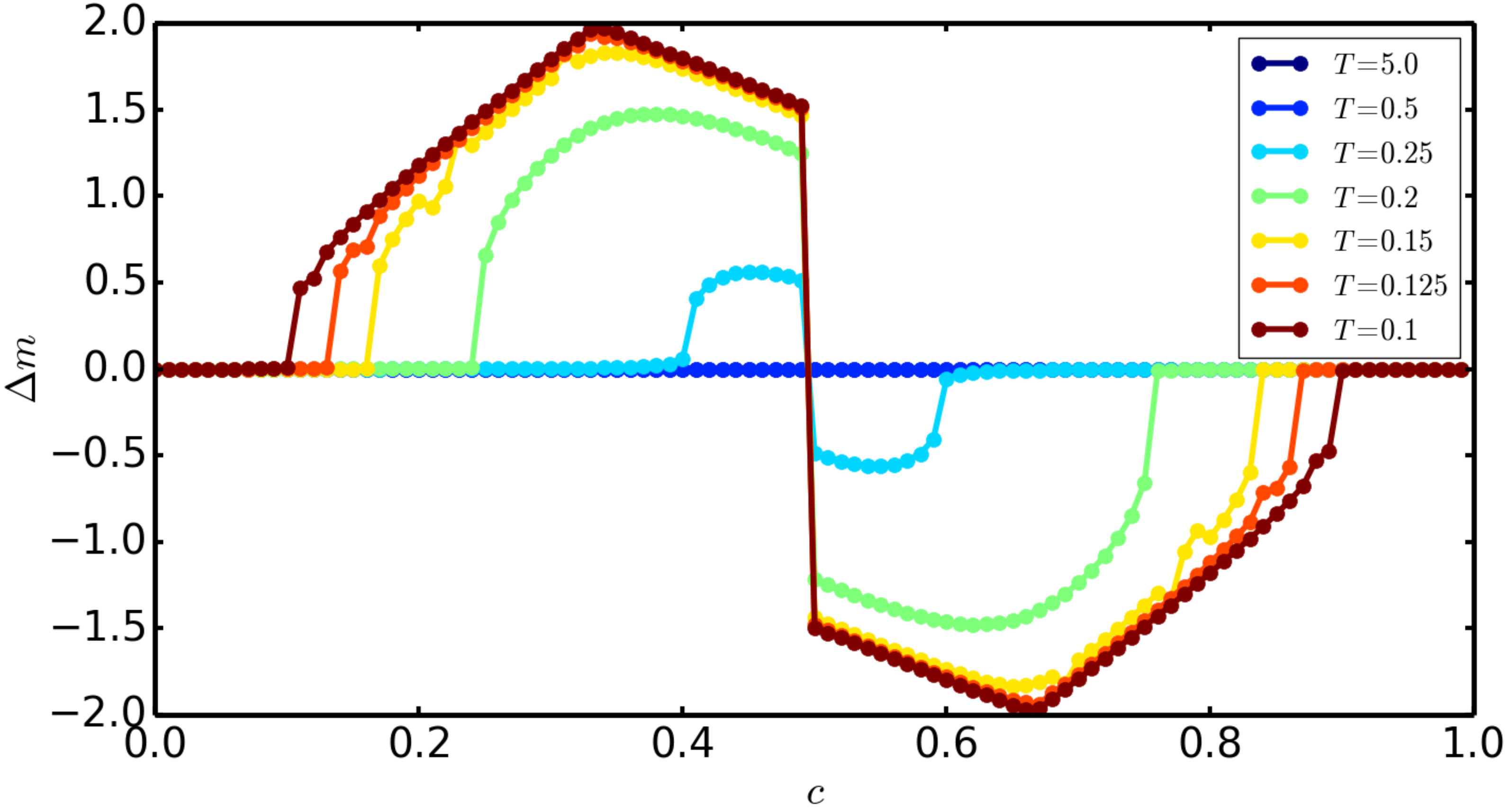
The interactions we see can be rationalized by considering the strain of the different impurity configurations.



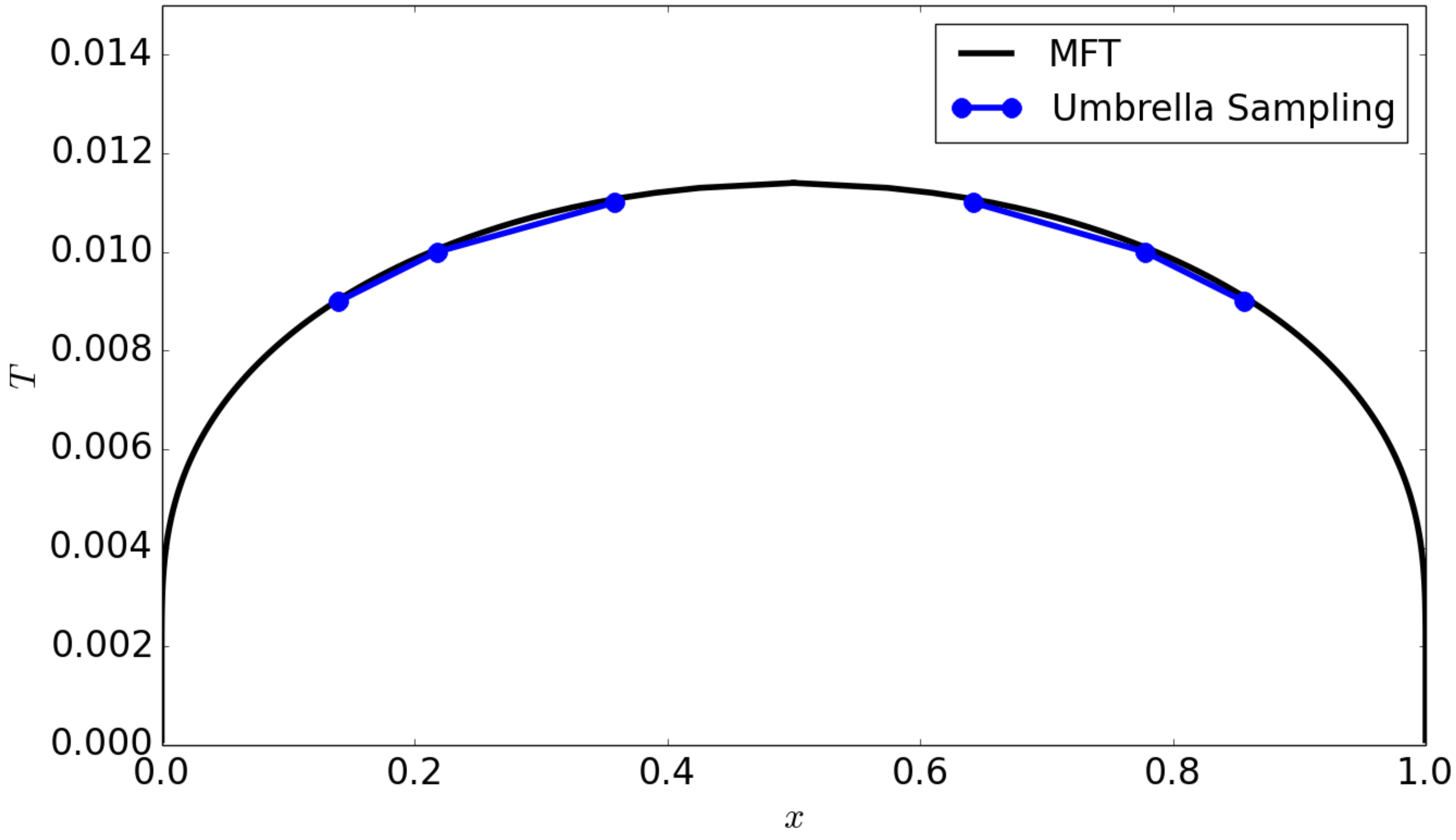
Fourier space potential

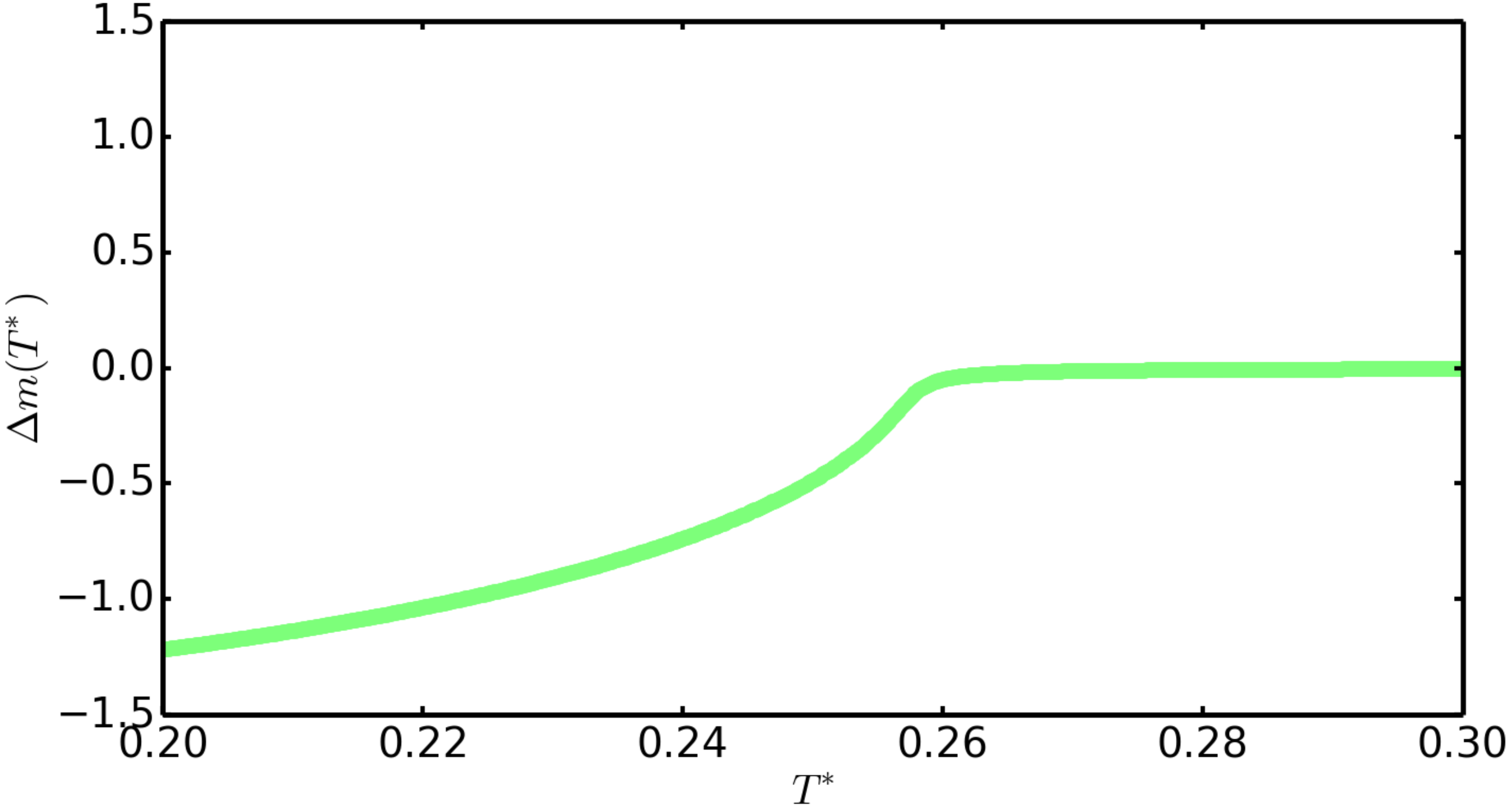


$$\hat{V}_{\mathrm{eff}}(\mathbf{q}) = \frac{K\Delta^2}{2} \frac{2\left(\cos(q_x\bar{l}) + 2\cos(q_x\bar{l}/2)\cos(\sqrt{3}q_y\bar{l}/2)\right)^2}{(\cos(q_x\bar{l}) - 2)\left(4\cos(q_x\bar{l}/2)\cos(\sqrt{3}q_y\bar{l}/2) - 3\right) + \cos(\sqrt{3}q_y\bar{l})}$$

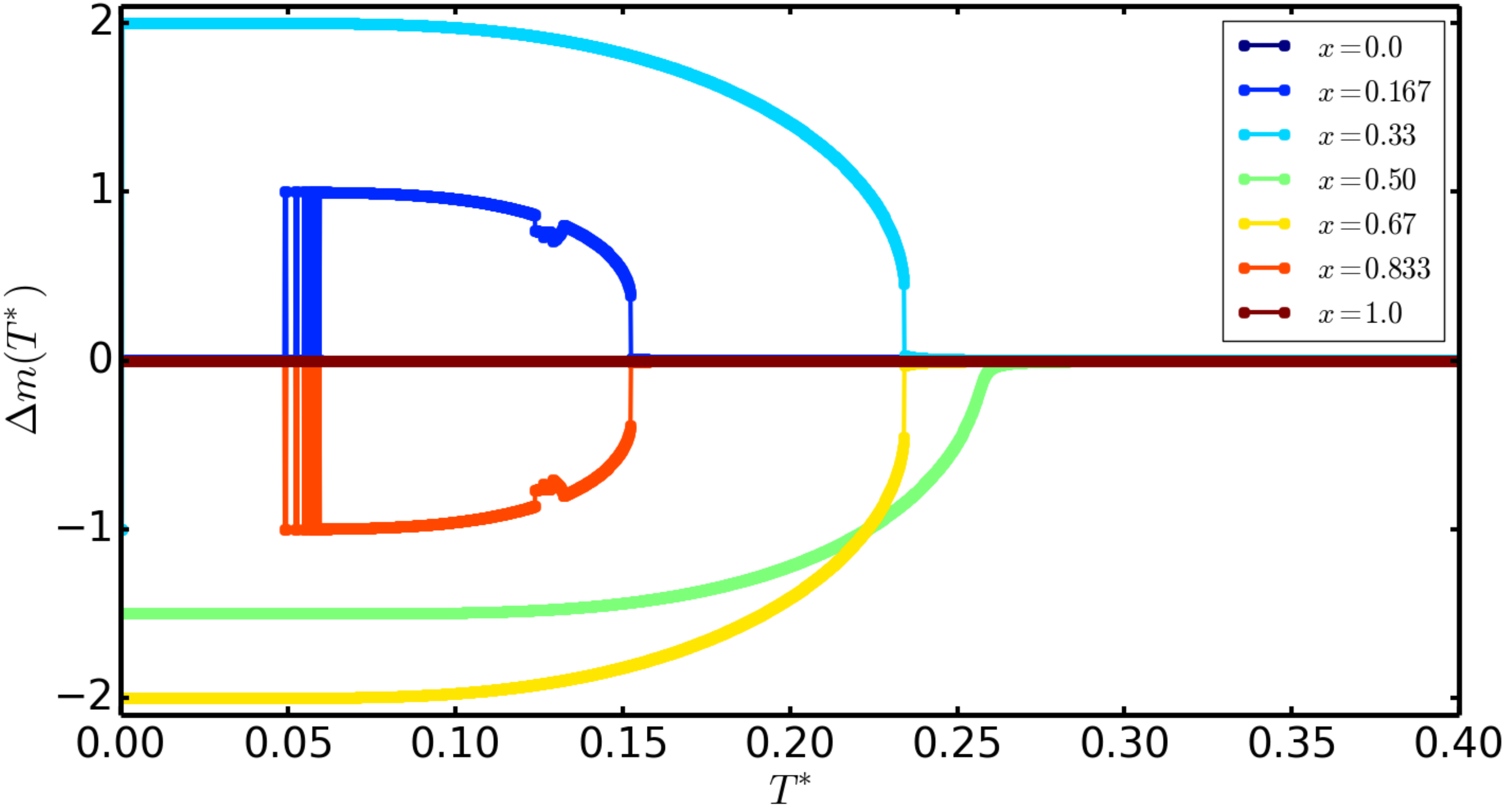


2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
Δm
0.0
0.2
0.4
0.6
0.8
1.0
c
$T\!=\!5.0$
$T\!=\!0.5$
$T\!=\!0.25$
$T\!=\!0.2$
$T\!=\!0.15$
$T\!=\!0.125$
$T\!=\!0.1$

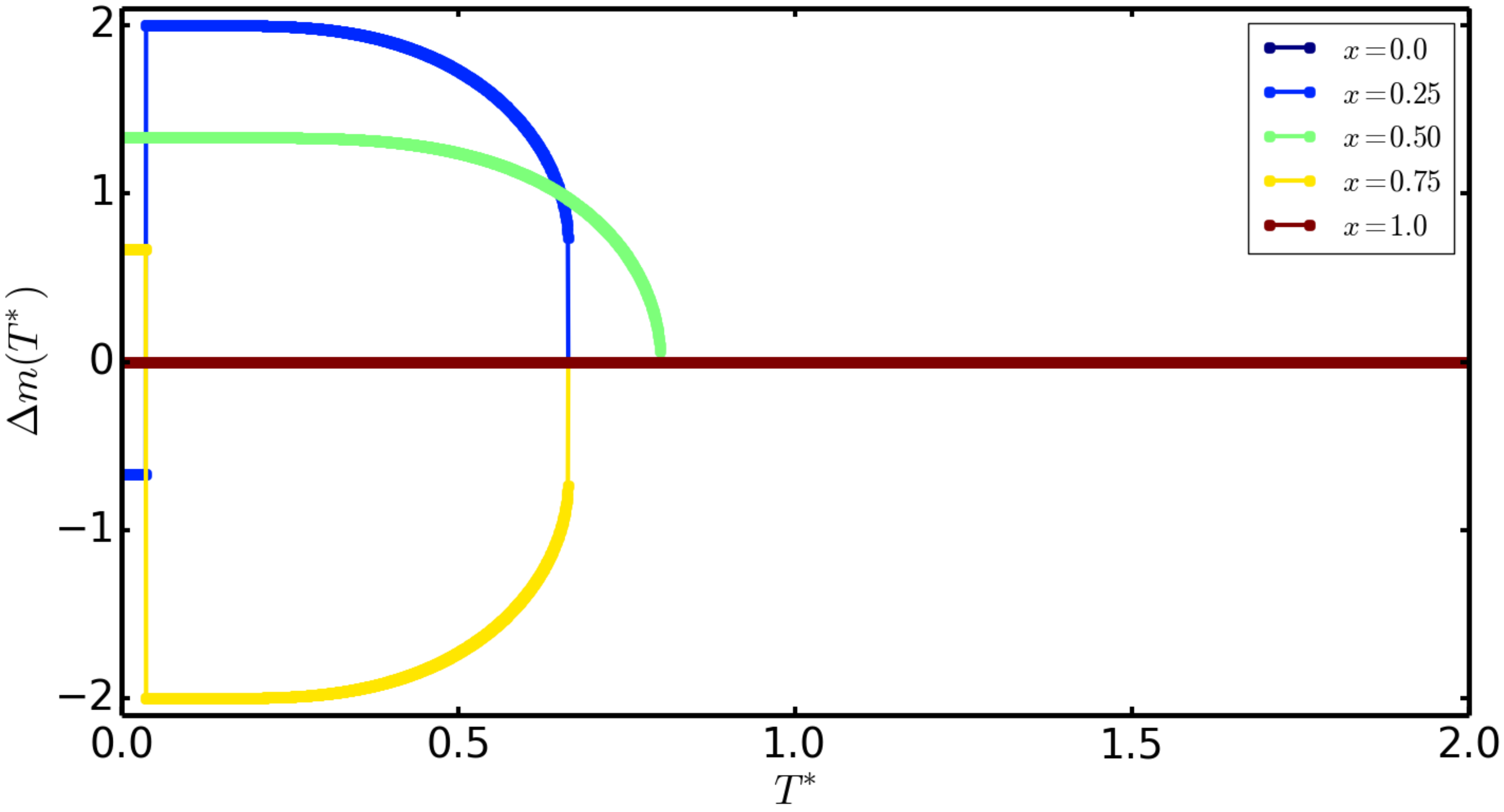

MFT
Umbrella Sampling
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
T
0.0
0.2
0.4
0.6
0.8
1.0
x



1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
$\Delta m(T^*)$
0.20
0.22
0.24
0.26
0.28
0.30
T^*



$x = 0.0$
$x = 0.167$
$x = 0.33$
$x = 0.50$
$x = 0.67$
$x = 0.833$
$x = 1.0$
$\Delta m(T^*)$
2
1
0
−1
−2
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
T^*



2
1
0
−1
−2
$\Delta m(T^*)$
0.0
0.5
1.0
1.5
2.0
T^*
$x = 0.0$
$x = 0.25$
$x = 0.50$
$x = 0.75$
$x = 1.0$