Cluster Expansions: Treating the effects of strain

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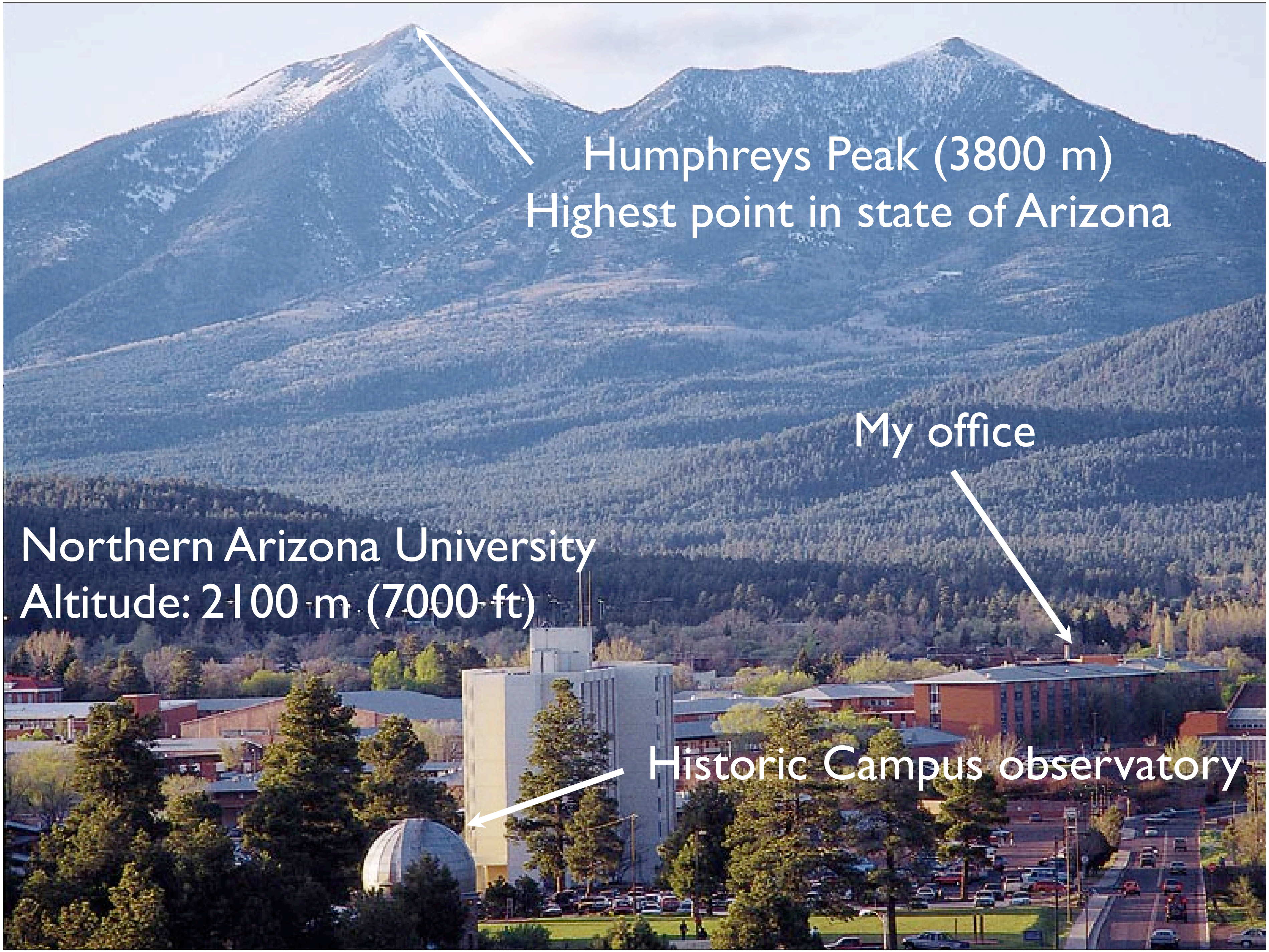
Flagstaff Arizona
It’s not hot!
Average July high/low: 28° C (82° F) and 10° C (50° F)
Average July relative humidity: 37% (afternoon)
Average yearly snowfall: 2.7 m (108 in)
Flagstaff is one of the 10 sunniest locations in the US
but...it is also one of the top 10 snowiest cities


Humphreys Peak (3800 m)
Highest point in state of Arizona
My office
Northern Arizona University
Altitude: 2100 m (7000 ft)
Historic Campus observatory

PLEASE!

Interrupt me
Ask questions
Make comments
Respond to questions

Generalized Ising model

$$Z = J_0 + J_1 \sum_i \hat{S}_i + \sum_{i<j} J_{ij} \hat{S}_i \hat{S}_j + \sum J_{ijk} \hat{S}_i \hat{S}_j \hat{S}_k + \ldots$$

where:

Z is any configurational-dependent quantity

$\{J\}$ are "interaction parameters" (to be fitted)

$\{S\}$ are the site variables ($S = \pm 1$)

Formally exact but useless unless sums can be truncated

An Illustration: Cluster expansion (Ising)

$$Z = J_0 + J_1 \sum_i \hat{S}_i + \sum_{i<j} J_{ij} \hat{S}_i \hat{S}_j + \sum J_{ijk} \hat{S}_i \hat{S}_j \hat{S}_k + \ldots$$

Approach:

Determine *Z* for a "few" structures via DFT

Use fitting to find values for { *J* }

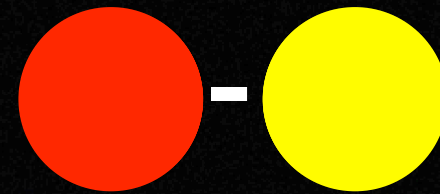
Predict *Z* for new structures, check against DFT

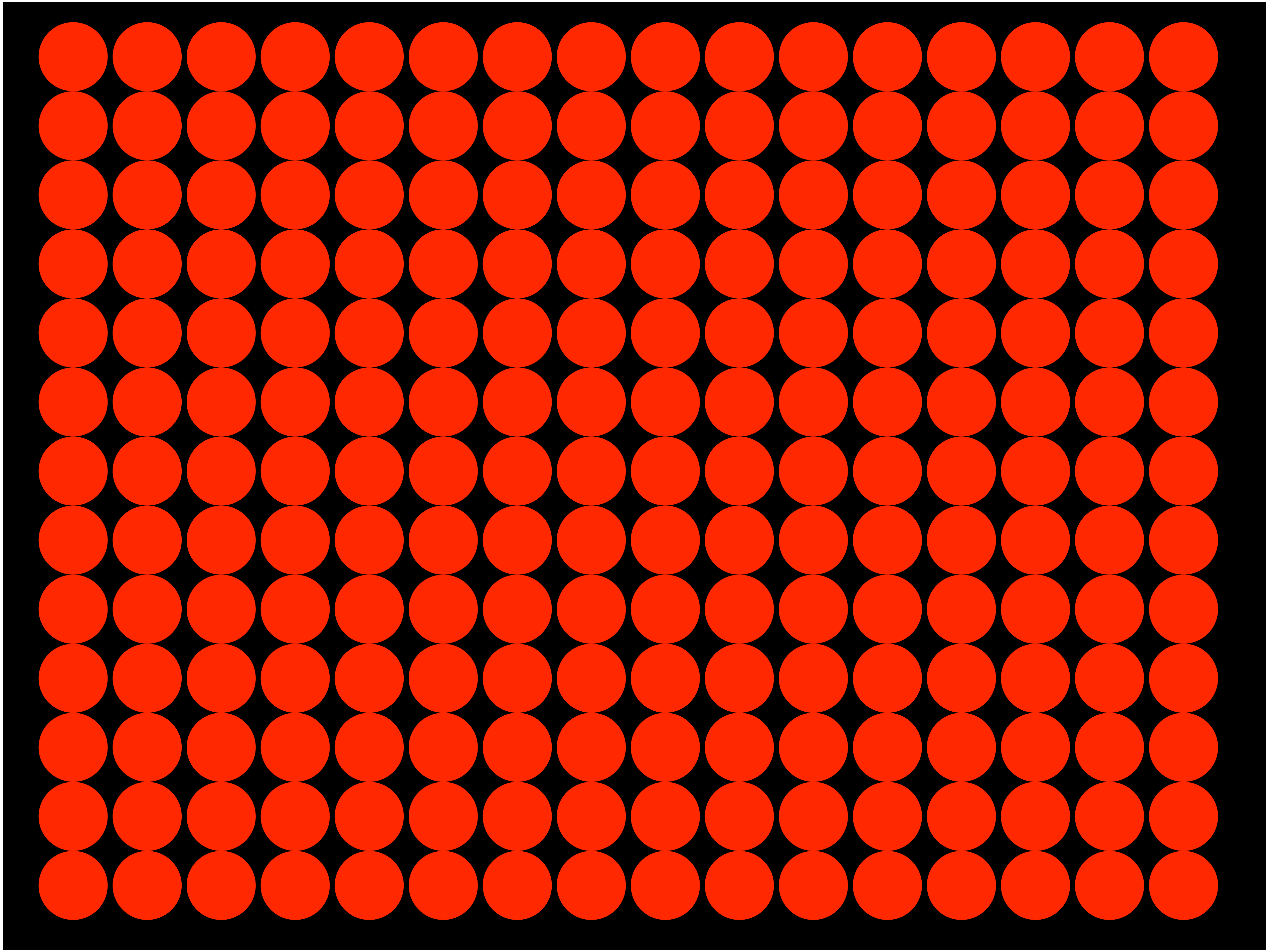
Add new structures to your computed set of *Z*'s

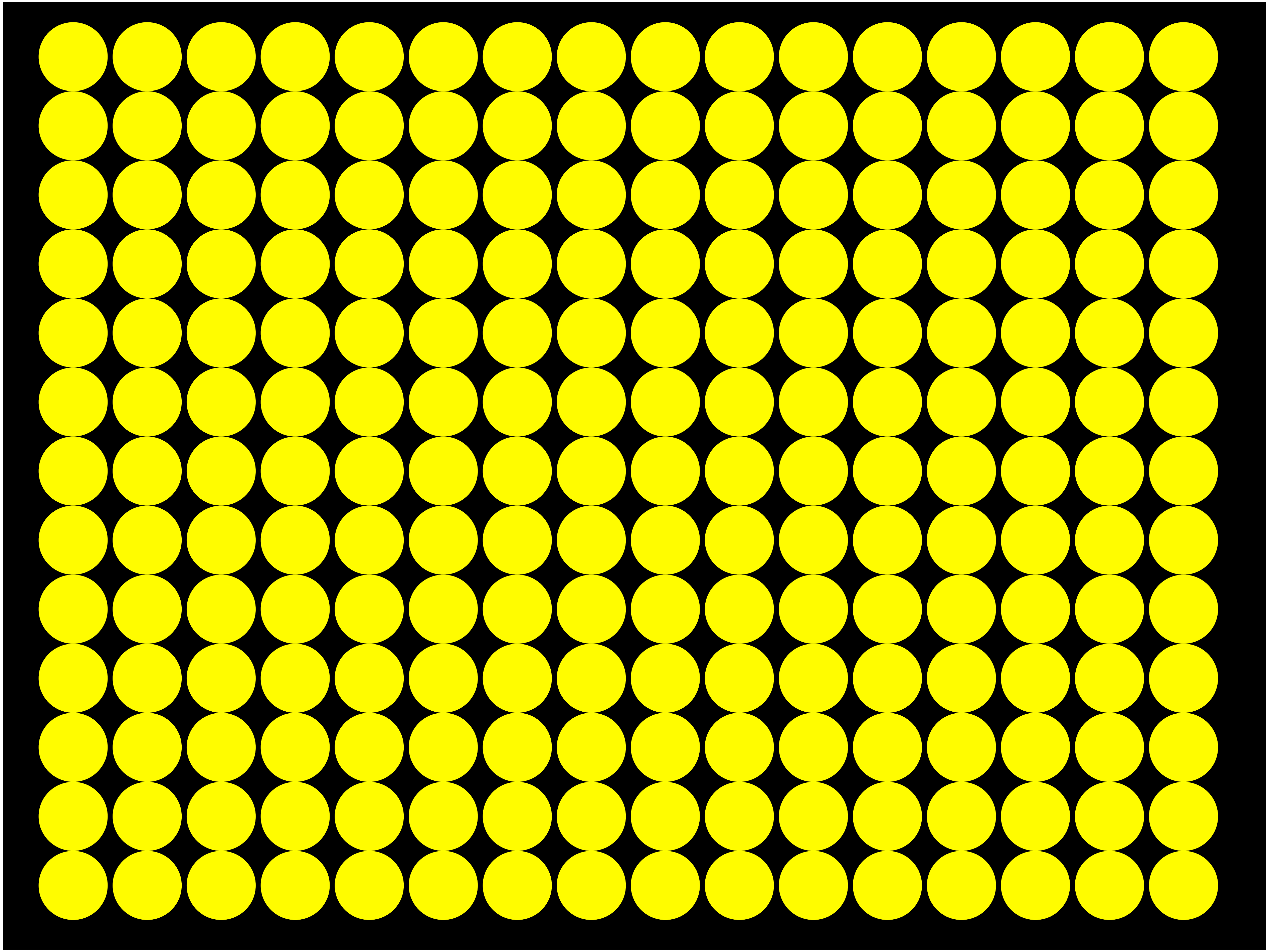
Iterate until we have a *universal* set of *J*'s

→ Result: a robust, *extremely fast*, model Hamiltonian

(millions of atoms, millions of configurations)

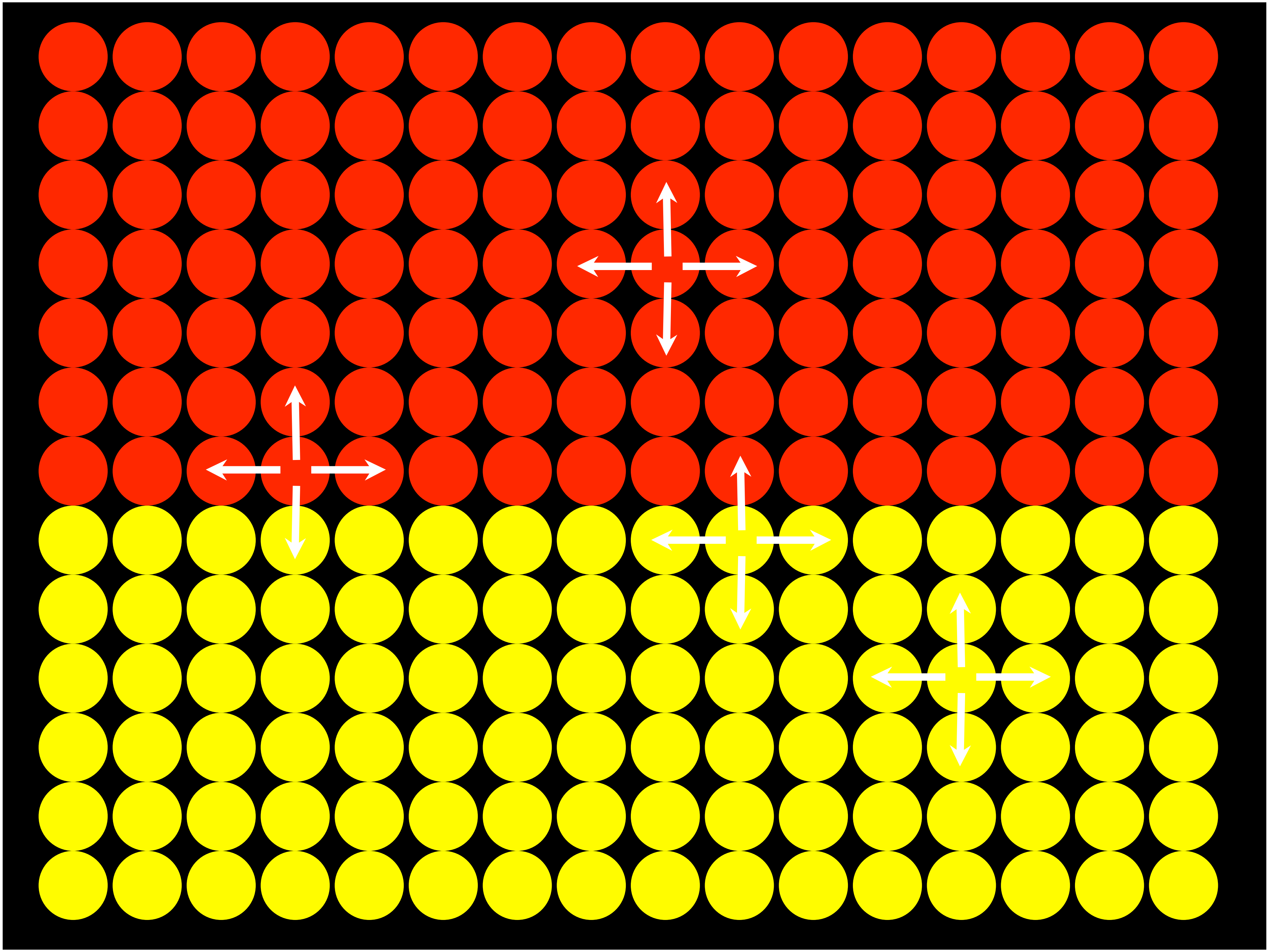
Cluster Expansion for 

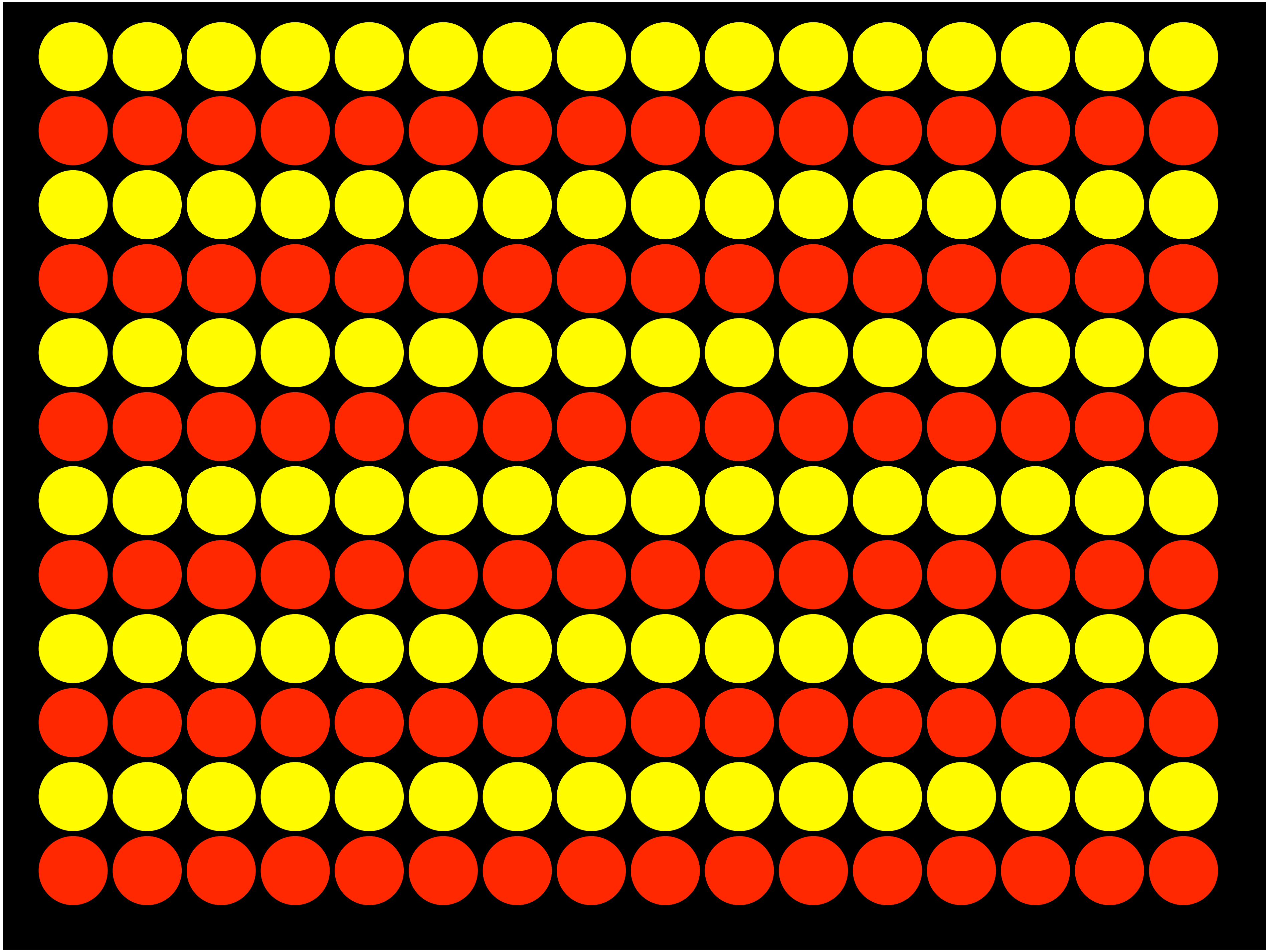


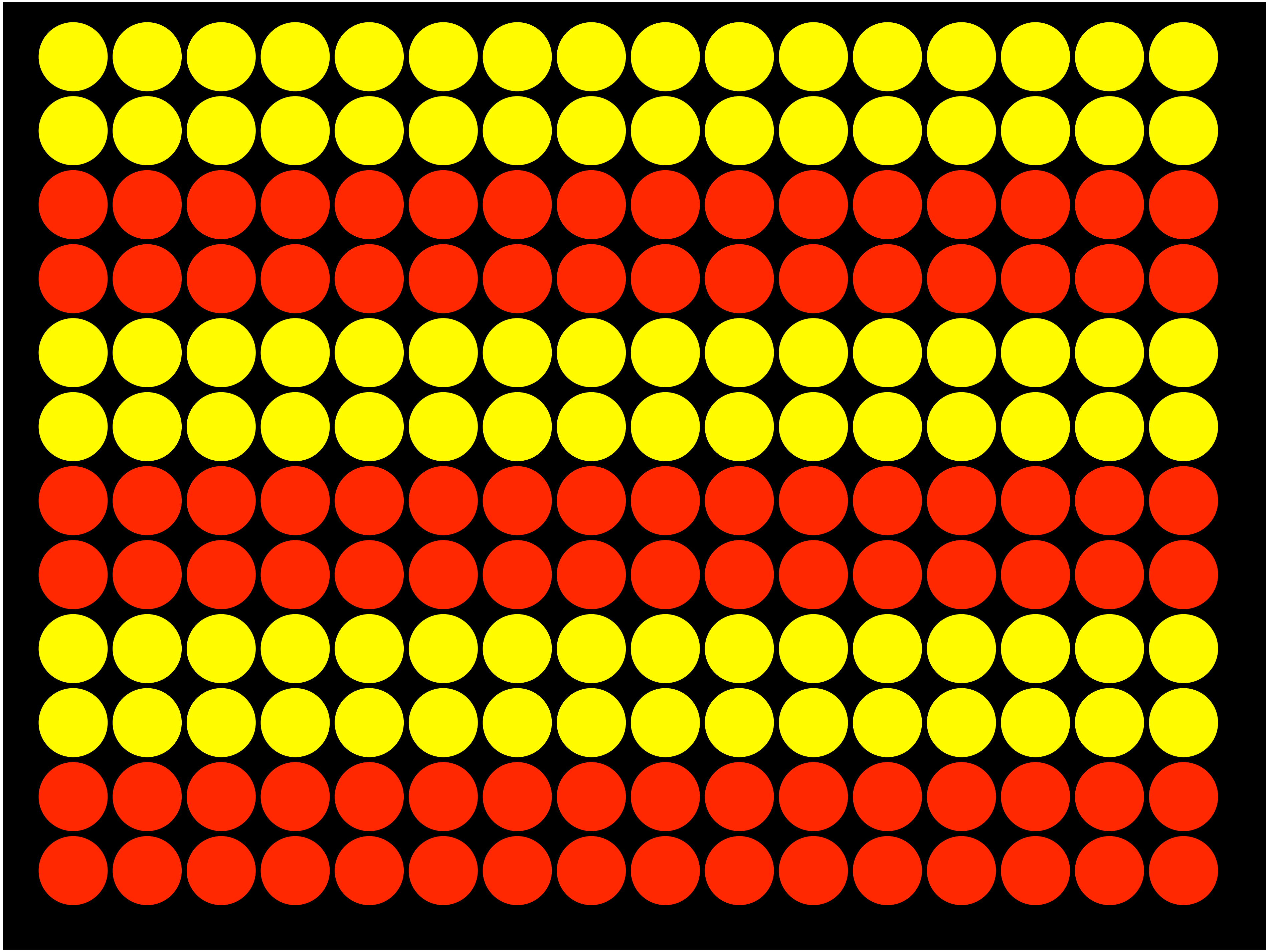


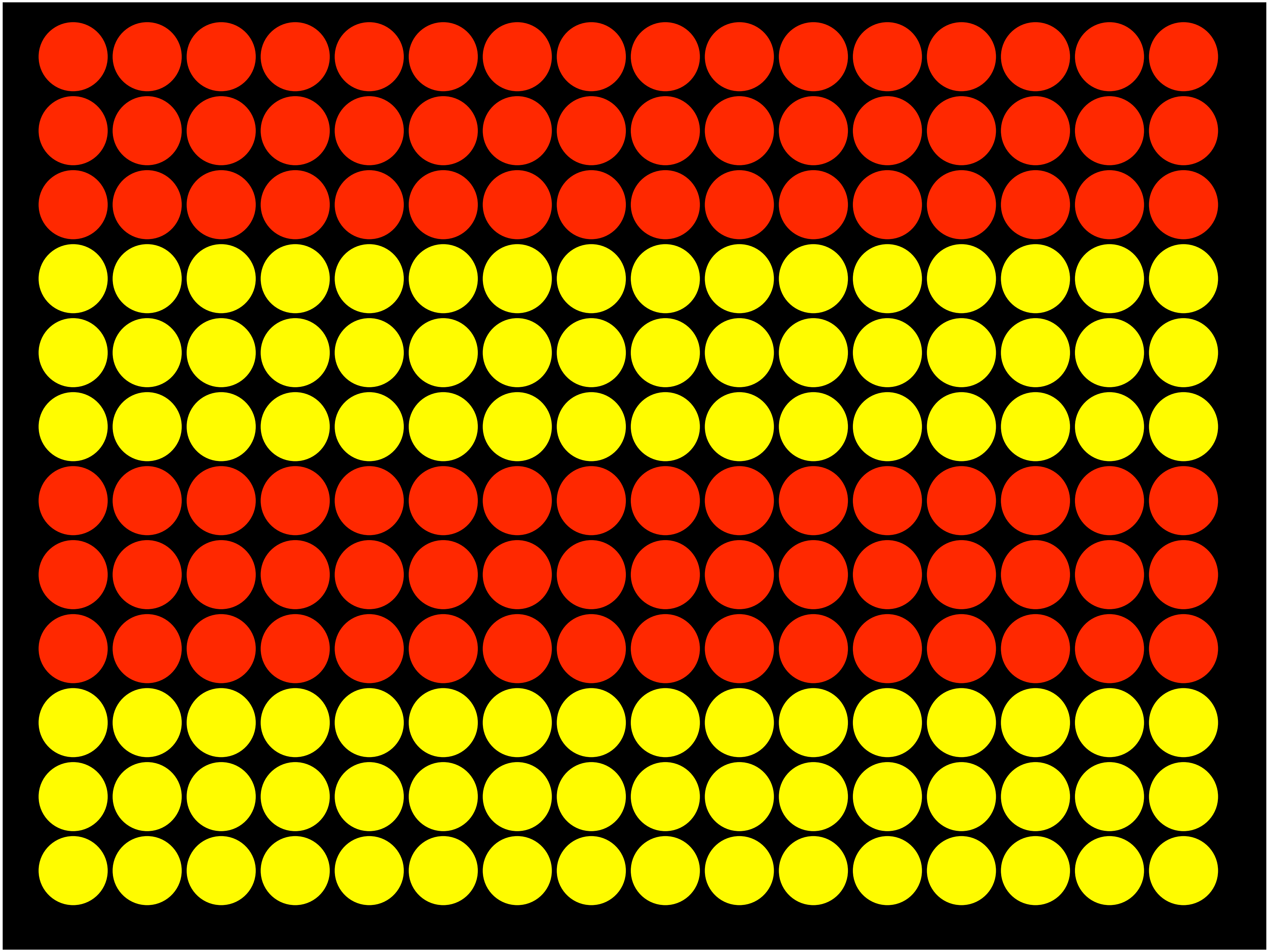
$$\Delta H = E_{AB}^{\text{alloy}} - \left[(1-x)E_A + xE_B\right]$$

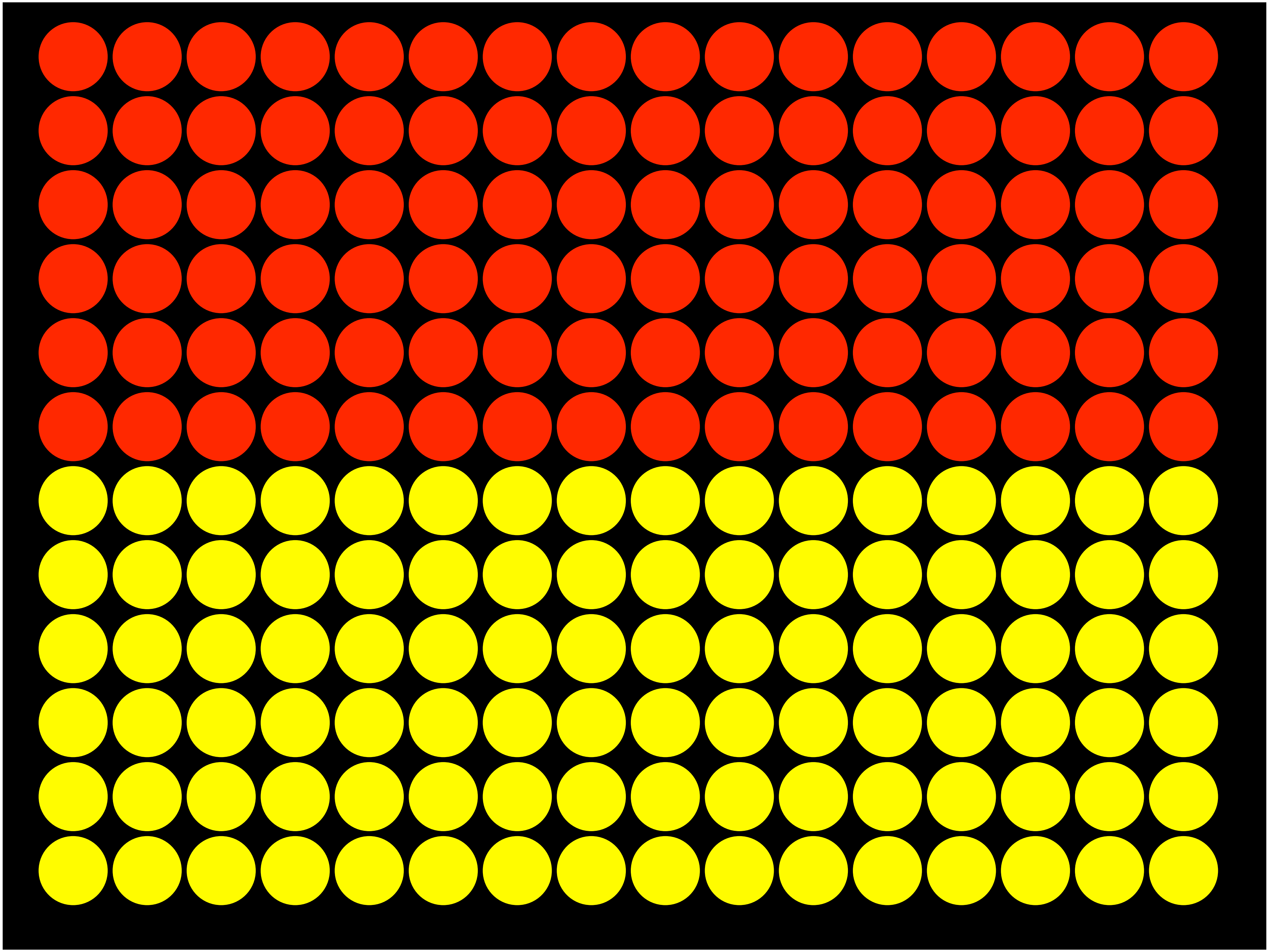
$$\Delta H = \frac{E_{AB}^{\mathrm{alloy}} - \left[nE_A + mE_B \right]}{n + m}$$









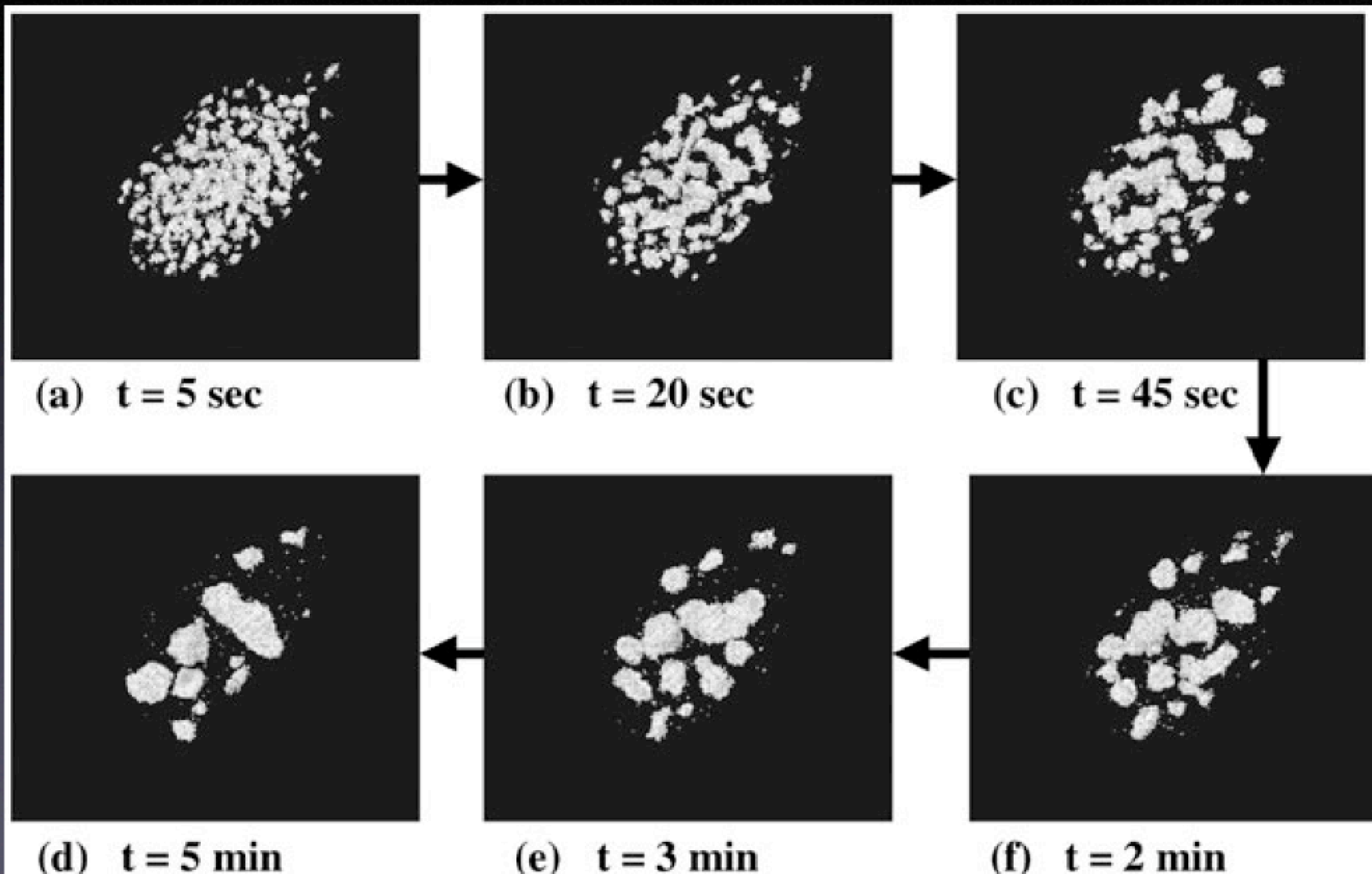


Coherent semi-infinite slabs

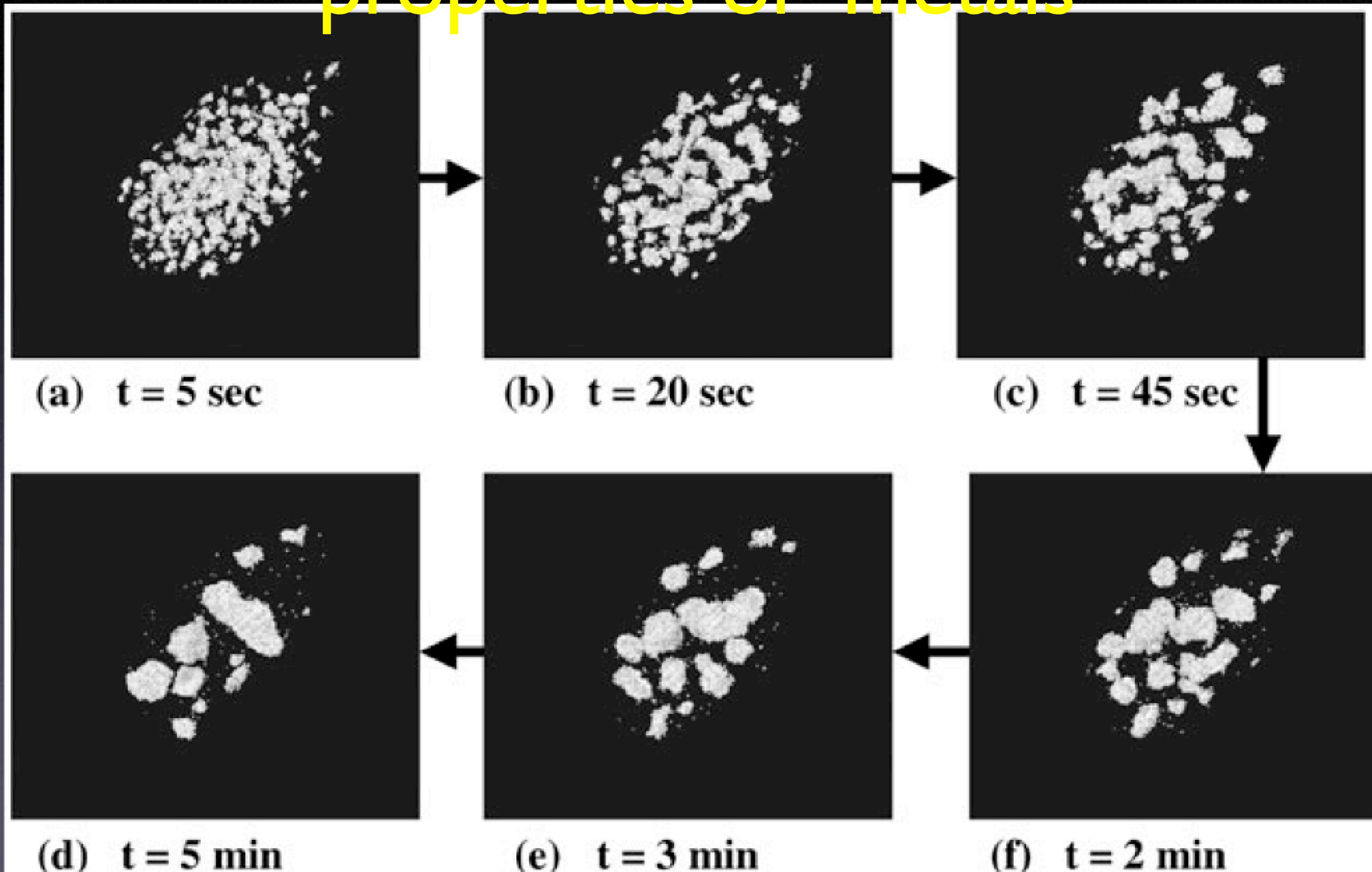
Cluster expansion predicts vanishing formation enthalpy

Who cares?

Precipitates!



Have a profound effect on the properties of metals



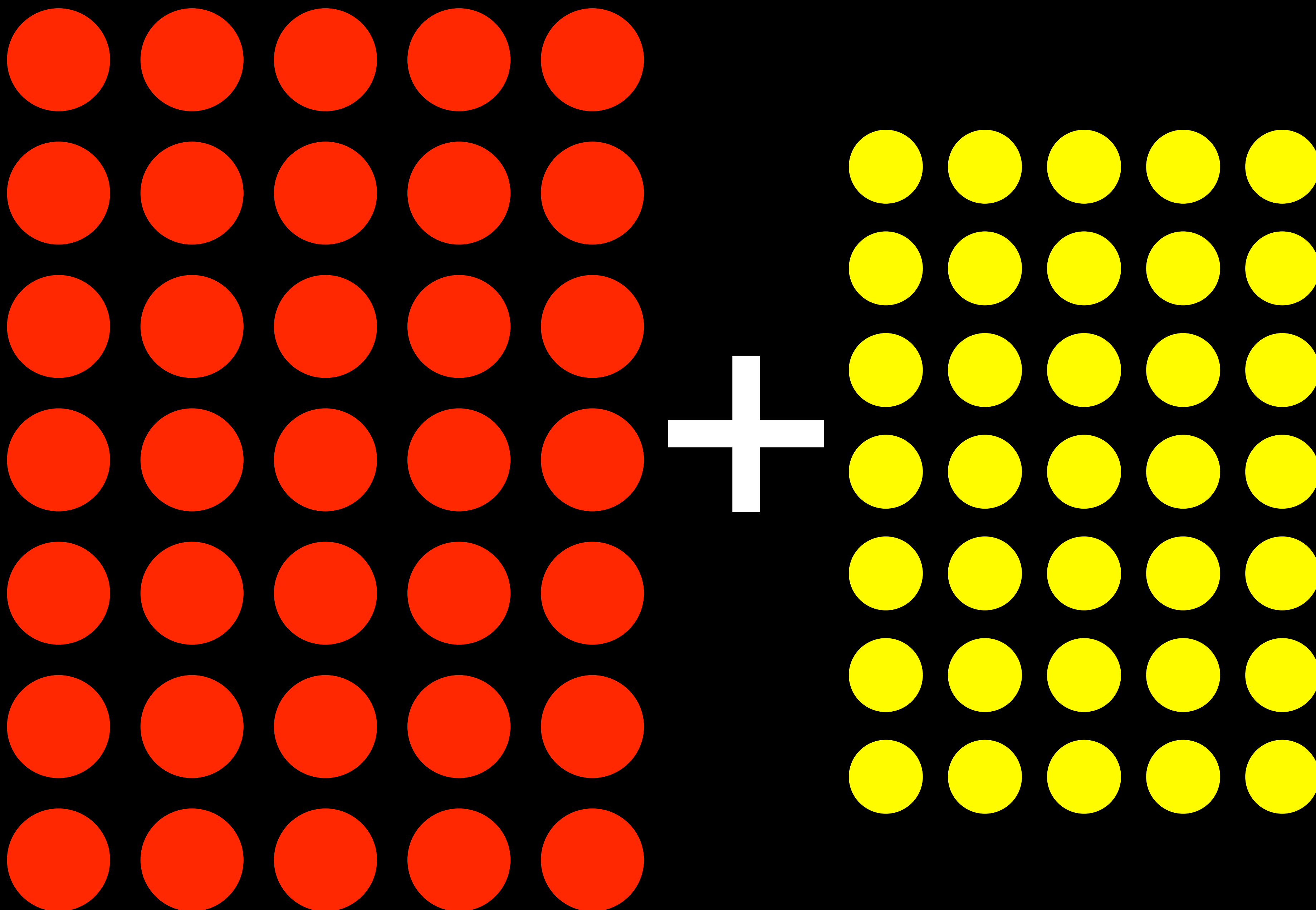
Huh?

What does that have to do with coherent semi-infinite slabs?

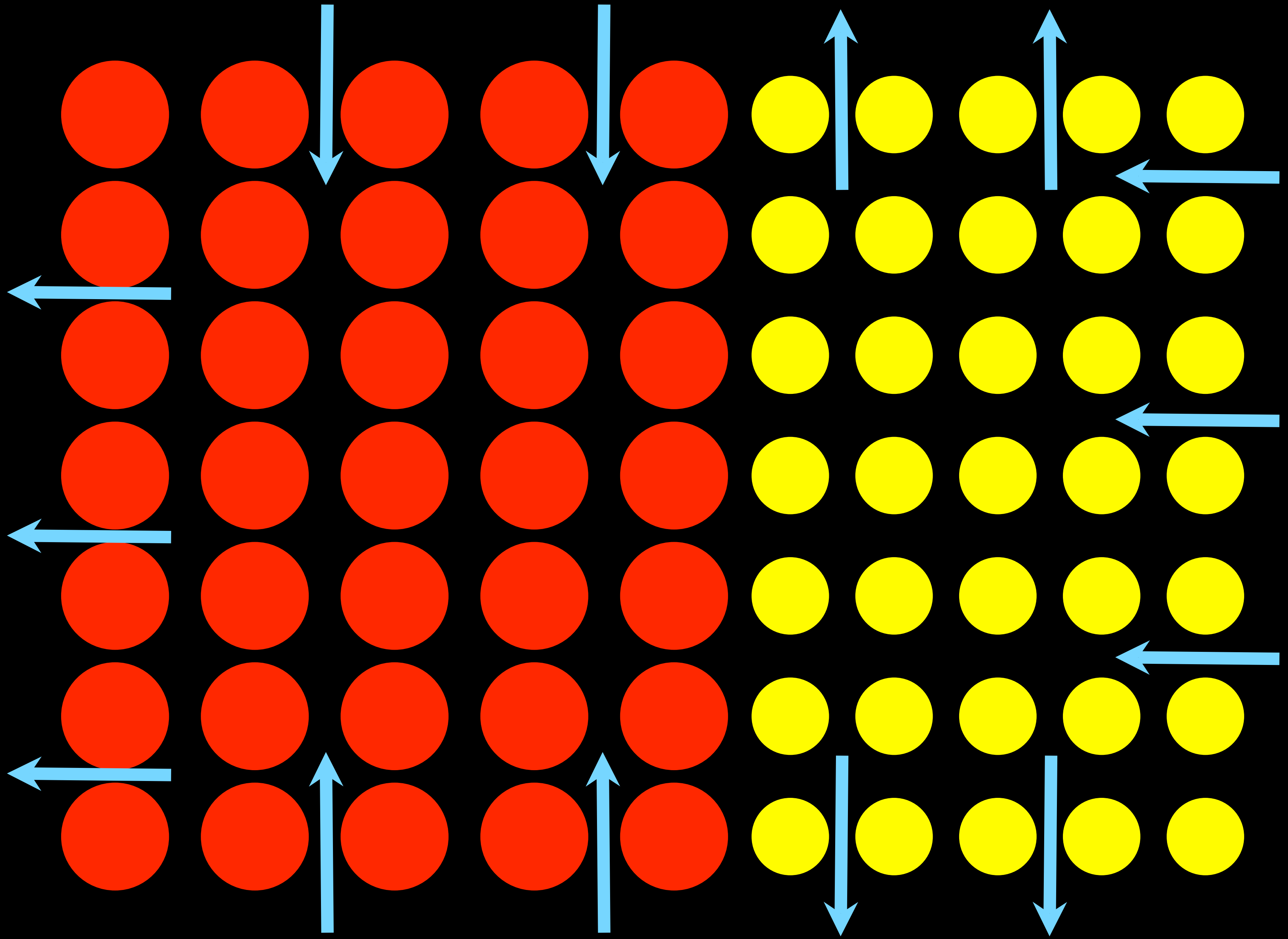
Coherent semi-infinite slabs

Cluster expansion predicts vanishing formation enthalpy

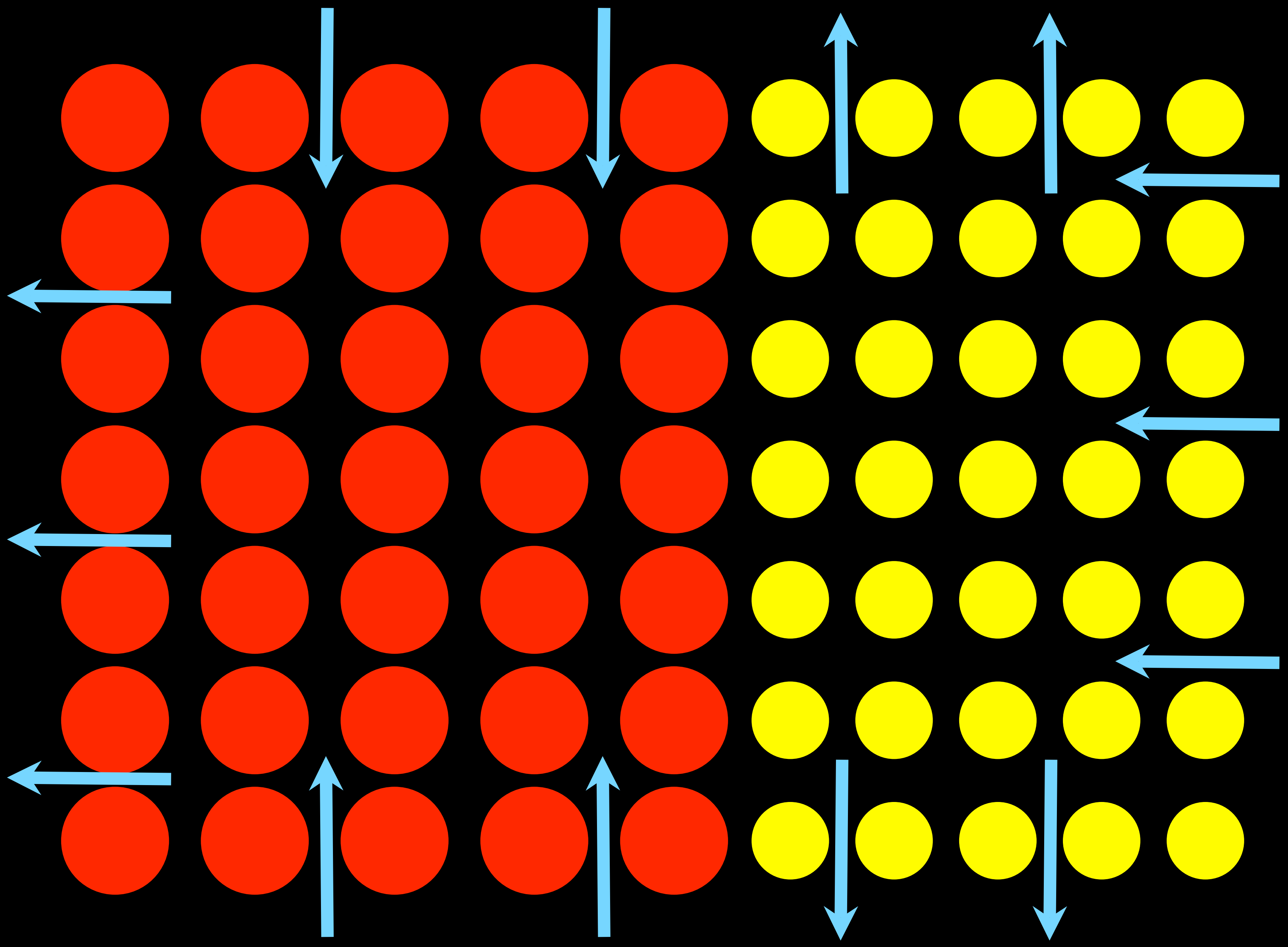
Is that correct?



Alloy of two mismatched components



What happens at an (coherent) interface?



And the energy?

The resulting strain energy is “long-range.”

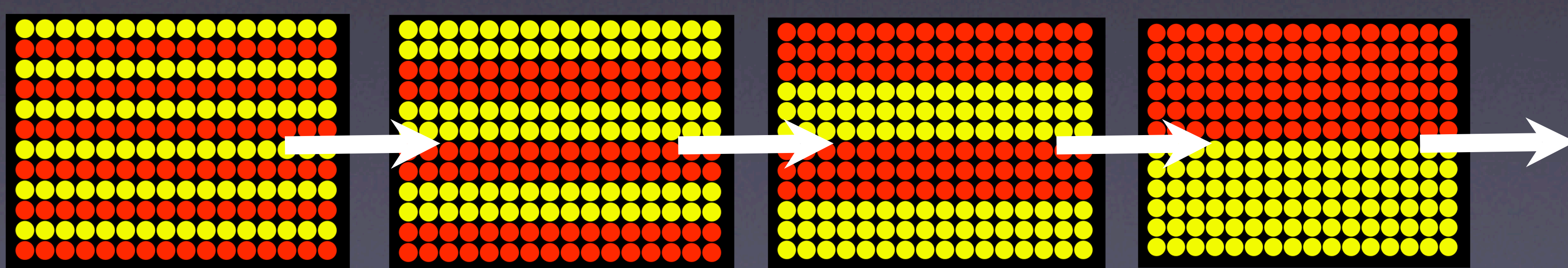
What do we mean by that?

How is it that the Ising model (cluster expansion) can’t handle this?

How can this be fixed?

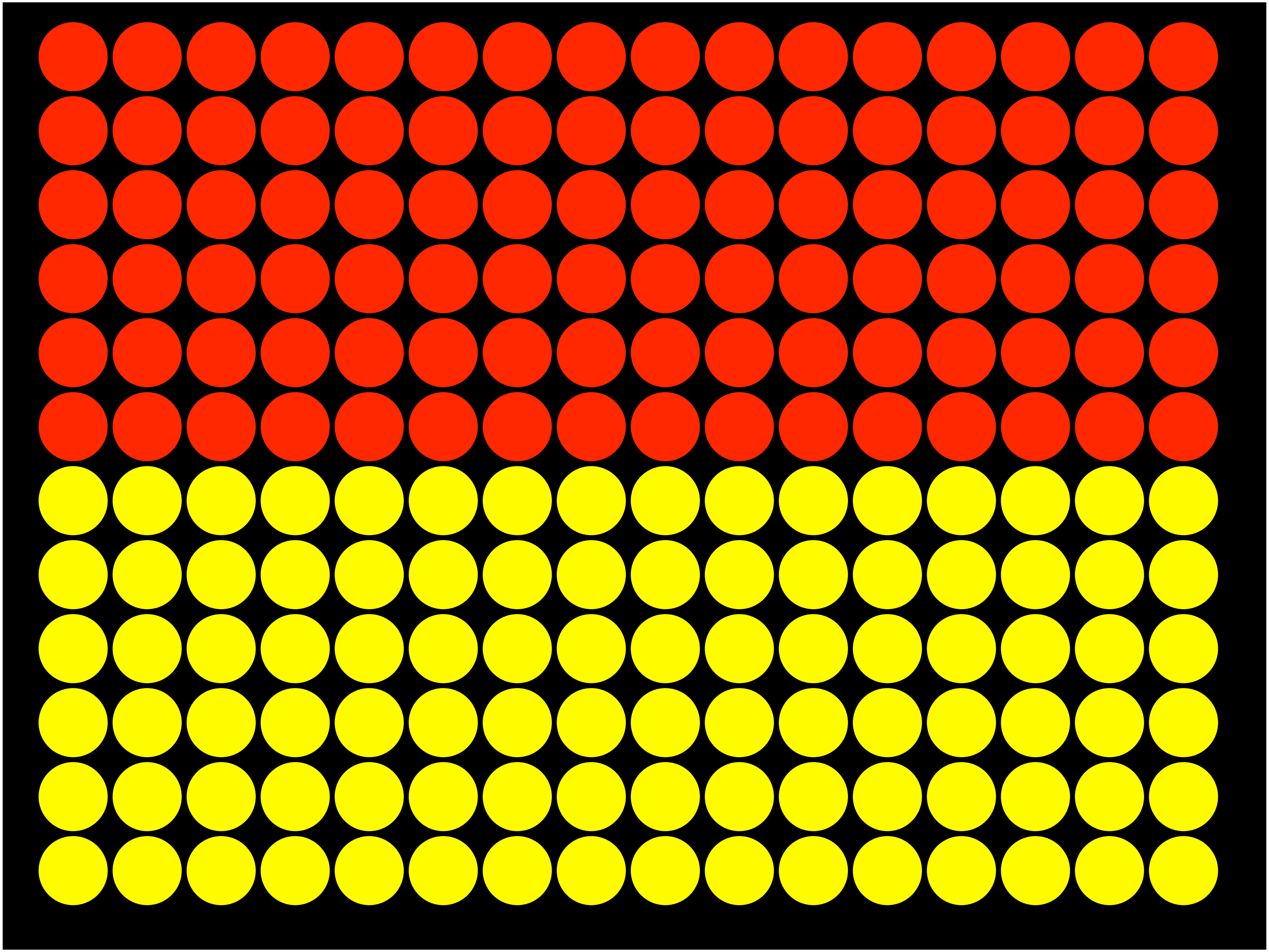
Superlattices...

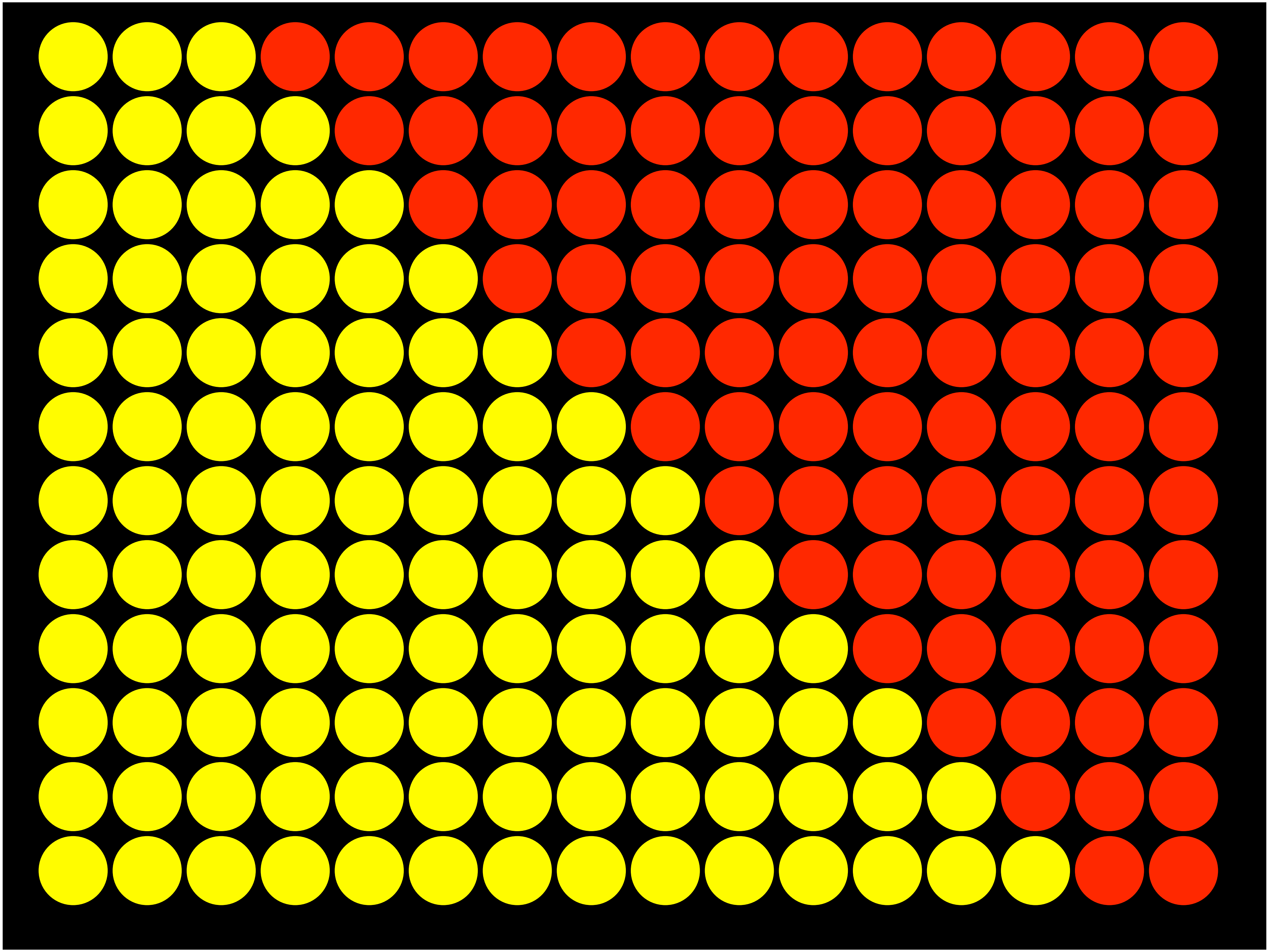
- A superlattice is like small, semi-infinite slabs (What the #$%@ does that mean?)
- Consider a 2n-layer superlattice A_nB_n
- What happens as n gets large? (Or as k gets small if we think in k-space?)



It's even worse...

Strain energy is *direction dependent*





Non-analyticity

In the limit of infinite-layers (k goes to zero) the strain reaches a finite value...

But that value depends on the orientation of the interface!

I.e., the limit $k \to 0$ depends on the direction in which we take the limit

Account for the "long-range" part of the energy by adding another term

$$\Delta H = E_{\text{chem}} + E_{\text{strain}}$$

Ising model handles this part

k-space strain model

In principle, any "correct" model for the strain can be used...

$$E_{\rm CS}(\vec{\sigma}) = \frac{1}{4x(1-x)} \sum_{\mathbf{k}} \Delta E^{\rm eq}_{\rm CS}(x,\hat{k}) |S(\mathbf{k},\sigma)|^2$$

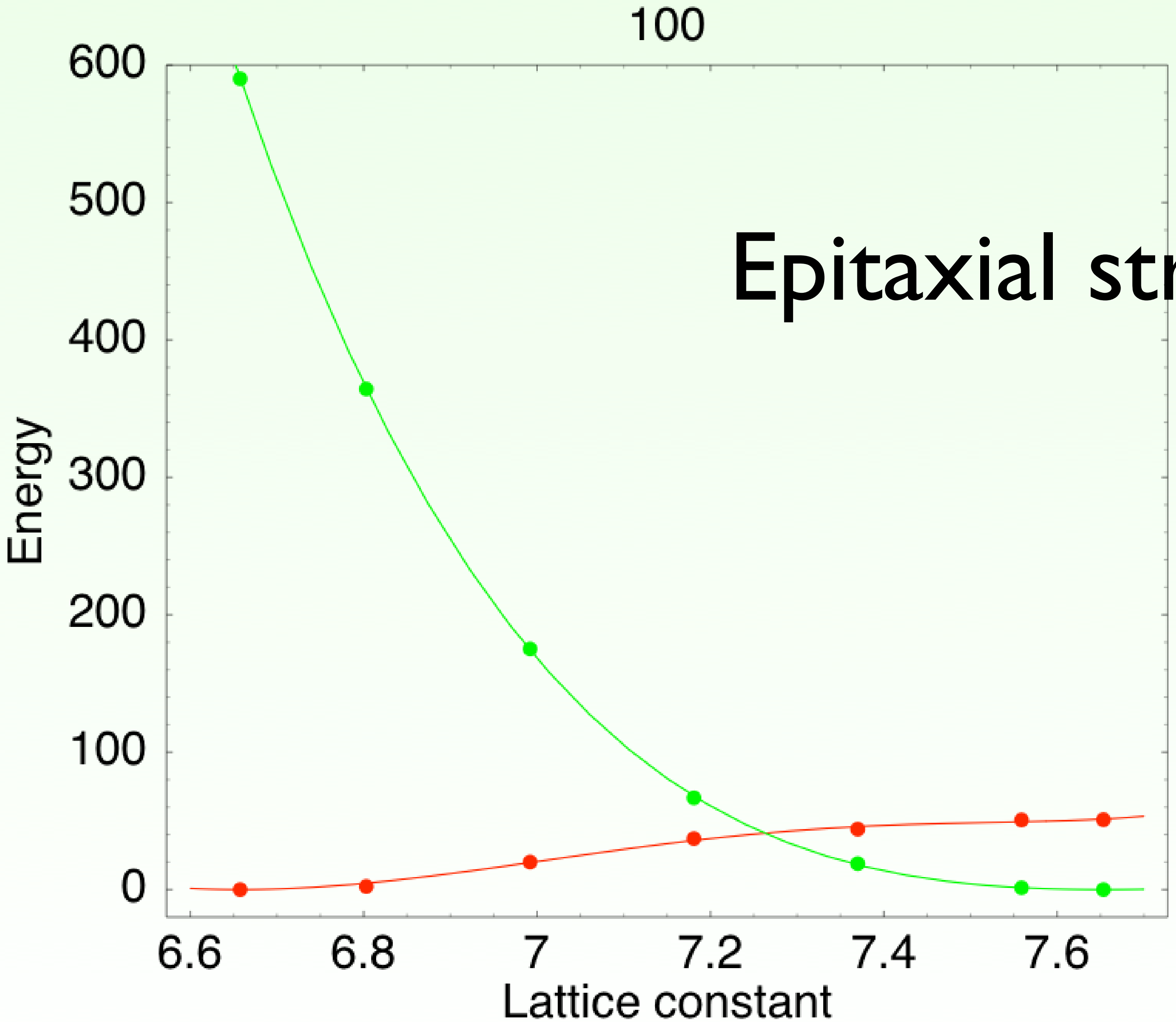
Must have the correct non-analyticity

We can still parameterize *ab-initio*

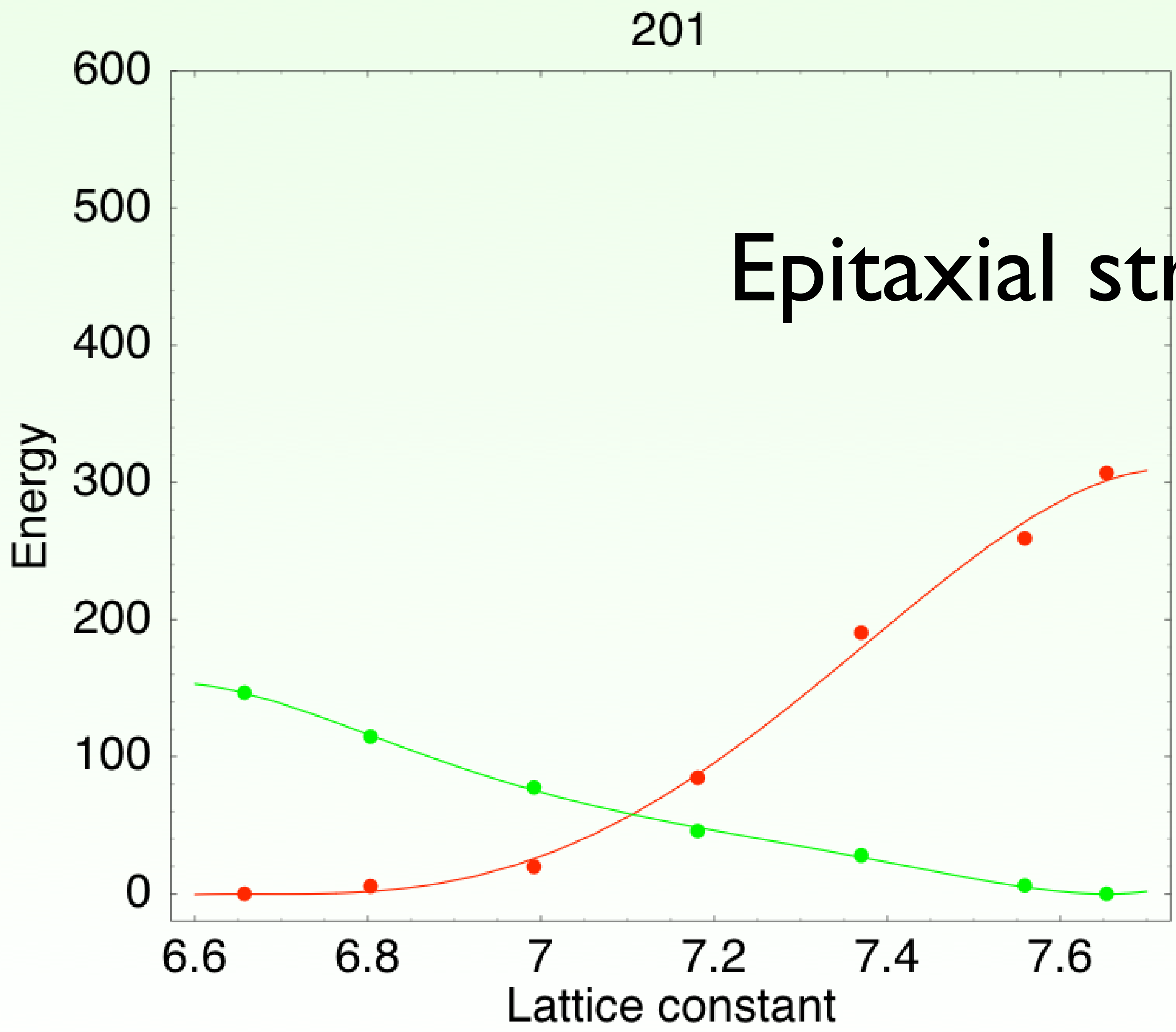
$$\Delta E_{\text{CS}} = \min_{a_\perp}[(1-x)\Delta E_A^{\text{epi}}(\hat{k}, a_\perp) + \Delta E_B^{\text{epi}}(\hat{k}, a_\perp)]$$

These terms can
come from one-atom-cell
DFT calculations

Epitaxial strains

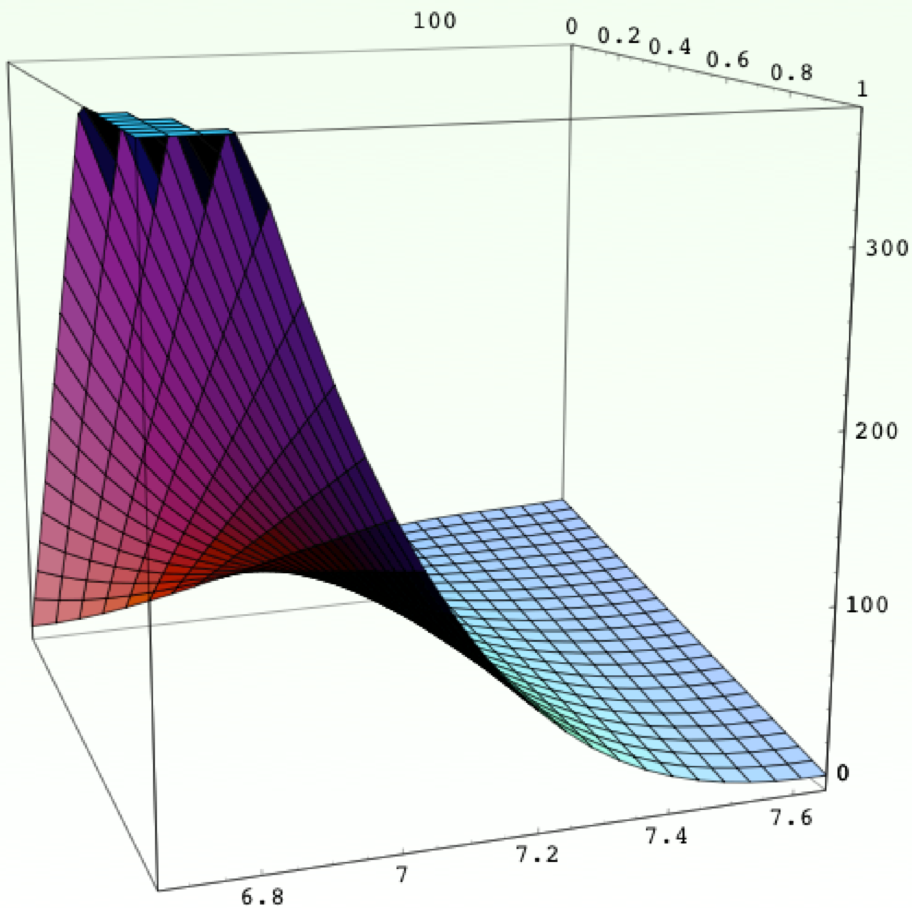


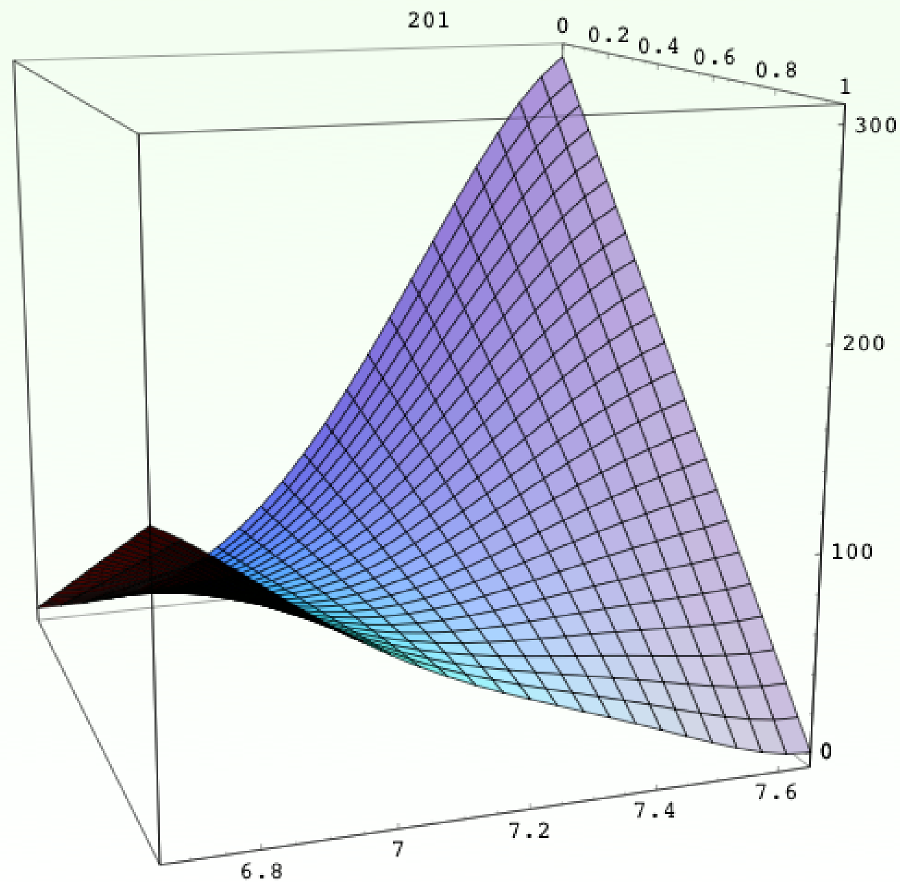
Epitaxial strains



Depends on both concentration and in-plane lattice constant

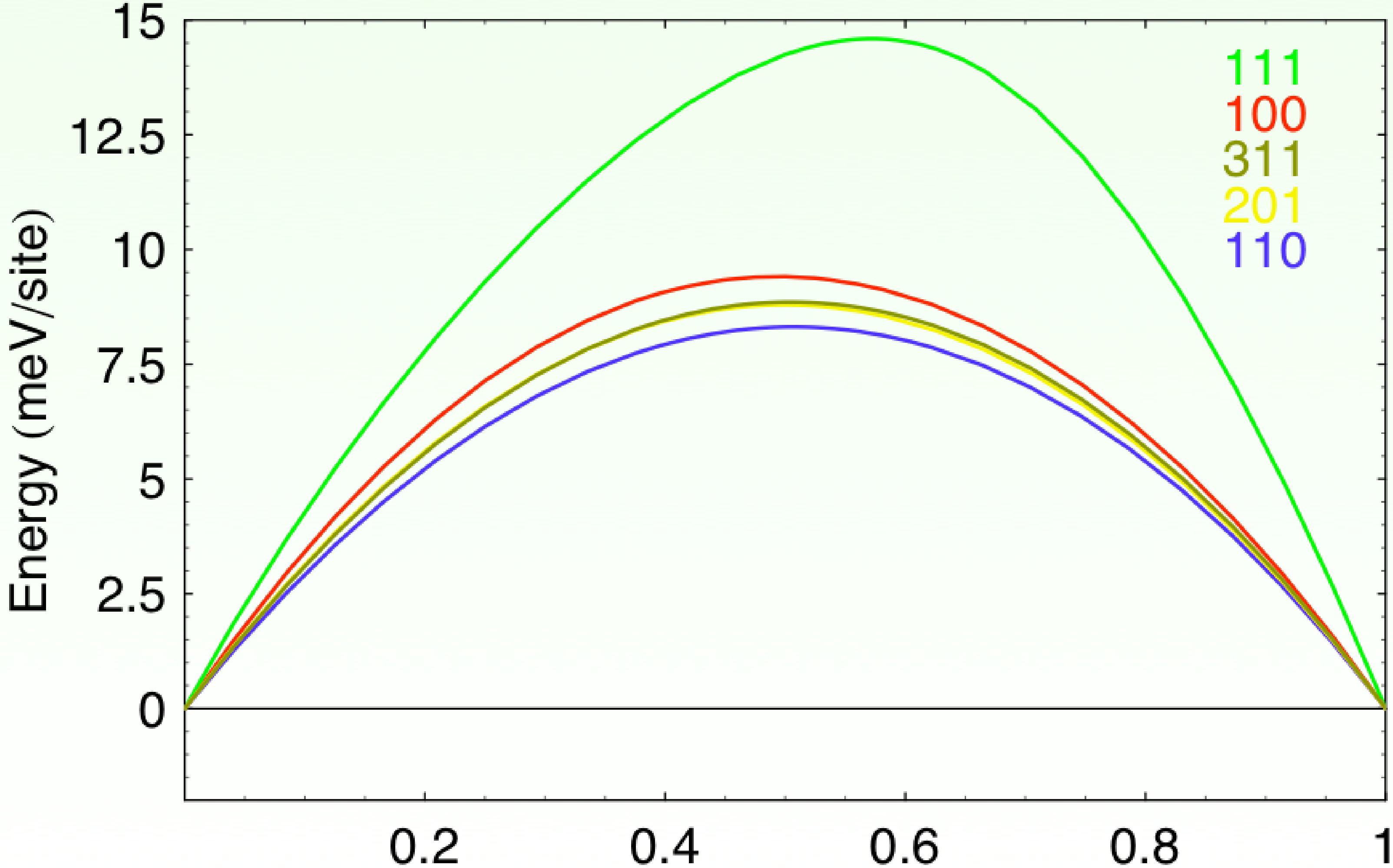
$$\Delta E_{\rm cs} = \min_{a_\perp}[(1-x)\Delta E_A^{\rm epi}(\hat{k}, a_\perp) + \Delta E_B^{\rm epi}(\hat{k}, a_\perp)]$$

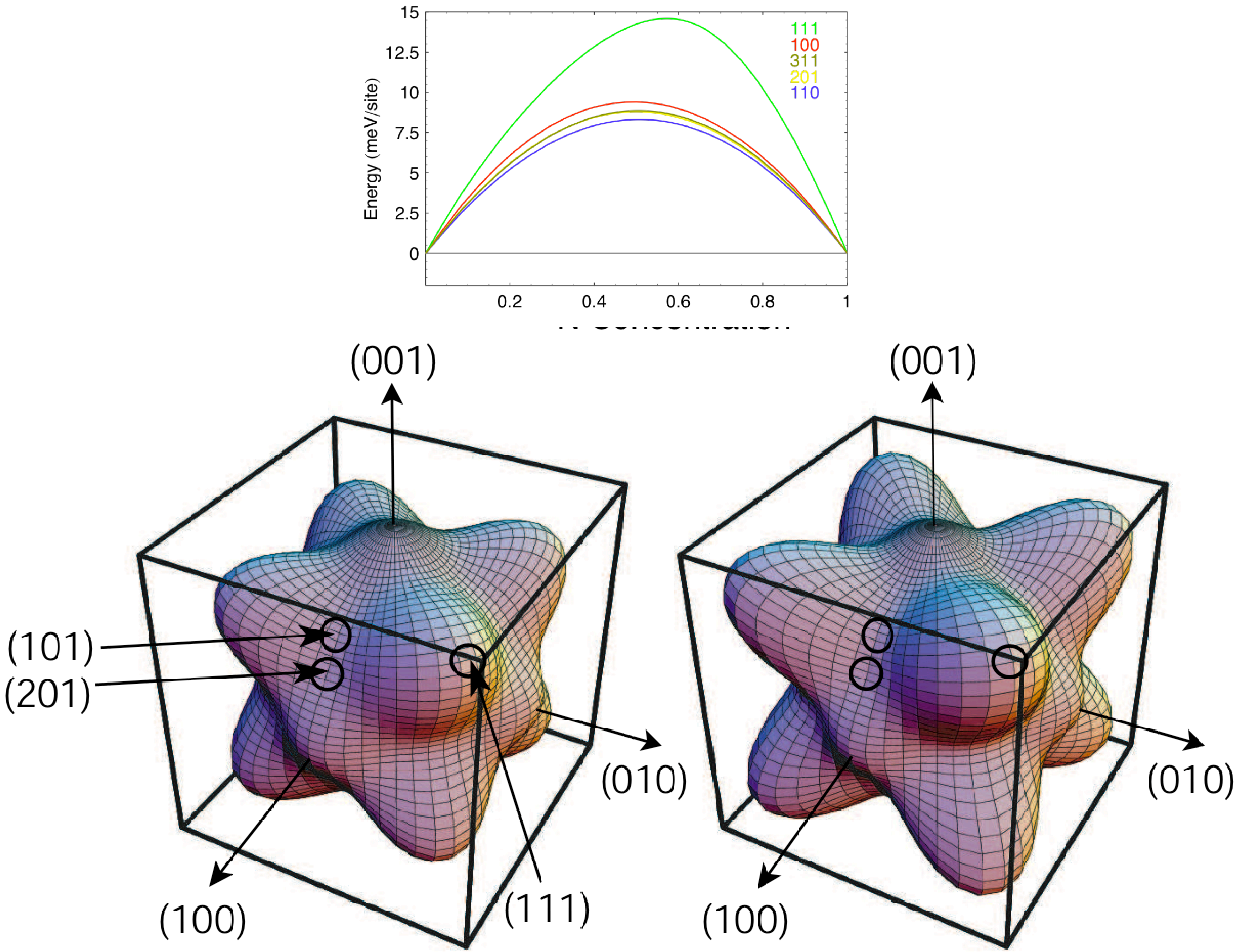


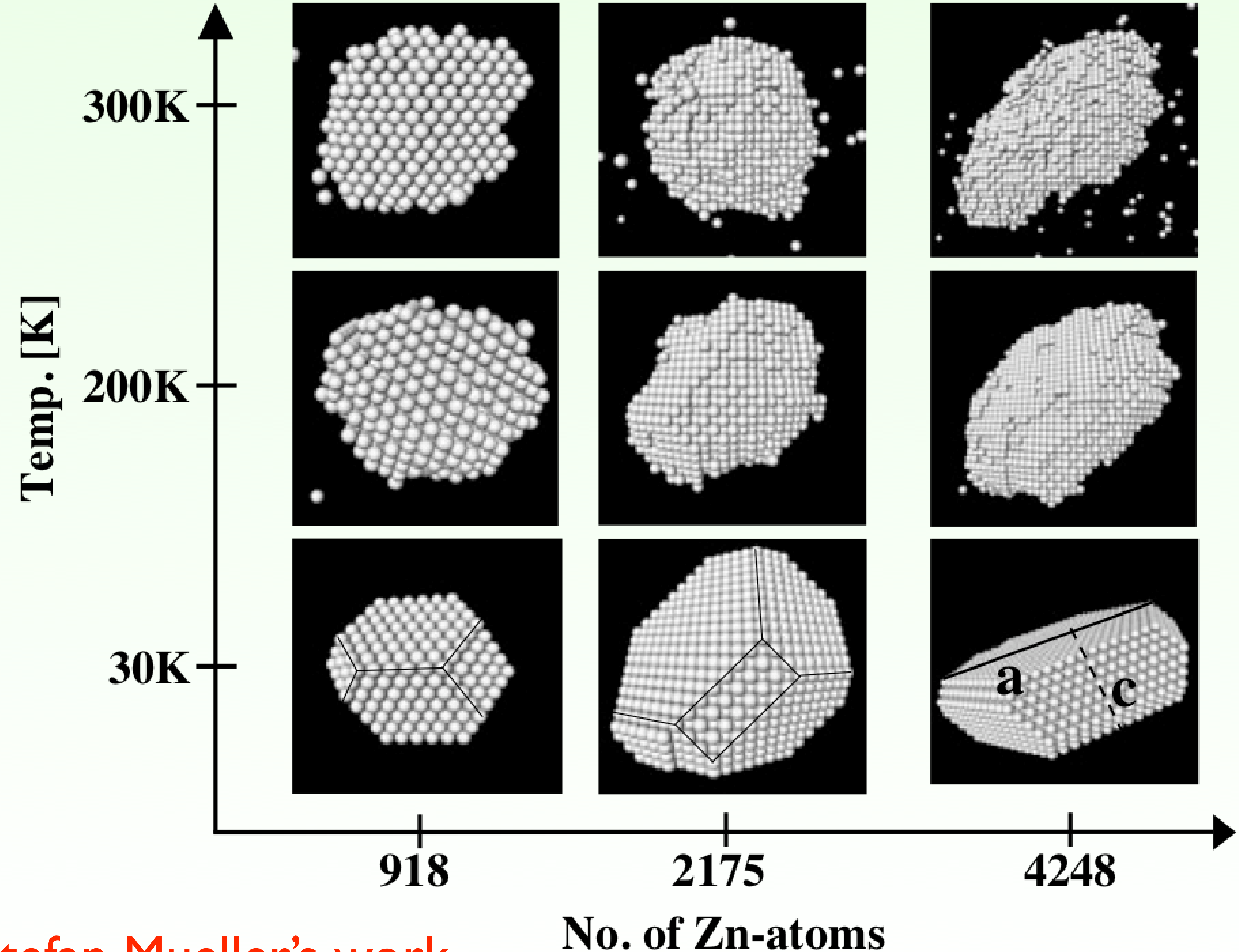


We end up with an "upside-down parabola" for each direction

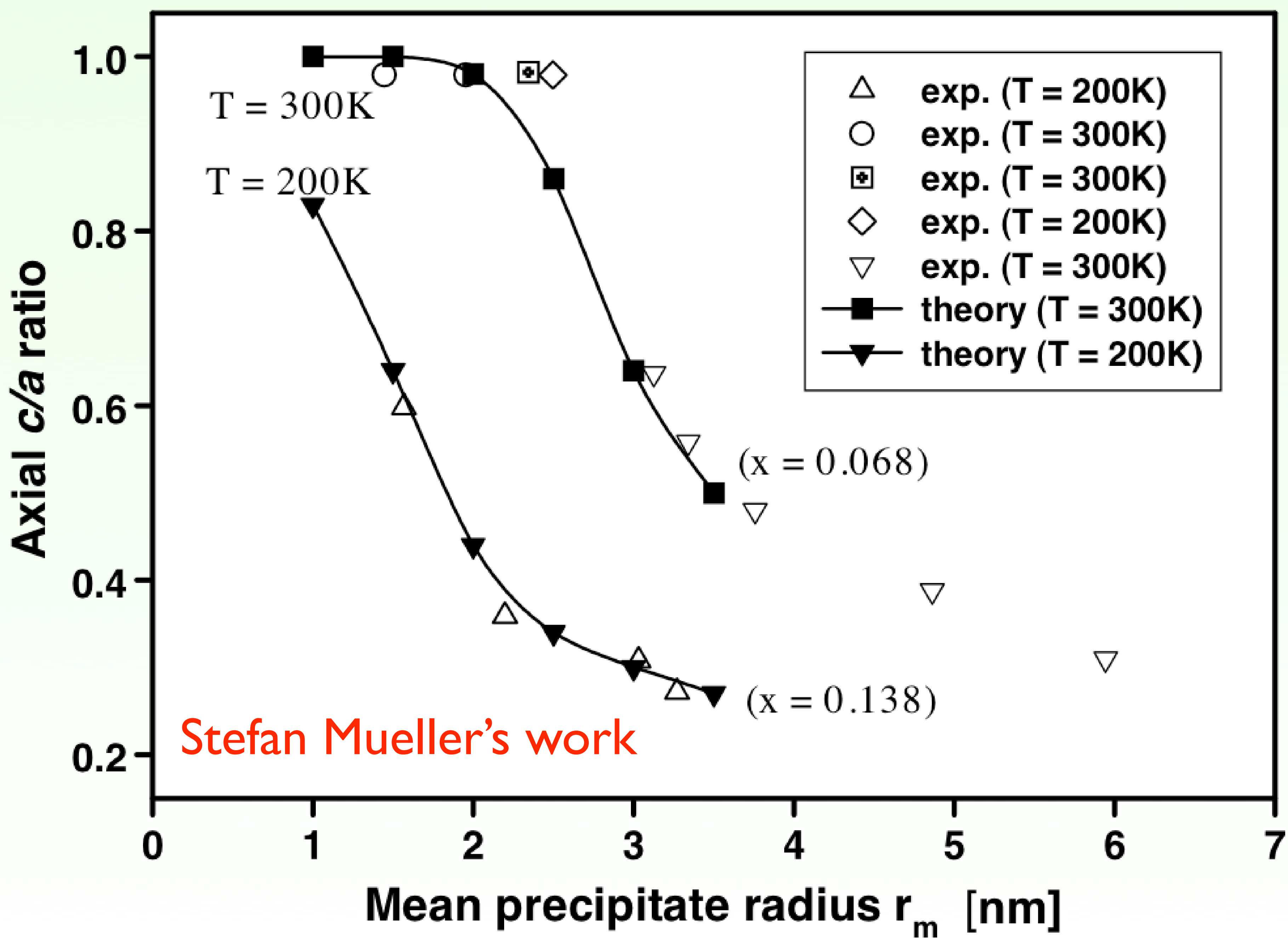
$$\Delta E_{\mathrm{cs}} = \min_{a_\perp} [(1-x)\Delta E_A^{\mathrm{epi}}(\hat{k}, a_\perp) + \Delta E_B^{\mathrm{epi}}(\hat{k}, a_\perp)]$$




Energy (meV/site)
15
12.5
10
7.5
5
2.5
0
0.2
0.4
0.6
0.8
1
111
100
311
201
110
(001)
(101)
(201)
(111)
(010)
(100)
(001)
(010)
(100)



Stefan Mueller's work



Axial c/a ratio
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
Mean precipitate radius r_m [nm]
T = 300K
T = 200K
(x = 0.068)
(x = 0.138)
exp. (T = 200K)
exp. (T = 300K)
exp. (T = 300K)
exp. (T = 200K)
exp. (T = 300K)
theory (T = 300K)
theory (T = 200K)
Stefan Mueller's work