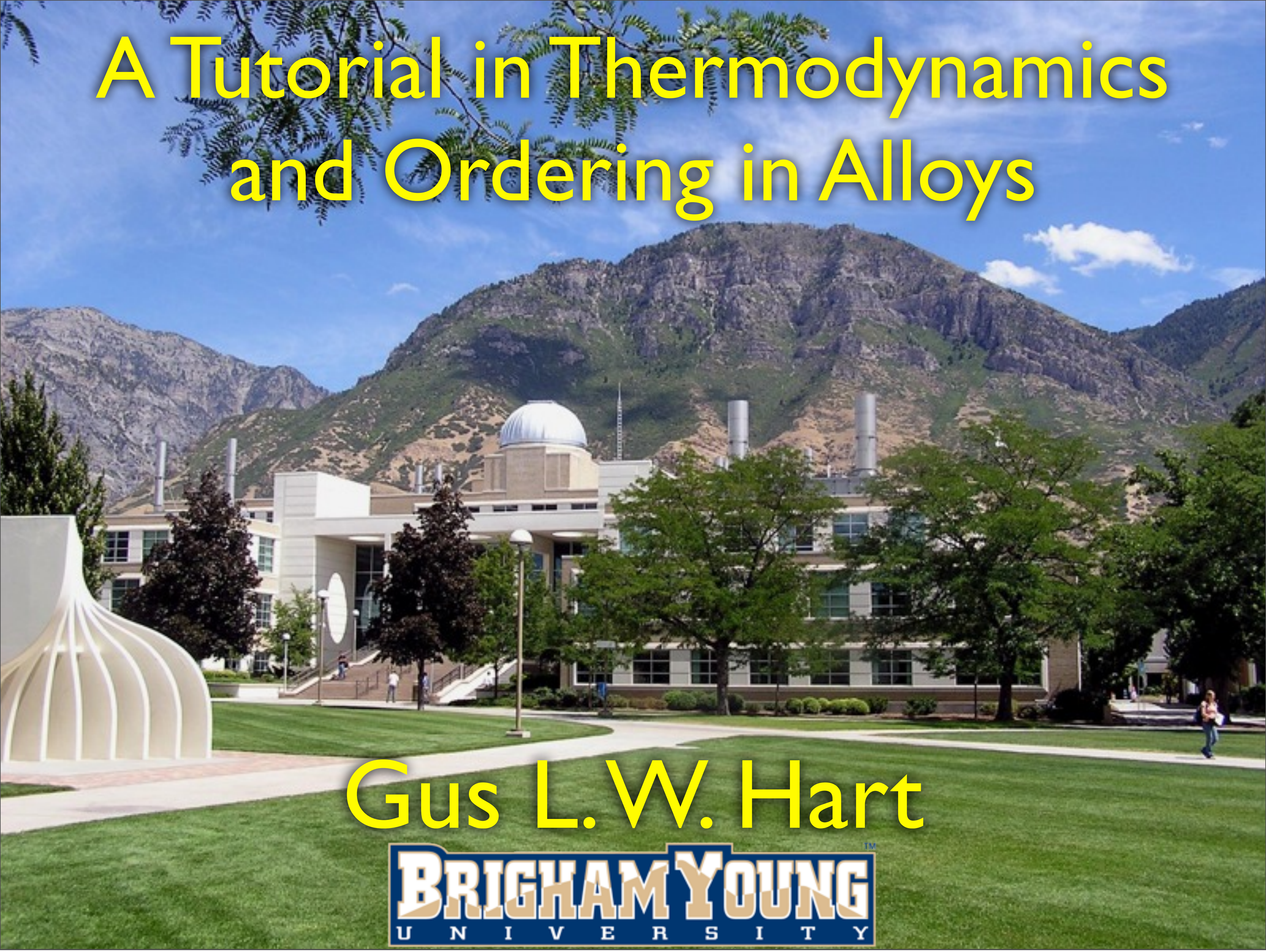
A Tutorial in Thermodynamics and Ordering in Alloys



Gus L. W. Hart

BRIGHAM YOUNG UNIVERSITY


A Tutorial

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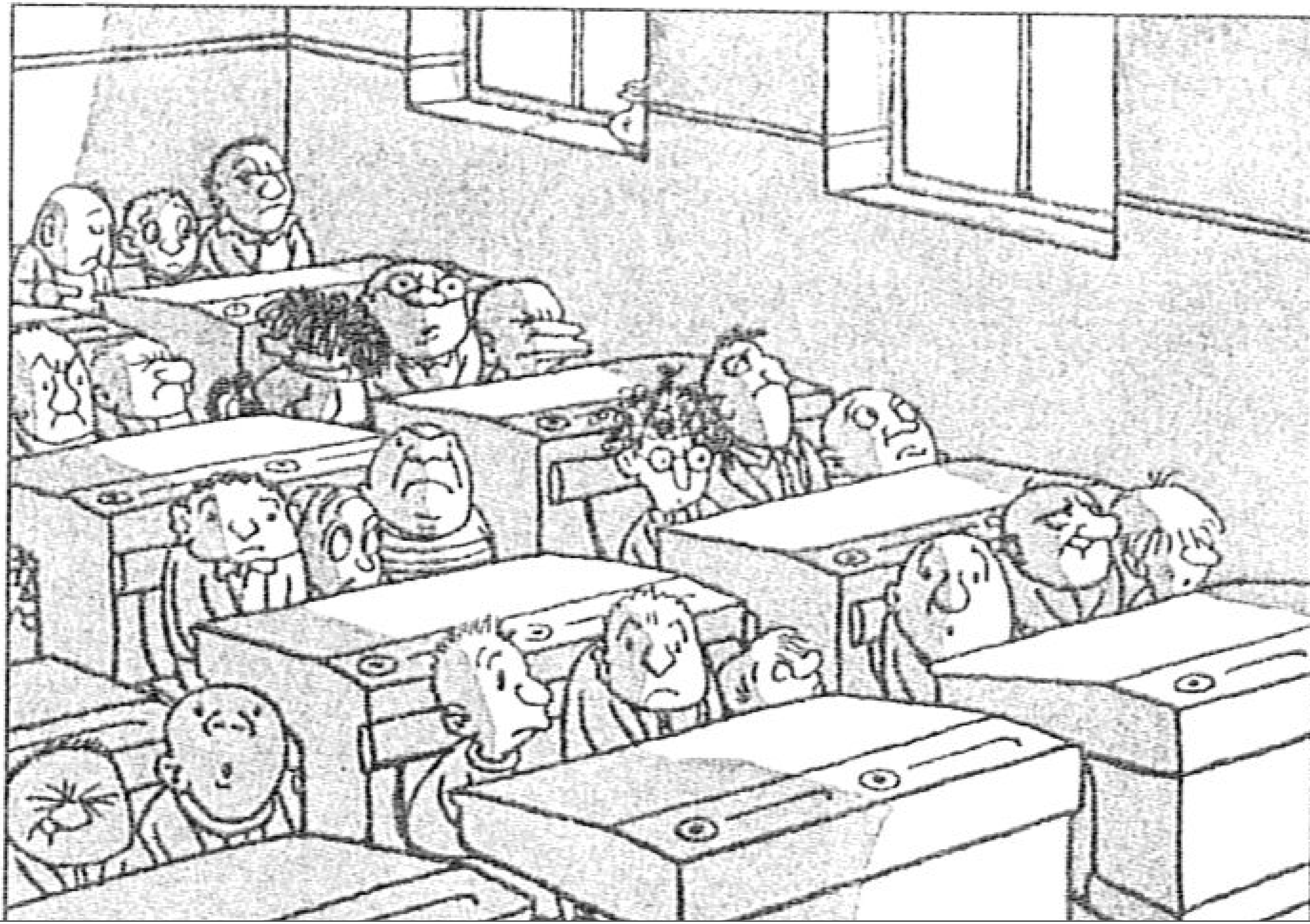
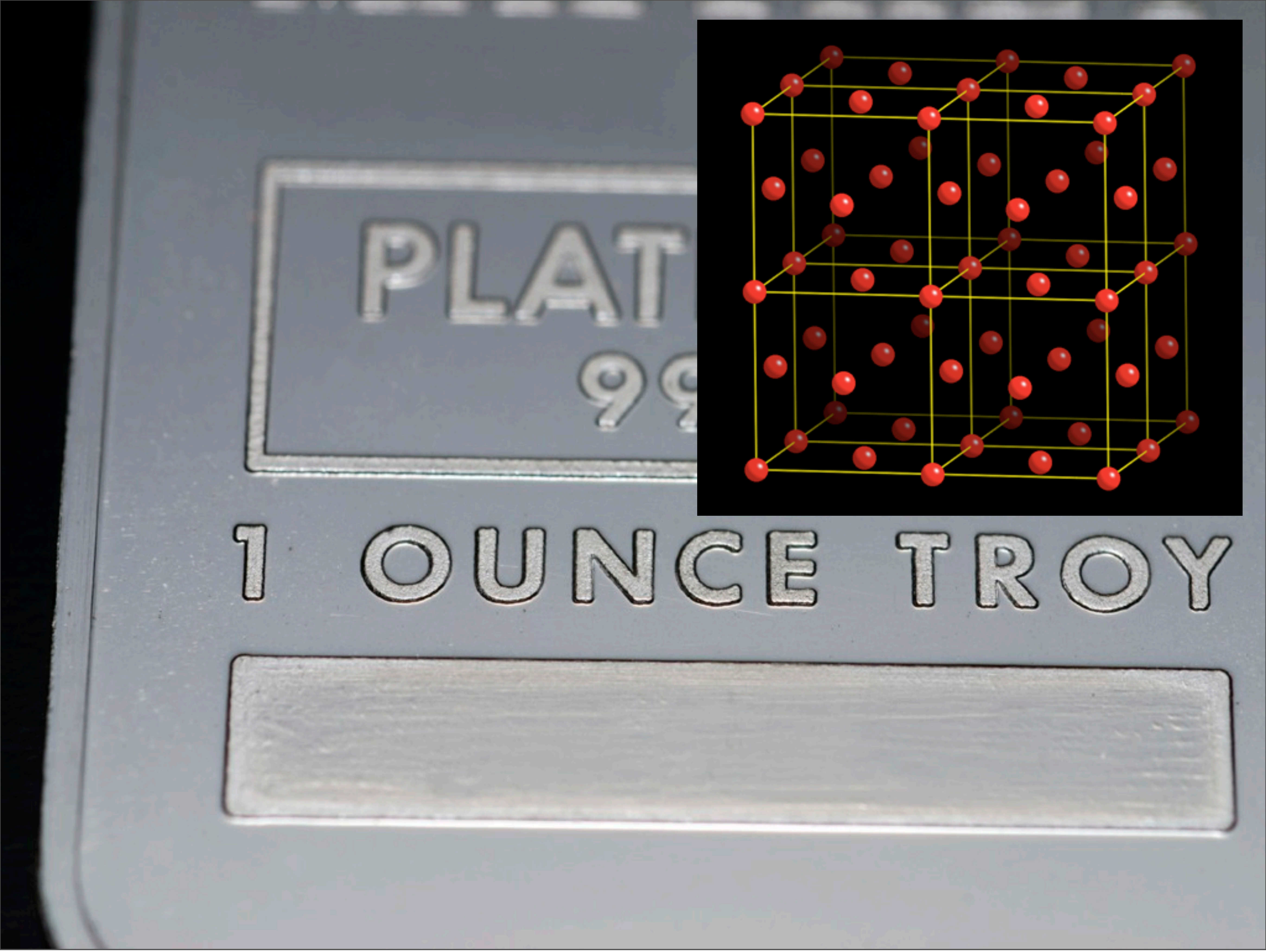


A Tutorial

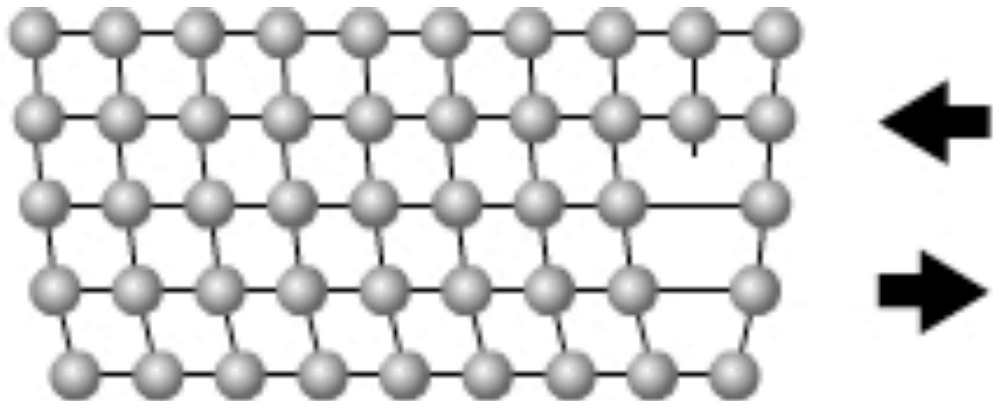
A Tutorial

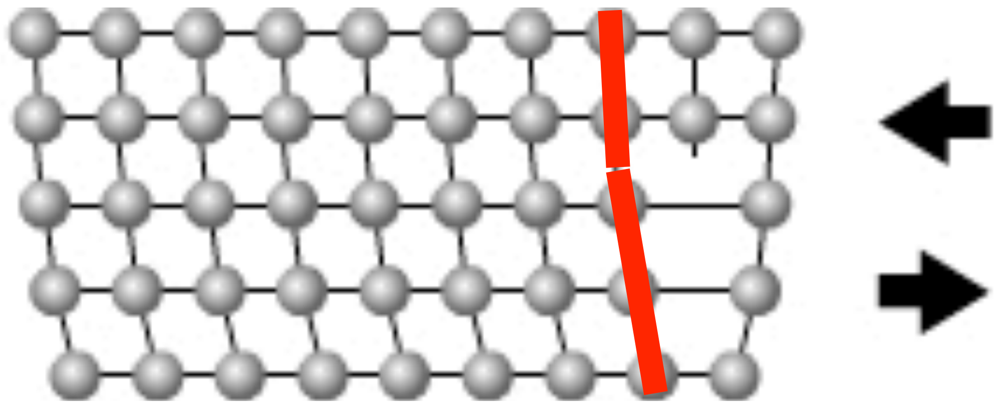
Interrupt me, please!

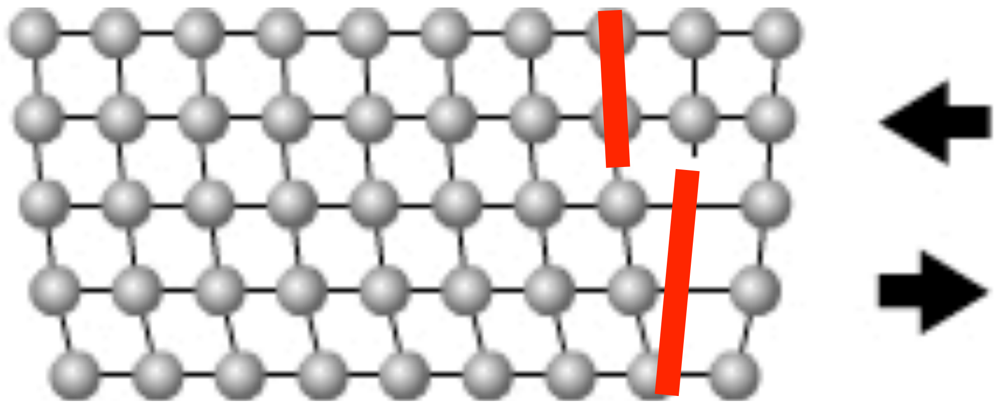

PLATINUM
9995
1 OUNCE TROY

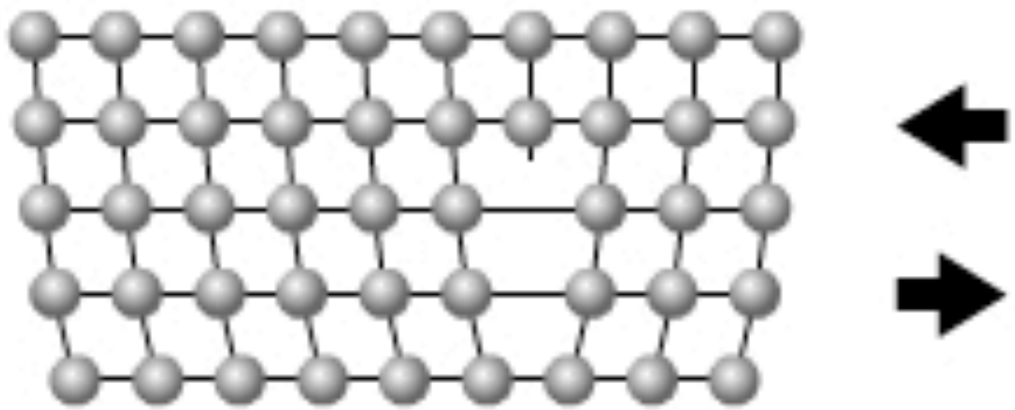

1 OUNCE TROY

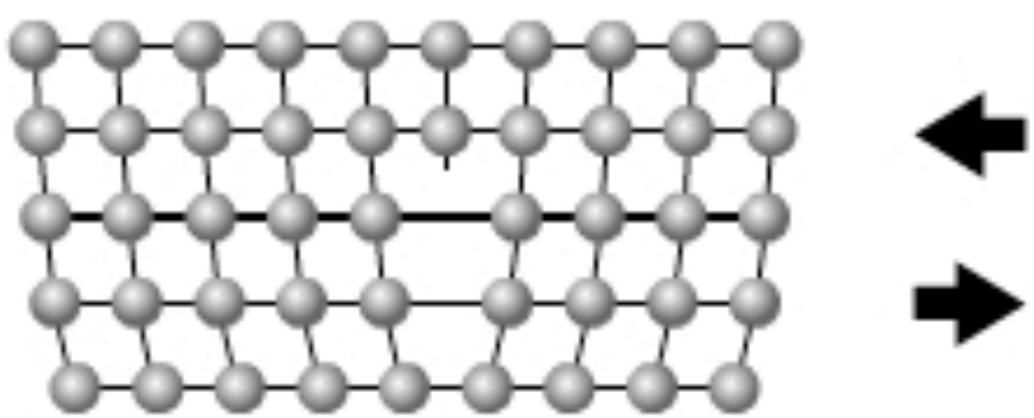
What makes a metal "soft"?

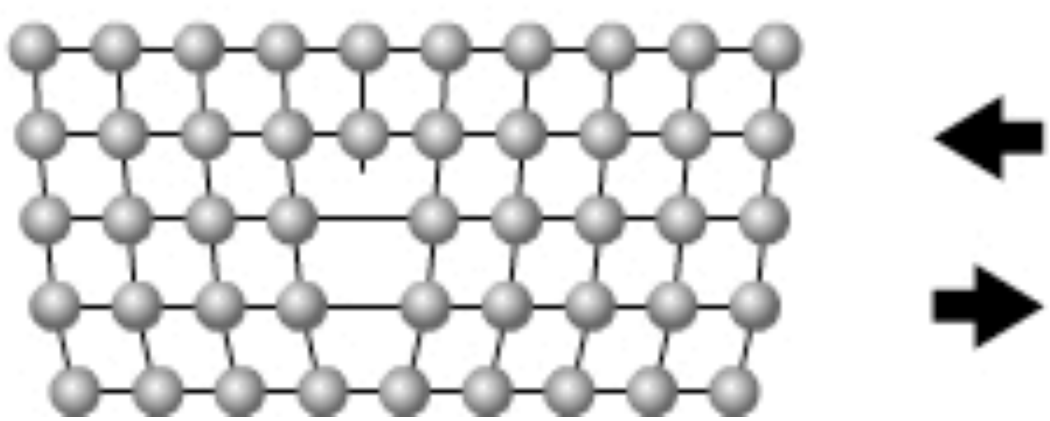


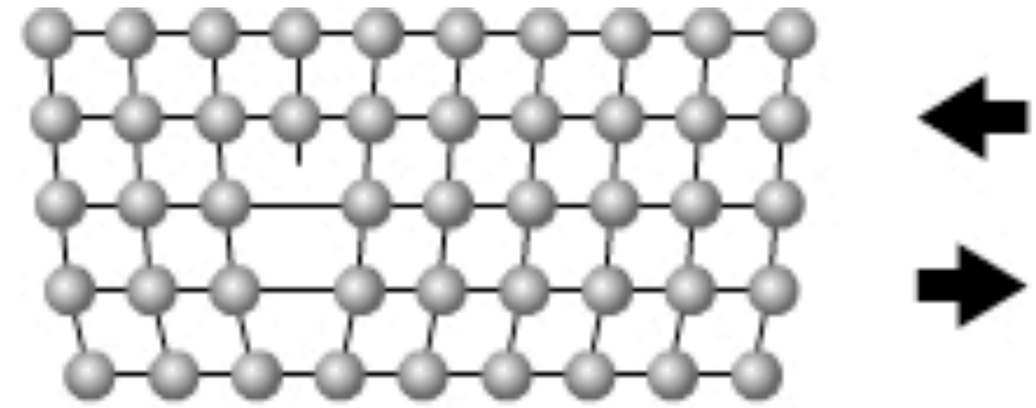


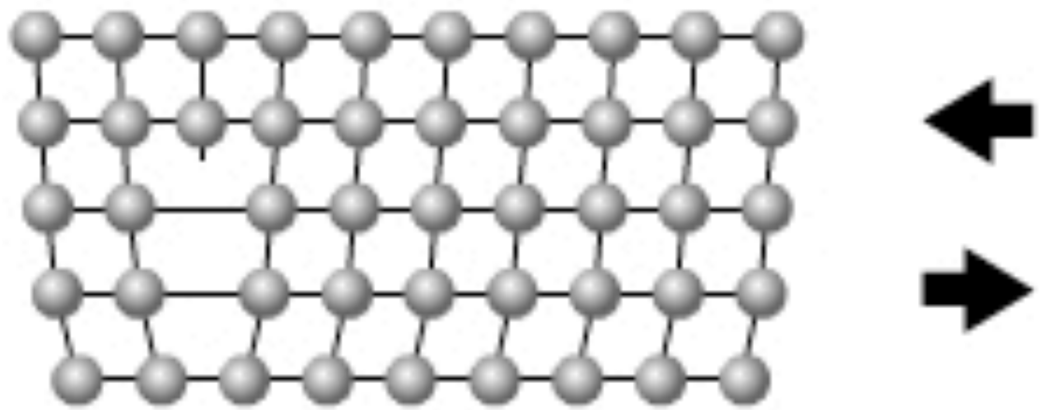


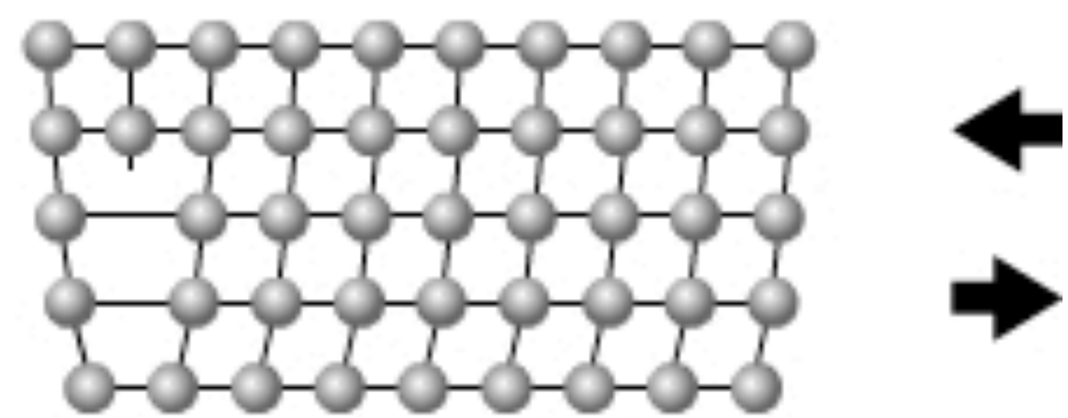


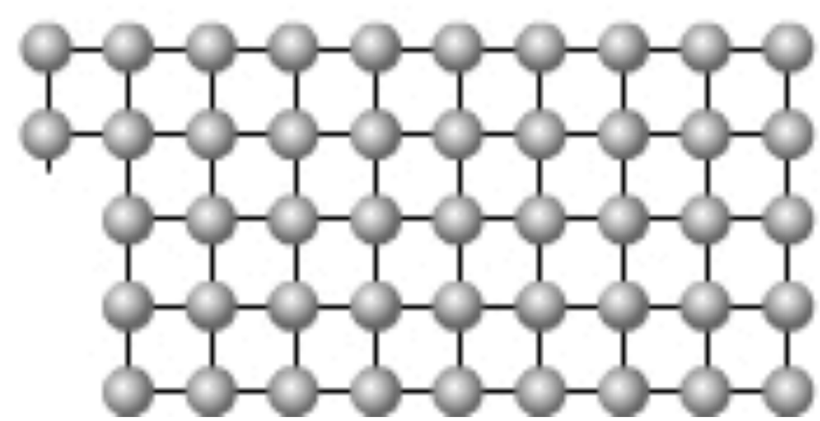




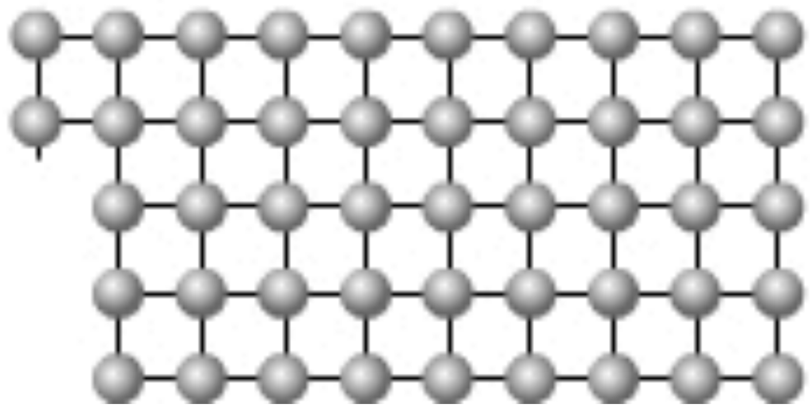








Dislocation motion leads to plastic deformation



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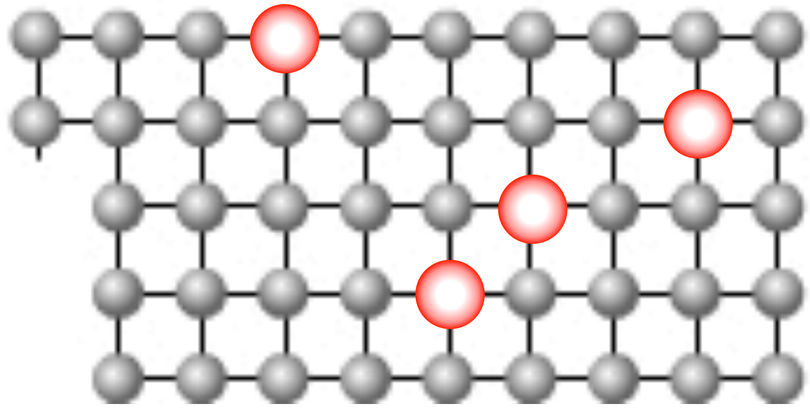
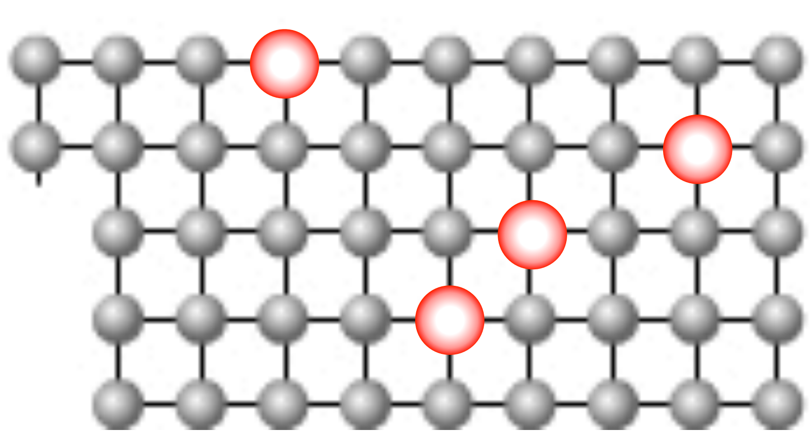
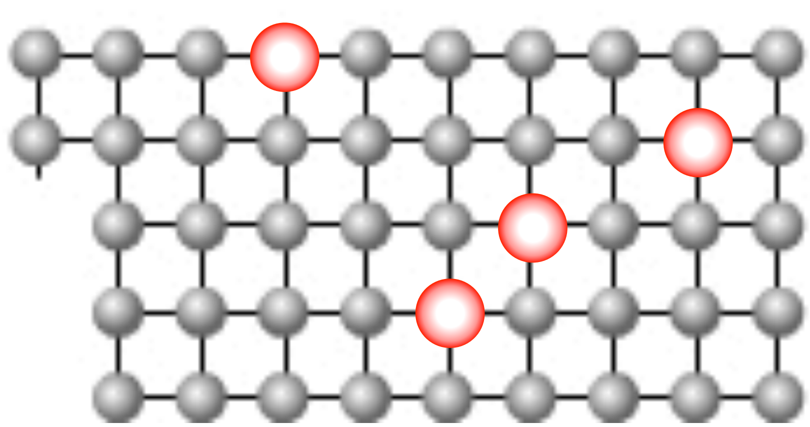


Dislocation motion leads to plastic deformation

Forming a solid solution inhibits dislocations



$$\leq 5\%$$



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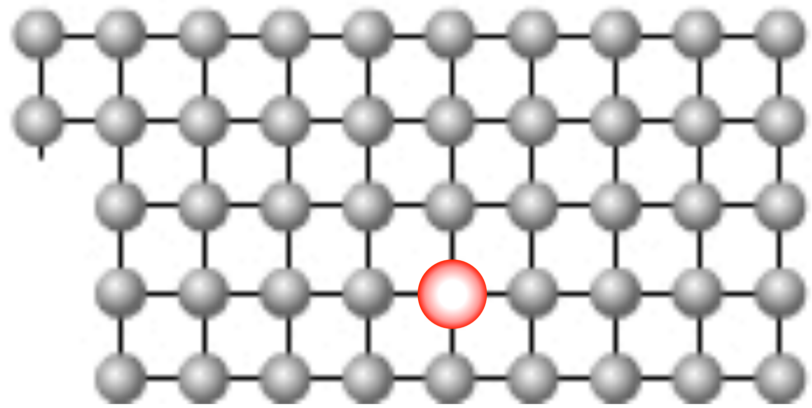
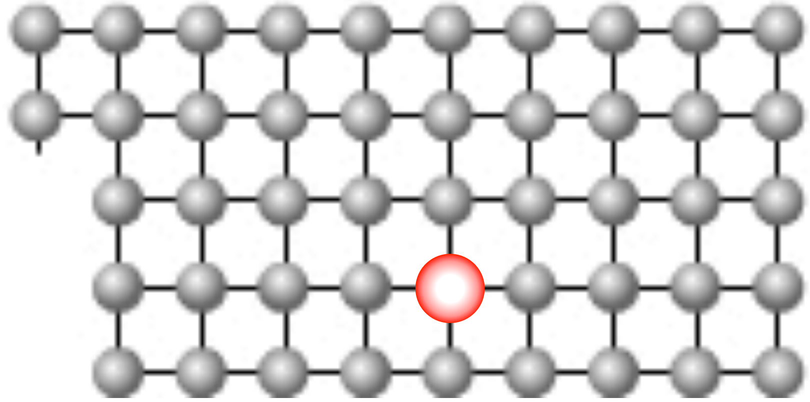
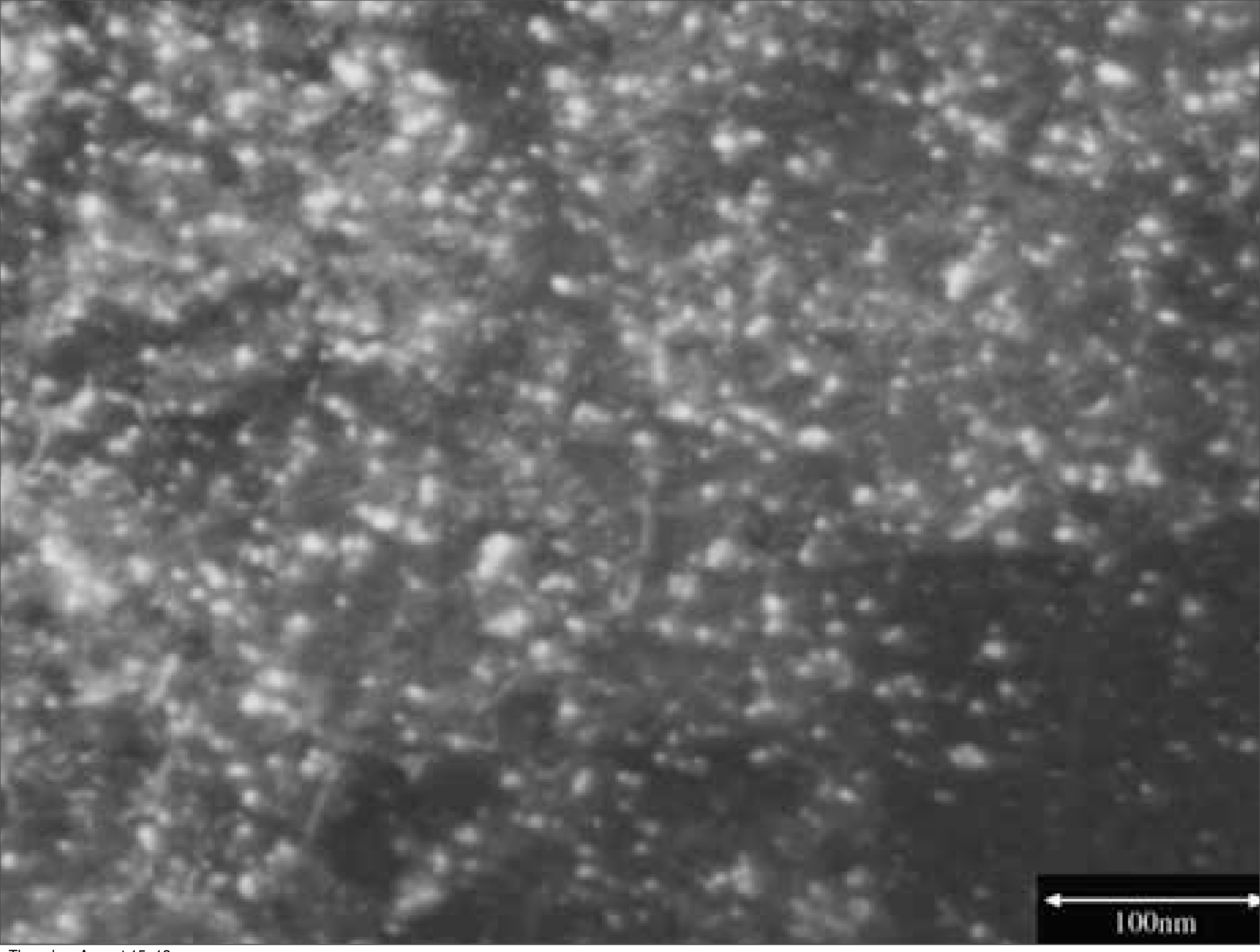
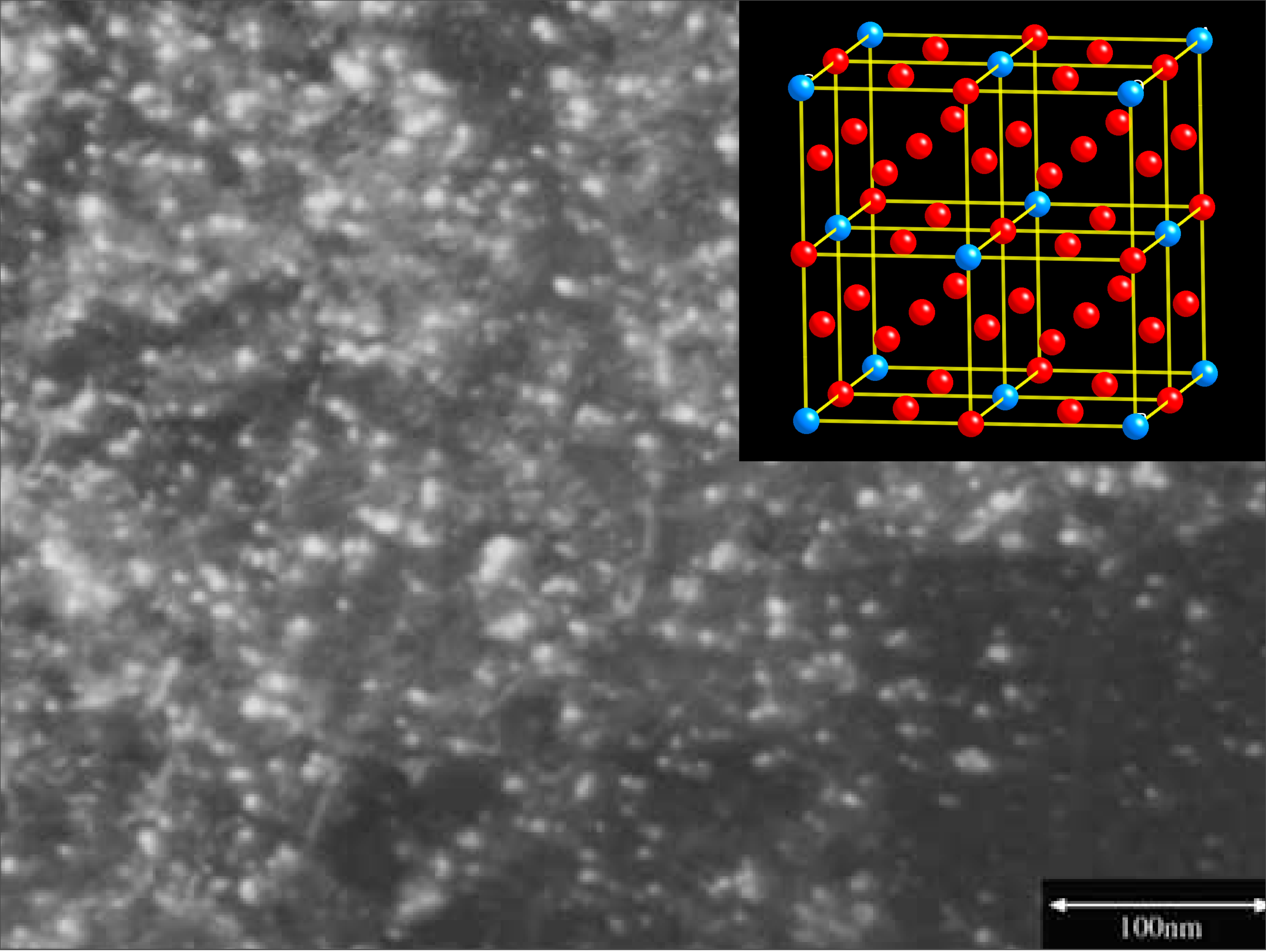


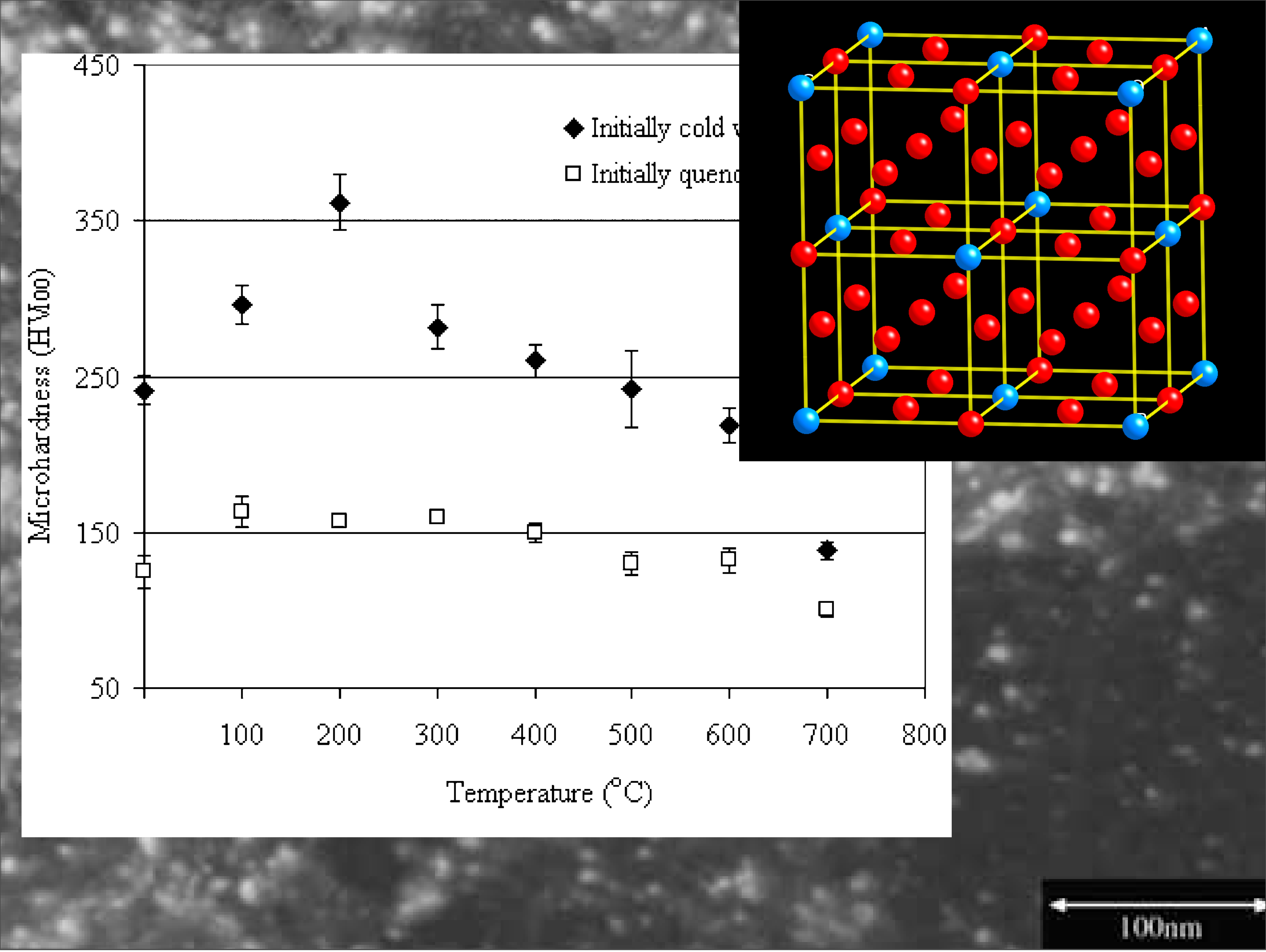
$$\leq 5\%$$

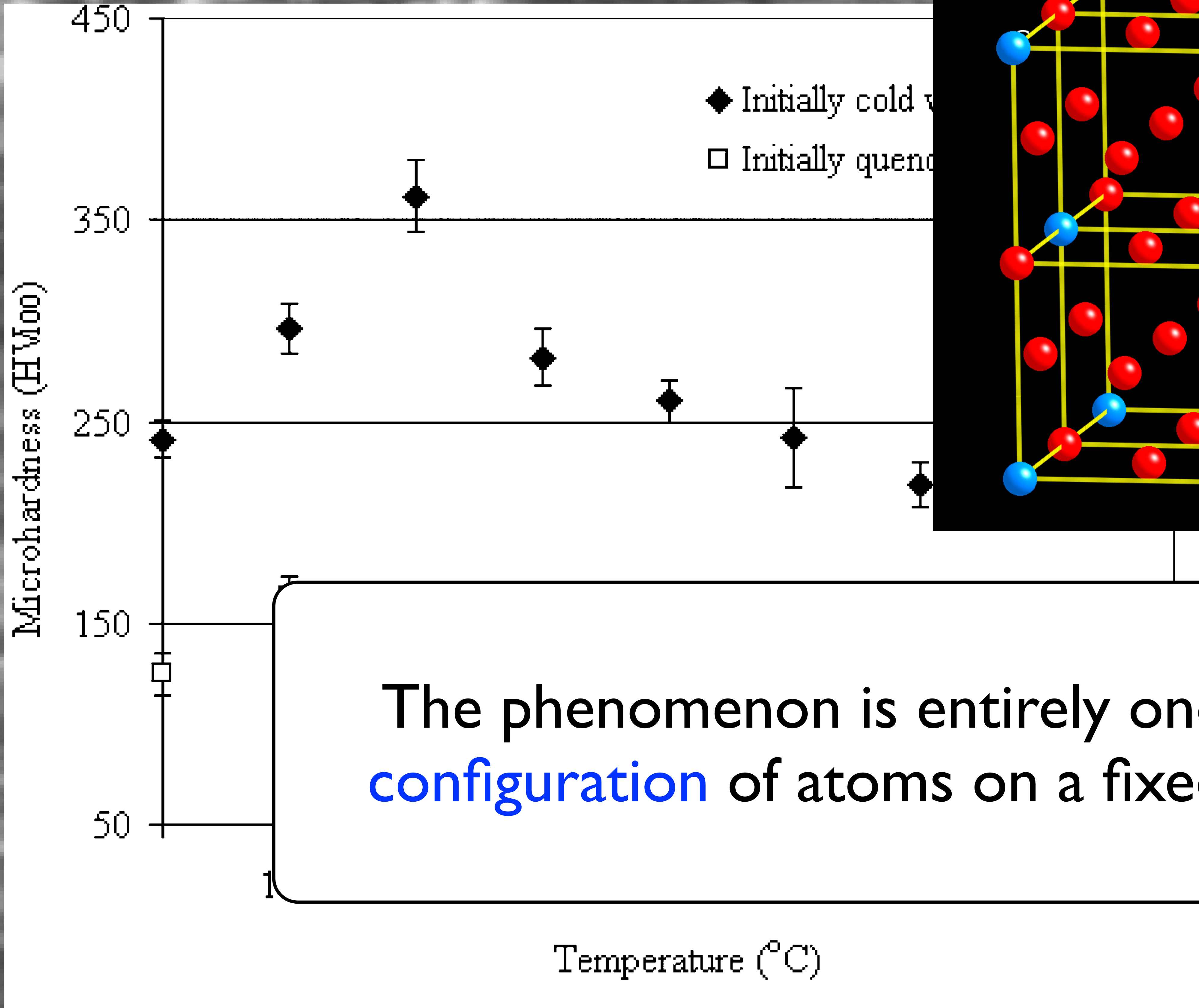
Solid solution hardening is ineffective jewelry alloys

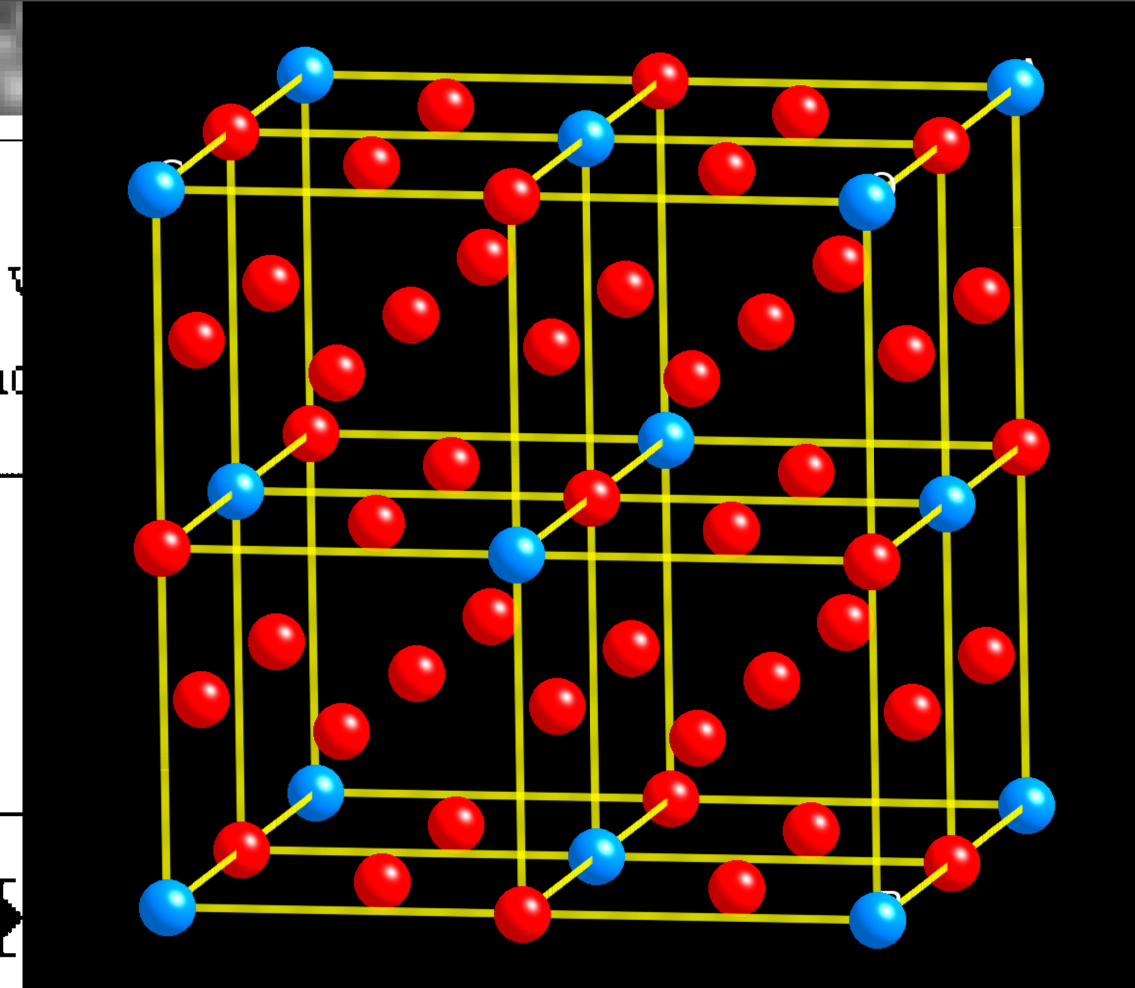



100nm

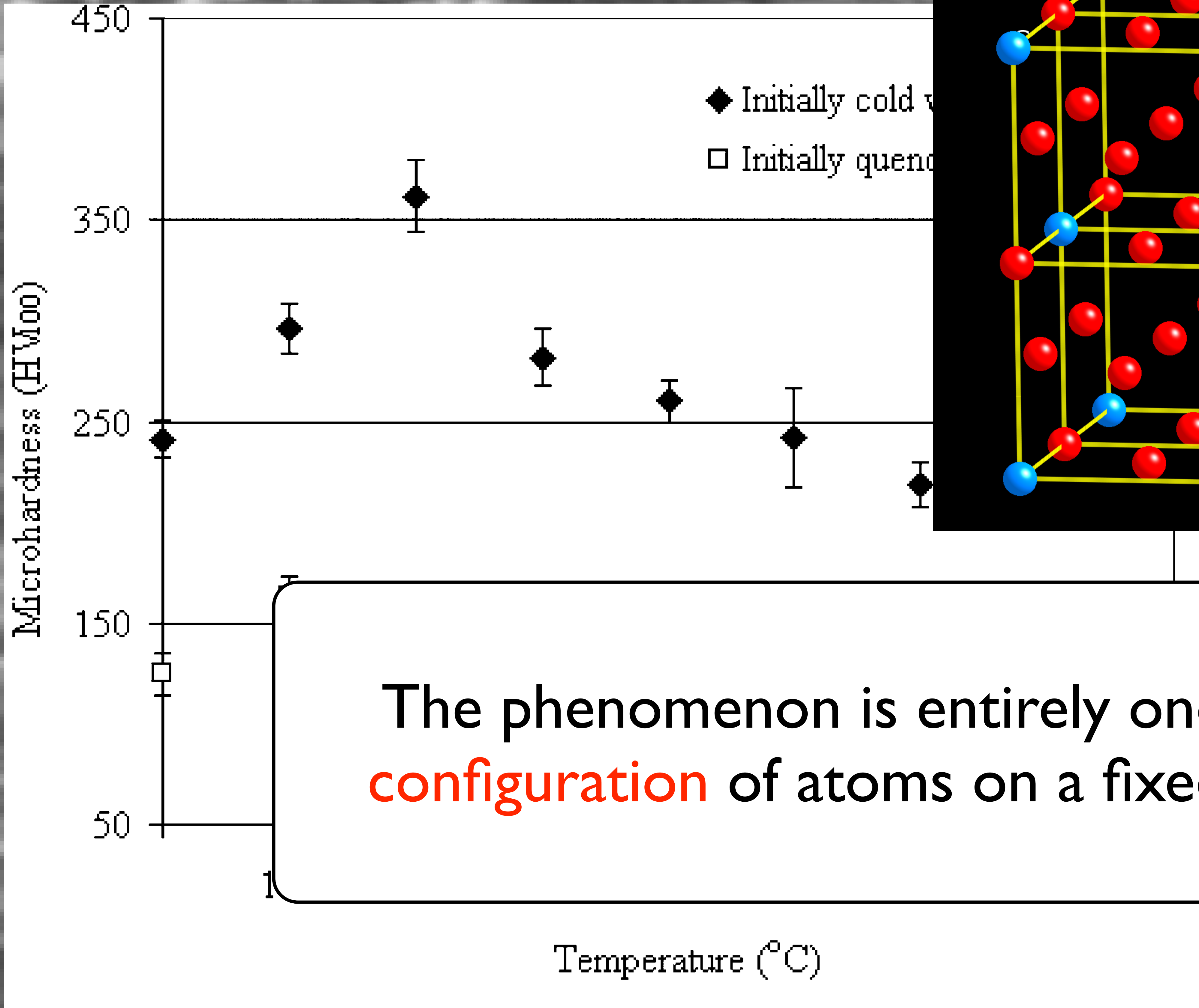

100nm

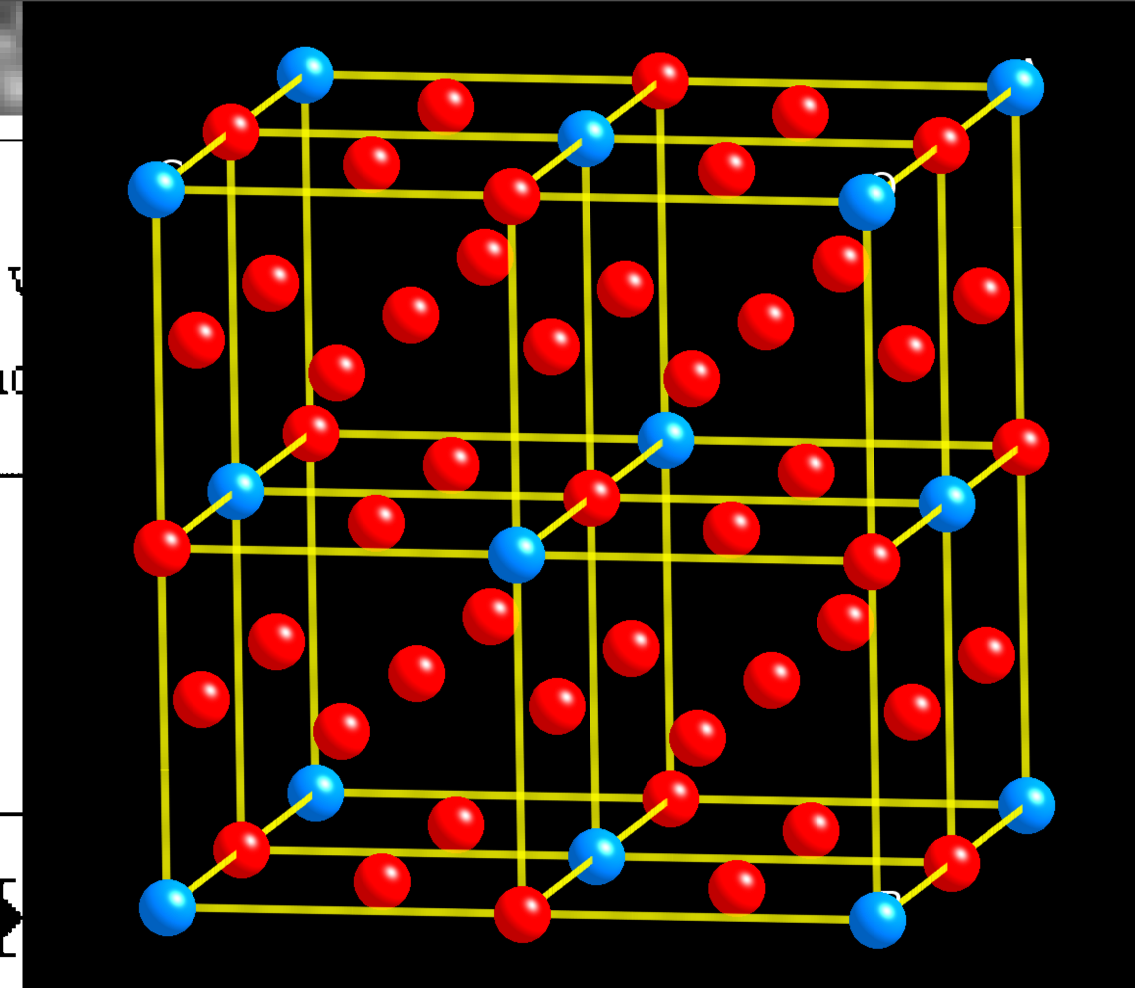

450
350
250
150
50
Microhardness (HV100)
Initially cold
Initially
100
200
300
400
500
600
700
800
Temperature (°C)
100nm





The phenomenon is entirely one of the configuration of atoms on a fixed lattice.





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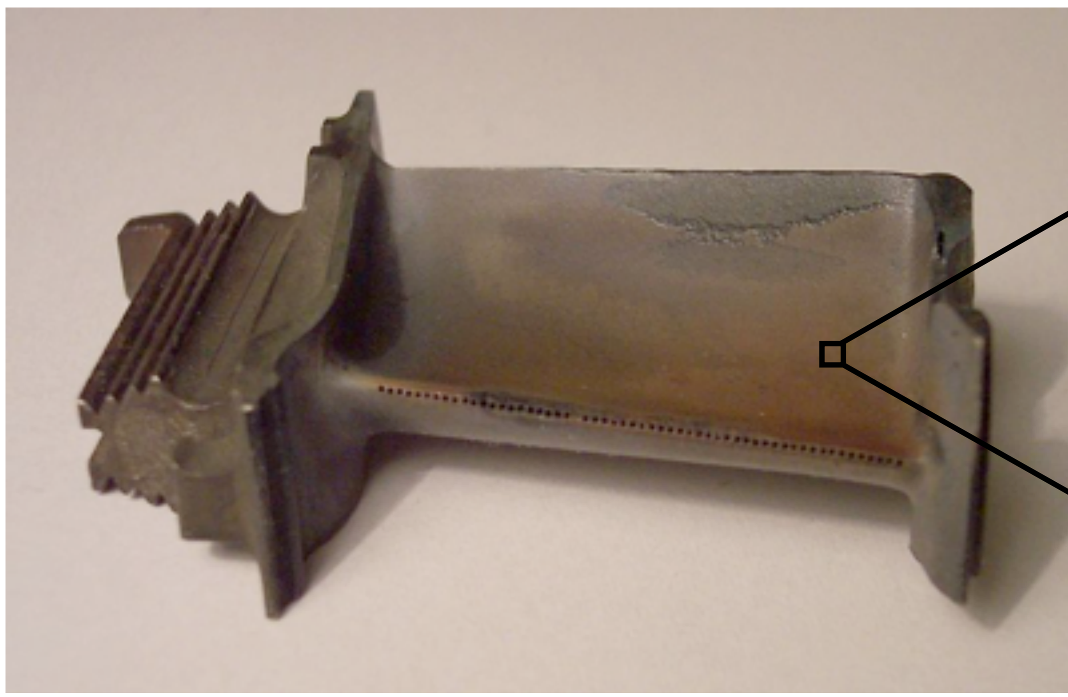
A second example

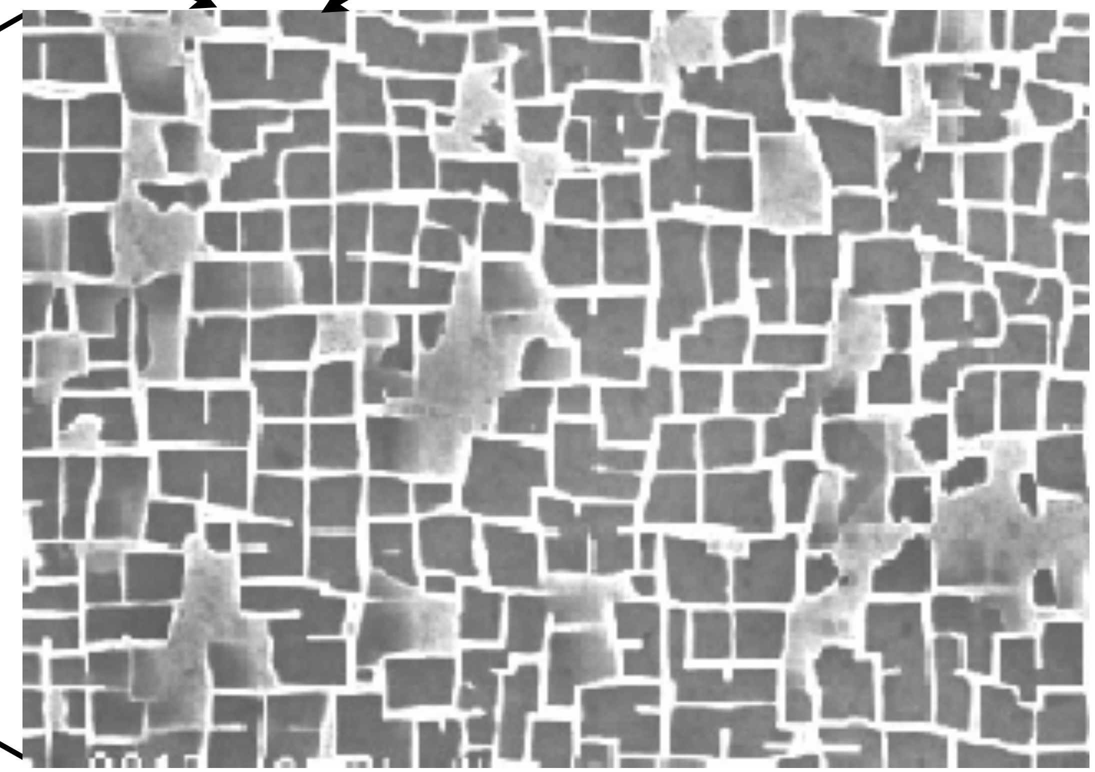
disordered fcc Ni+(Co,Cr,Mo,W,...)

ordered $Ni_3(Al,Ti)$



Nickel superalloy jet engine turbine blade

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



http://www.tms.org/meetings/specialty/superalloys2000/superalloyshistory.html

Configurational problems

- Precipitate hardening (Pt-Cu, Al-Cu)
- New phases in metallic alloys (8:1)
- Vacancies in TiC, ScS, etc.
- Oxygen diffusion in fuel cell materials
- Hydrogen in storage materials
- Li in battery materials

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Can you think of other problems that are configurational in nature?
Other lattice problems?

Configurational problems

- Precipitate hardening (Pt-Cu, Al-Cu)

Interrupt me, please!

configurational in nature?
Other lattice problems?

If we had a fast lattice Hamiltonian...

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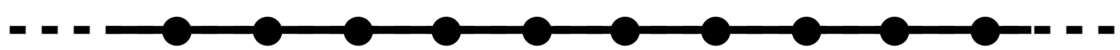
1. Search for new phases (step through millions of candidate configurations)

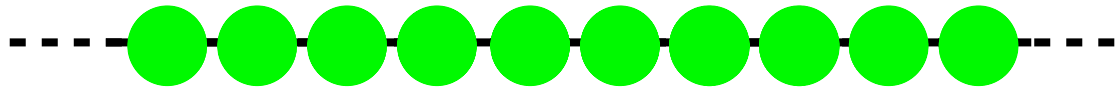
2. Apply thermodynamic modeling (to identify phase transitions)

3. Build a kinetic simulation (to model time evolution)

One-Dim. configurational problem



One-Dim. configurational problem



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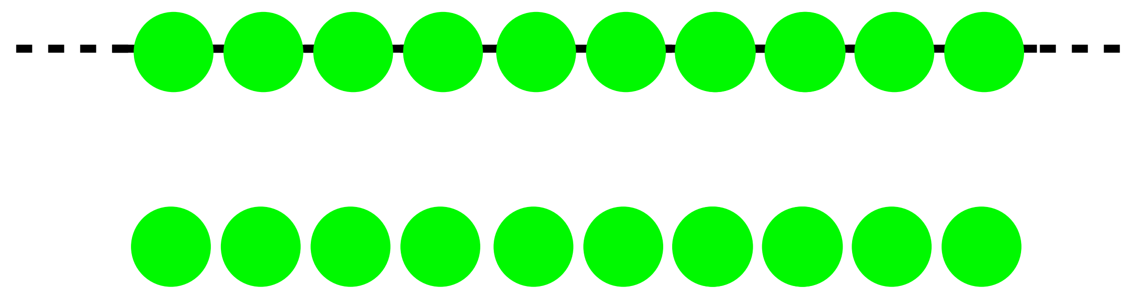

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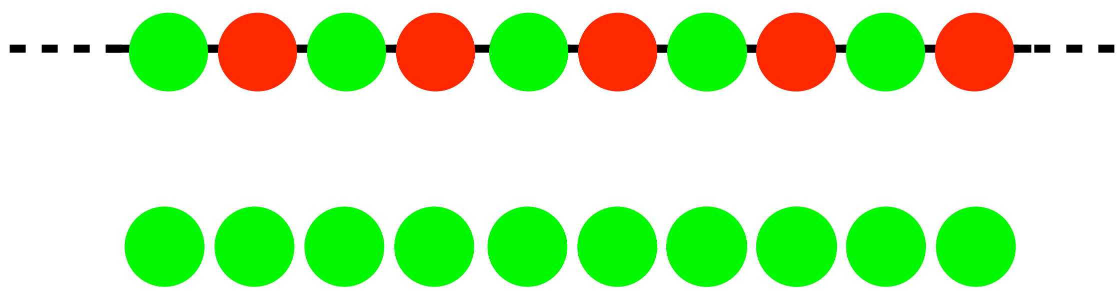

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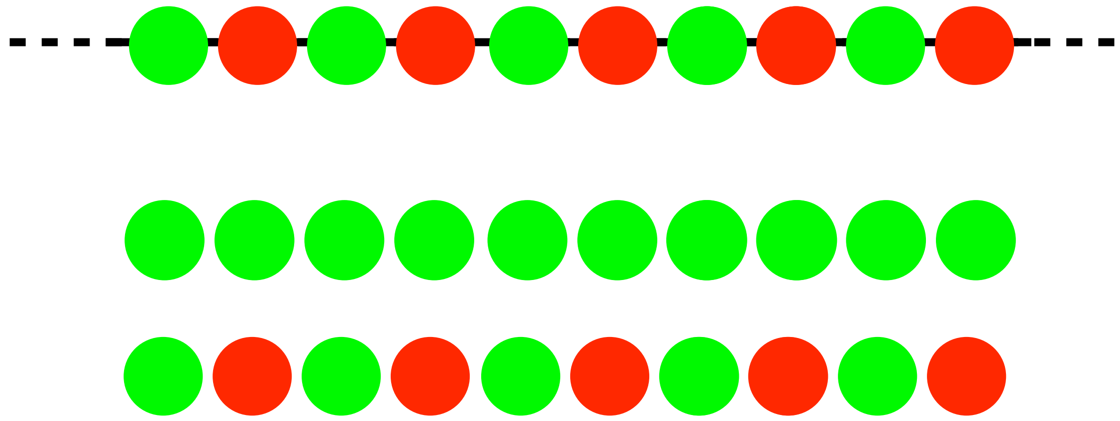

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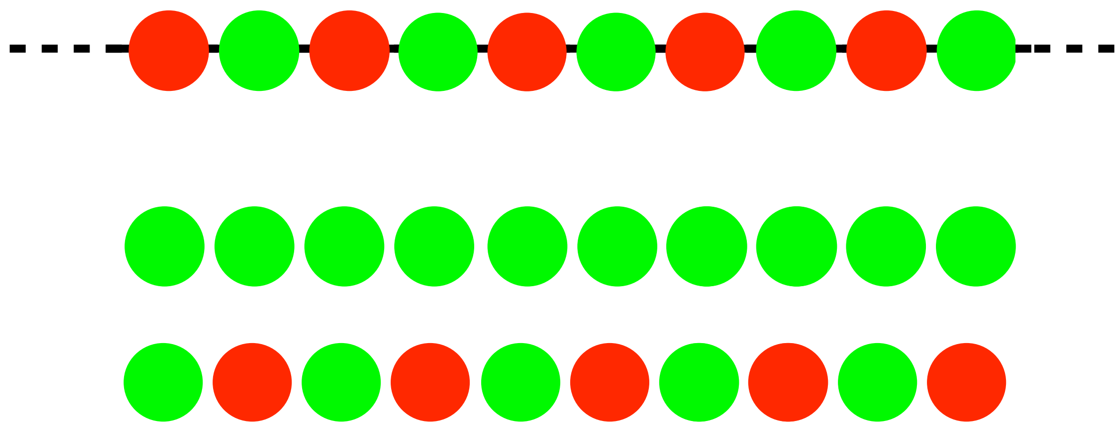

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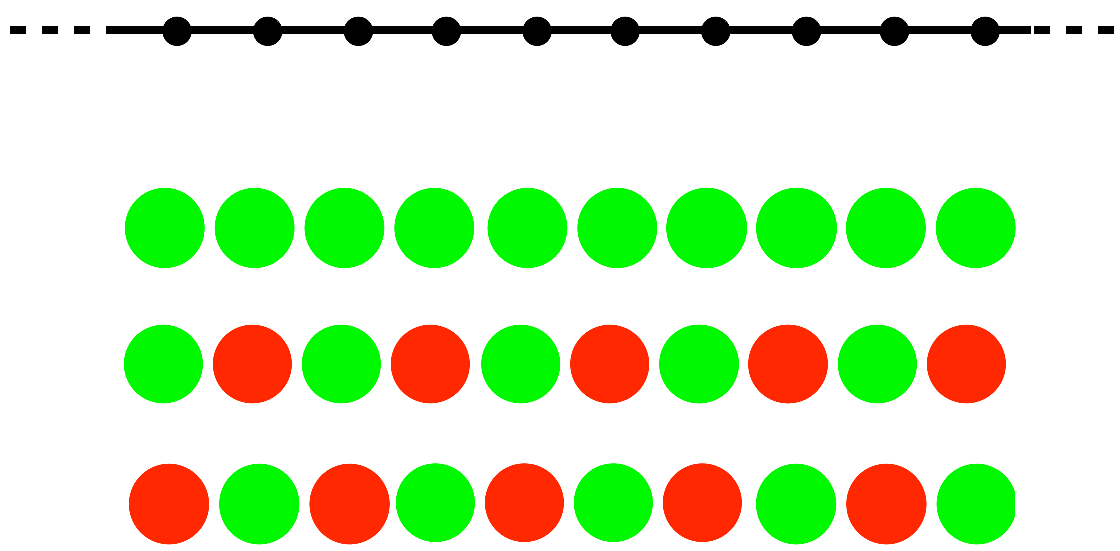

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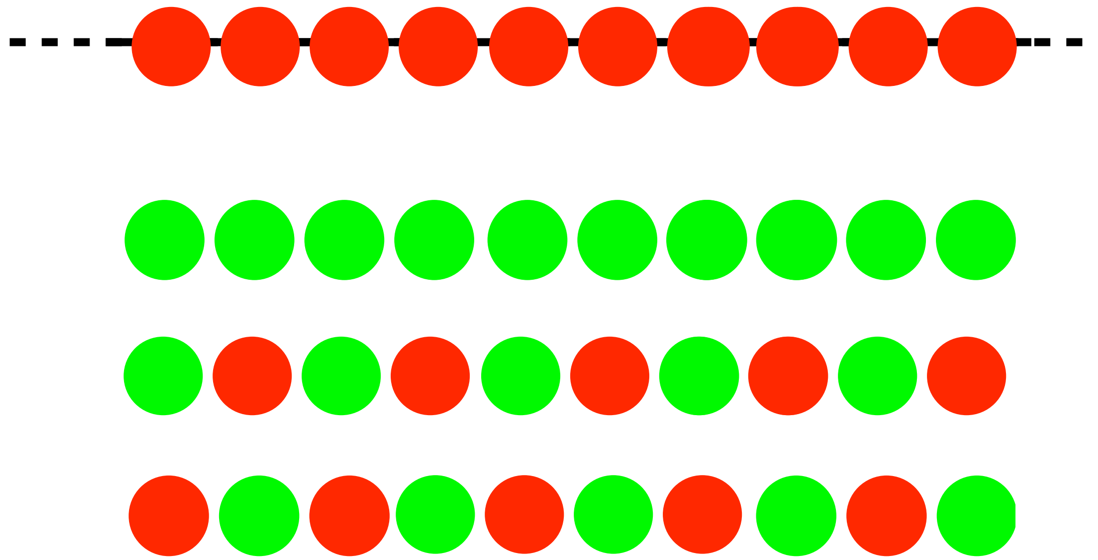

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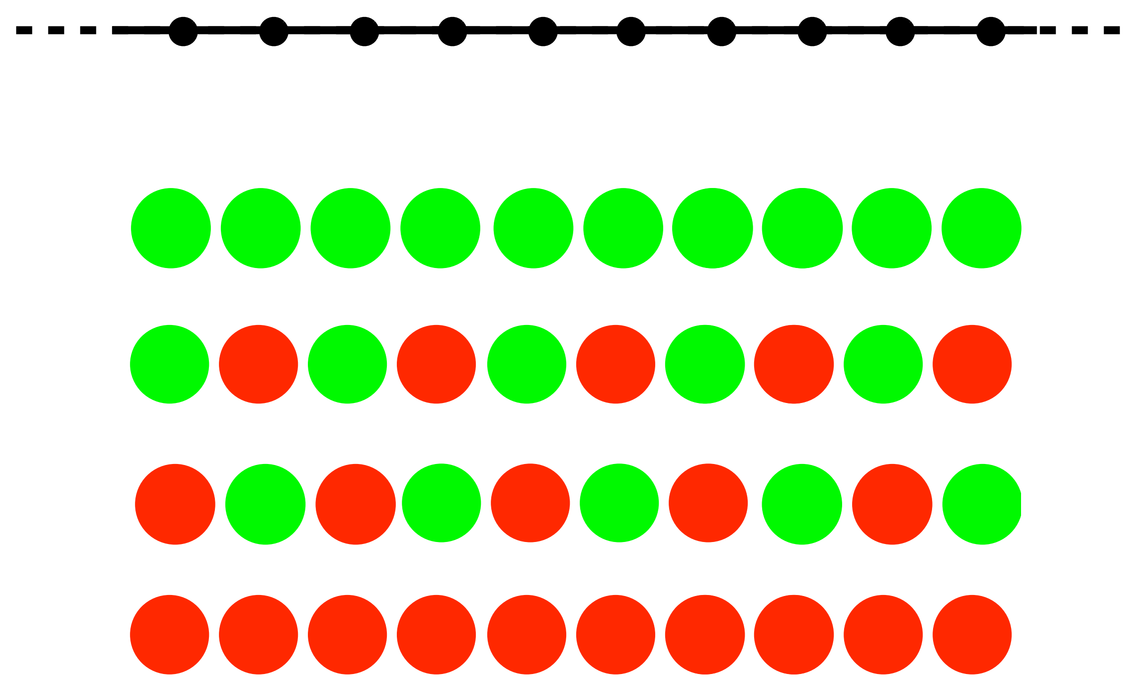

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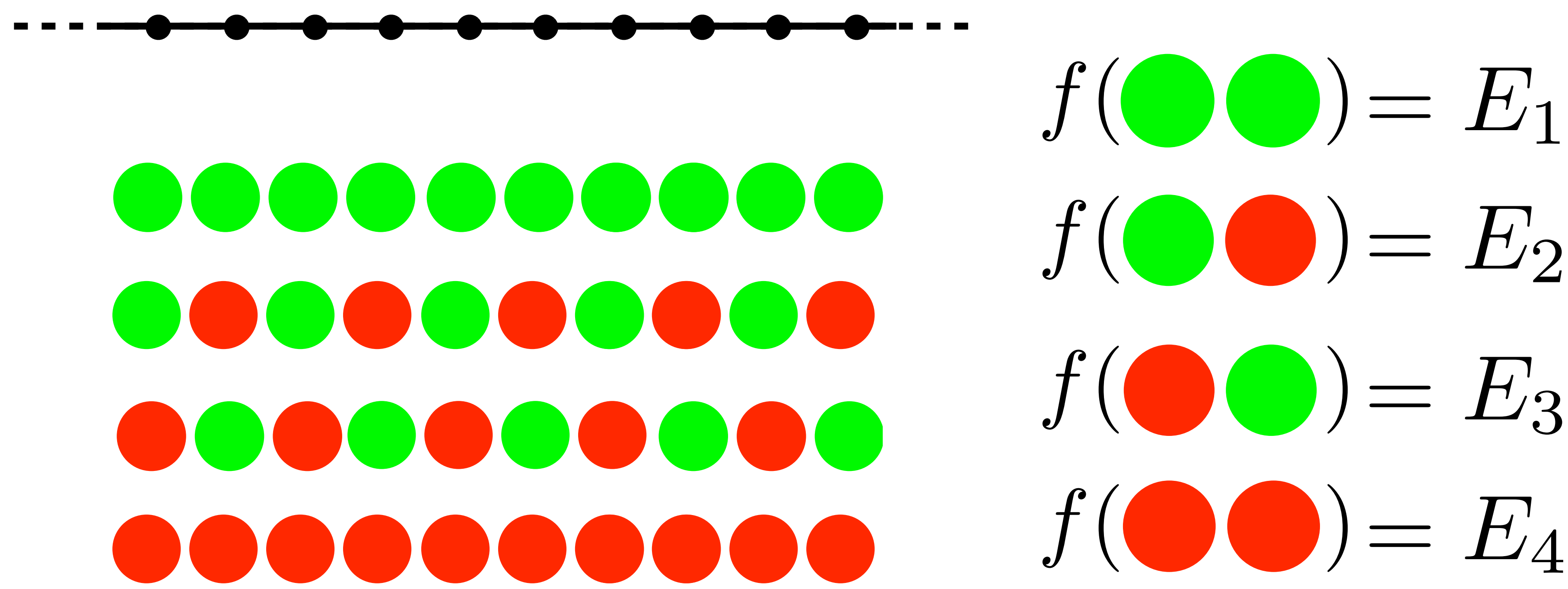
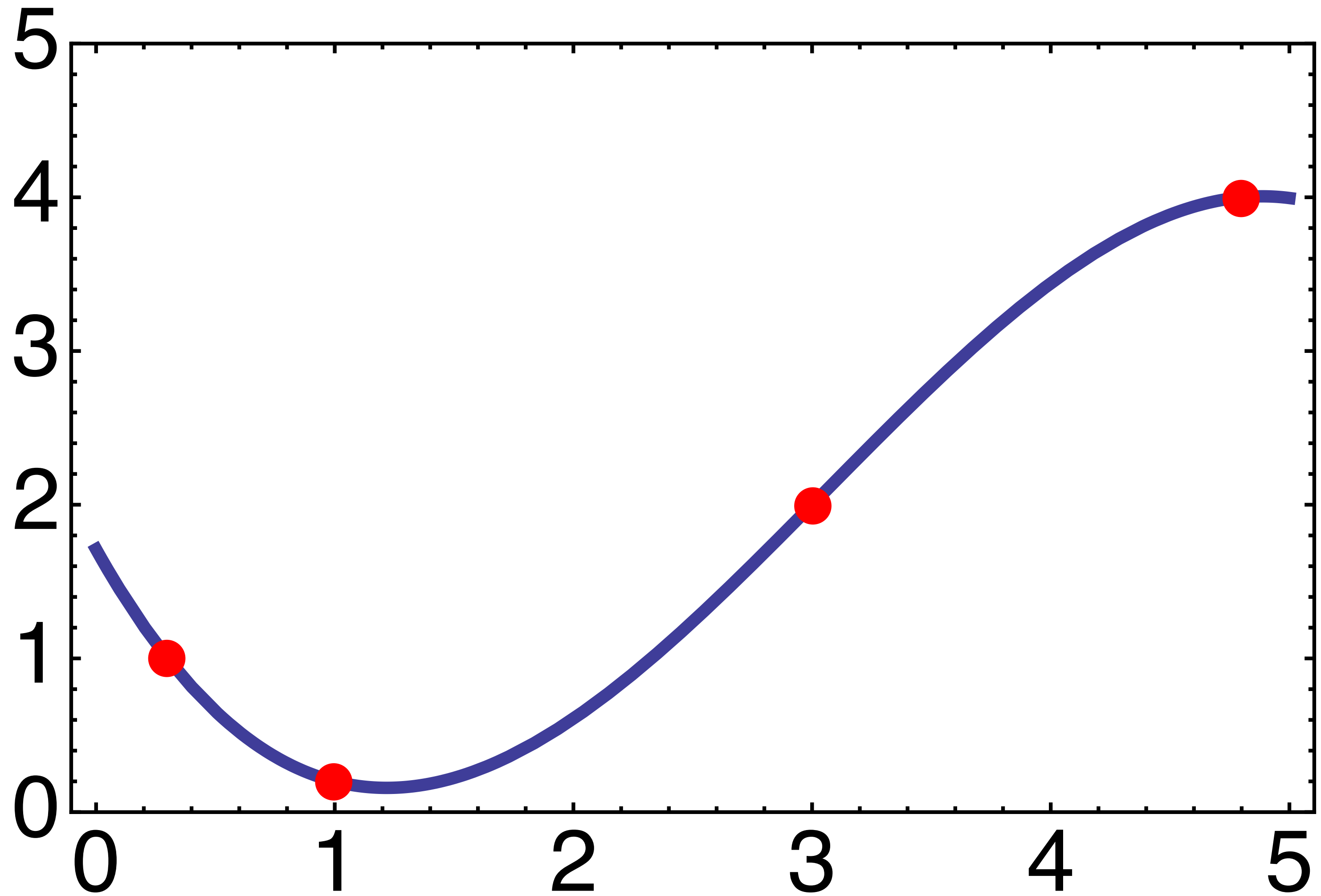


Expanding in a power series



$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots$$

optimize $\{a_0,\ a_1,\ a_2,\ \ldots\}$ to minimize error

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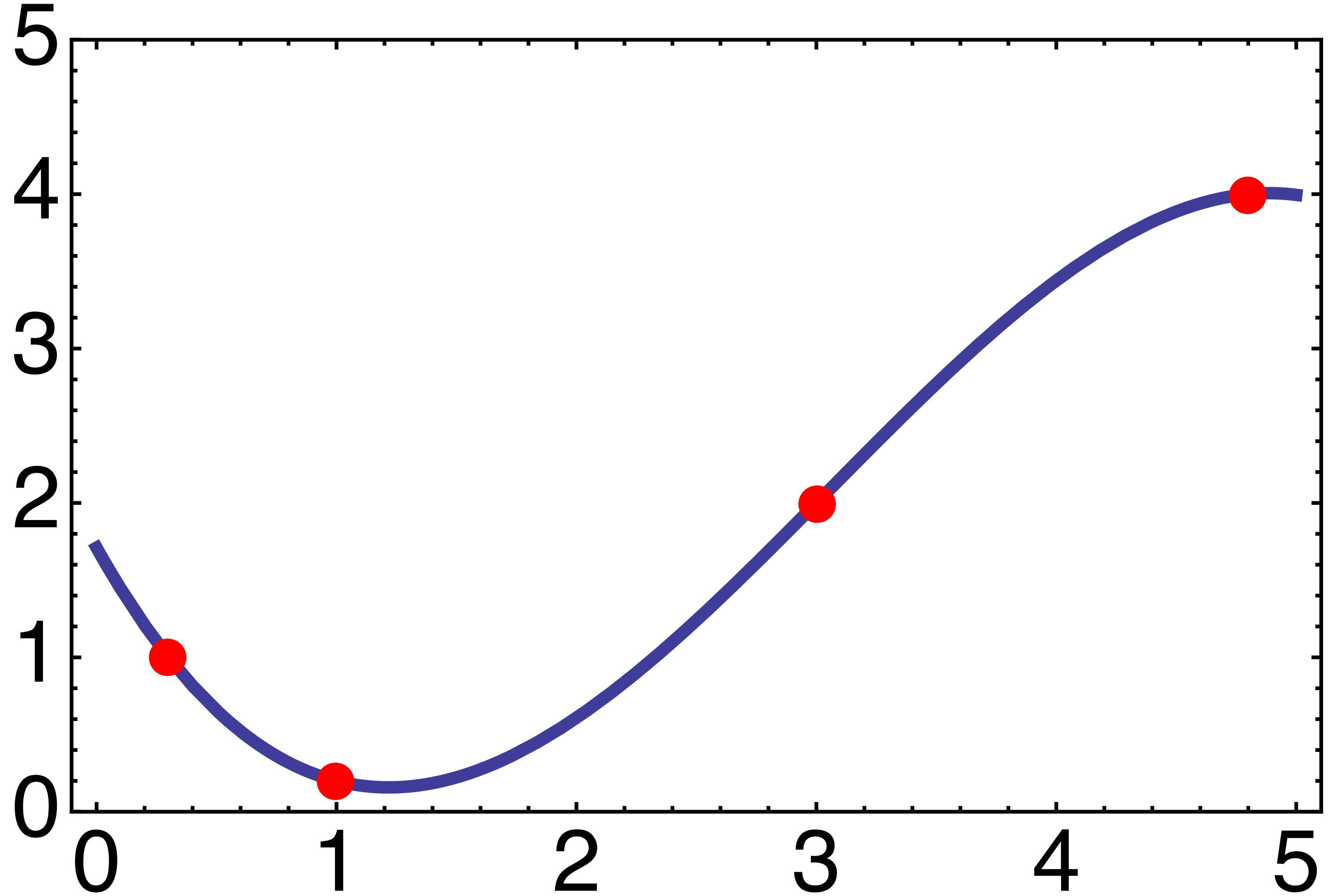
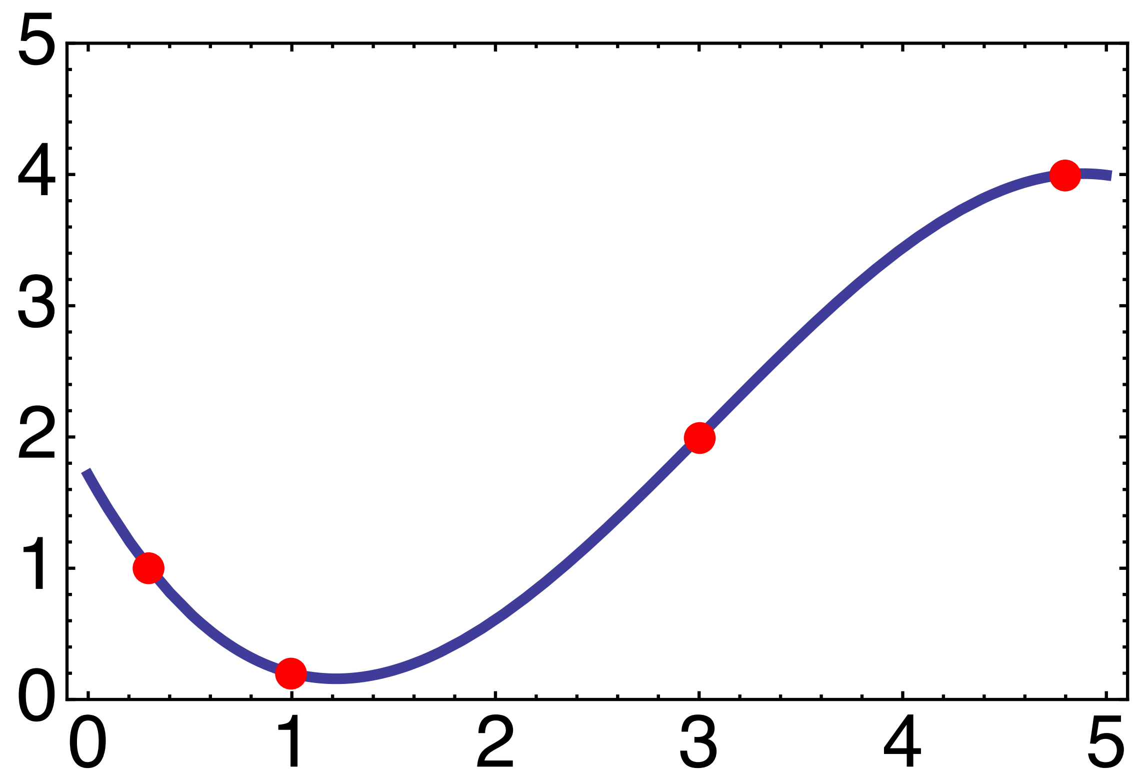


$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots$$

optimize $\{a_0,\, a_1,\, a_2,\, \ldots\}$ to minimize error

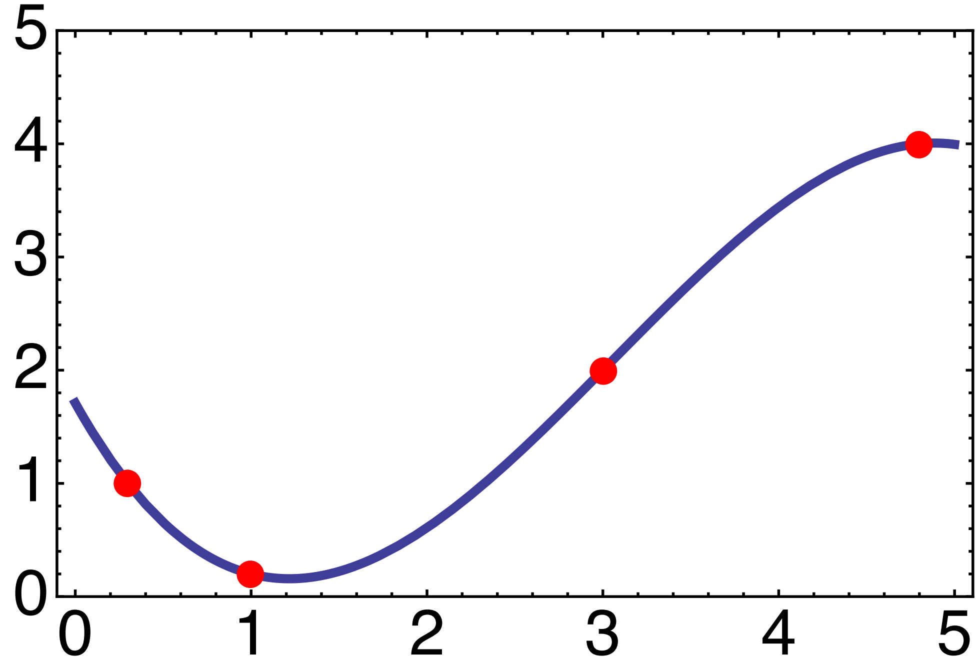
How do we find the coefficients?

Expanding in a power series



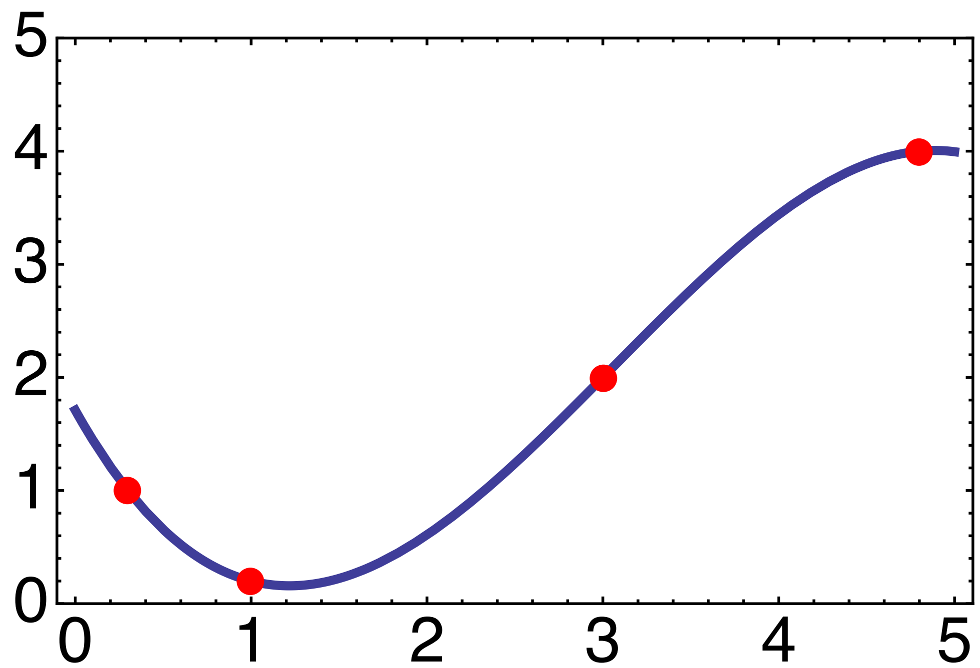
$$f(x_1) = a_0 + a_1 x_1 + a_2 x_1^2 + a_3 x_1^3$$
$$f(x_2) = a_0 + a_1 x_2 + a_2 x_2^2 + a_3 x_2^3$$
$$f(x_3) = a_0 + a_1 x_3 + a_2 x_3^2 + a_3 x_3^3$$
$$f(x_4) = a_0 + a_1 x_4 + a_2 x_4^2 + a_3 x_4^3$$

Expanding in a power series



$$\begin{pmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ f(x_4) \end{pmatrix} = \begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 \\ 1 & x_2 & x_2^2 & x_2^3 \\ 1 & x_3 & x_3^2 & x_3^3 \\ 1 & x_4 & x_4^2 & x_4^3 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

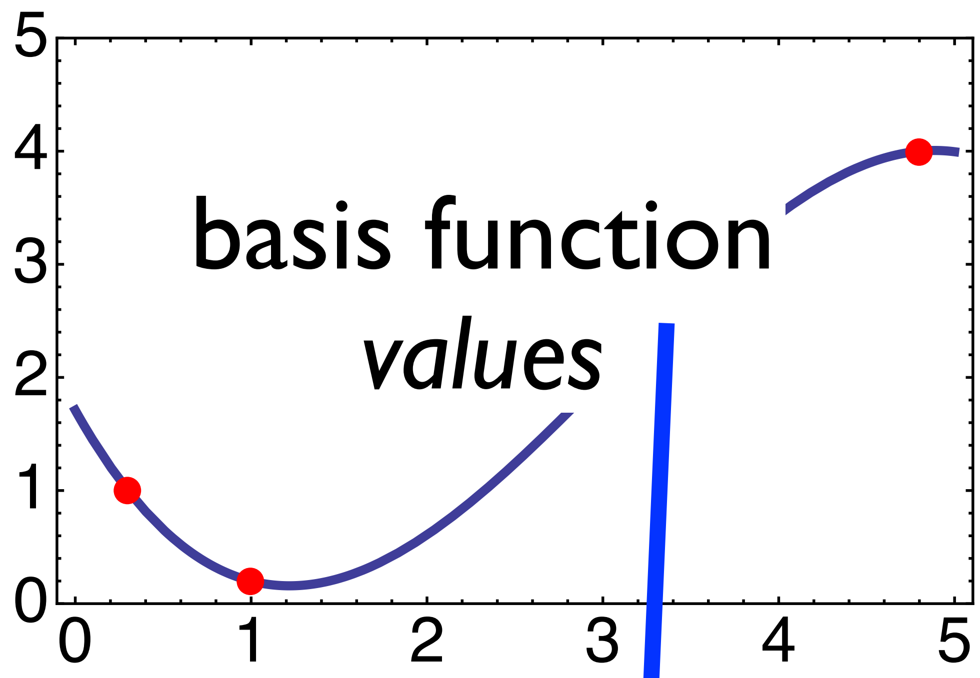
Expanding in a power series



Data

$$\begin{pmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ f(x_4) \end{pmatrix} = \begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 \\ 1 & x_2 & x_2^2 & x_2^3 \\ 1 & x_3 & x_3^2 & x_3^3 \\ 1 & x_4 & x_4^2 & x_4^3 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

Expanding in a power series



basis function *values*

Data

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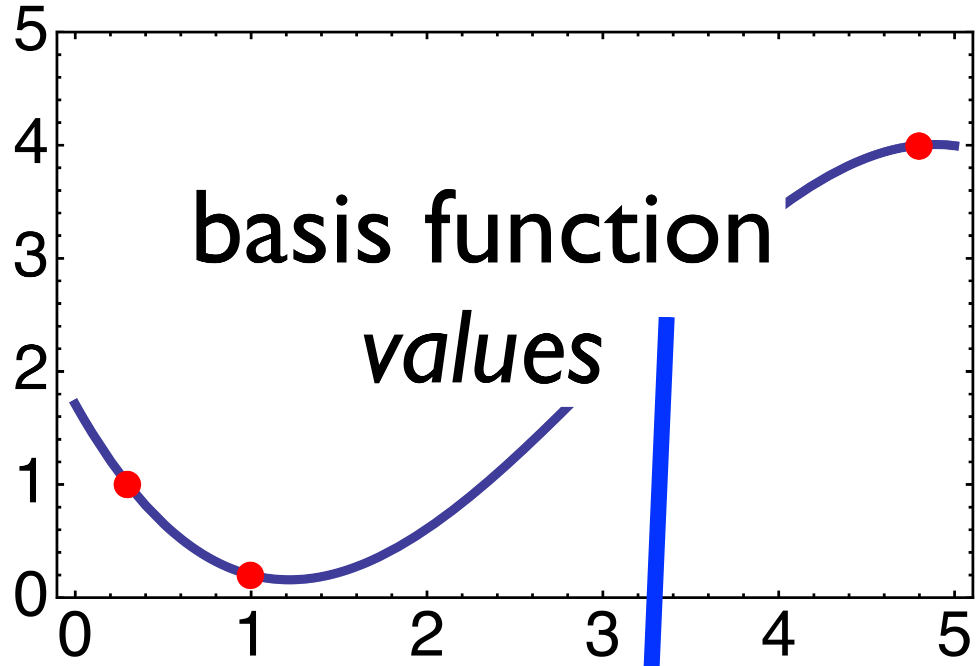

Data

basis function *values*

coefficients of the model

$$\begin{pmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ f(x_4) \end{pmatrix} = \begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 \\ 1 & x_2 & x_2^2 & x_2^3 \\ 1 & x_3 & x_3^2 & x_3^3 \\ 1 & x_4 & x_4^2 & x_4^3 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

Expanding configurational functions

$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots$$

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 + J_1 \bar{\Pi}^{\circ} + J_2 \bar{\Pi}^{\circ\circ} + J_3 \bar{\Pi}^{\circ\circ\circ} + \cdots$$

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$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \bigcirc + J_1 \bigcirc + J_2 \bigcirc\bigcirc + J_3 \bigcirc\bigcirc\bigcirc + \cdots$$

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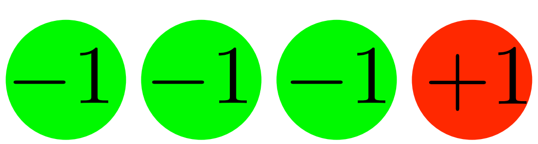

Expanding configurational functions

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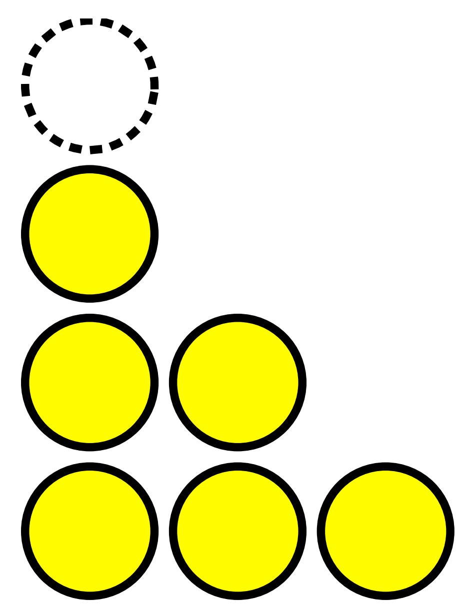
$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \, \circ + J_1 \bullet + J_2 \bullet\bullet + J_3 \bullet\bullet\bullet + \cdots$$

These are the "effective cluster interactions" (unknown expansion coefficients)

$$\{J_0, J_1, J_2, J_3, \cdots\}$$

These are the "clusters" or "figures" (basis functions)



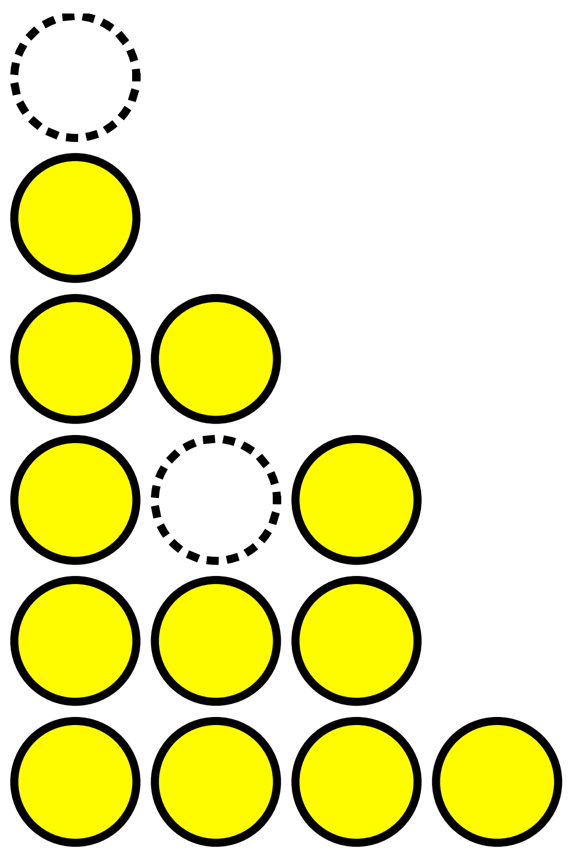
Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 + J_1\bar{\Pi}^{\circ} + J_2\bar{\Pi}^{\circ\circ} + J_3\bar{\Pi}^{\circ\circ\circ} + \cdots$$

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0\,\bigcirc + J_1\,\bullet + J_2\,\bullet\bullet + J_3\,\bullet\bullet\bullet + \cdots$$

Calculate the correlations...



Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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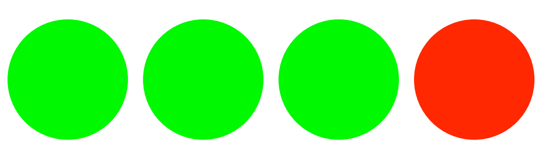
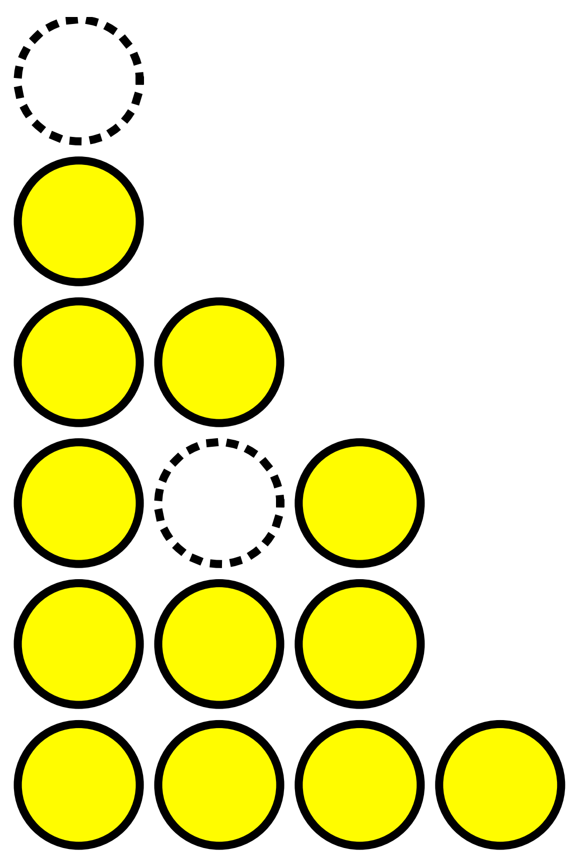
$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \bigcirc + J_1 \bigcirc + J_2 \bigcirc\bigcirc + J_3 \bigcirc\bigcirc\bigcirc + \cdots$$

Calculate the correlations...





Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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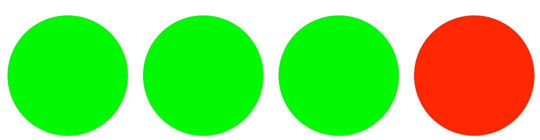
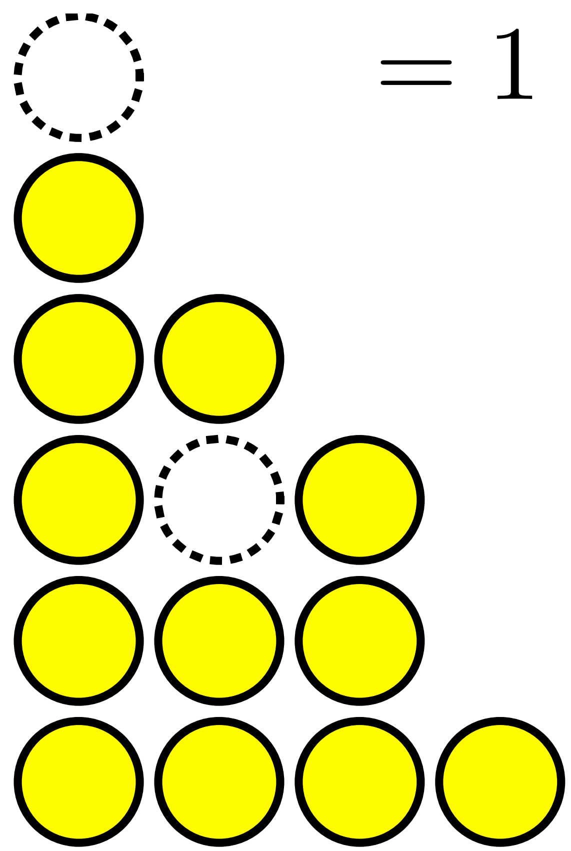
Calculate the correlations...





$= 1$

Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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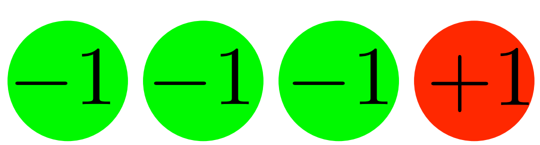

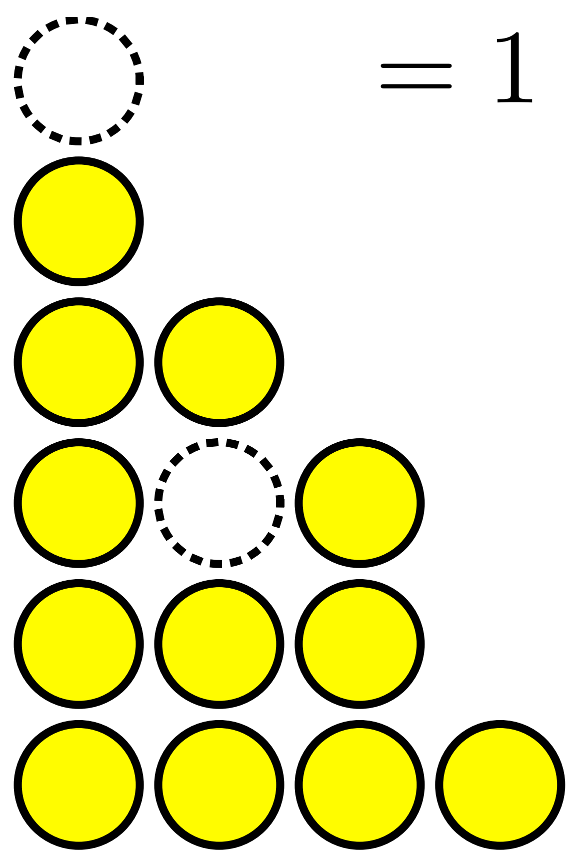

Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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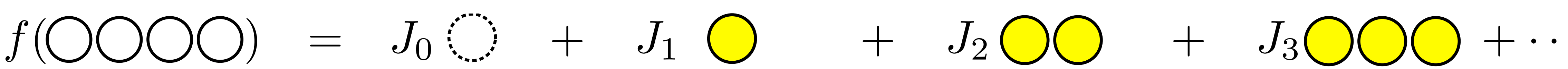
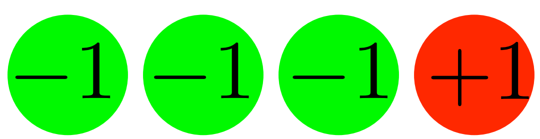
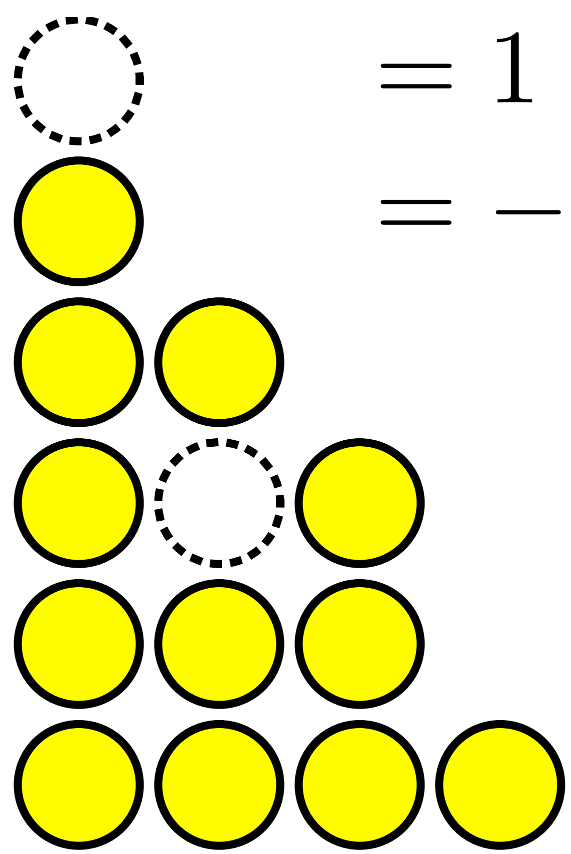


Calculate the correlations...





$= 1$

$= -\frac{1}{2}$

Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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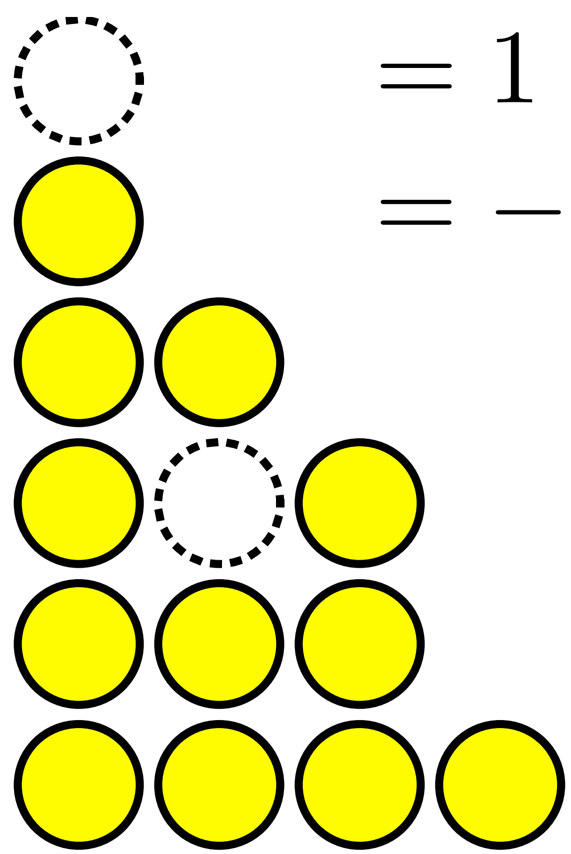

$$= 1$$

$$= -\frac{1}{2}$$

Cluster Expansion: Example

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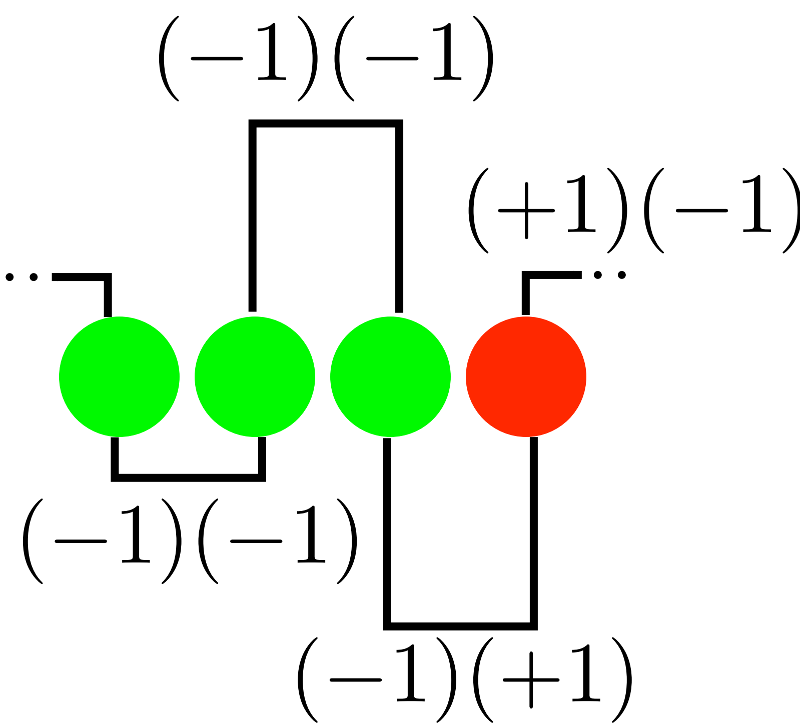

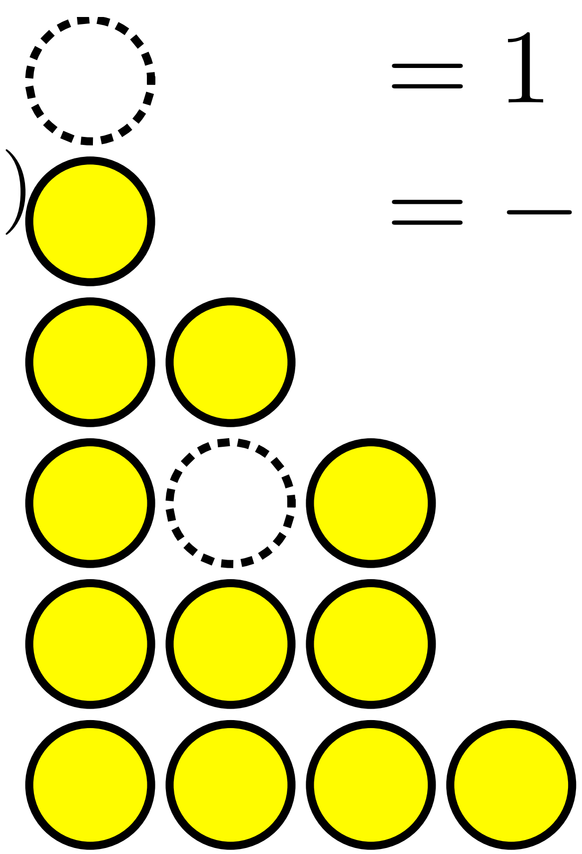

$= 1$

$= -\frac{1}{2}$

Cluster Expansion: Example

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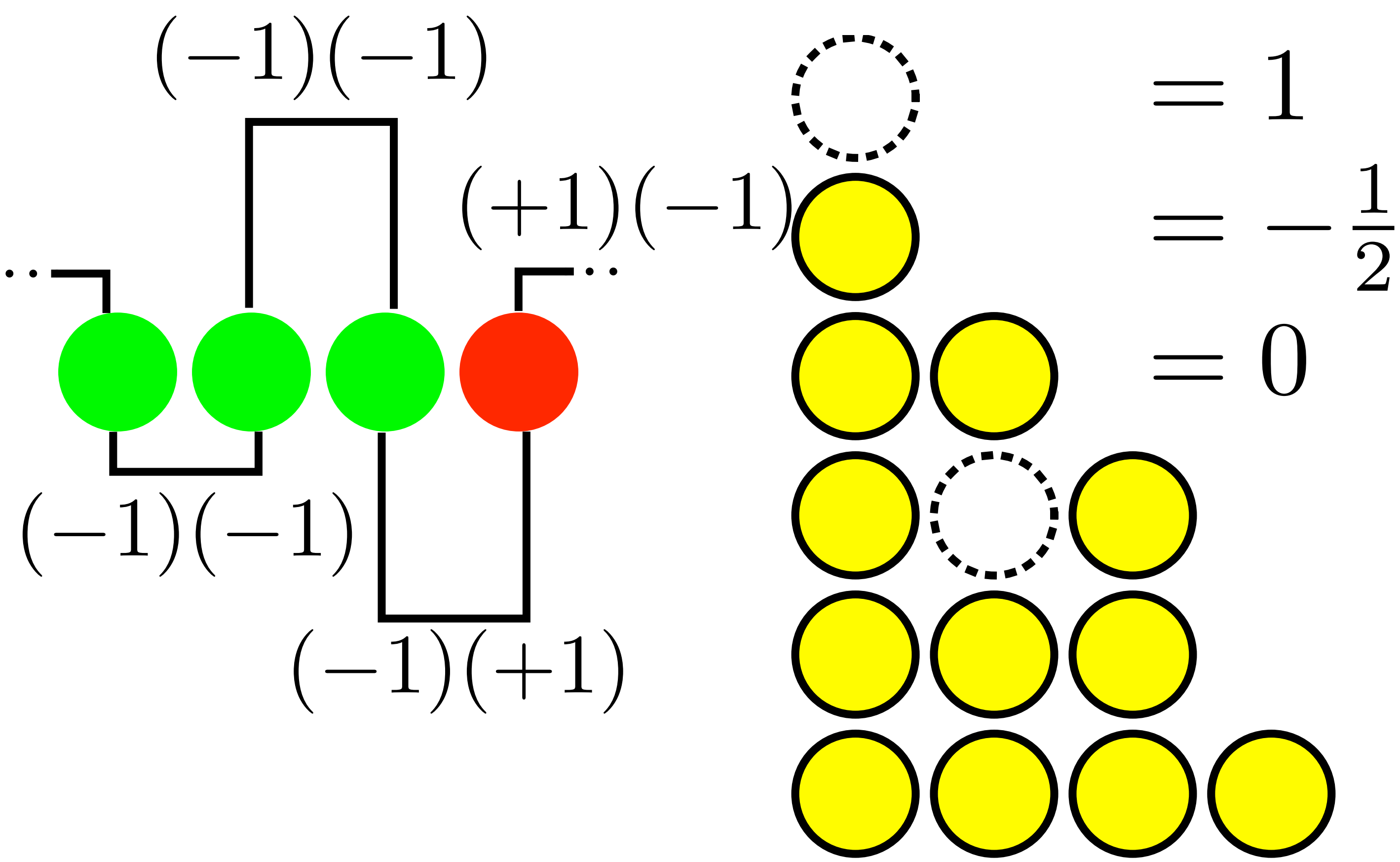
$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \, (\text{empty cluster}) + J_1 \, \bullet + J_2 \, \bullet\bullet + J_3 \, \bullet\bullet\bullet + \cdots$$

Calculate the correlations...



Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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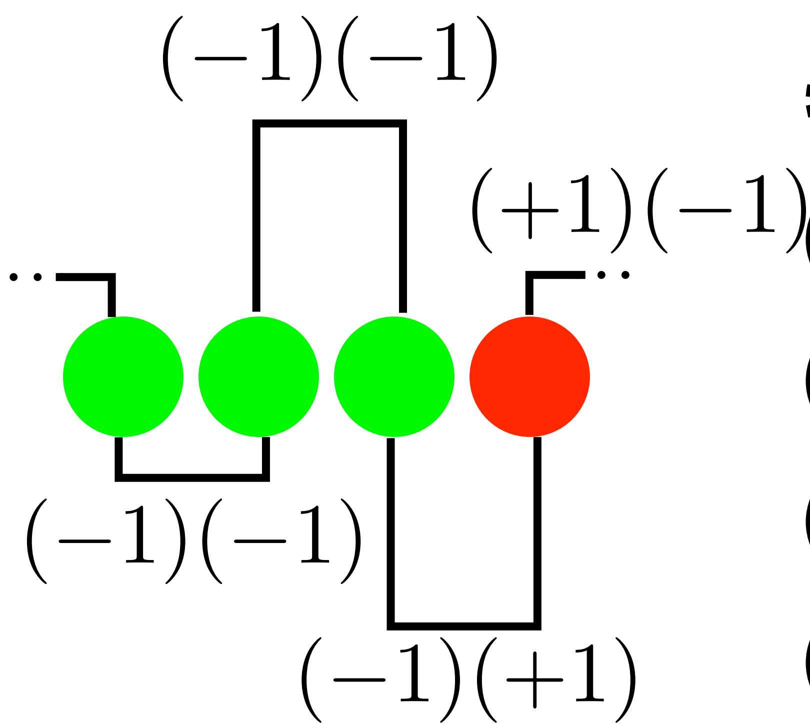

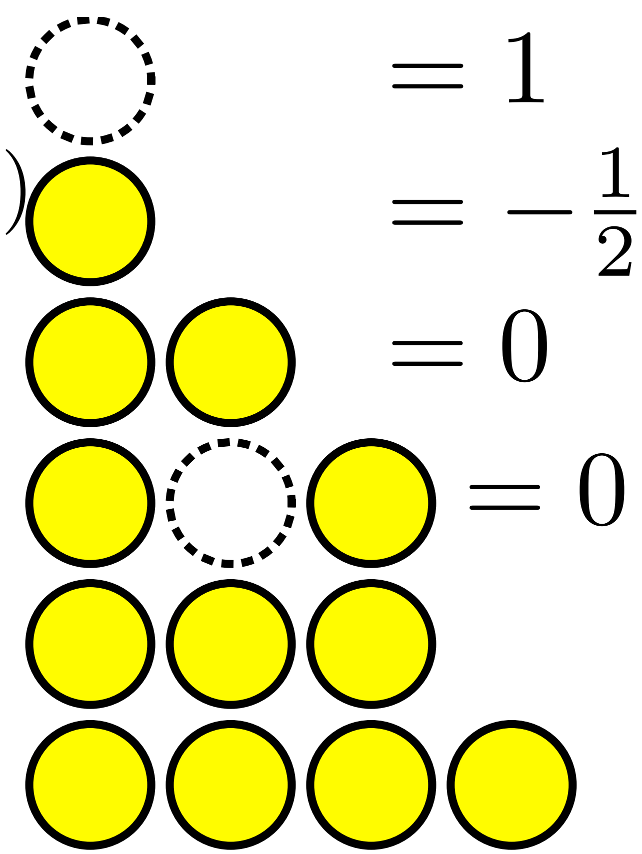

Cluster Expansion: Example

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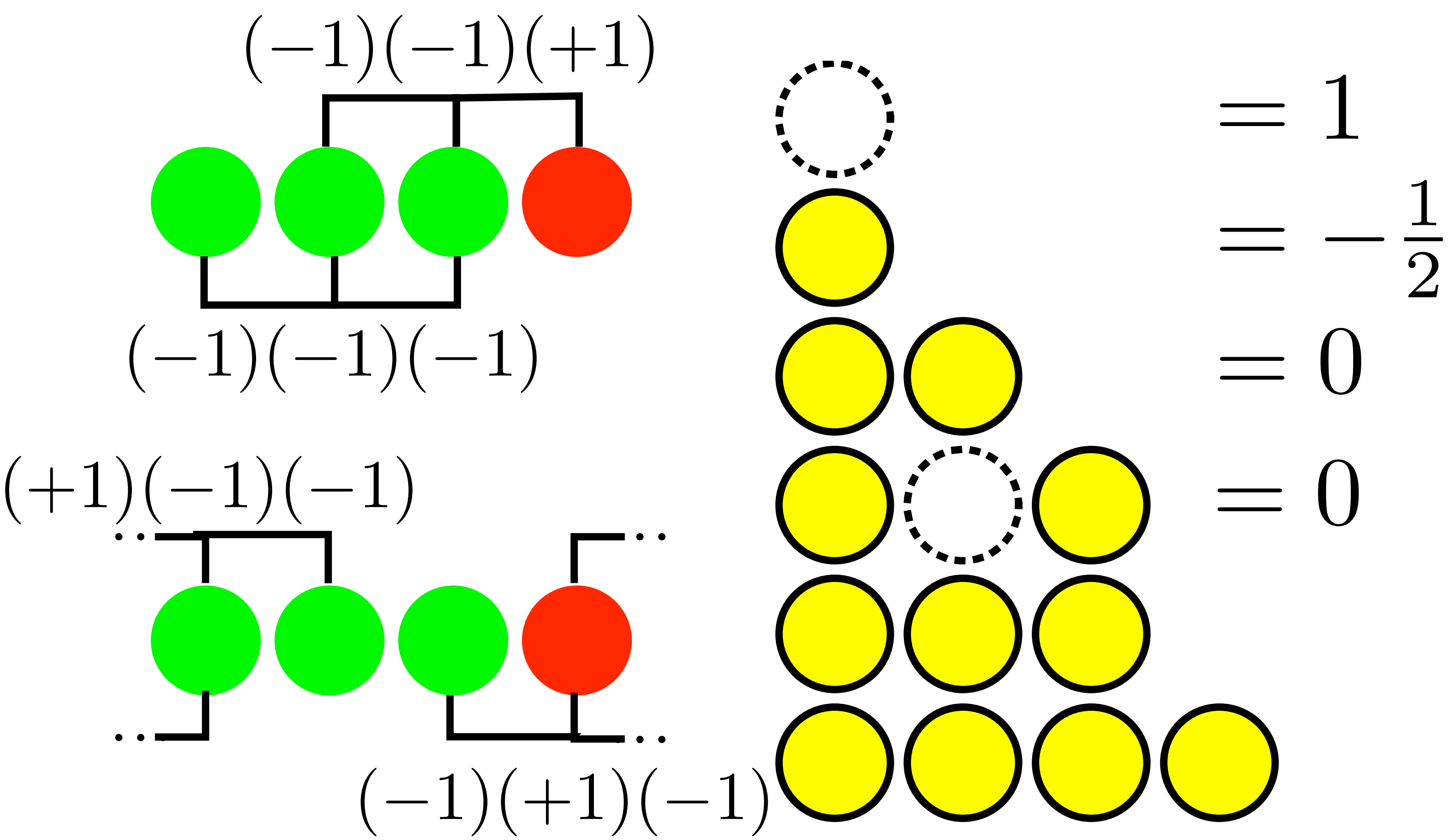

Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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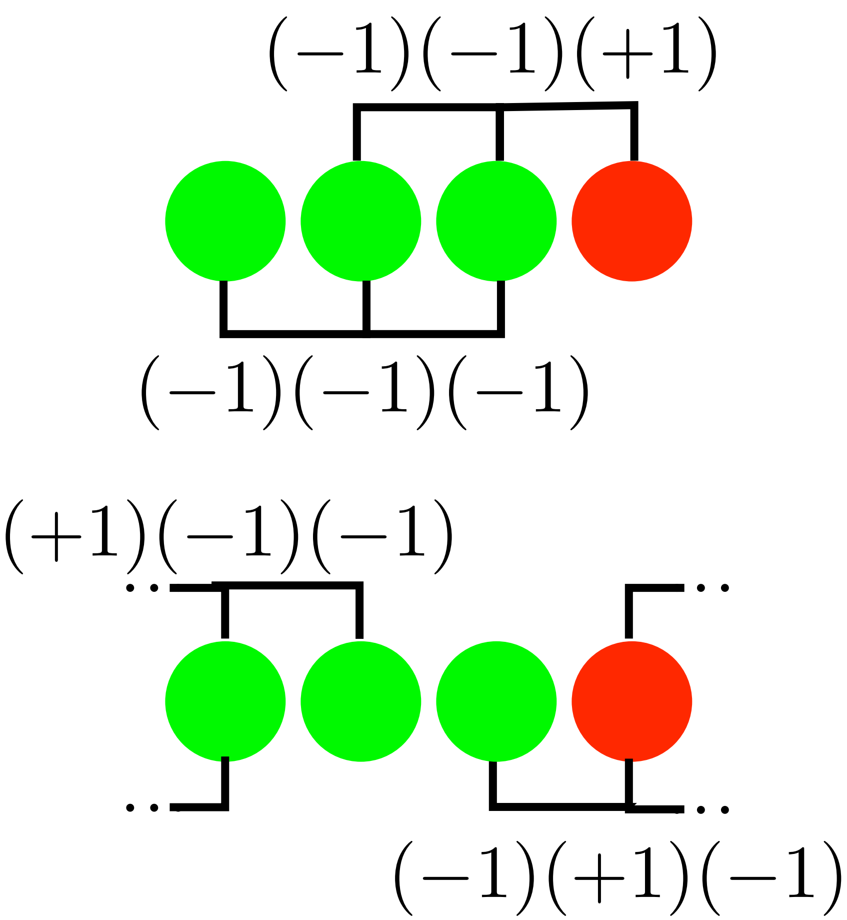

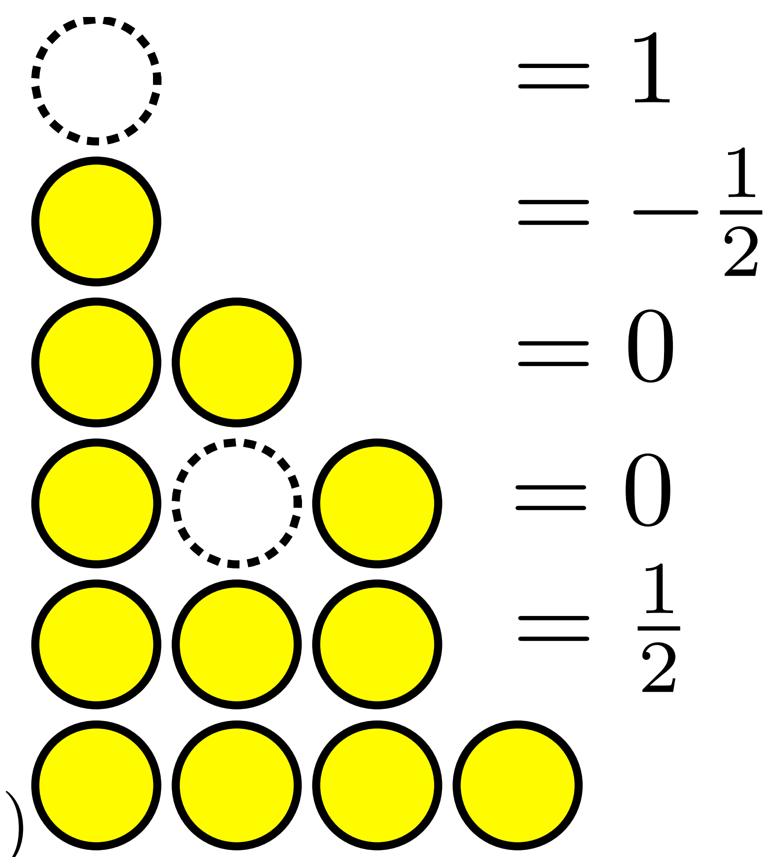

Cluster Expansion: Example

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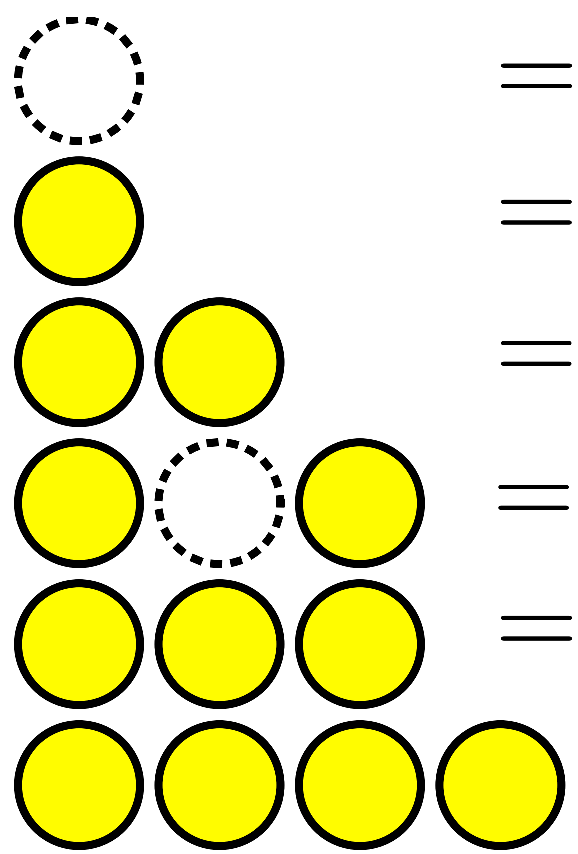

$= 1$

$= -\frac{1}{2}$

$= 0$

$= 0$

$= \frac{1}{2}$

$= -1$

Cluster Expansion: Example

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = \frac{J_0}{N}\sum_i^{\circ\circ\circ\circ} 1 + J_1 \sum_i^{\circ\circ\circ\circ} \bigcirc_i + J_2 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} + J_3 \sum_i^{\circ\circ\circ\circ} \bigcirc_i \bigcirc_{i+1} \bigcirc_{i+2} + \cdots$$

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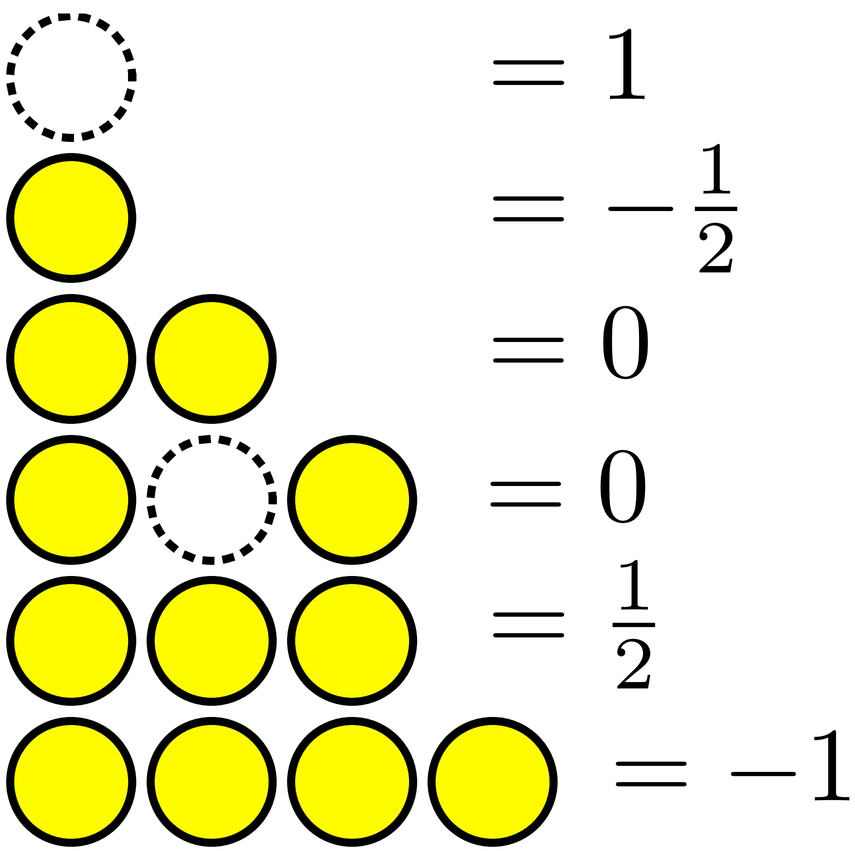
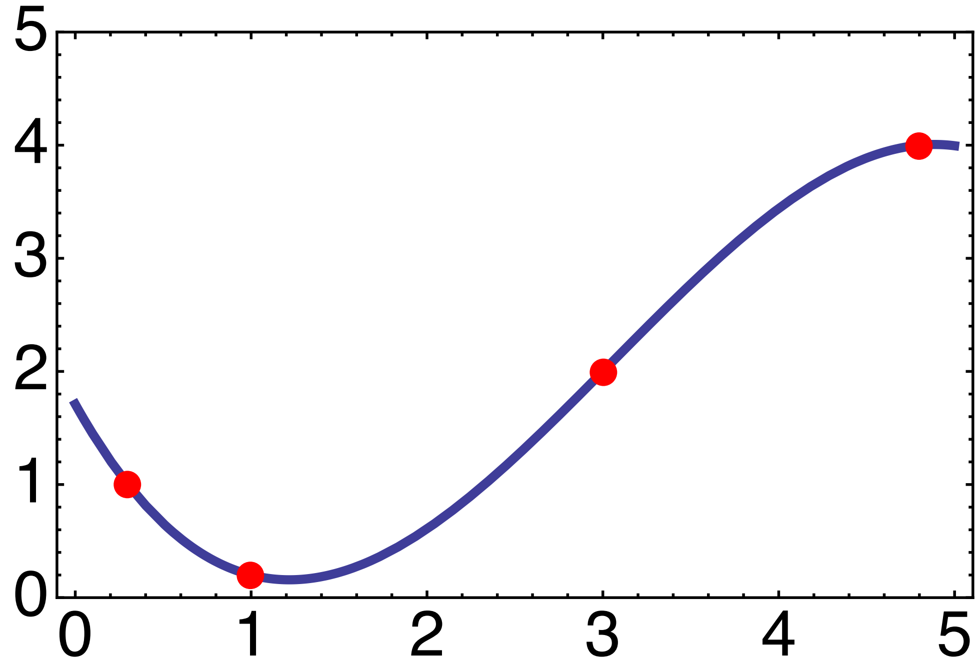
$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \circ + J_1 \bullet + J_2 \bullet\bullet + J_3 \bullet\bullet\bullet + \cdots$$



$$\begin{pmatrix} 1 & -\frac{1}{2} & 0 & 0 & \frac{1}{2} & -1 \end{pmatrix}$$

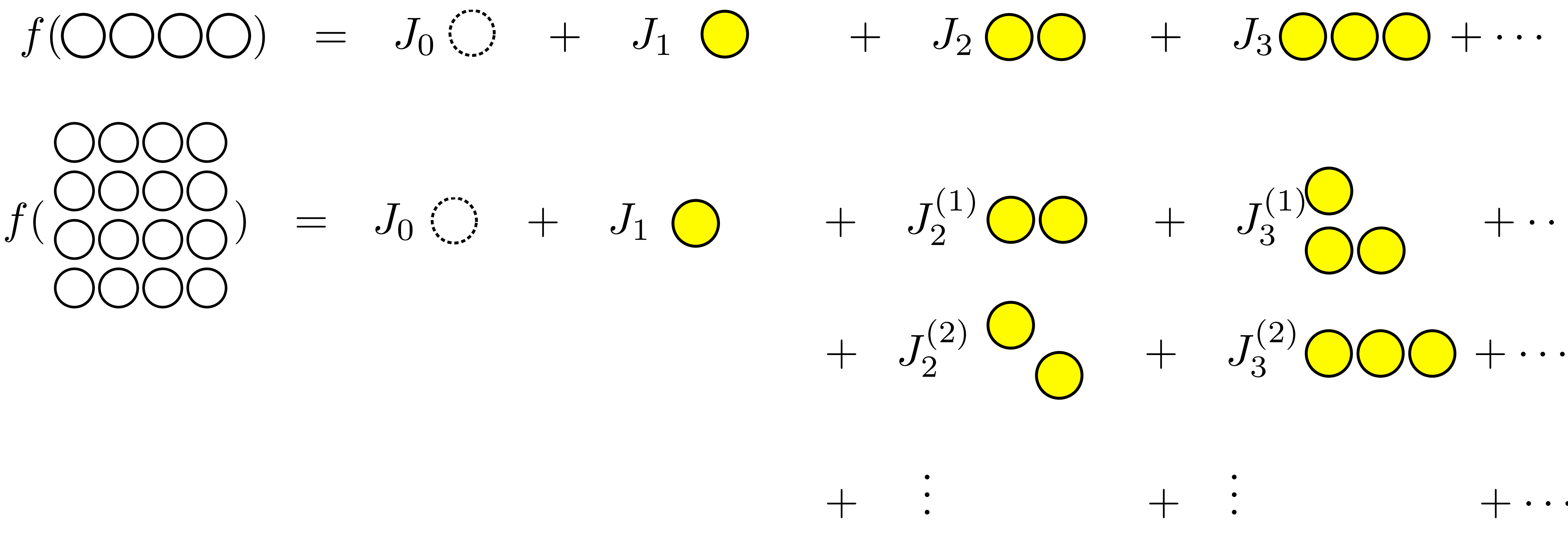
Expanding in a power series



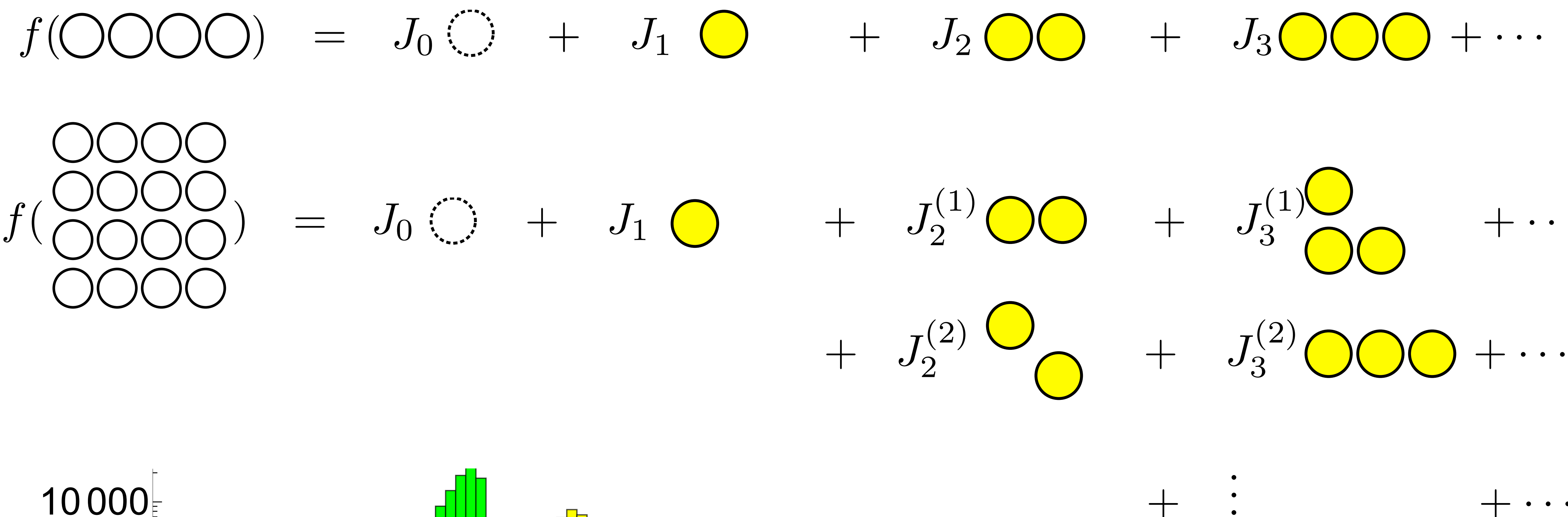
$$\begin{pmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ f(x_4) \end{pmatrix} = \begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 \\ 1 & x_2 & x_2^2 & x_2^3 \\ 1 & x_3 & x_3^2 & x_3^3 \\ 1 & x_4 & x_4^2 & x_4^3 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

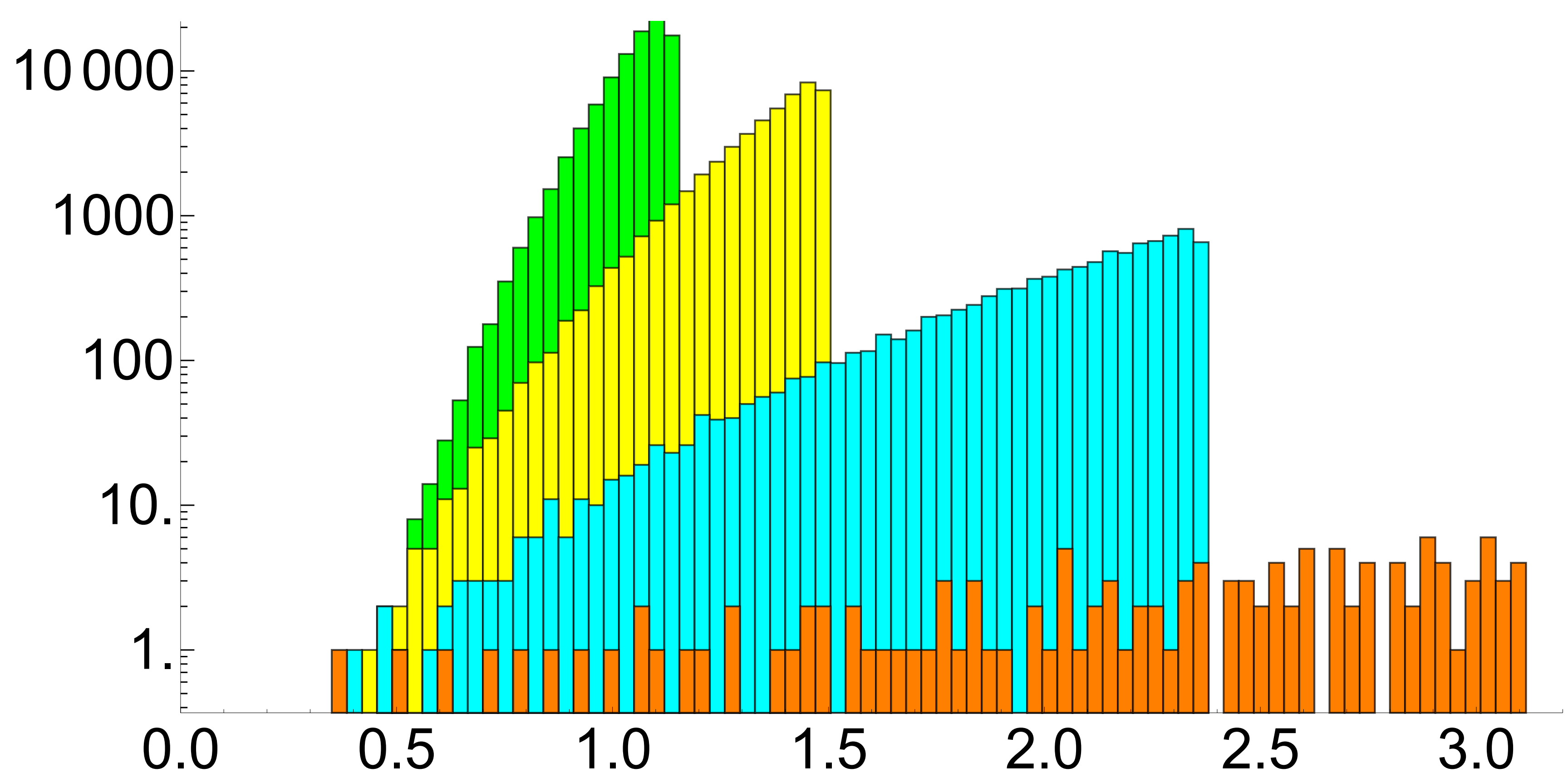
$$\vec{\Pi} = \begin{pmatrix} 1 & -\frac{1}{2} & 0 & 0 & \frac{1}{2} & -1 \end{pmatrix}$$

In more than one dimension...

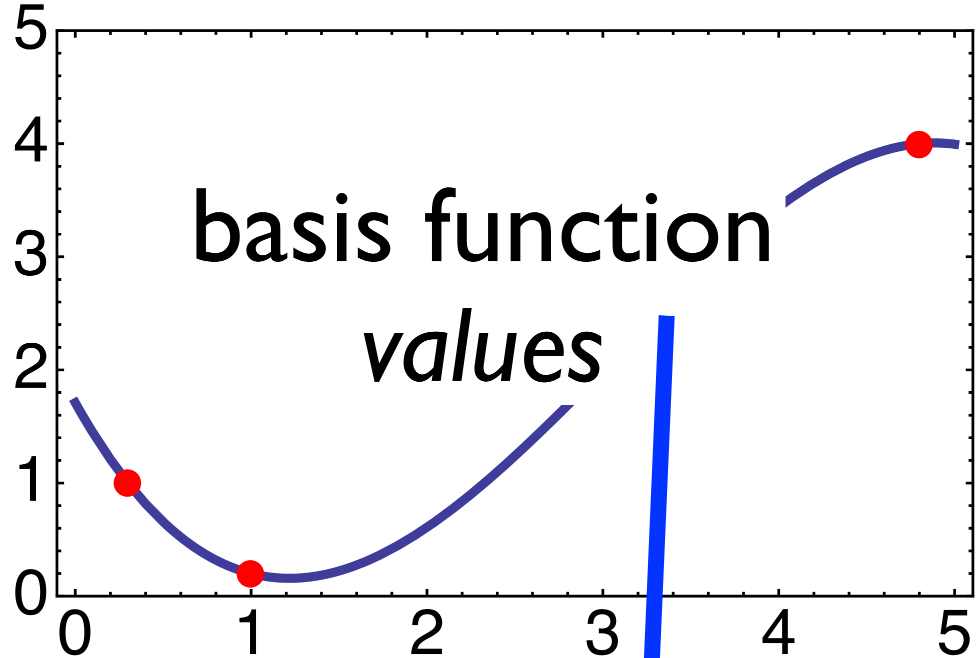


In more than one dimension...





Expanding in a power series



Data

basis function *values*

coefficients of the model

$$\begin{pmatrix} f(x_1) \\ f(x_2) \\ f(x_3) \\ f(x_4) \end{pmatrix} = \begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 \\ 1 & x_2 & x_2^2 & x_2^3 \\ 1 & x_3 & x_3^2 & x_3^3 \\ 1 & x_4 & x_4^2 & x_4^3 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

Compressive sensing: It's like magic

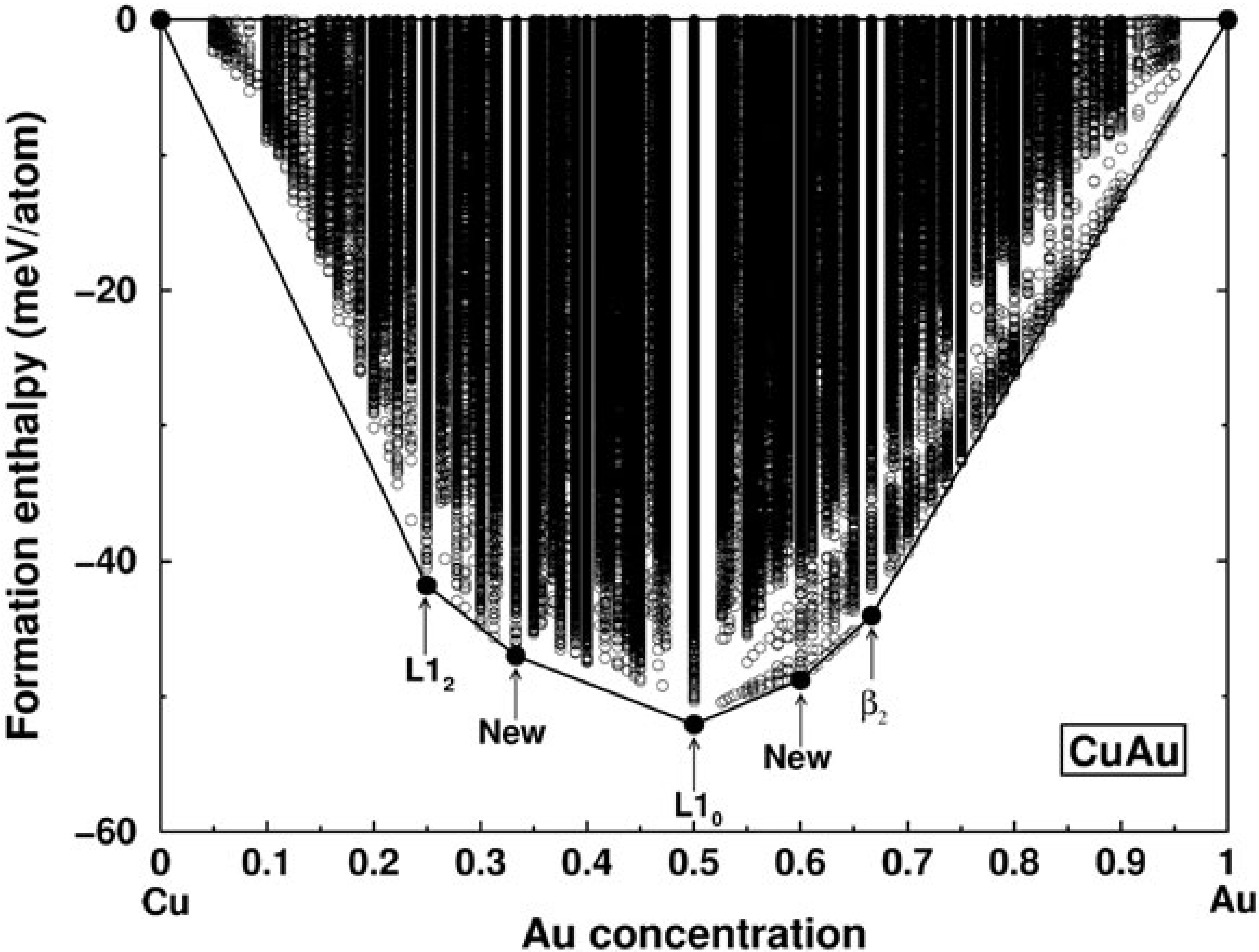
More info at the end of the talk

Once you have a good physical model, what can you do with it?

Once you have a good physical model, what can you do with it?

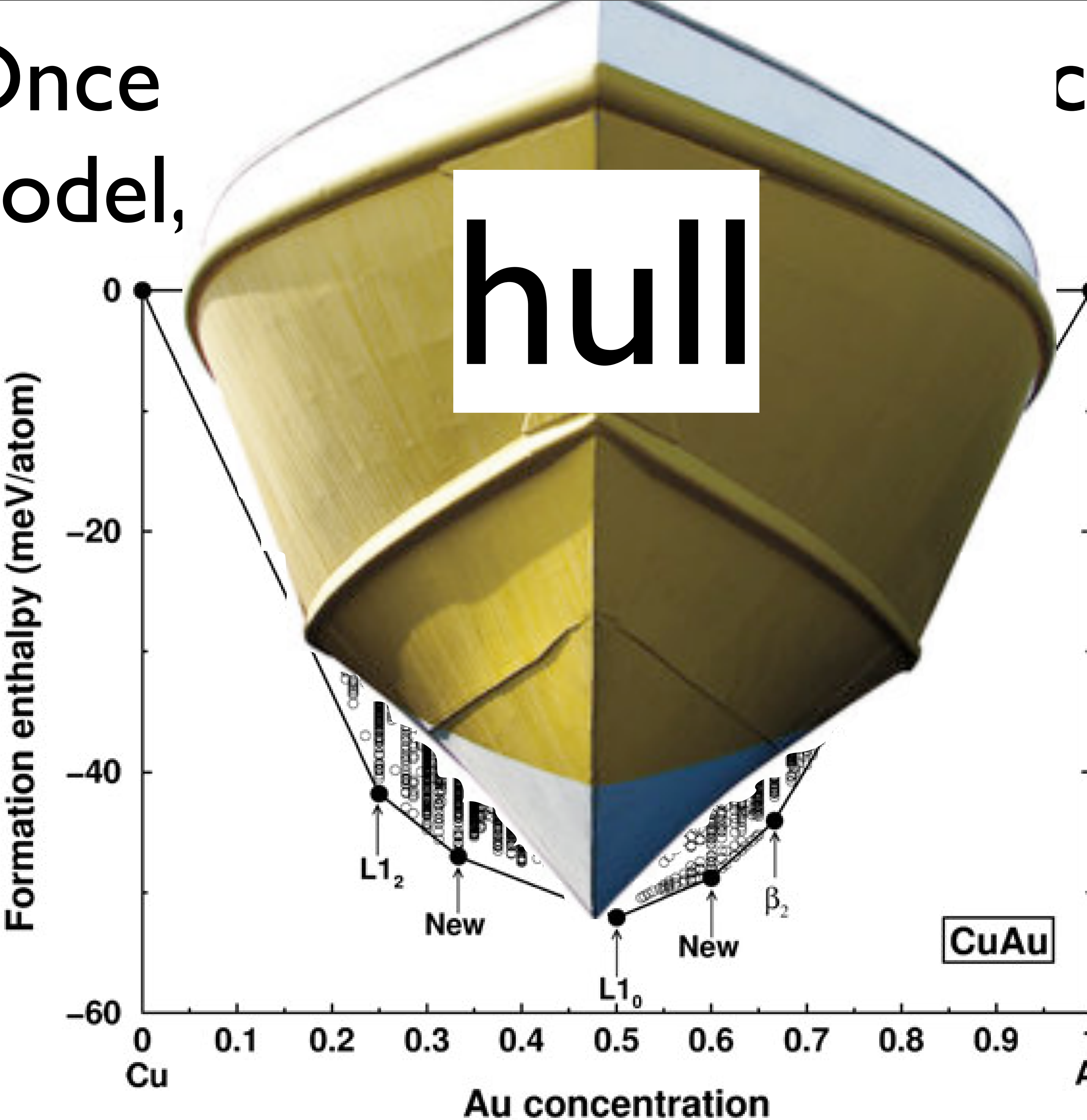
Calculate the energy of
millions of configurations

Once you have a good physical model, what can you do with it?



Once cal
model, it?

hull



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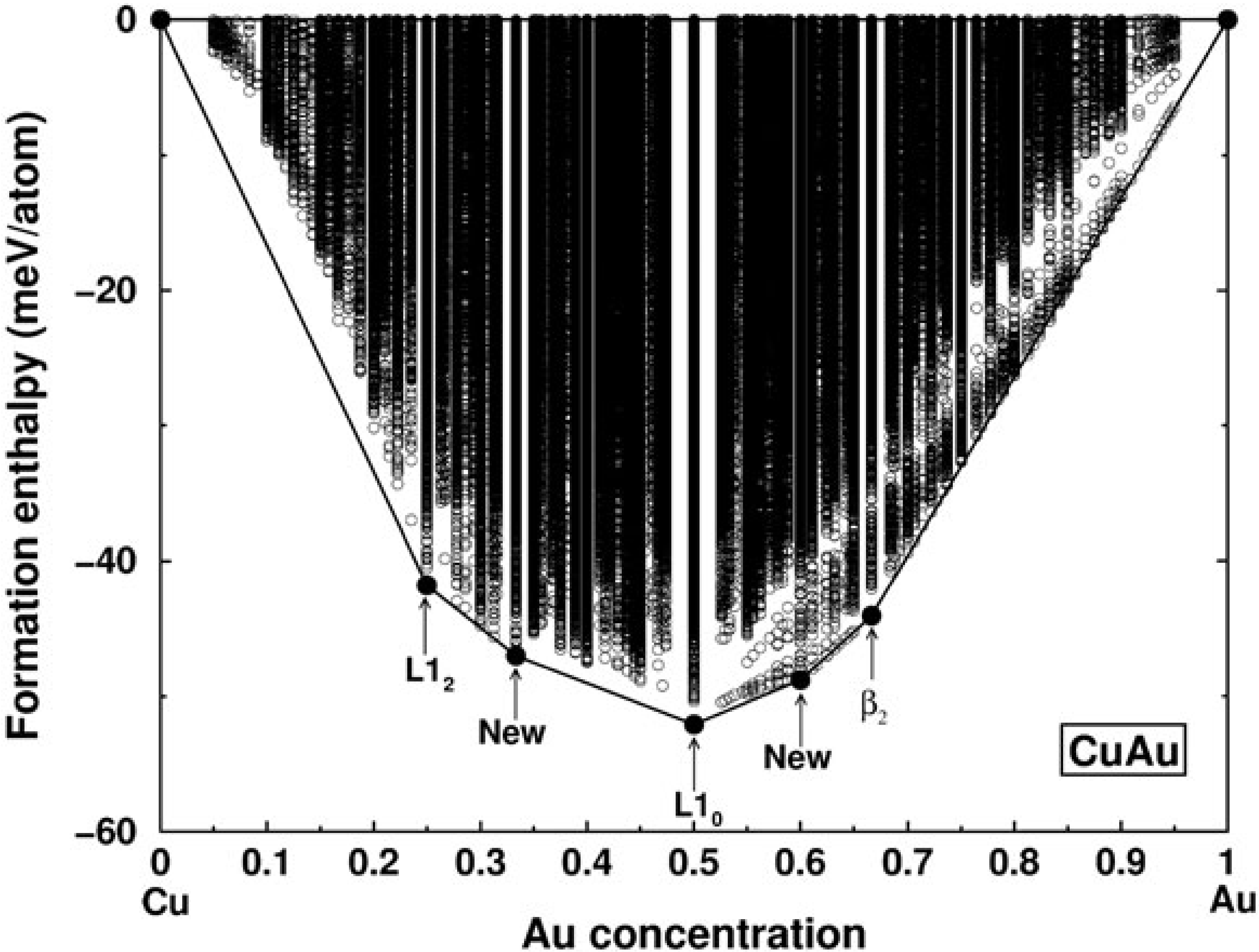
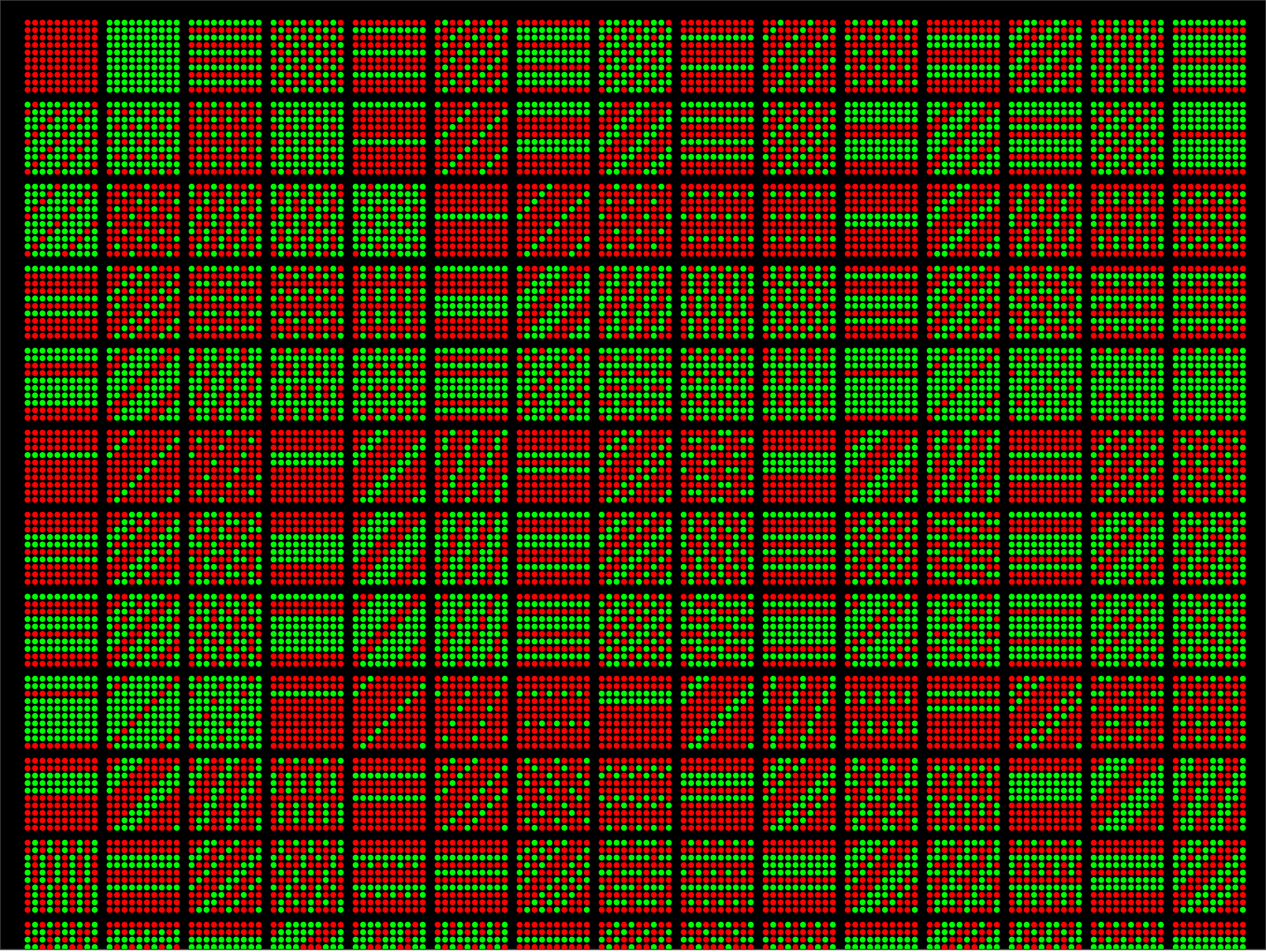
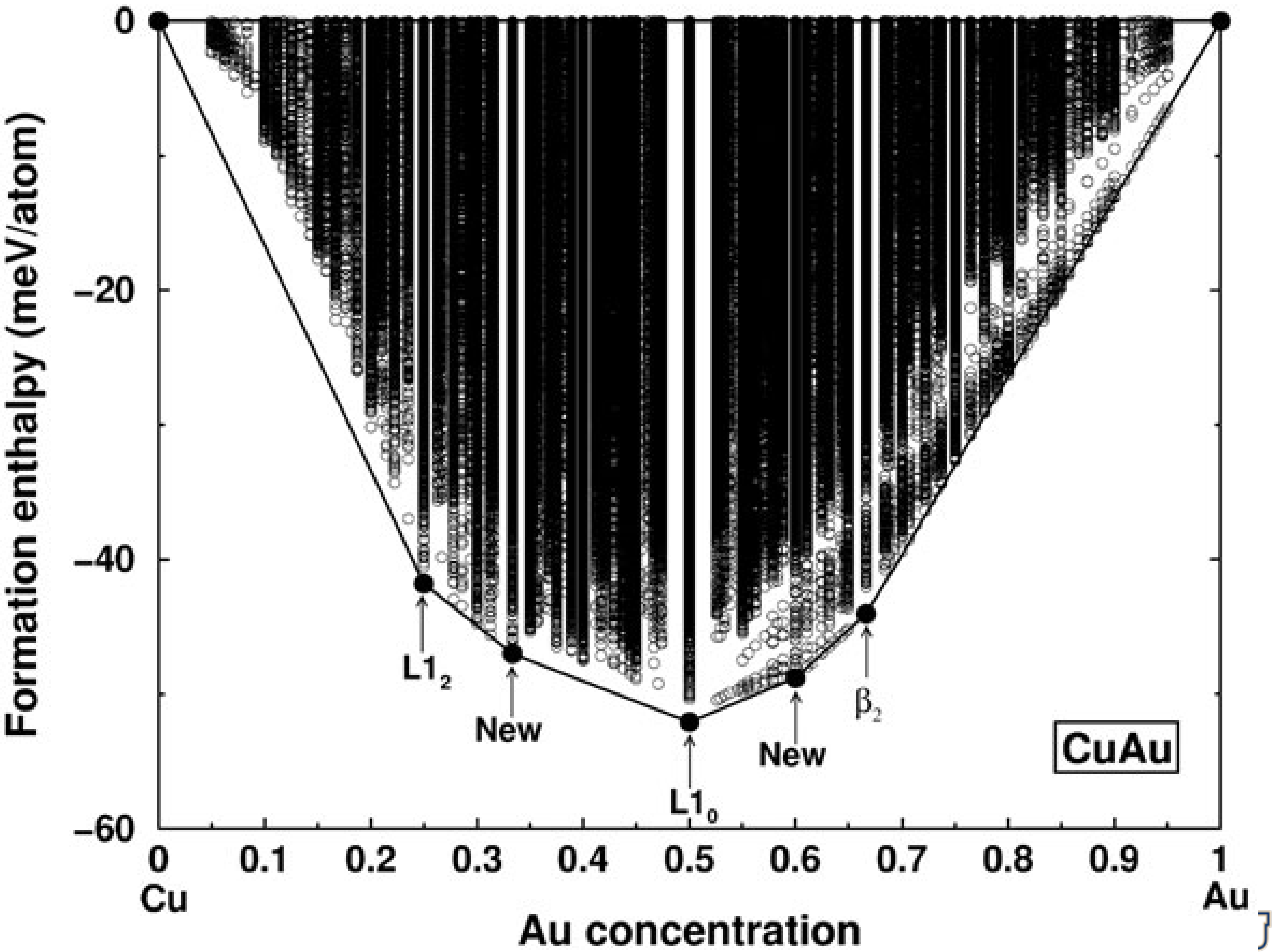
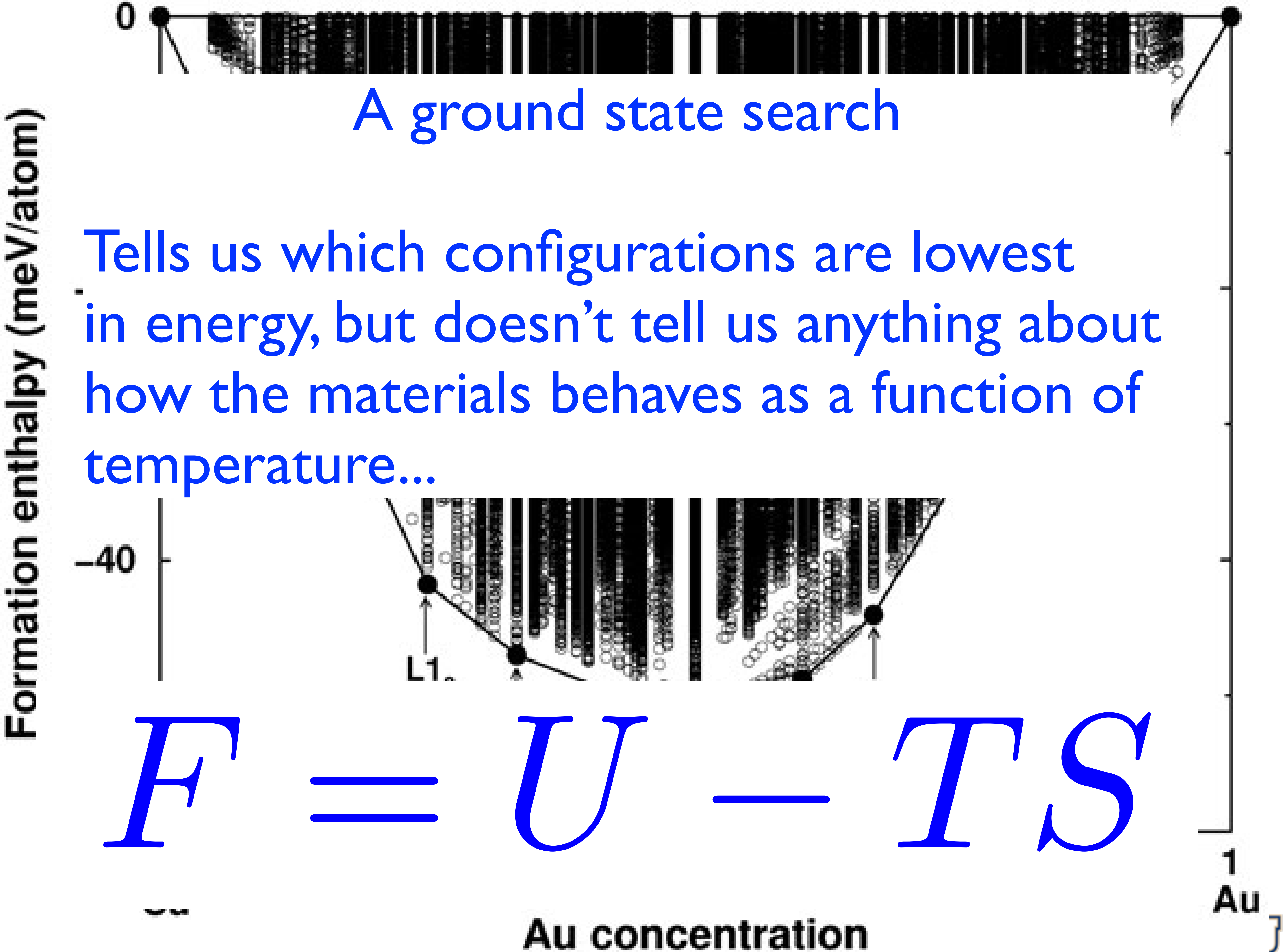





Formation enthalpy (meV/atom)
0
−20
−40
−60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Cu
Au
Au concentration
L1$_2$
New
L1$_0$
New
β$_2$
CuAu

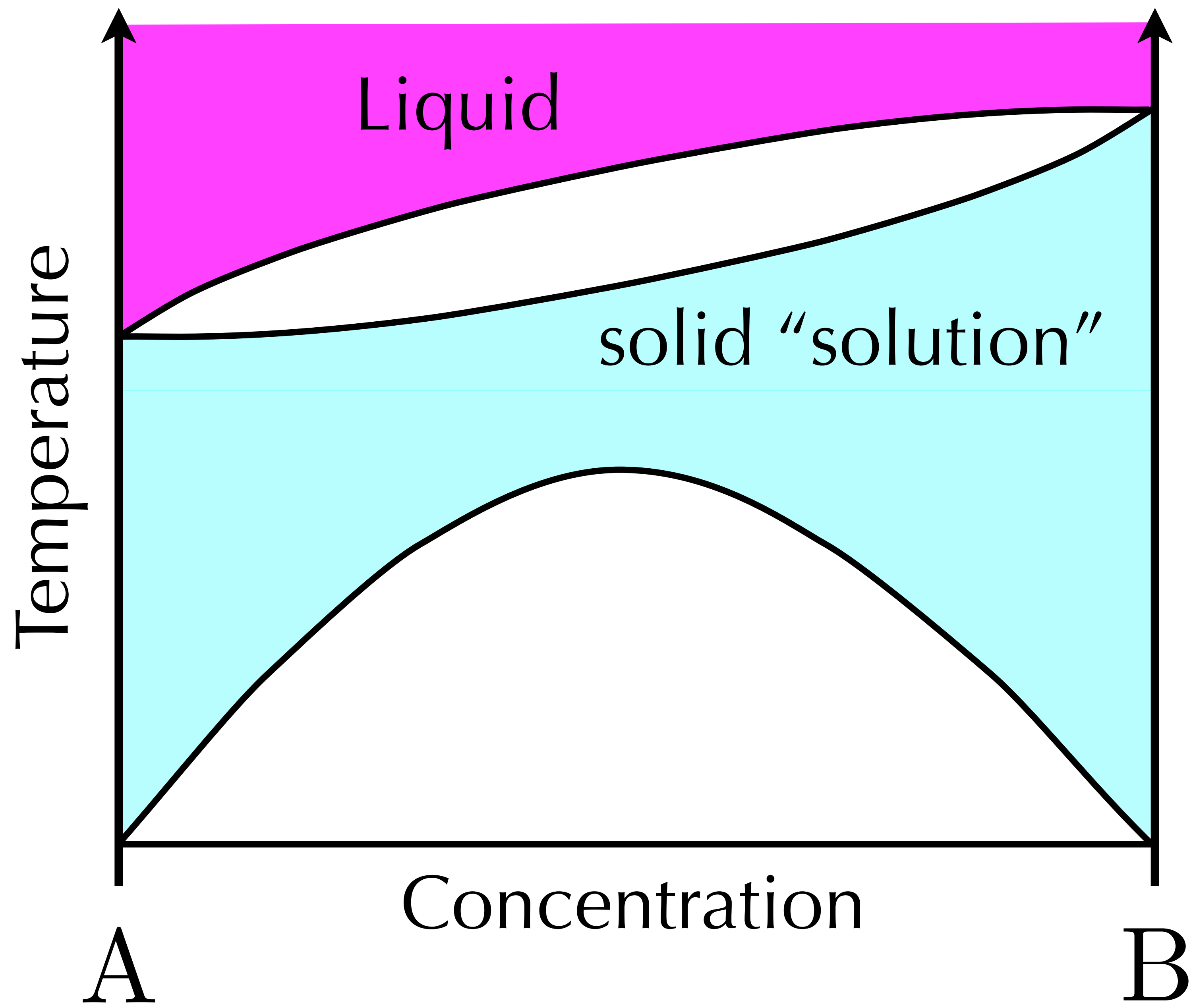


A ground state search

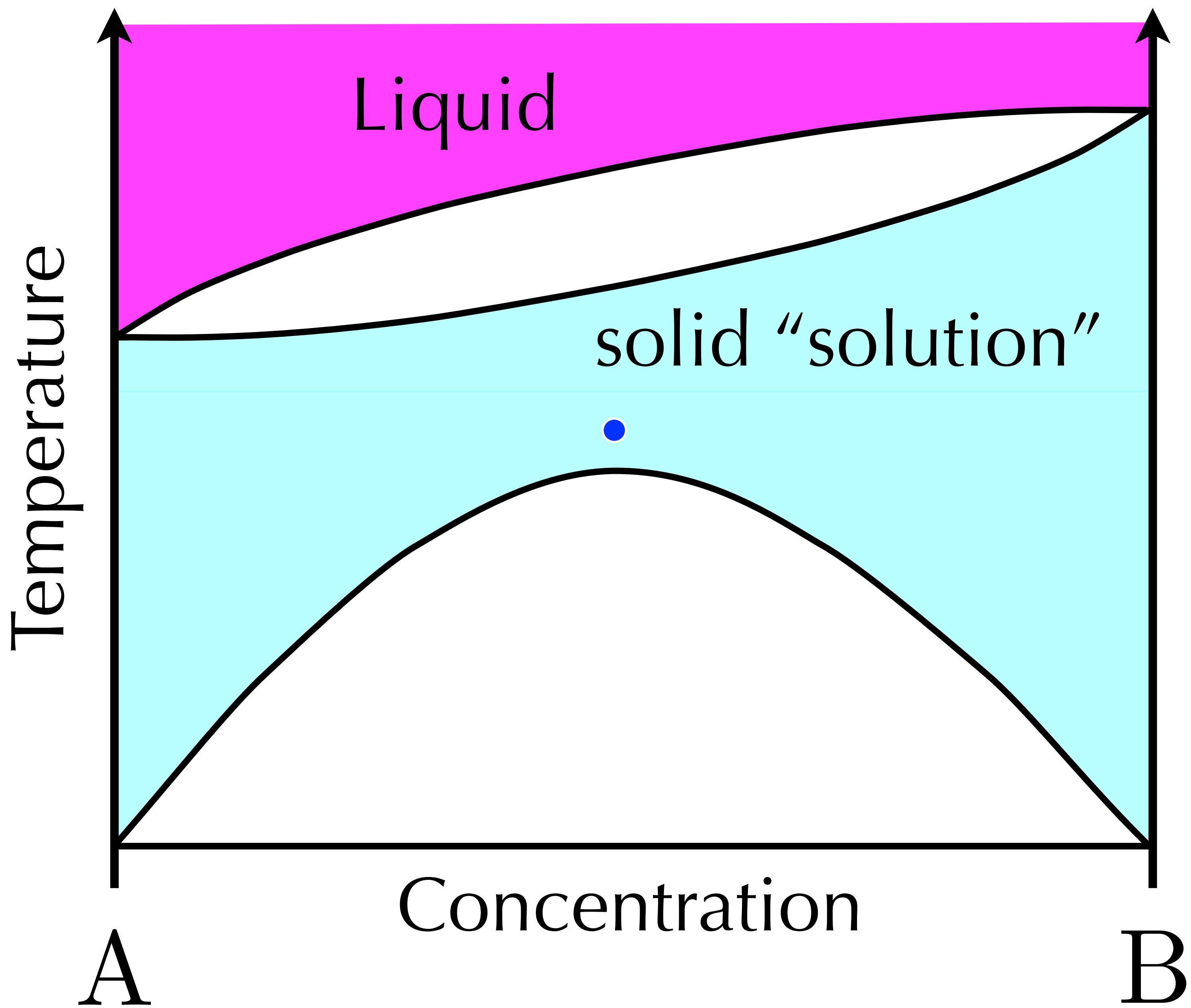
Tells us which configurations are lowest in energy, but doesn't tell us anything about how the materials behaves as a function of temperature...

$$F = U - TS$$

Alloy phase diagrams



What happens as it cools?



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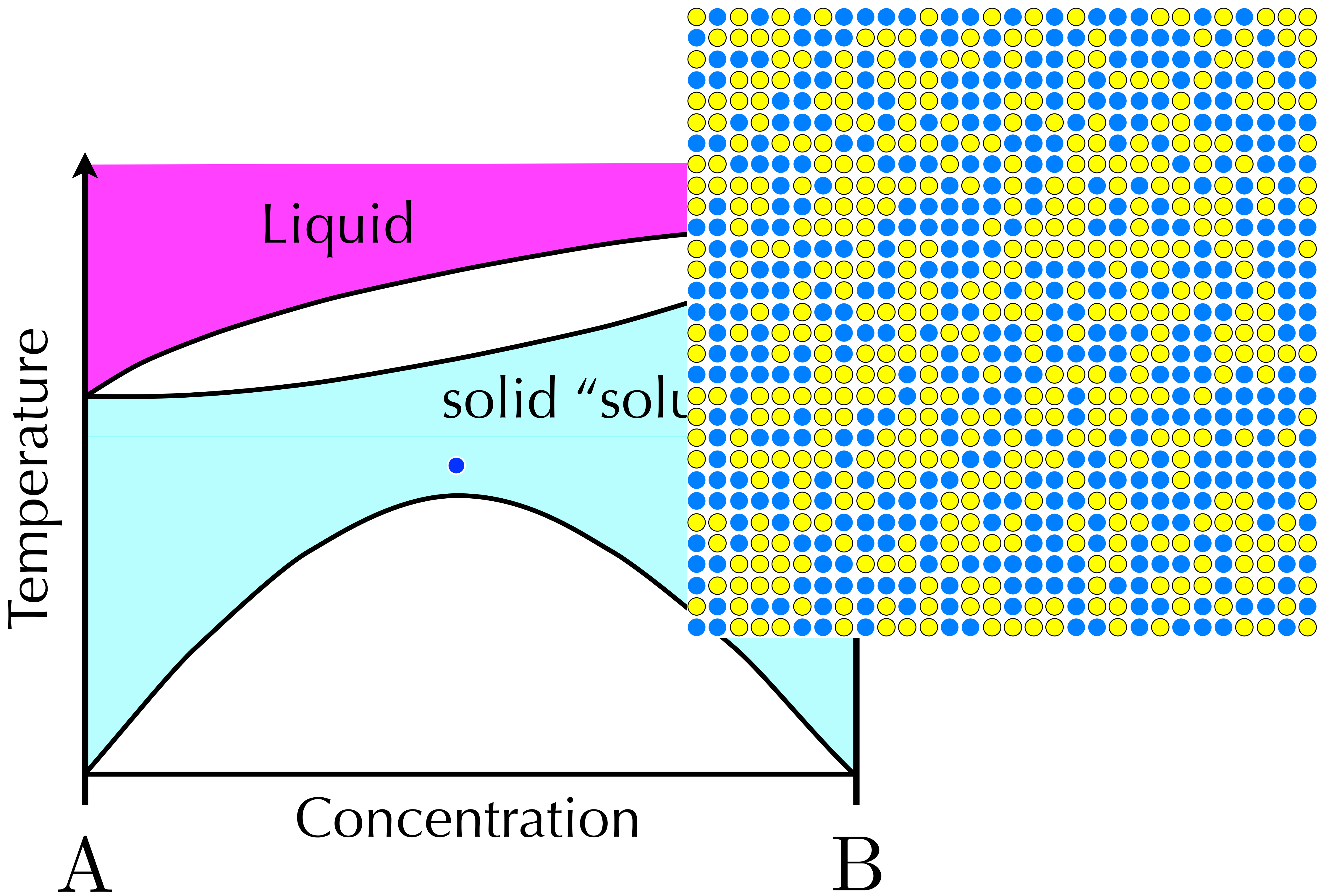

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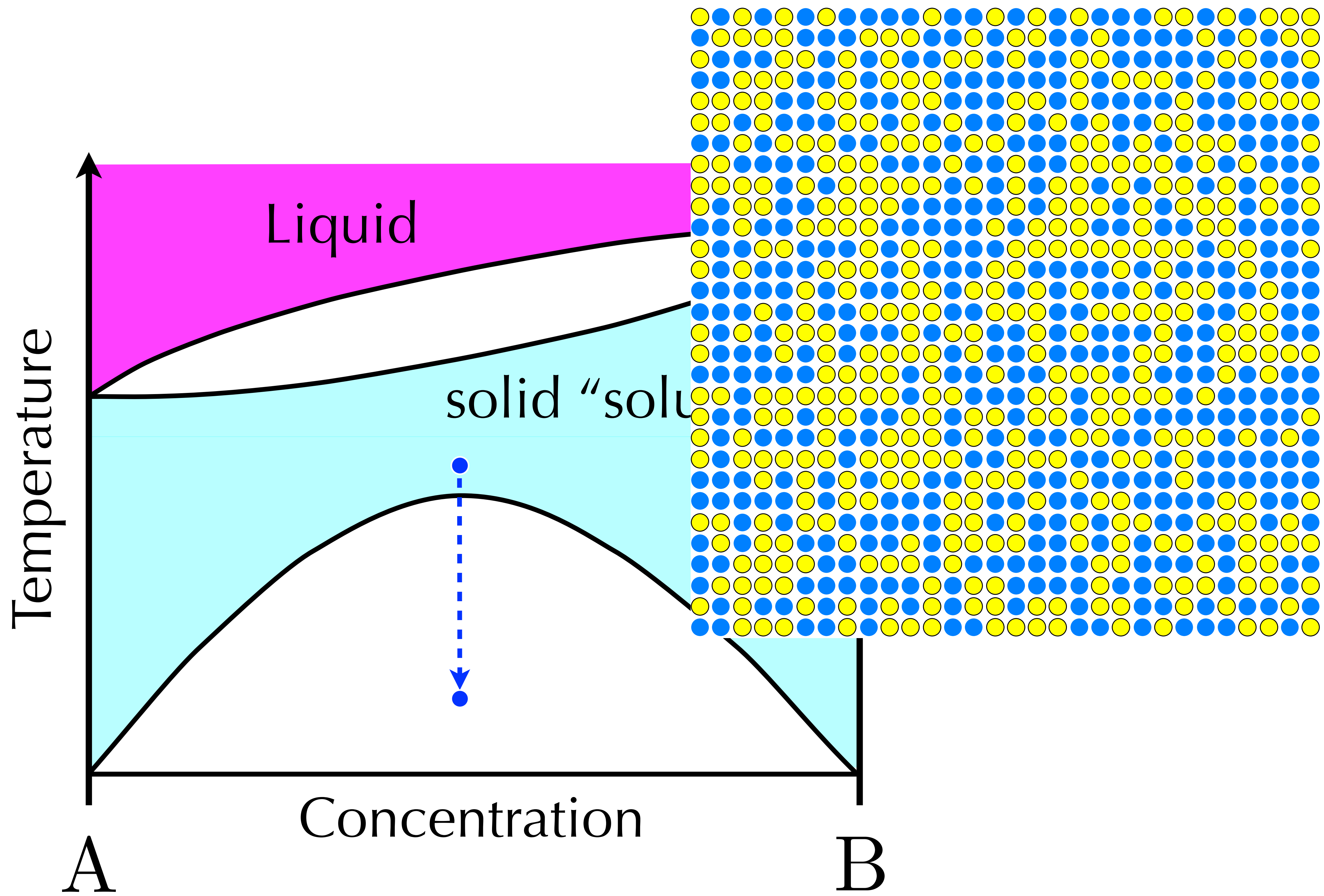

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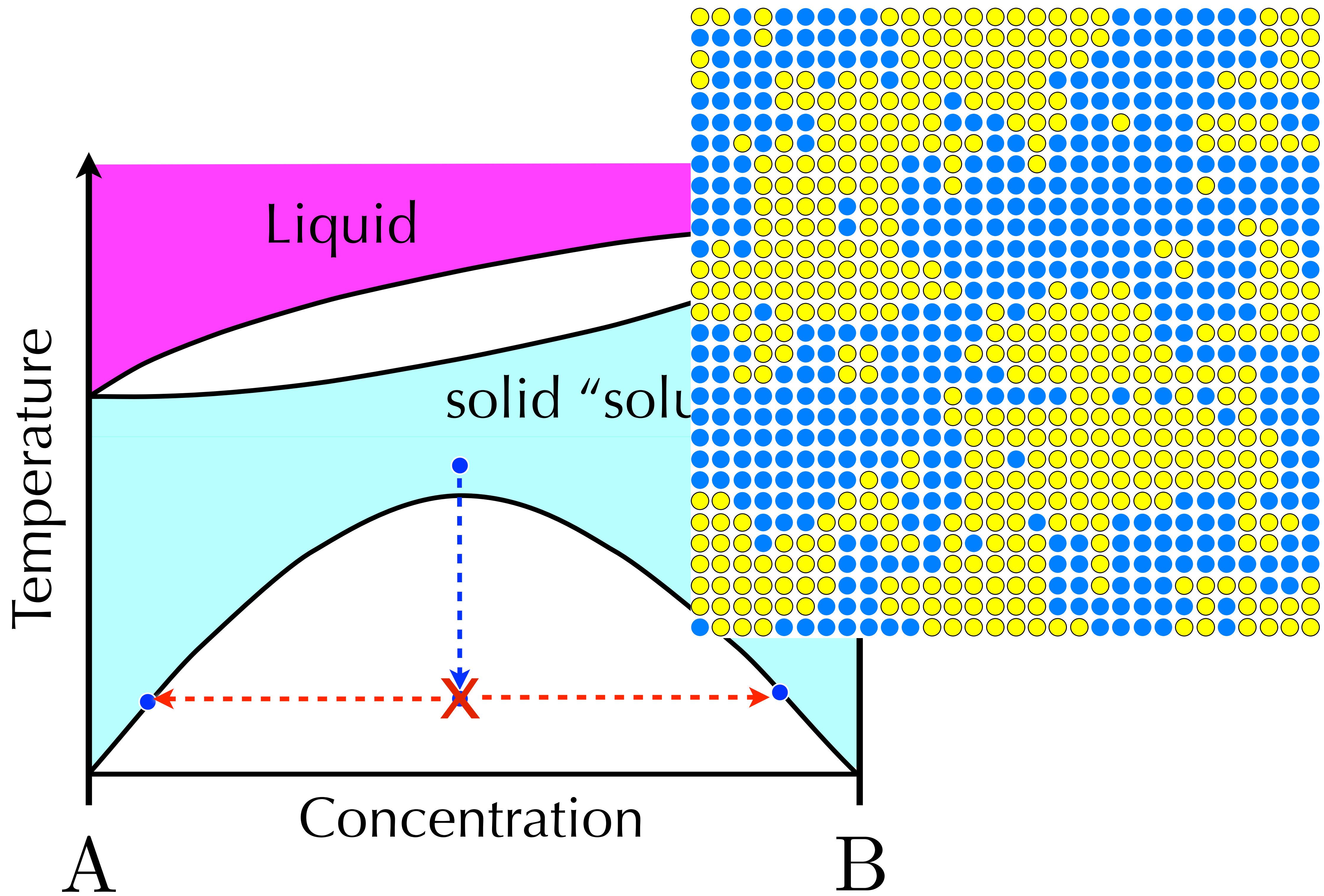
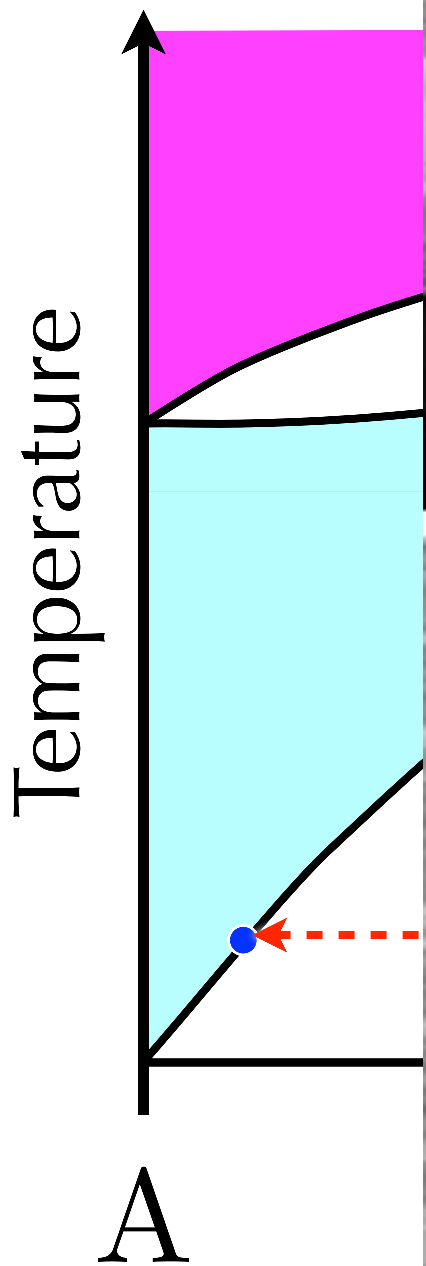
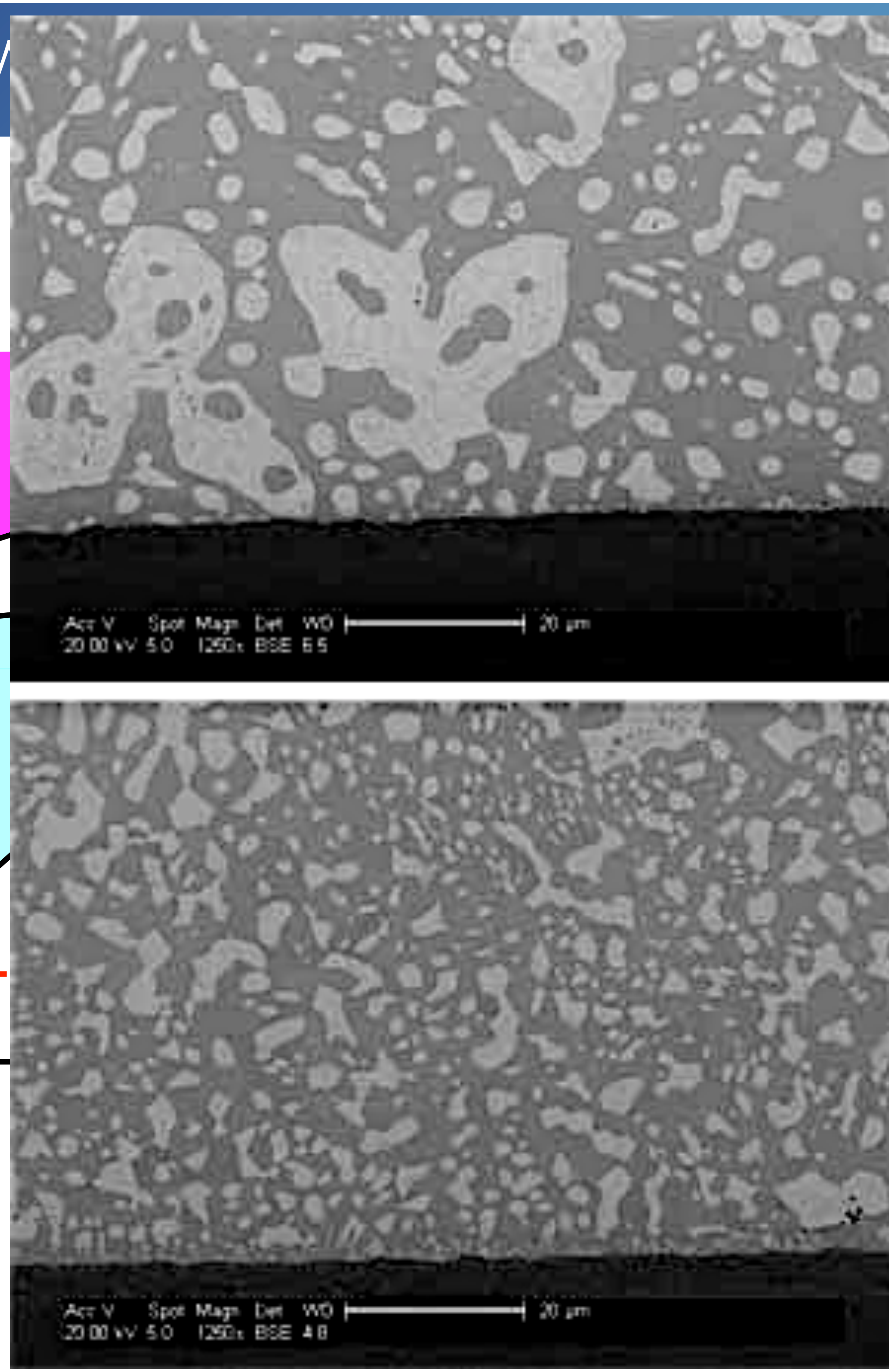
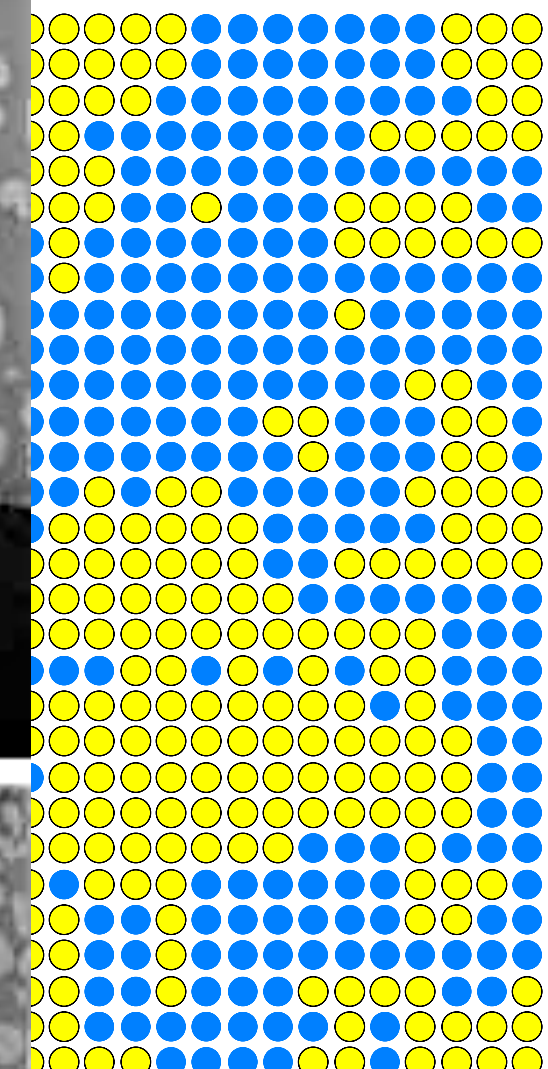


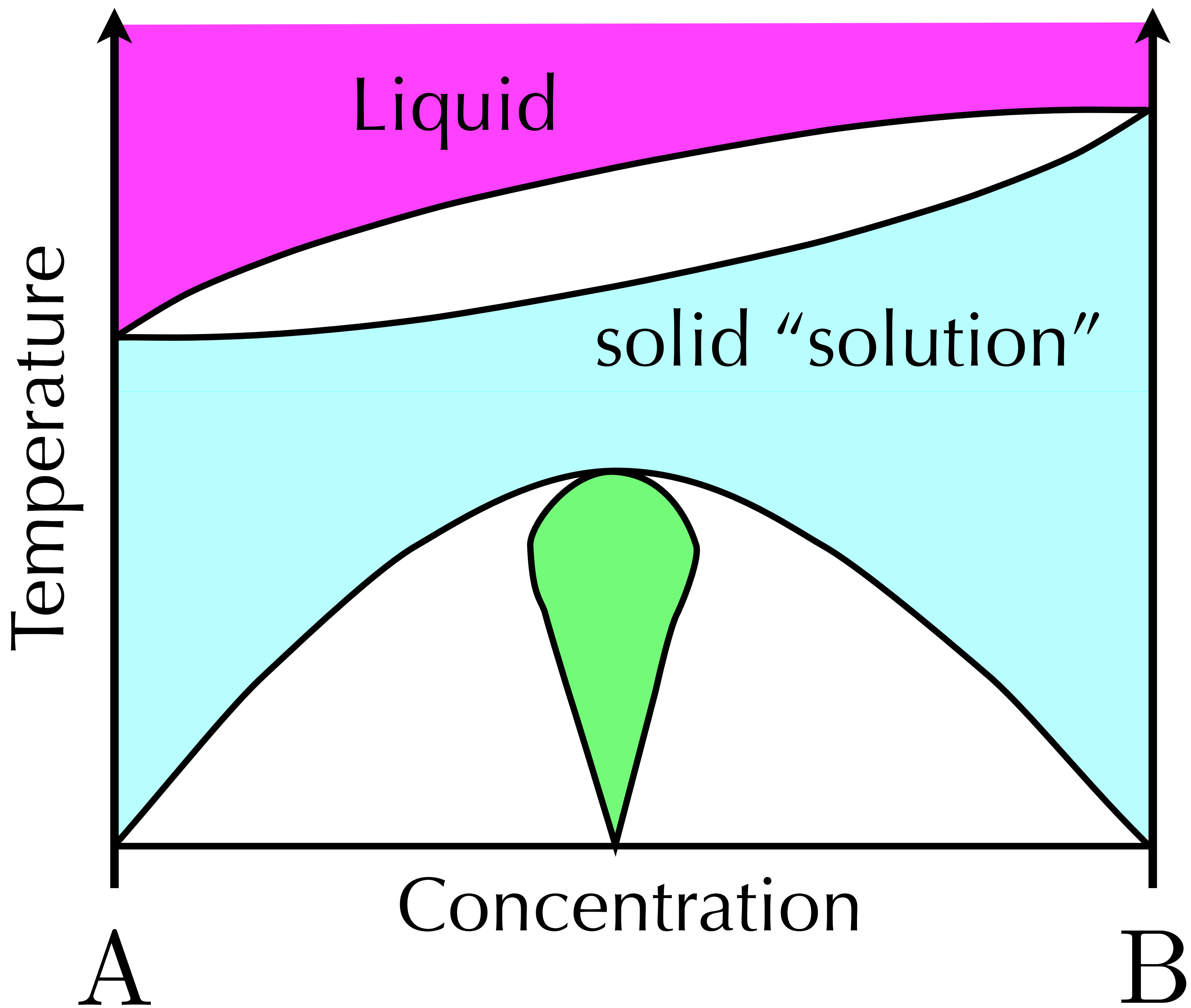
V


Temperature
A


Acc V Spot Magn Det WD 20 µm
20.00 kV 5.0 1250x BSE 6.5
Acc V Spot Magn Det WD 20 µm
20.00 kV 5.0 1250x BSE 4.8



Alloy phase diagrams: Ordering



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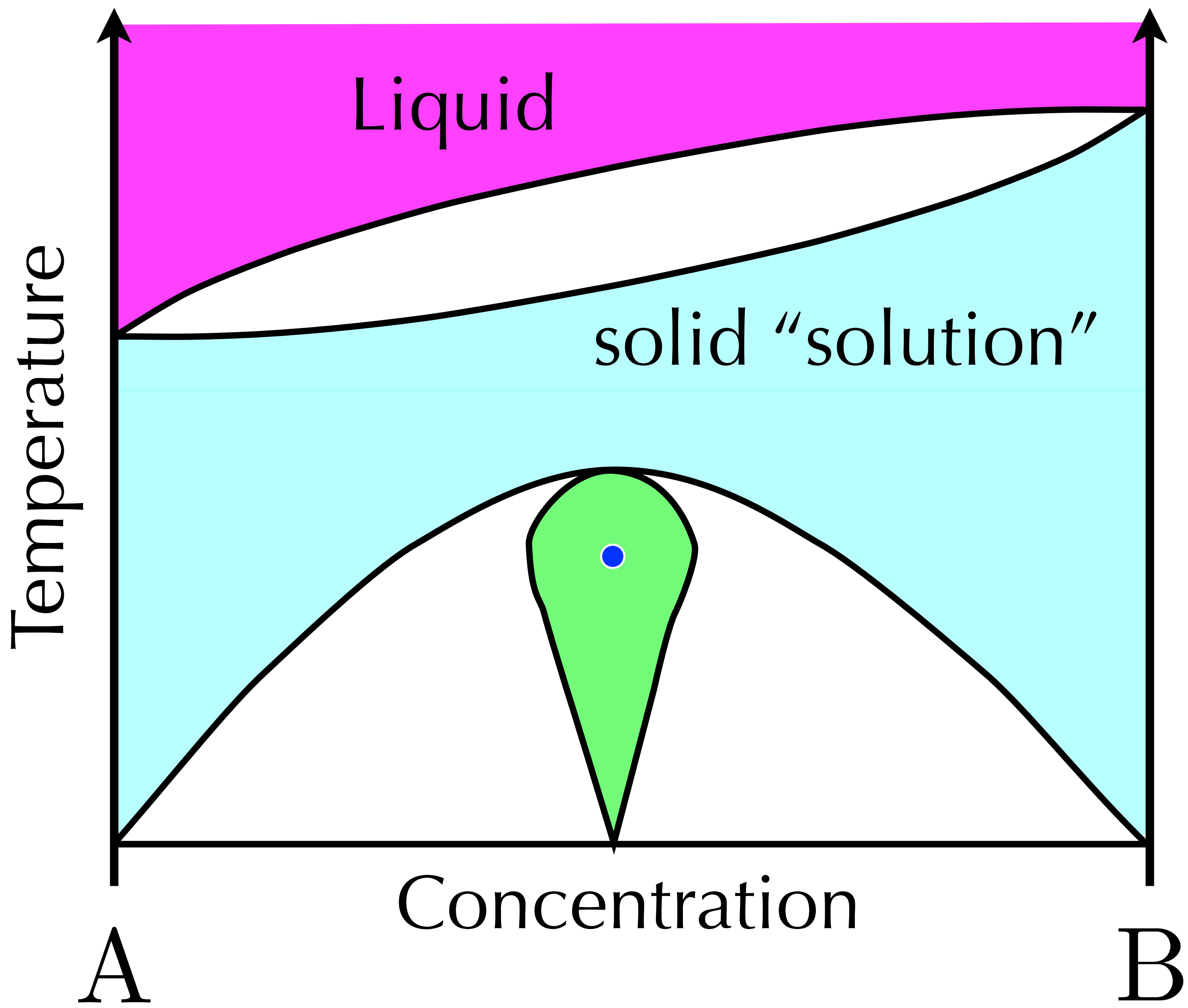

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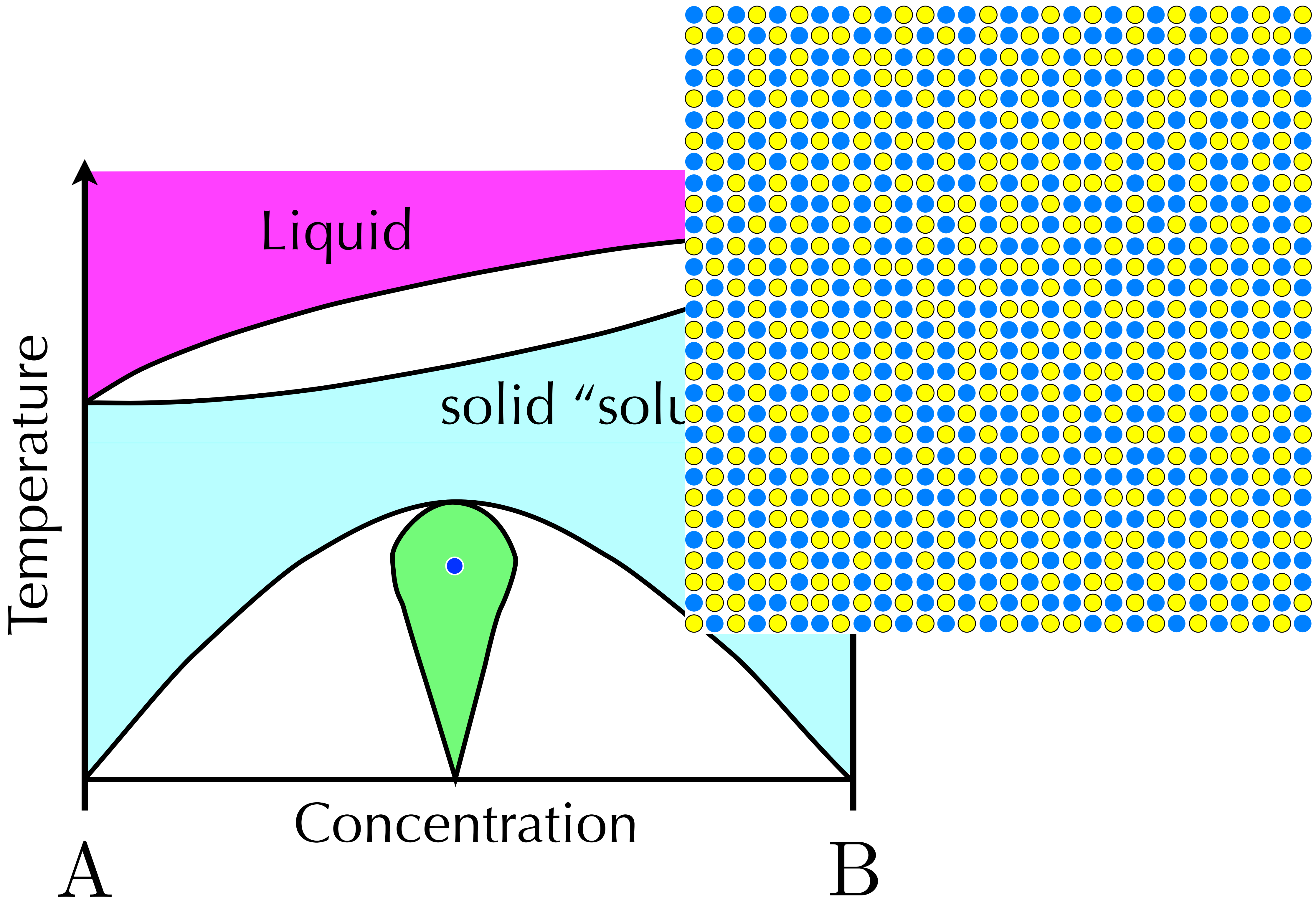

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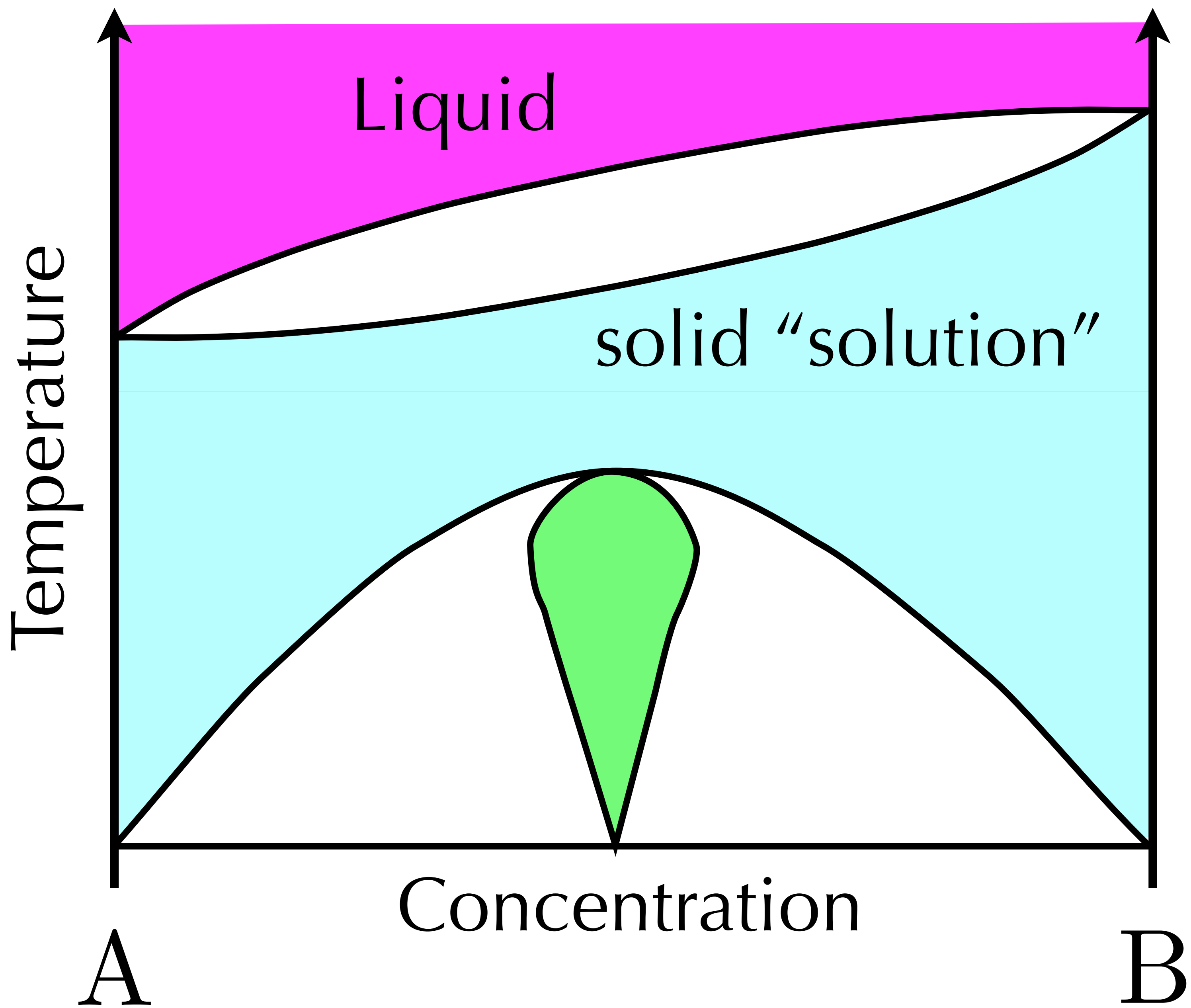

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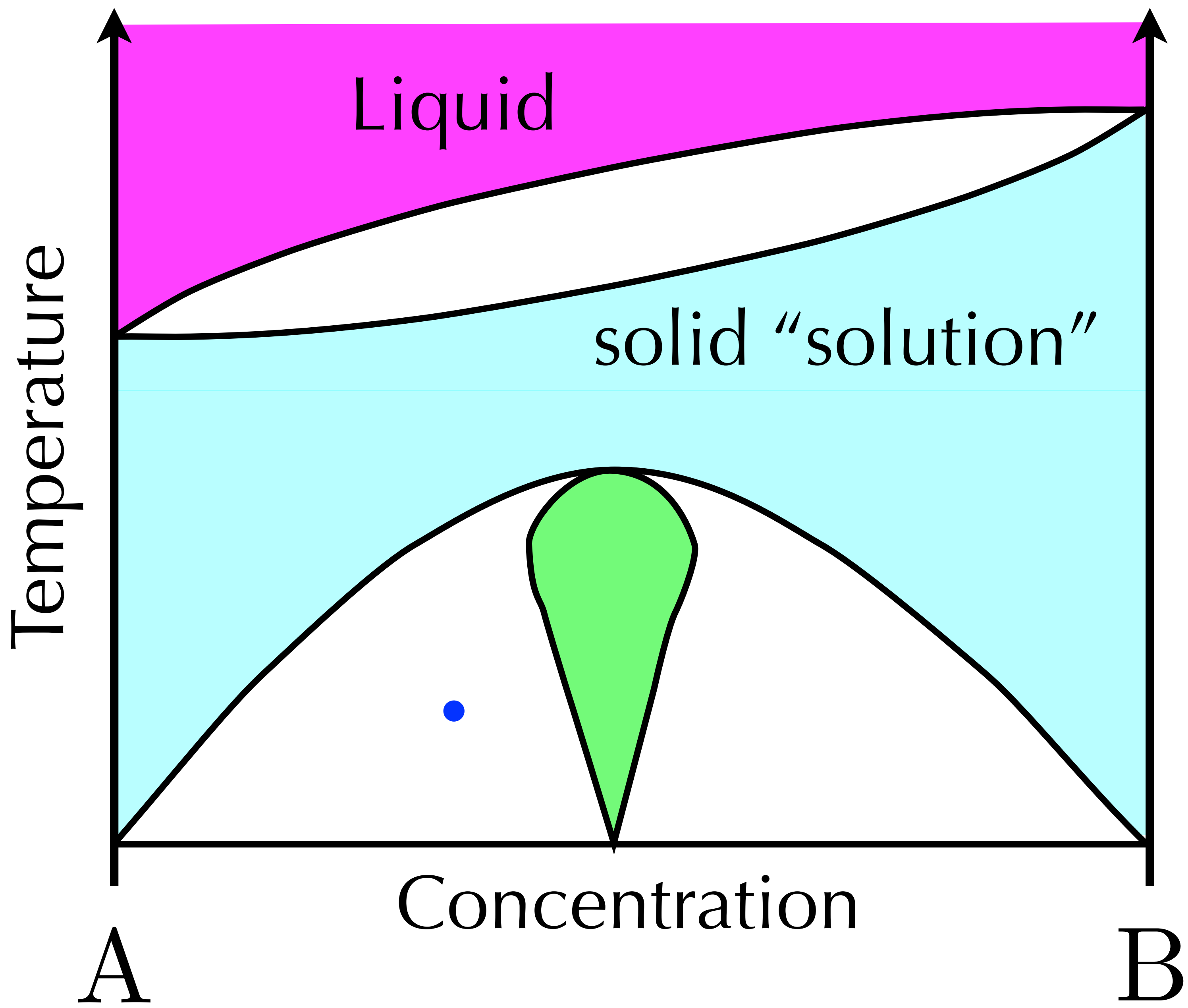

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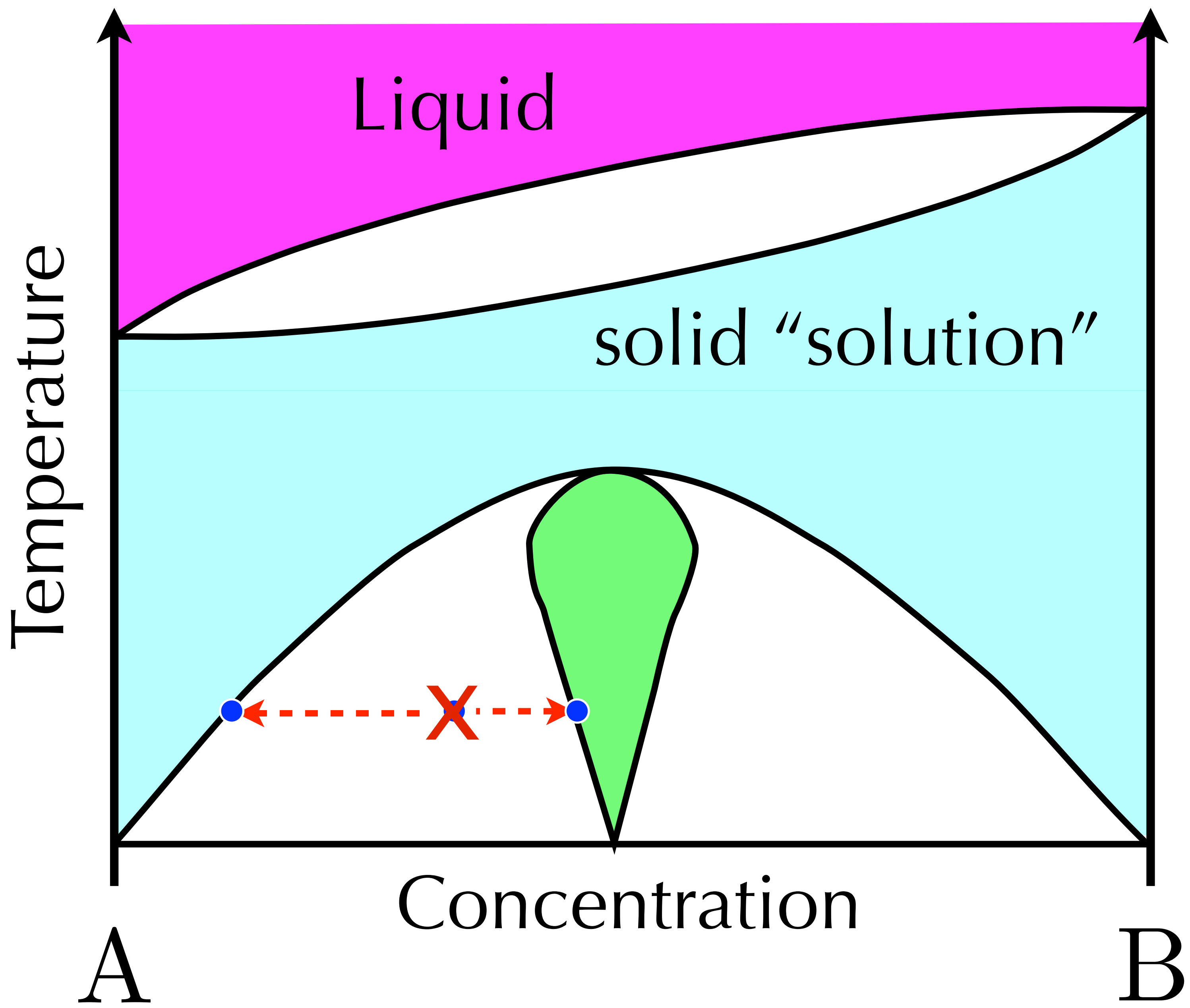

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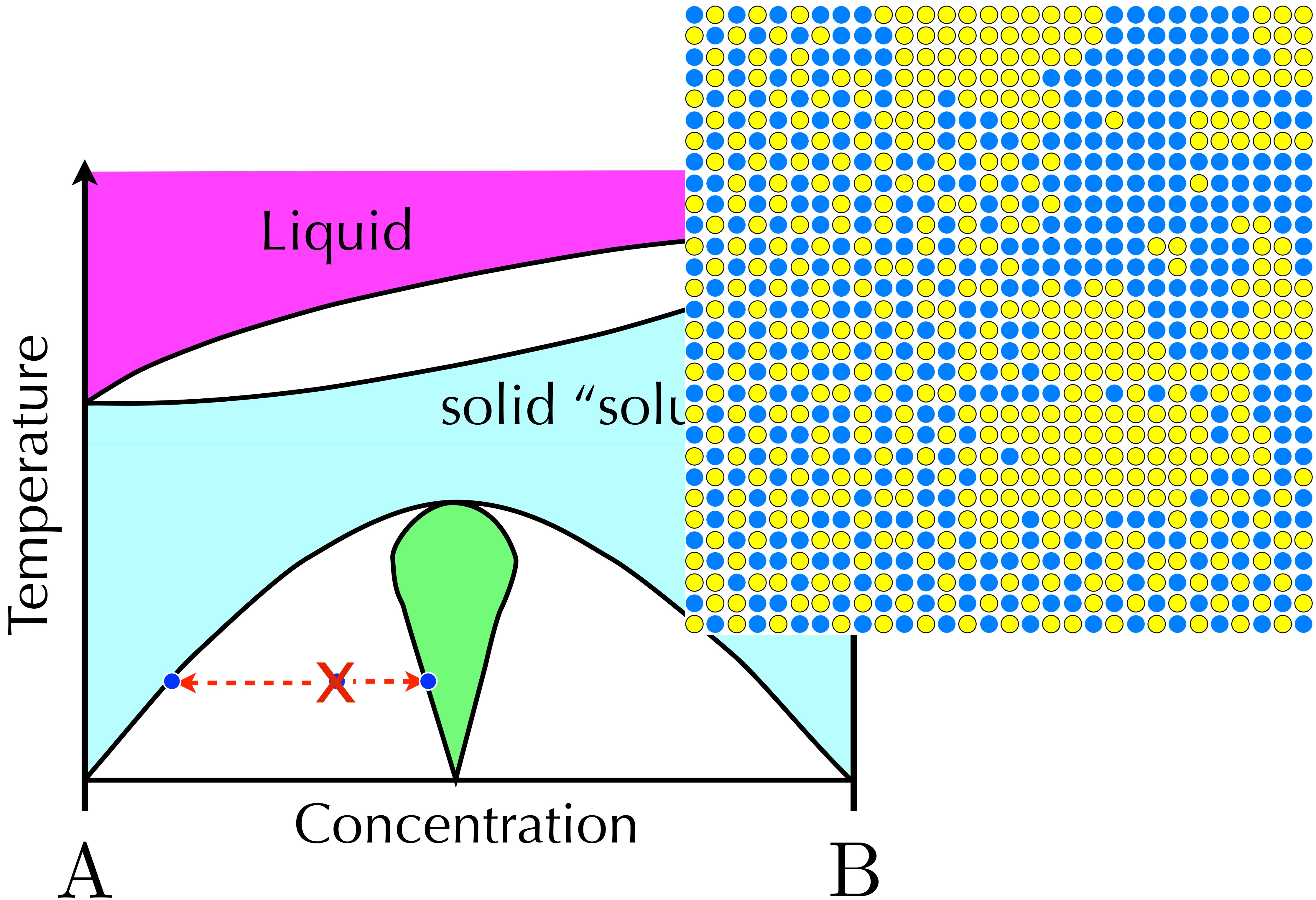

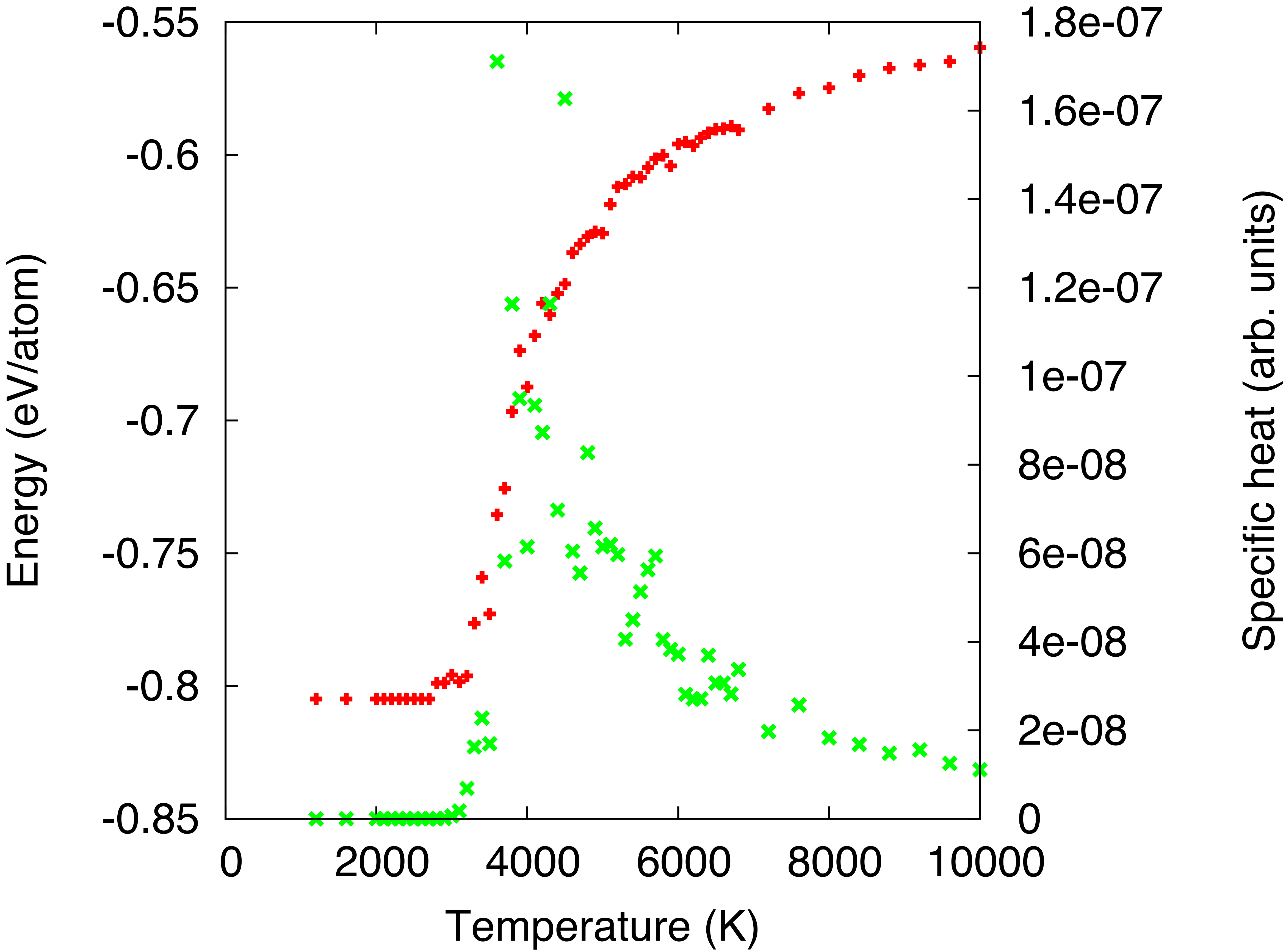
-0.55
-0.6
-0.65
-0.7
-0.75
-0.8
-0.85
Energy (eV/atom)
1.8e-07
1.6e-07
1.4e-07
1.2e-07
1e-07
8e-08
6e-08
4e-08
2e-08
0
Specific heat (arb. units)
0
2000
4000
6000
8000
10000
Temperature (K)

Recap: with a fast lattice Hamiltonian we can...

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1. Search for new phases (try millions of trial configurations) **Ground State Search**

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3. Build a kinetic simulation (to model time evolution) **Kinetic MC**

In a nutshell: **Better models, faster**

Basic idea:

Instead of adding complexity (terms) to a model until it fits the data and predicts well...(normal approach)...

...start with an infinite set of models (containing all possible terms). Discard all models except the simplest one (Compressive Sensing approach). Surprisingly perhaps, this is really efficient.

Going beyond a linear model fit (adding terms)

$$f(x,y) = \boxed{a_0 + a_1 x + a_2 y + a_3 xy + a_4 x^2 + a_5 y^2} + \cdots$$

$$\begin{pmatrix} 1 & x_1 & y_1 & x_1 y_1 & x_1^2 & y_1^2 \\ 1 & x_2 & y_2 & x_2 y_2 & x_2^2 & y_2^2 \\ 1 & x_3 & y_3 & x_3 y_3 & x_3^2 & y_3^2 \\ 1 & x_4 & y_4 & x_4 y_4 & x_4^2 & y_4^2 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \end{pmatrix} = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{pmatrix}$$

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$$\mathbb{M}\vec{a} = \vec{f}$$

"Solving" an under-determined problem

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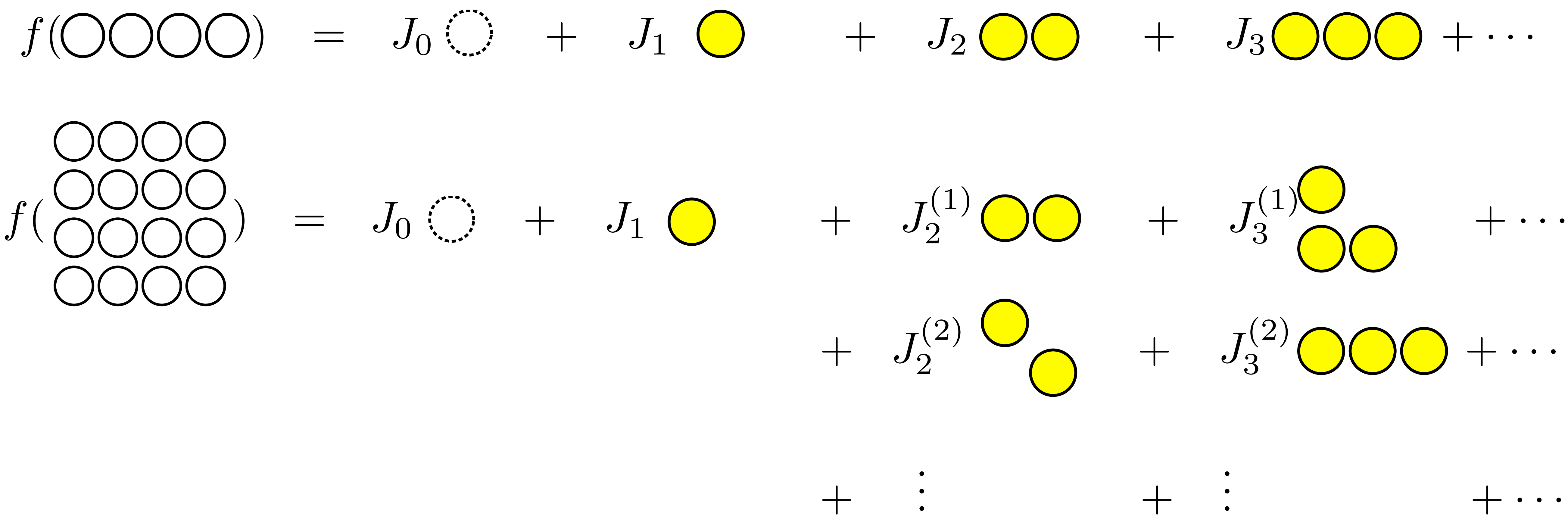
$$\min_{\vec{a}} \left\{ \|\vec{a}\|_1 : \mathbb{M}\vec{a} = \vec{f} \right\}$$

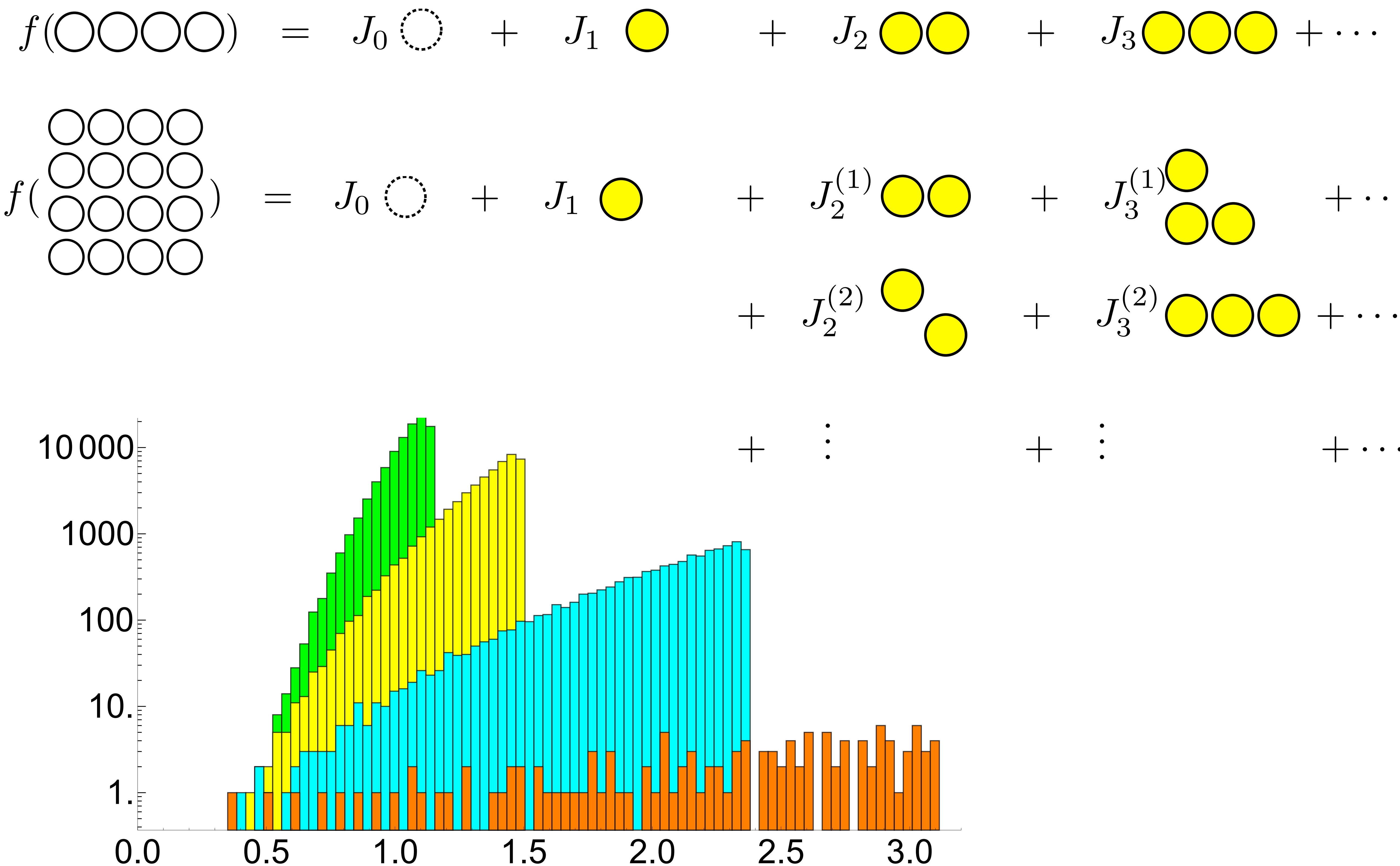
$$\ell_1 \equiv \|\vec{u}\| = \sum_i |u_i|$$

$$\ell_2 \equiv \left(\sum_i |u_i|^2 \right)^{\frac{1}{2}} \qquad \ell_1 \equiv \left(\sum_i |u_i|^1 \right)^{\frac{1}{1}}$$

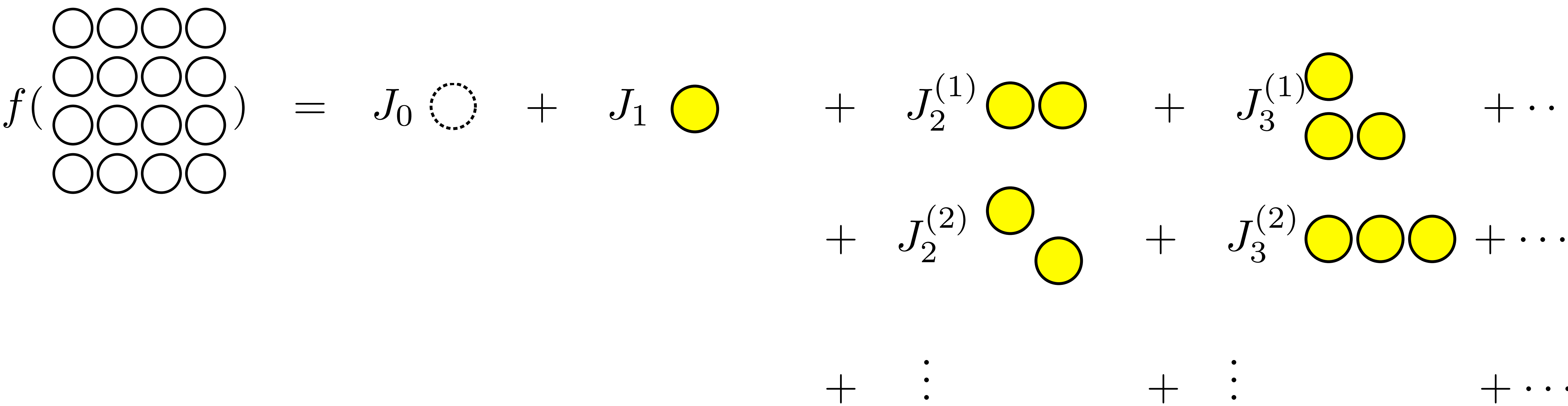
In more than one dimension...



In more than one dimension...



Models built via Compressive Sensing



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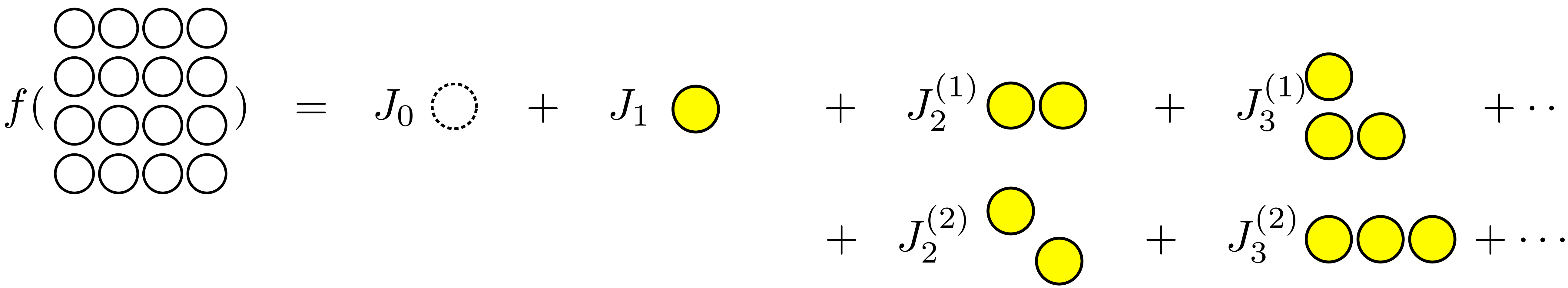
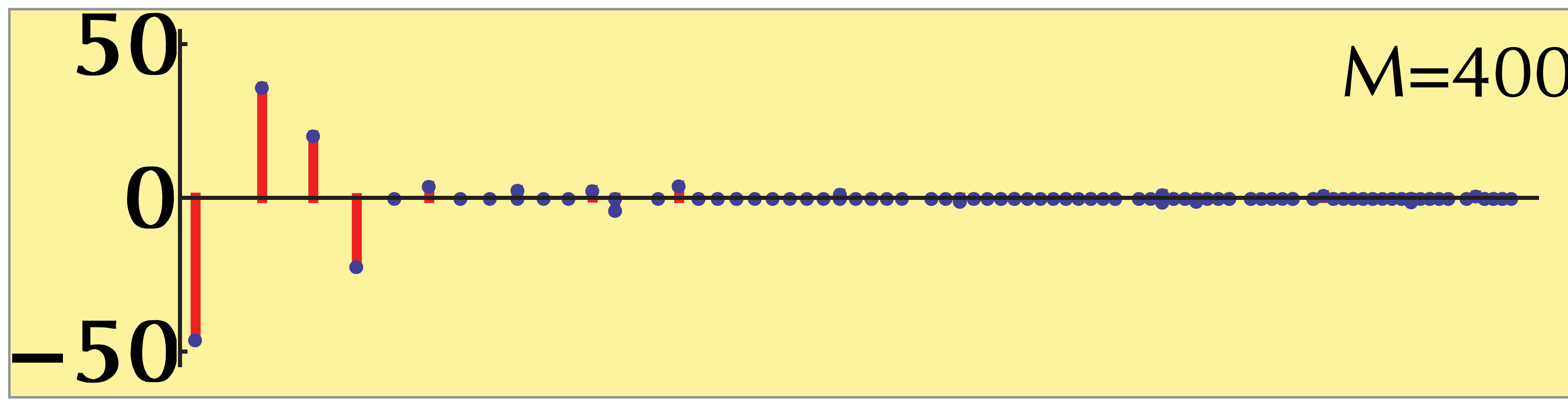


Pairs



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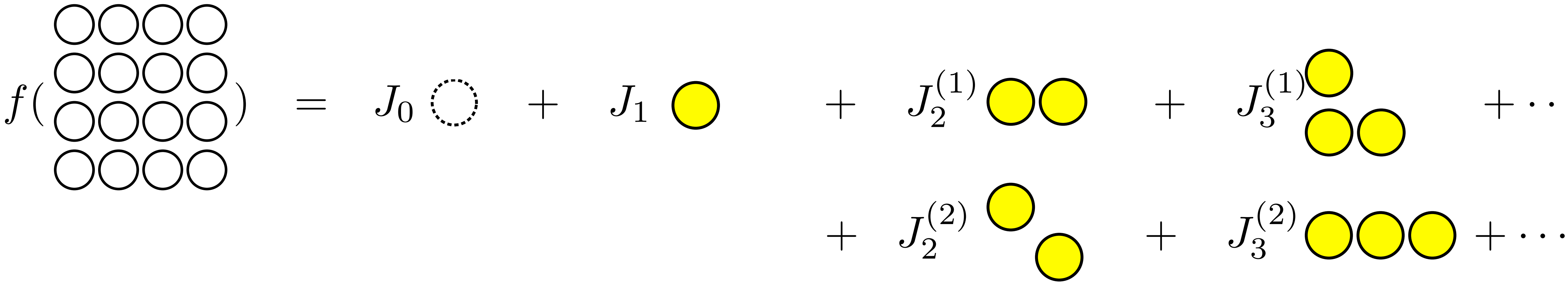

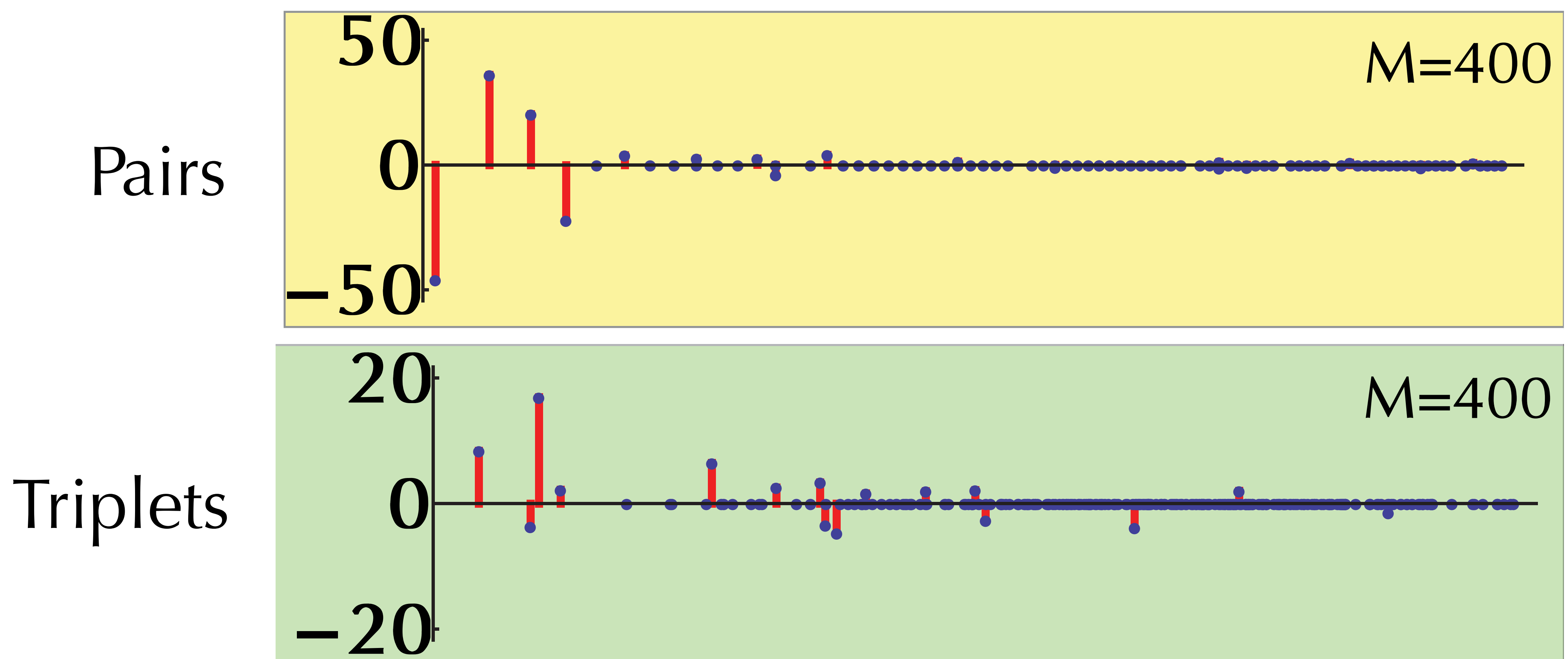

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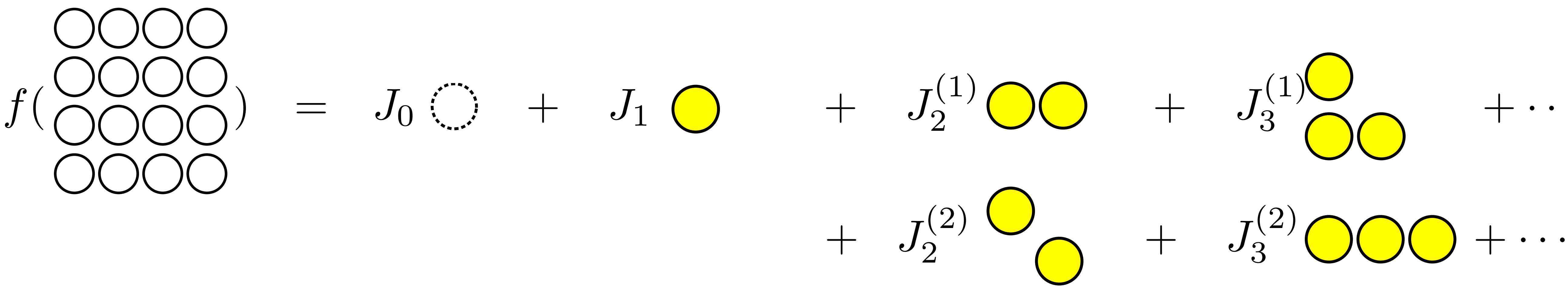
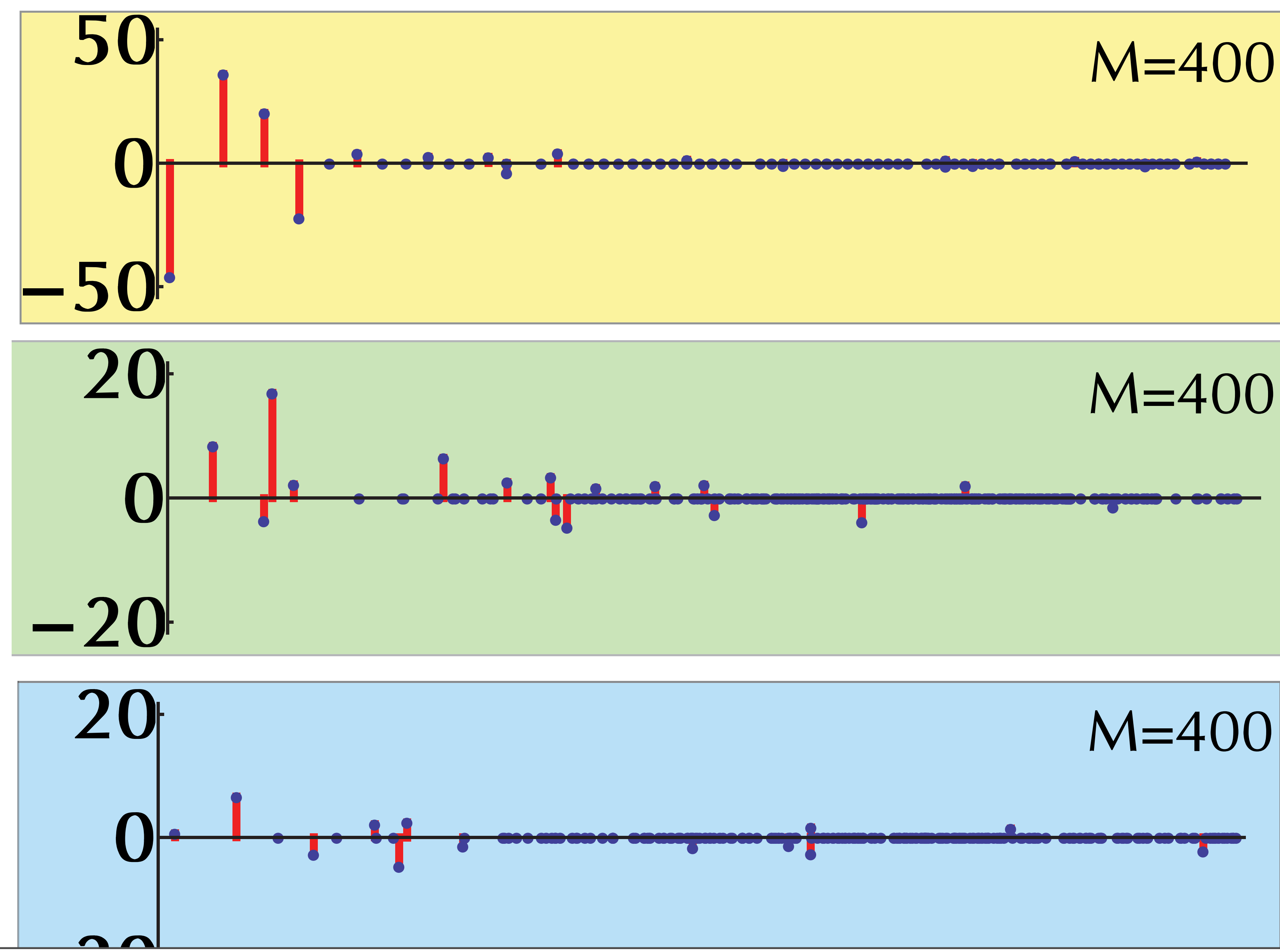


Pairs

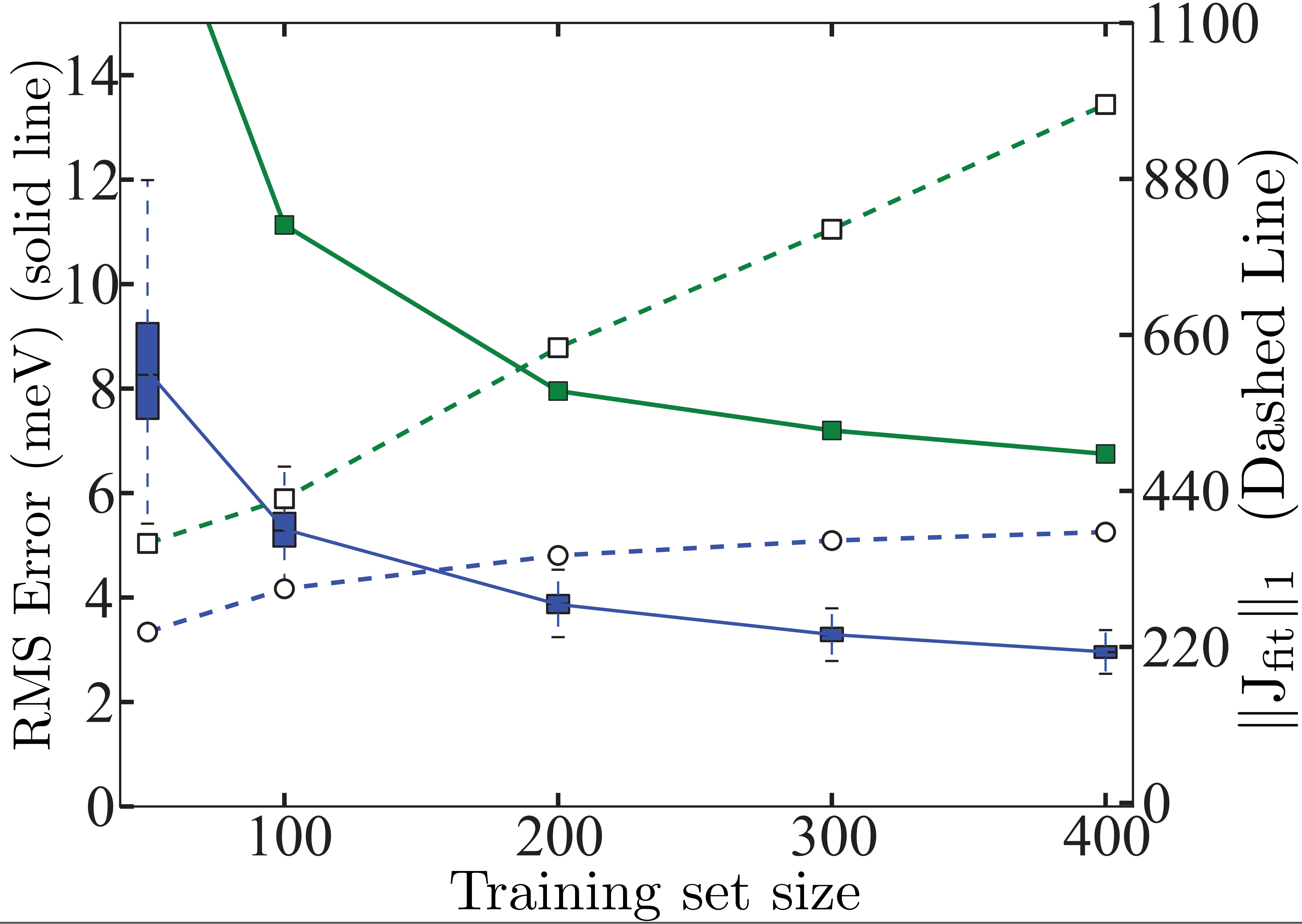
Triplets

Quadruplets



CSCE: Compressive sensing-based CE

UNCLE



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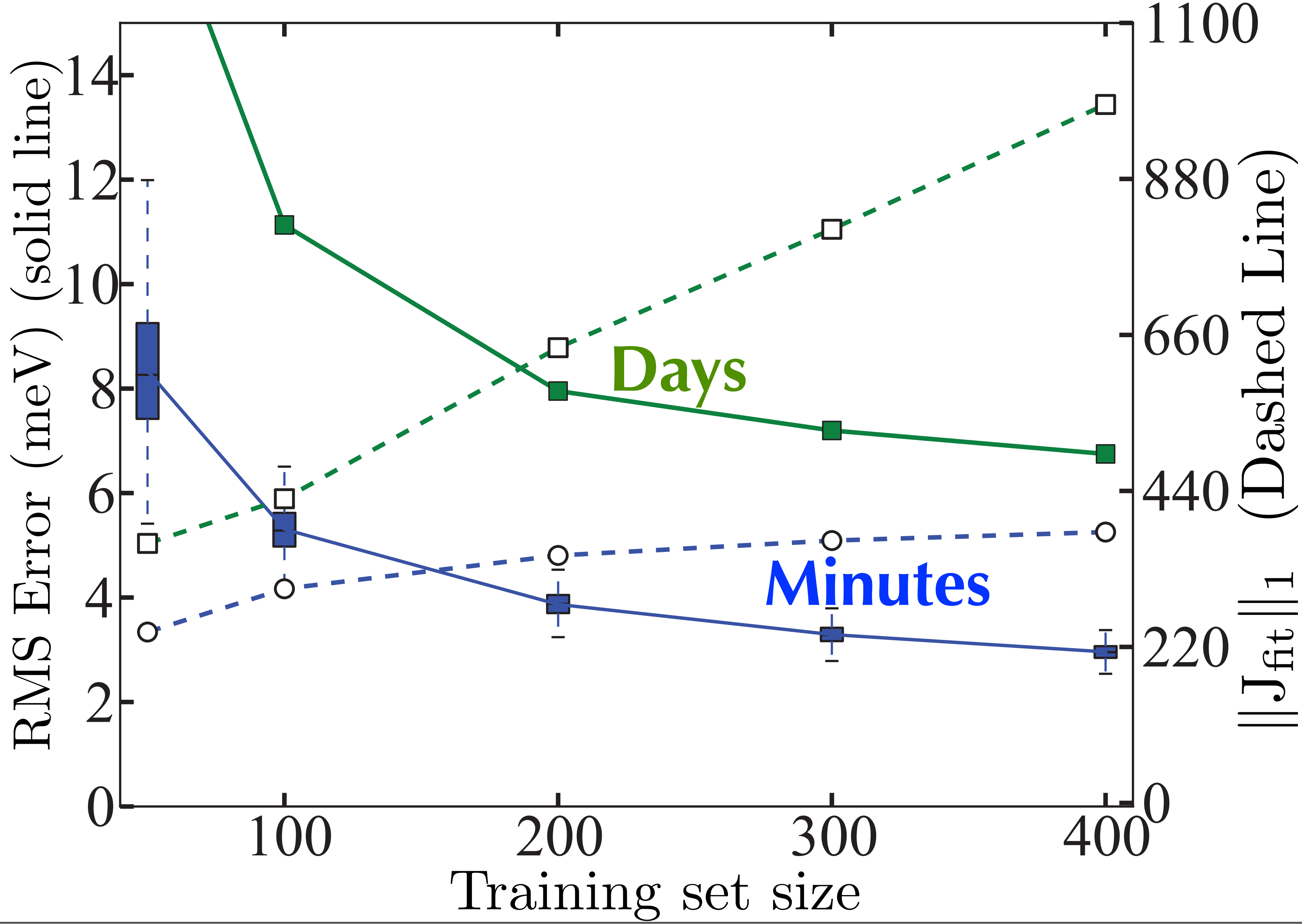
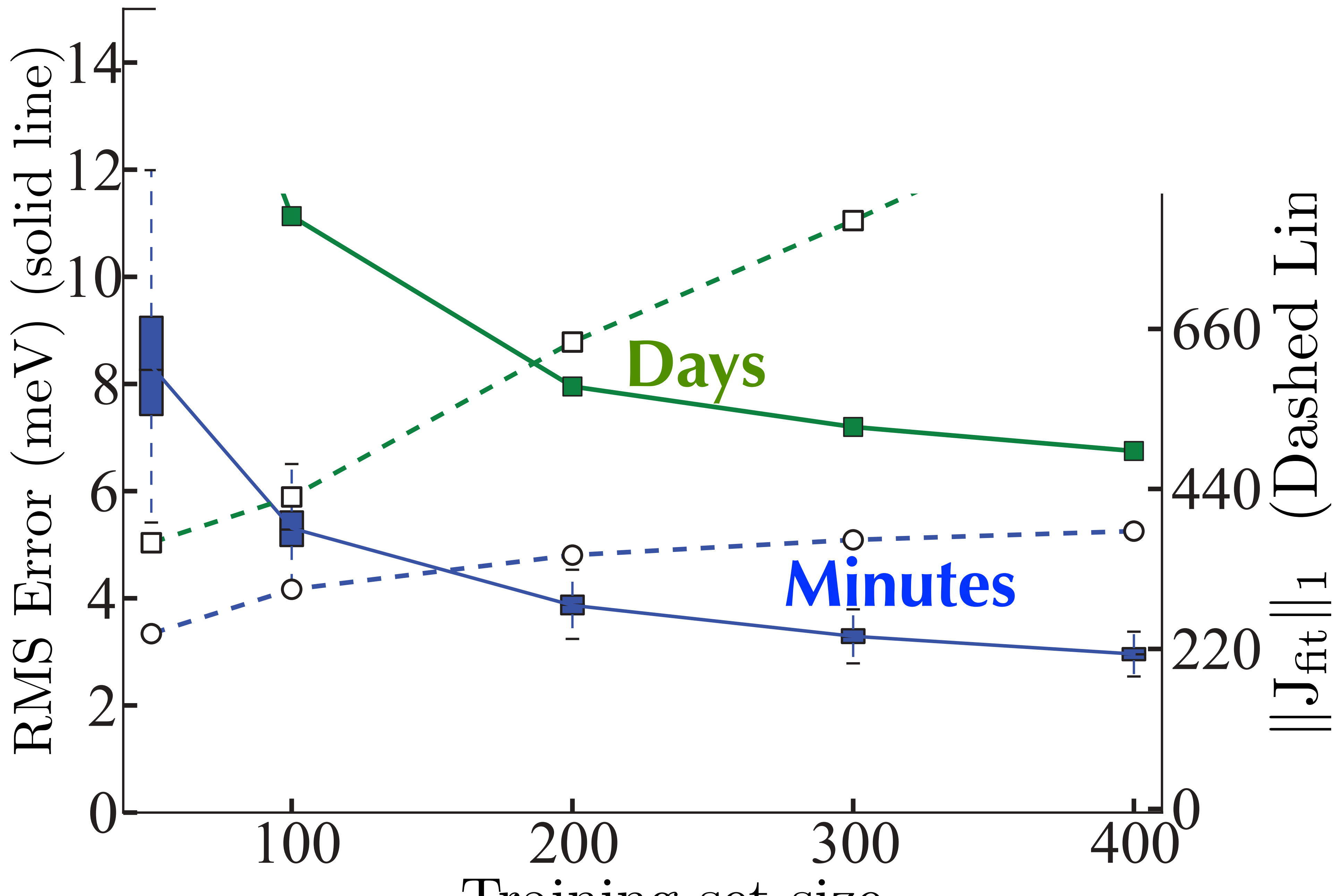


CSCE: Compressive sensing-based CE

- Faster(!)



CSCE: Compressive sensing-based CE

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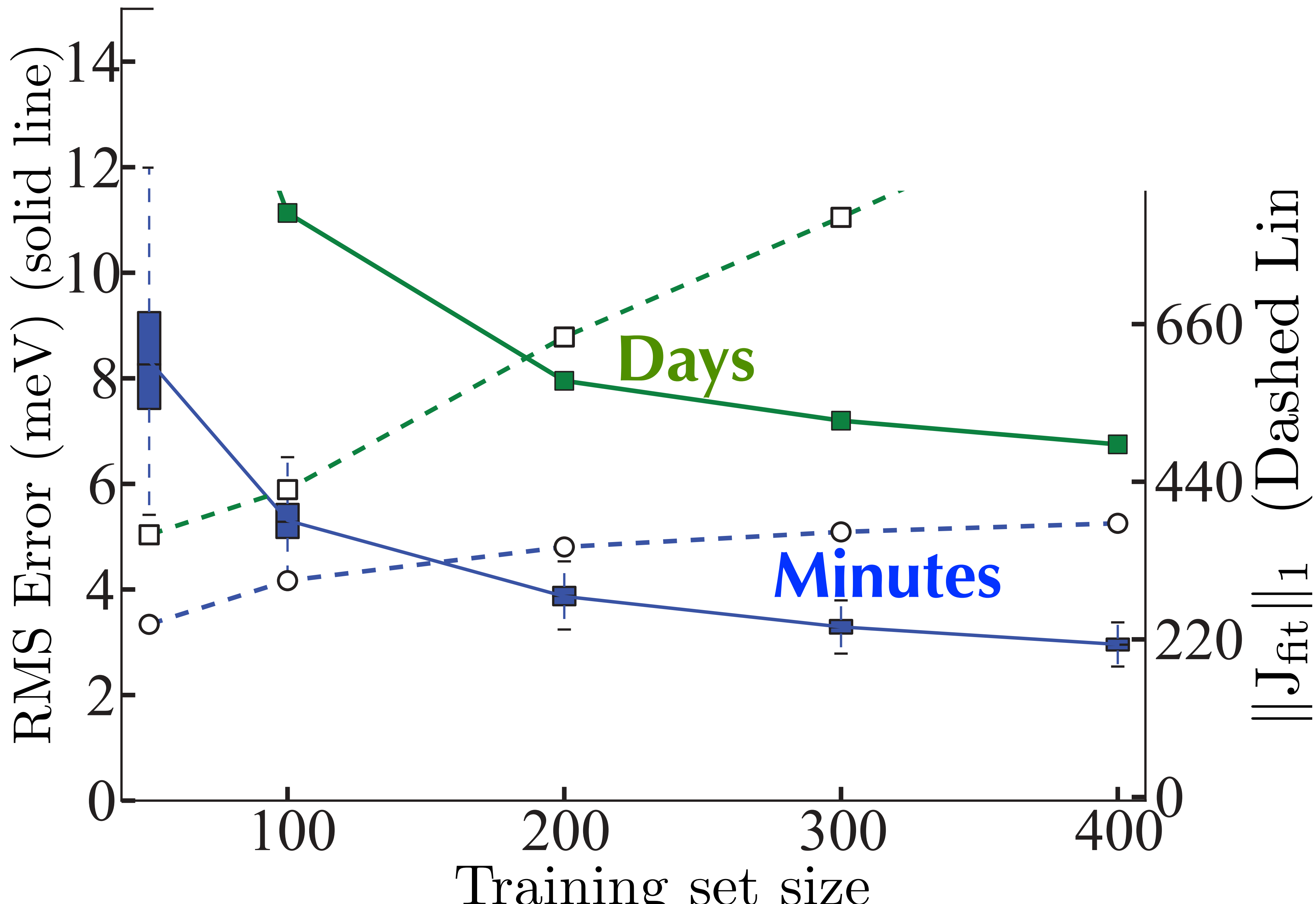
- Better predictions



CSCE: Compressive sensing-based CE

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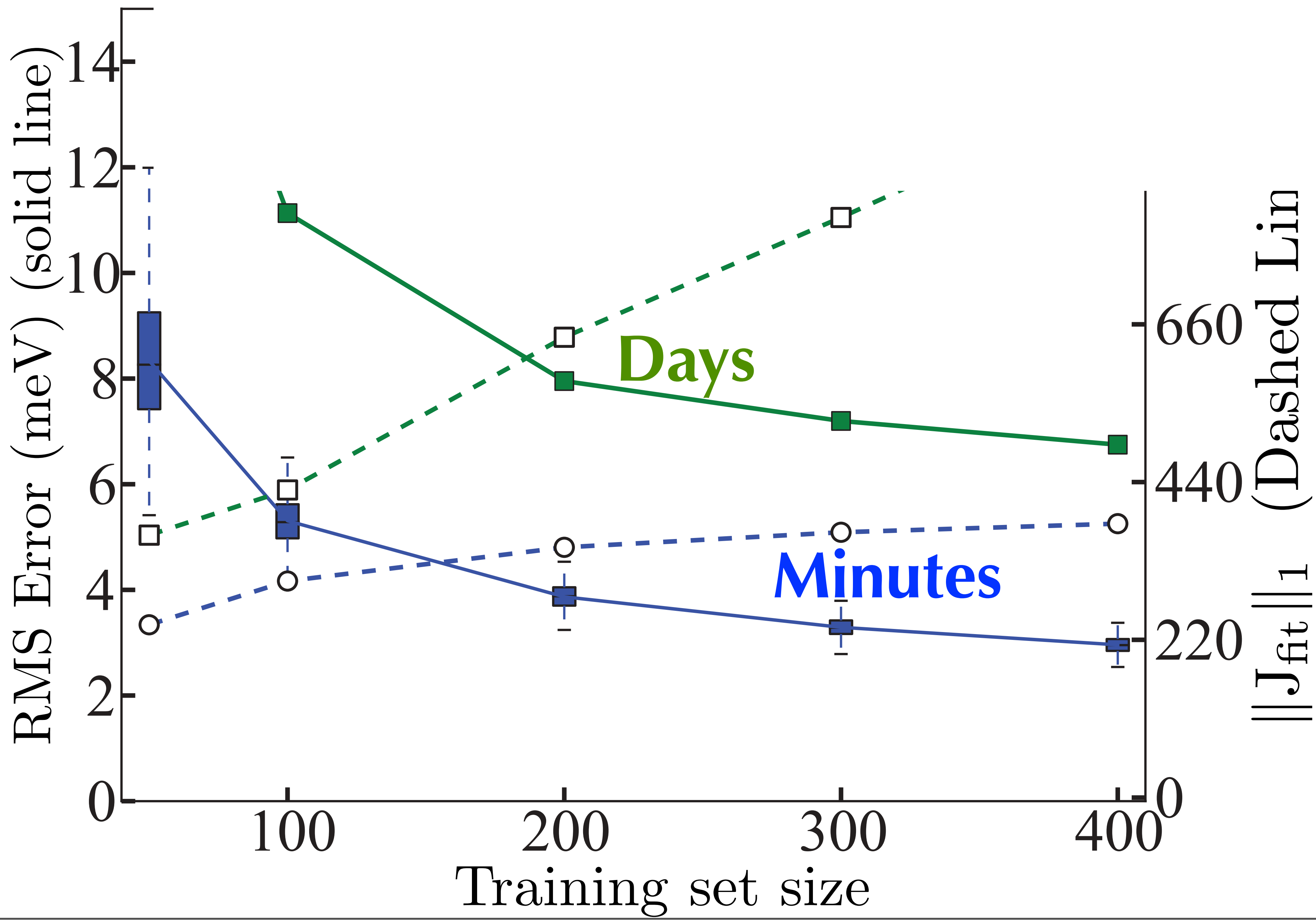
- Easier to implement



CSCE: Compressive sensing-based CE

UNCLE

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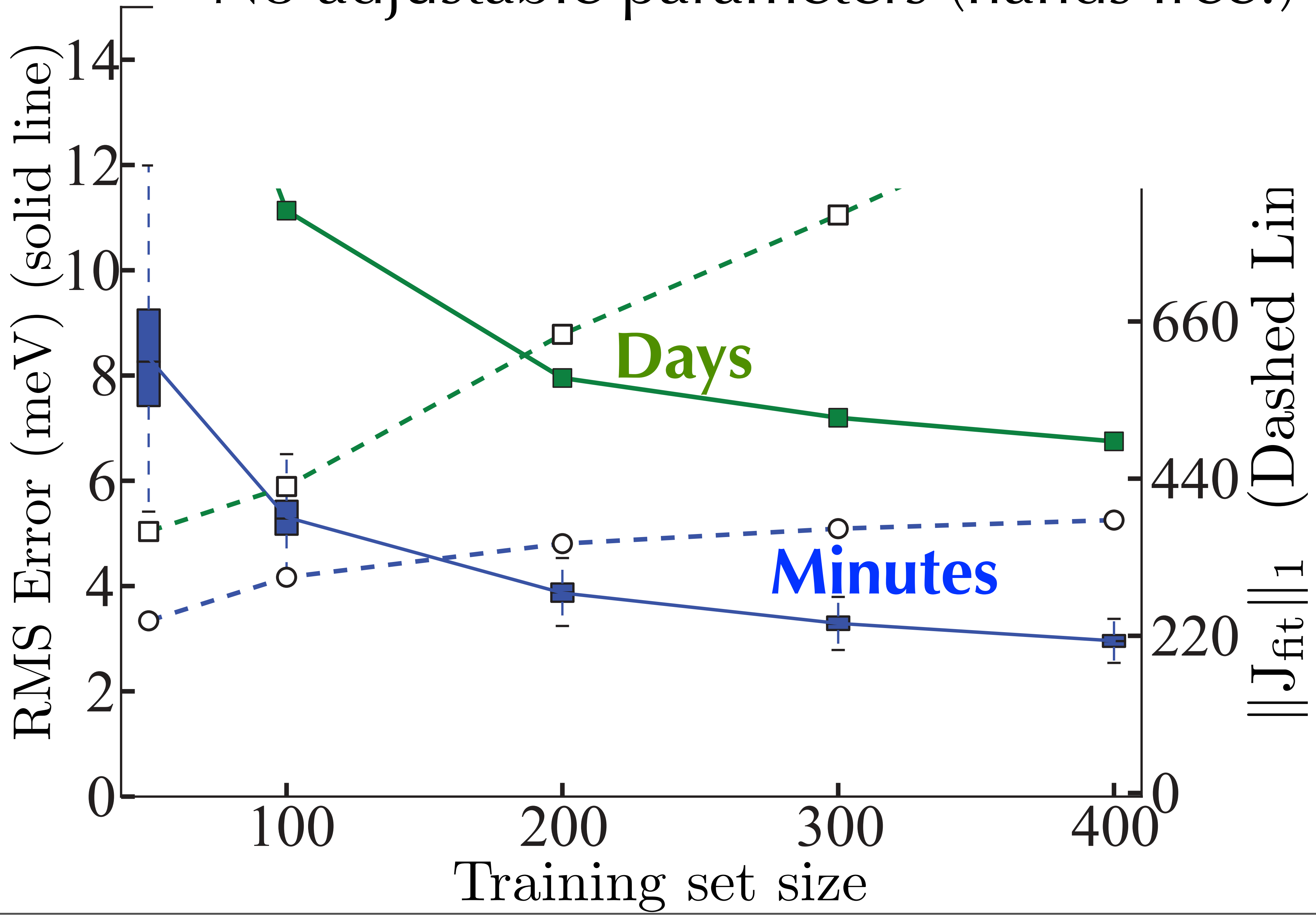
- Easier to implement
- No adjustable parameters (hands free!)



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UNCLE

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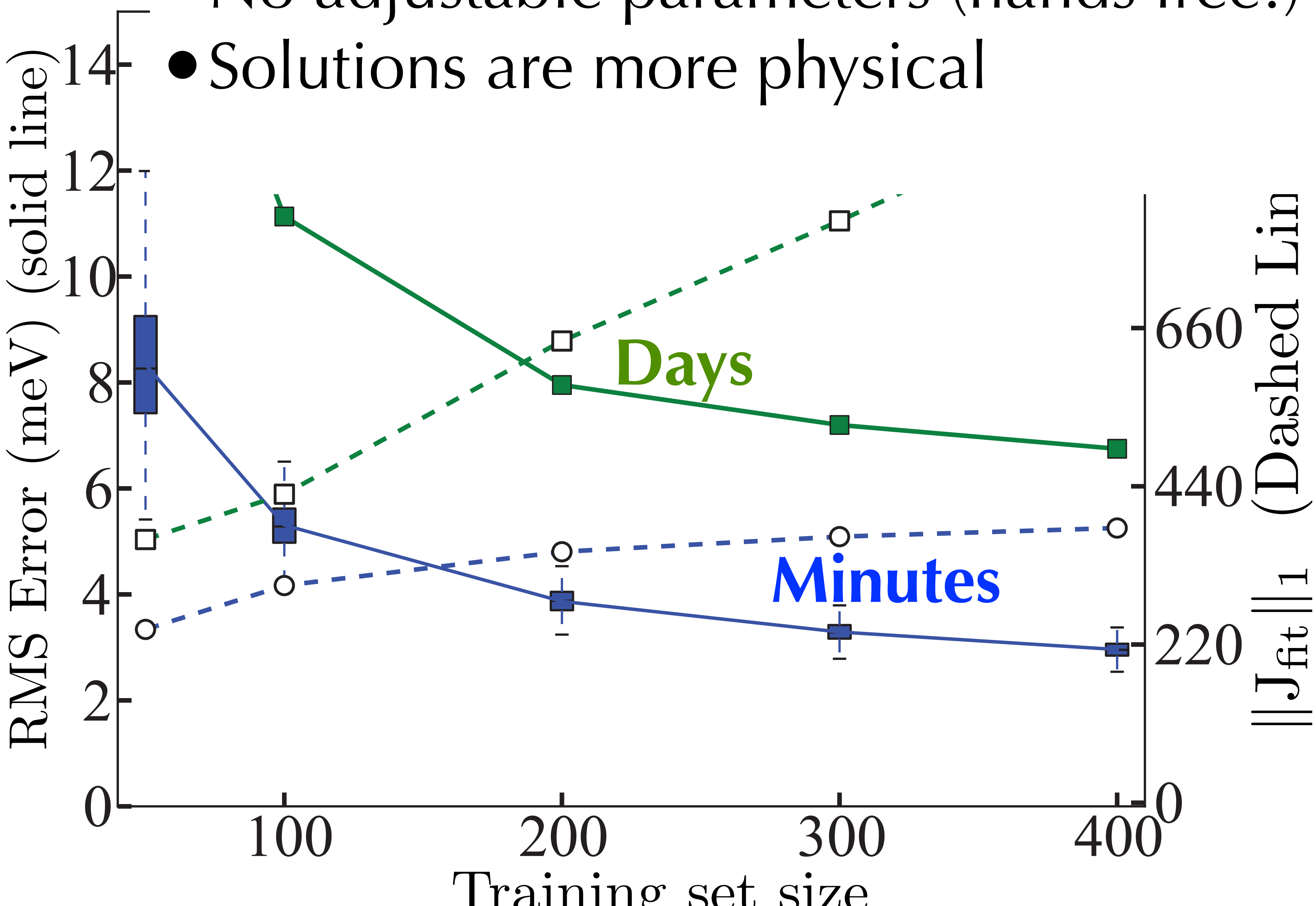
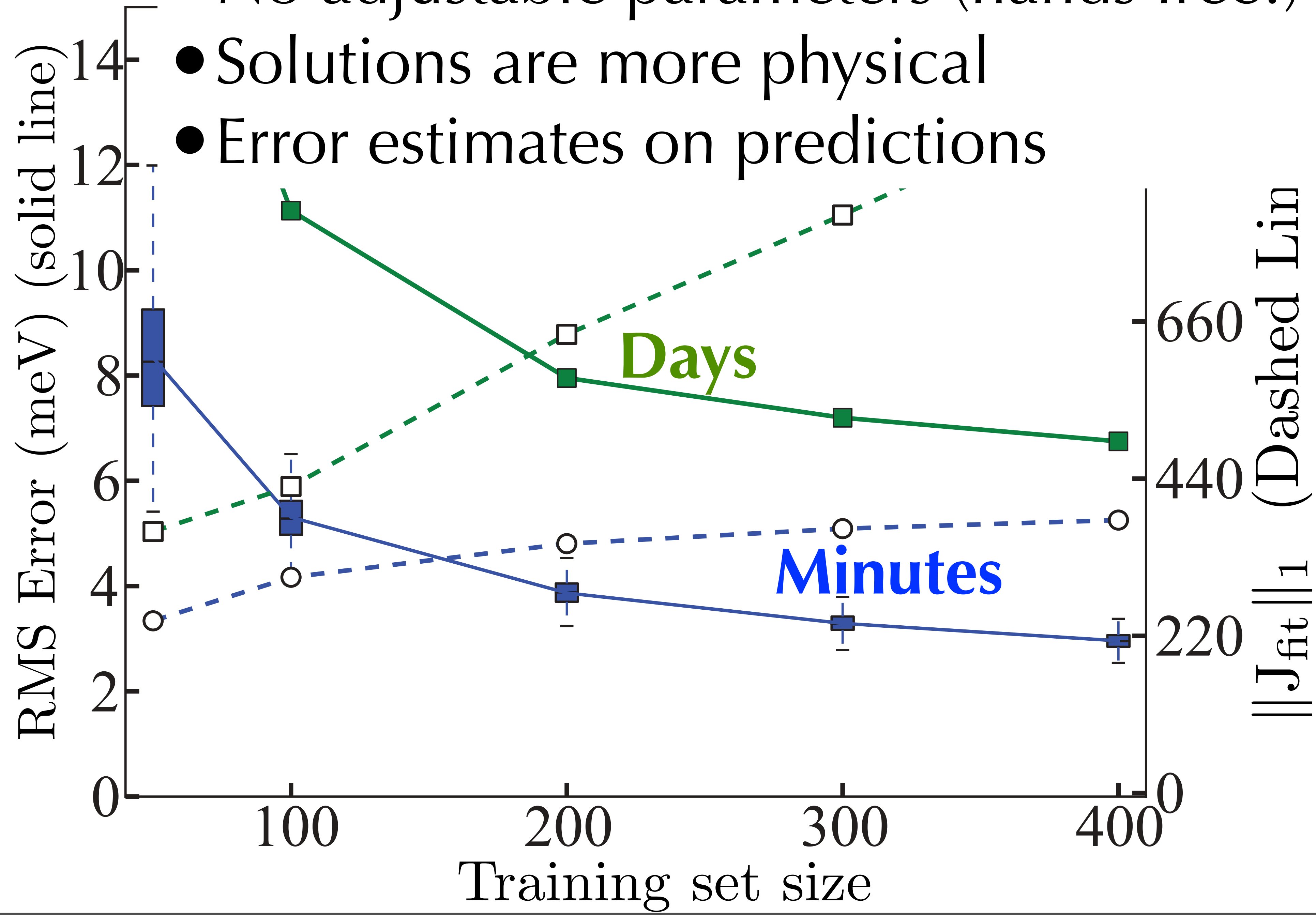


CSCE: Compressive sensing-based CE

UNCLE

- Faster(!)
- Better predictions
- Easier to implement
- No adjustable parameters (hands free!)
- Solutions are more physical
- Error estimates on predictions



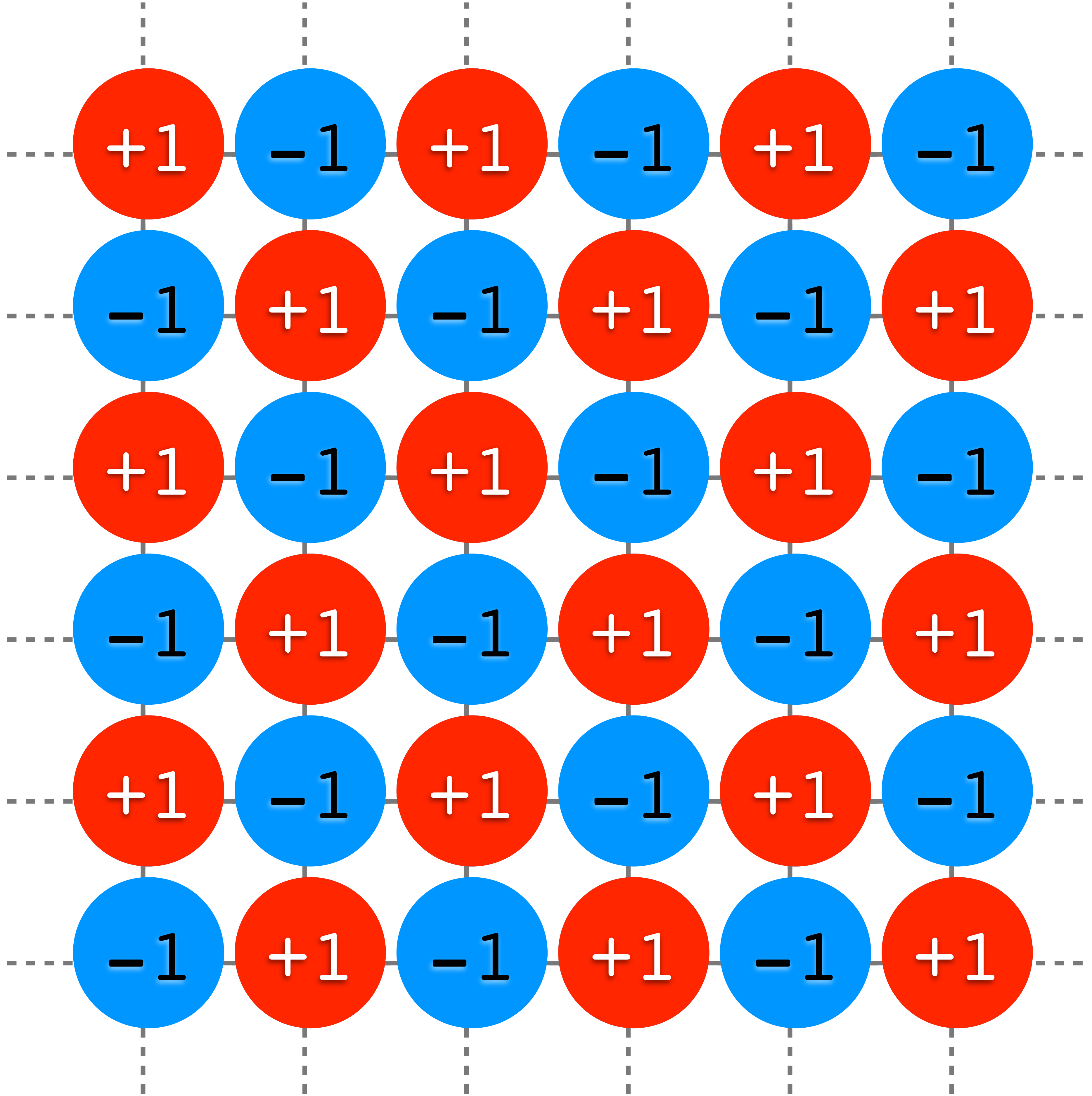
Further reading

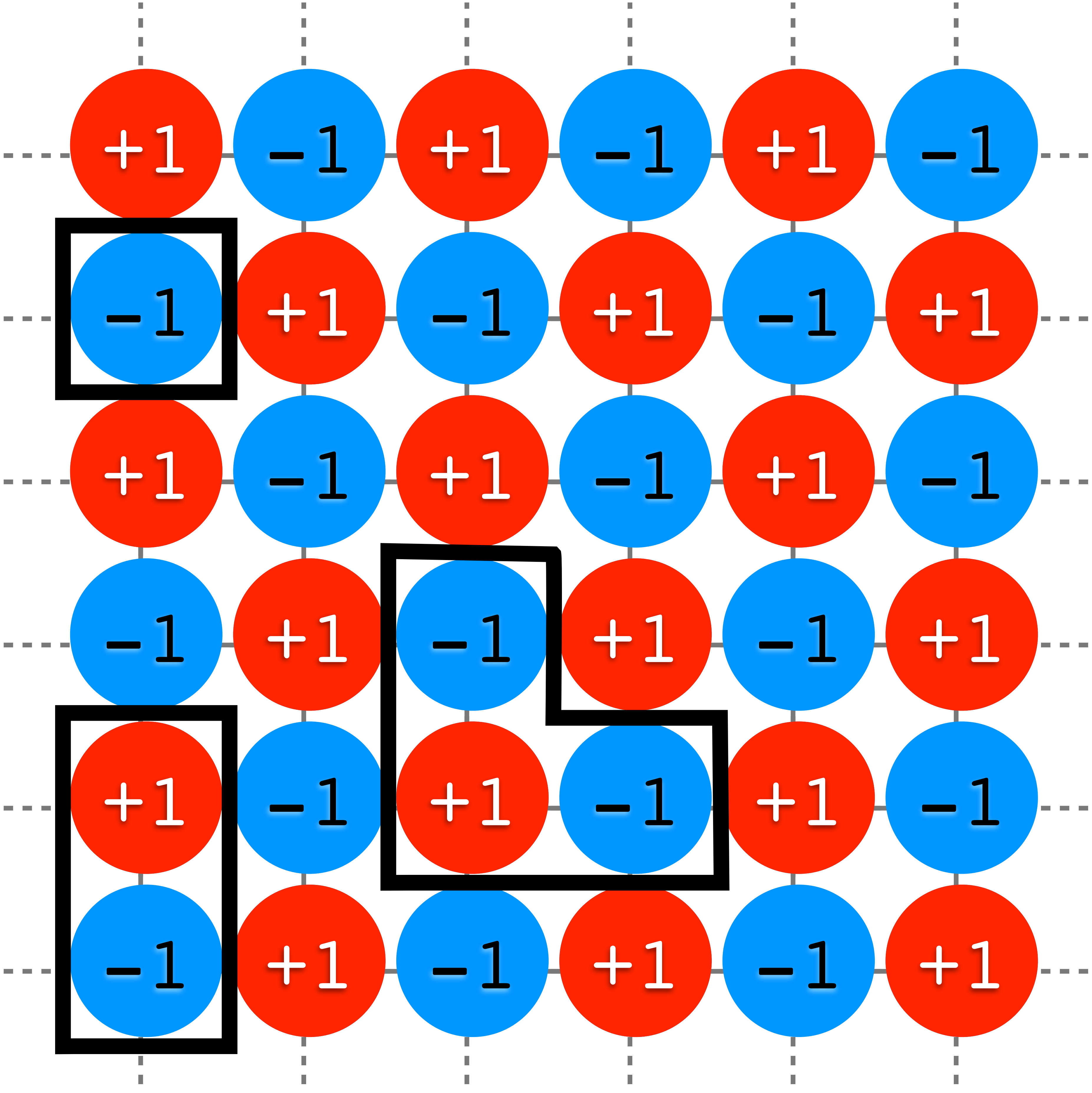
Lance J. Nelson, Gus L. W. Hart, Fei Zhou, and Vidvuds Ozolins, "*Cluster expansion made easy with Bayesian compressive sensing*," arXiv:1307.2938 [cond-mat.mtrl-sci]

Lance J. Nelson, Gus L. W. Hart, Fei Zhou, and Vidvuds Ozolins, "*Compressive sensing as a paradigm for building physics models*," Phys. Rev. B **87** 035125 (2013).

E. J. Candès and M. B. Wakin, "*An introduction to compressive sampling*," Signal Processing Magazine, IEEE, vol. 25, no. 2, pp. 21–30 (2008).

T. Strohmer, "*Measure What Should be Measured: Progress and Challenges in Compressive Sensing*," Signal Processing Letters **19** 887 (2012).

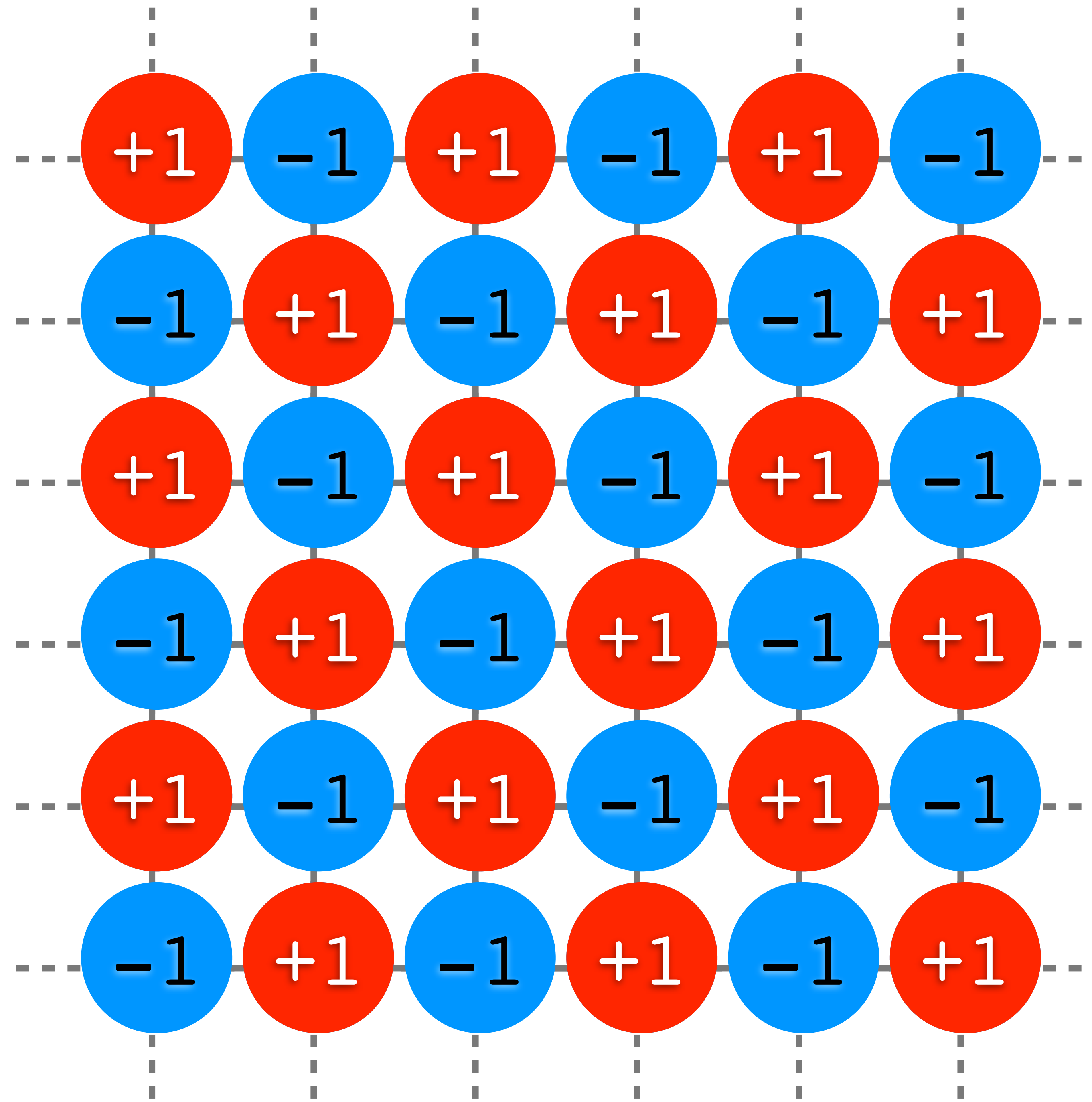

+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1


+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \bigcirc + J_1 \bigcirc + J_2 \bigcirc\bigcirc + J_3 \bigcirc\bigcirc\bigcirc + \cdots$$

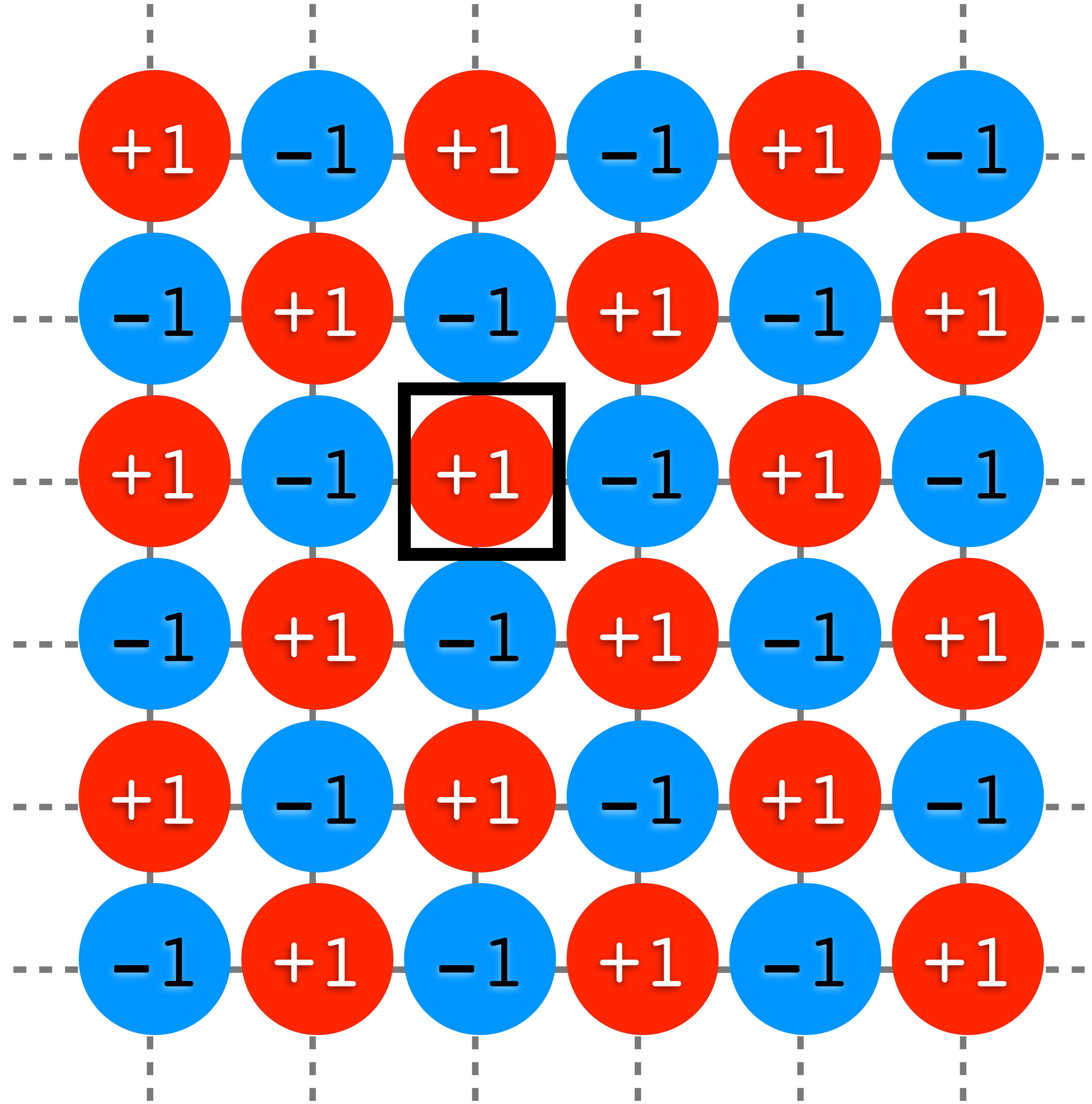
Empty cluster is trivial

$$1 = \frac{1}{N} \sum_{i}^{\text{lattice}} S_i^0$$



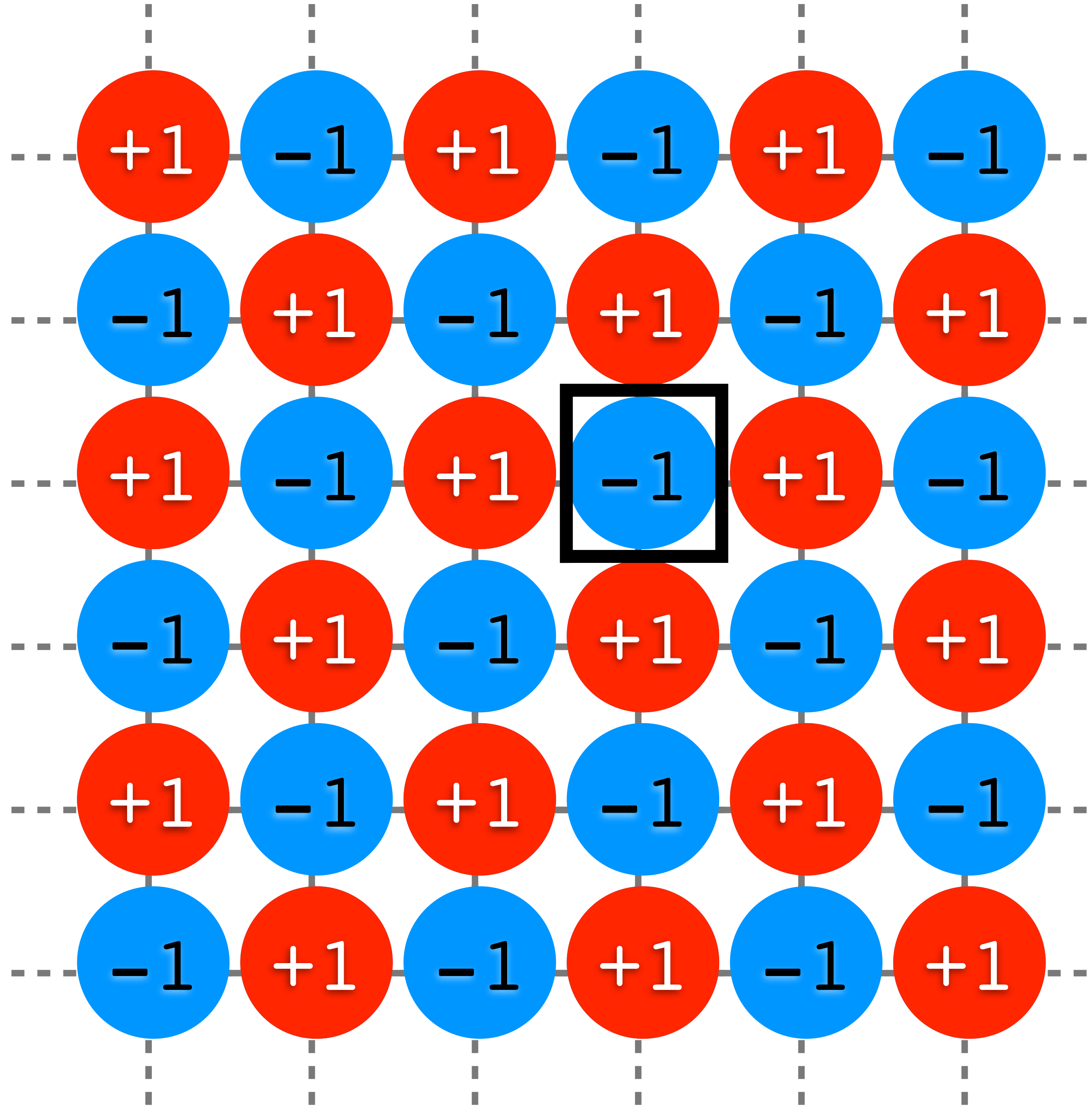
$$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0 \, \bigcirc + J_1 \, \bullet + J_2 \, \bullet\bullet + J_3 \, \bullet\bullet\bullet + \cdots$$

$$? = \frac{1}{N} \sum_i^{\text{lattice}} S_i$$



$$0 = (-1) + (+1) + (-1) + (+1) + \cdots$$

$$? = \frac{1}{N}\sum_{i}^{\text{lattice}} S_i$$



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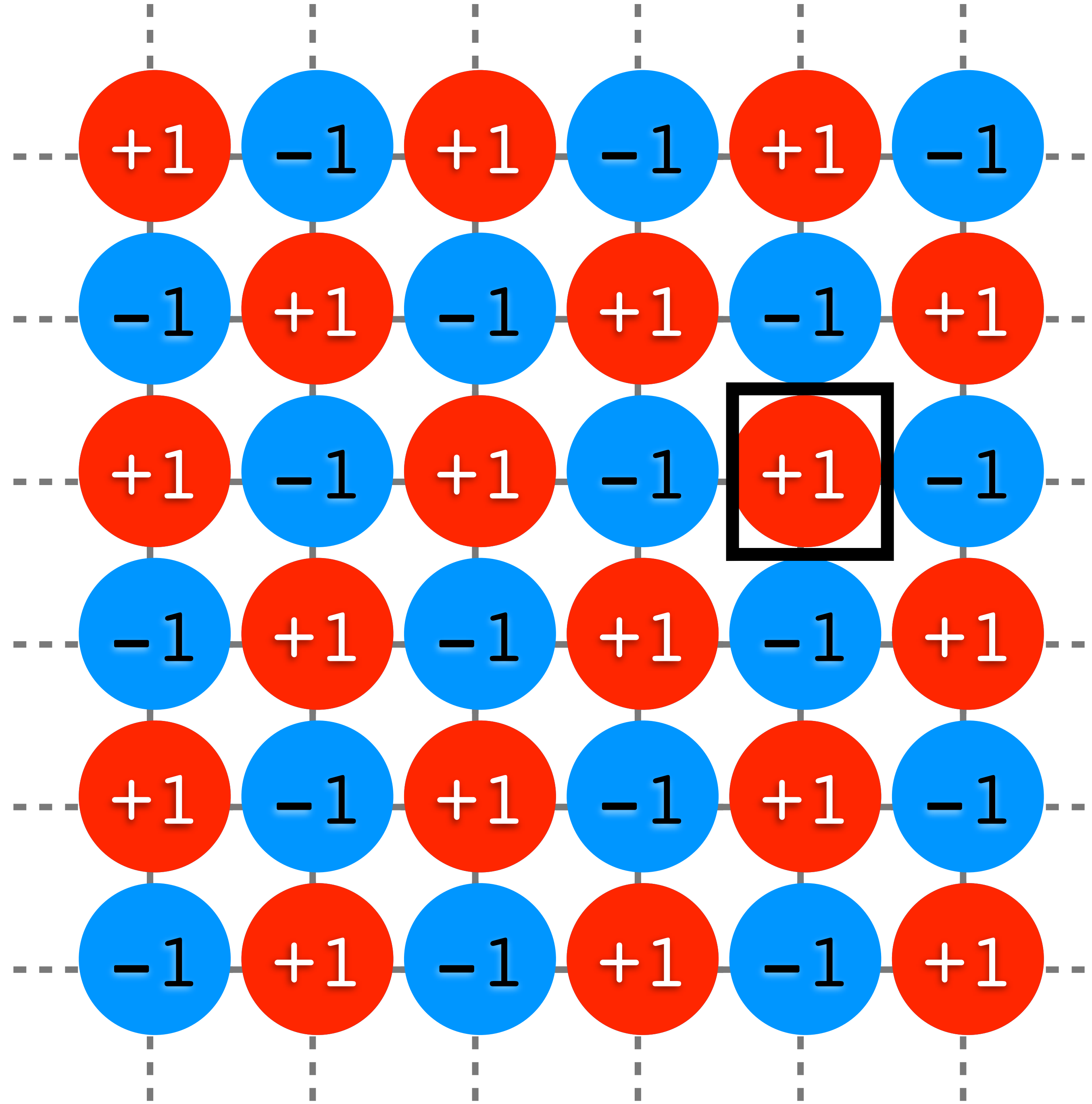

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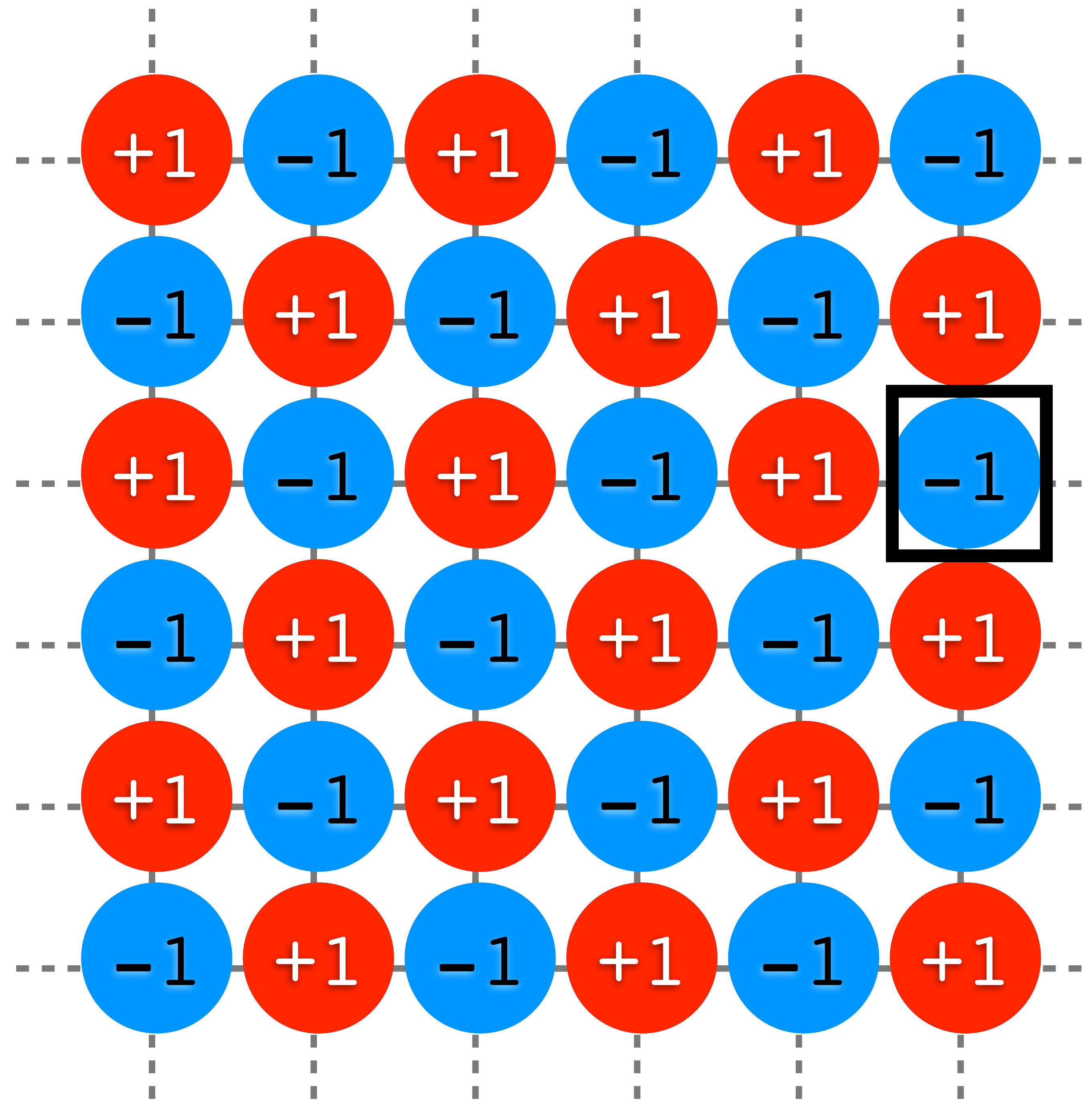

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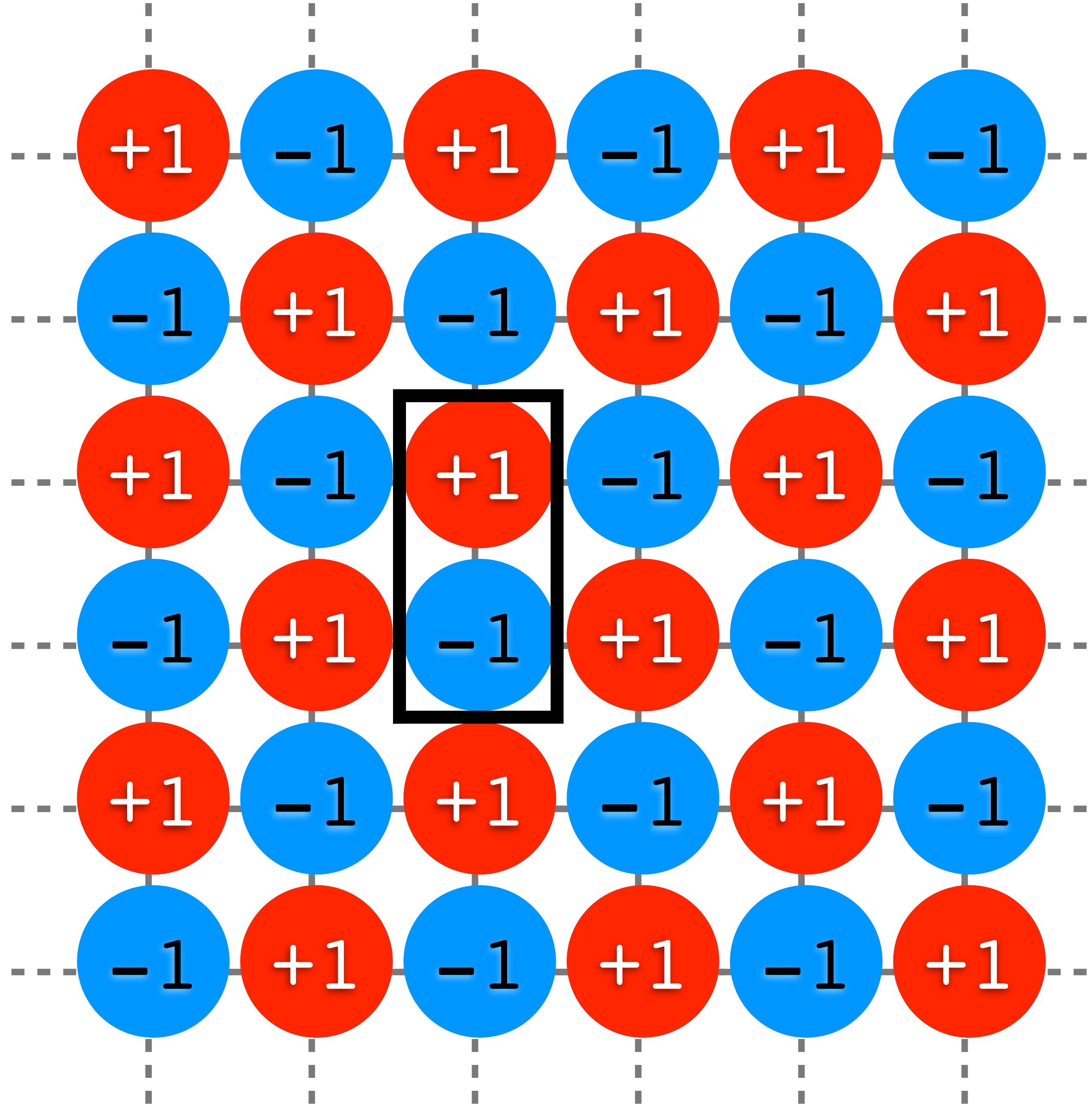
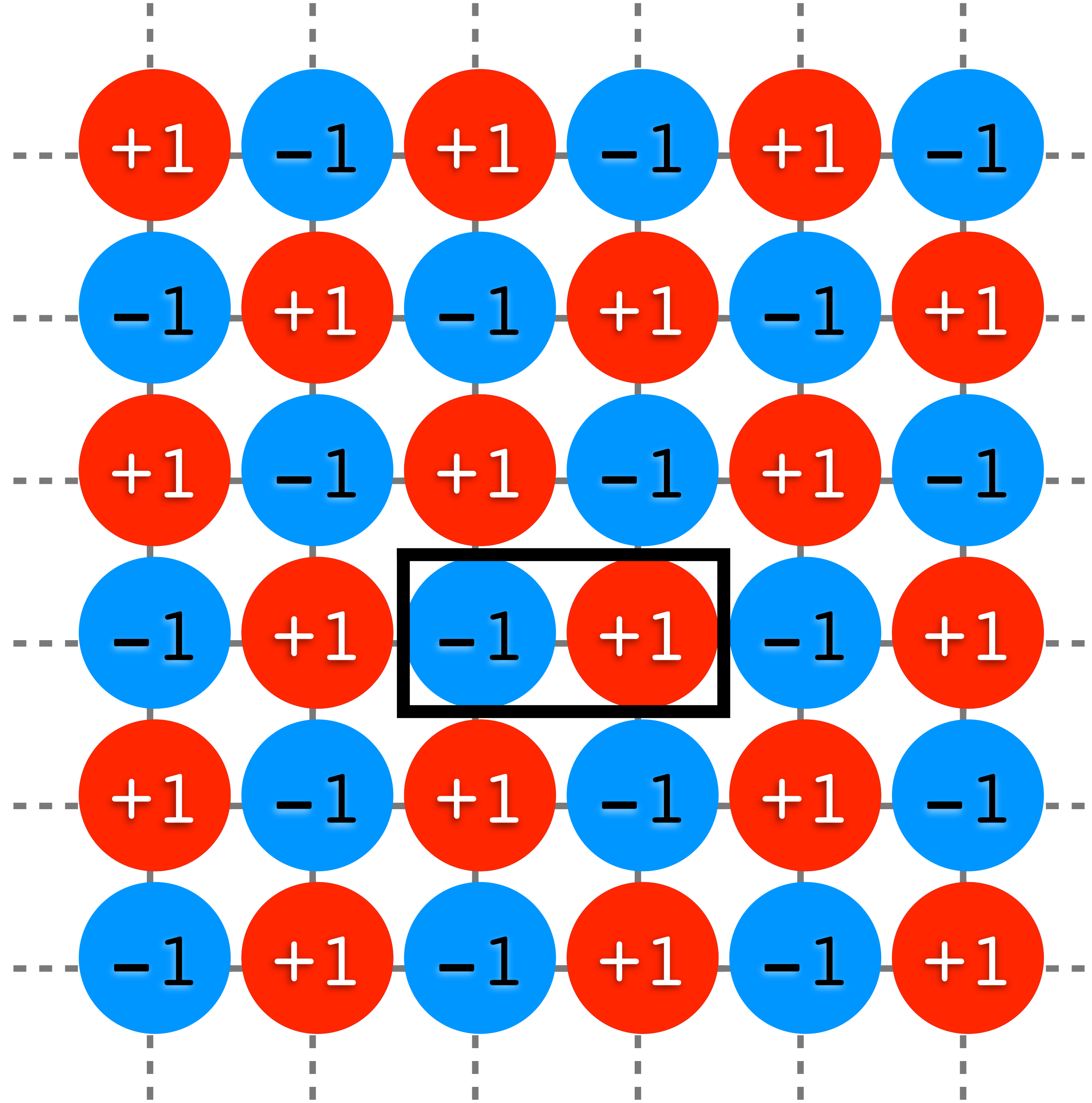
$f(\bigcirc\bigcirc\bigcirc\bigcirc) = J_0$ ◌ $+ \; J_1$ ● $+ \; J_2$ ●● $+ \; J_3$ ●●● $+ \cdots$



$$? = \frac{1}{N} \sum_{<i,j>_{\mathrm{N.N.}}}^{\mathrm{lattice}} S_i S_j$$

$$-1 = \left(\frac{1}{2}\right)\left(\frac{1}{4}\right)[(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)$$
$$[(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)]$$

$$f(\bigcirc\bigcirc\bigcirc\bigcirc) \;=\; J_0 \,\bigcirc \;+\; J_1 \,\bigcirc \;+\; J_2 \,\bigcirc\bigcirc \;+\; J_3 \,\bigcirc\bigcirc\bigcirc \;+\cdots$$



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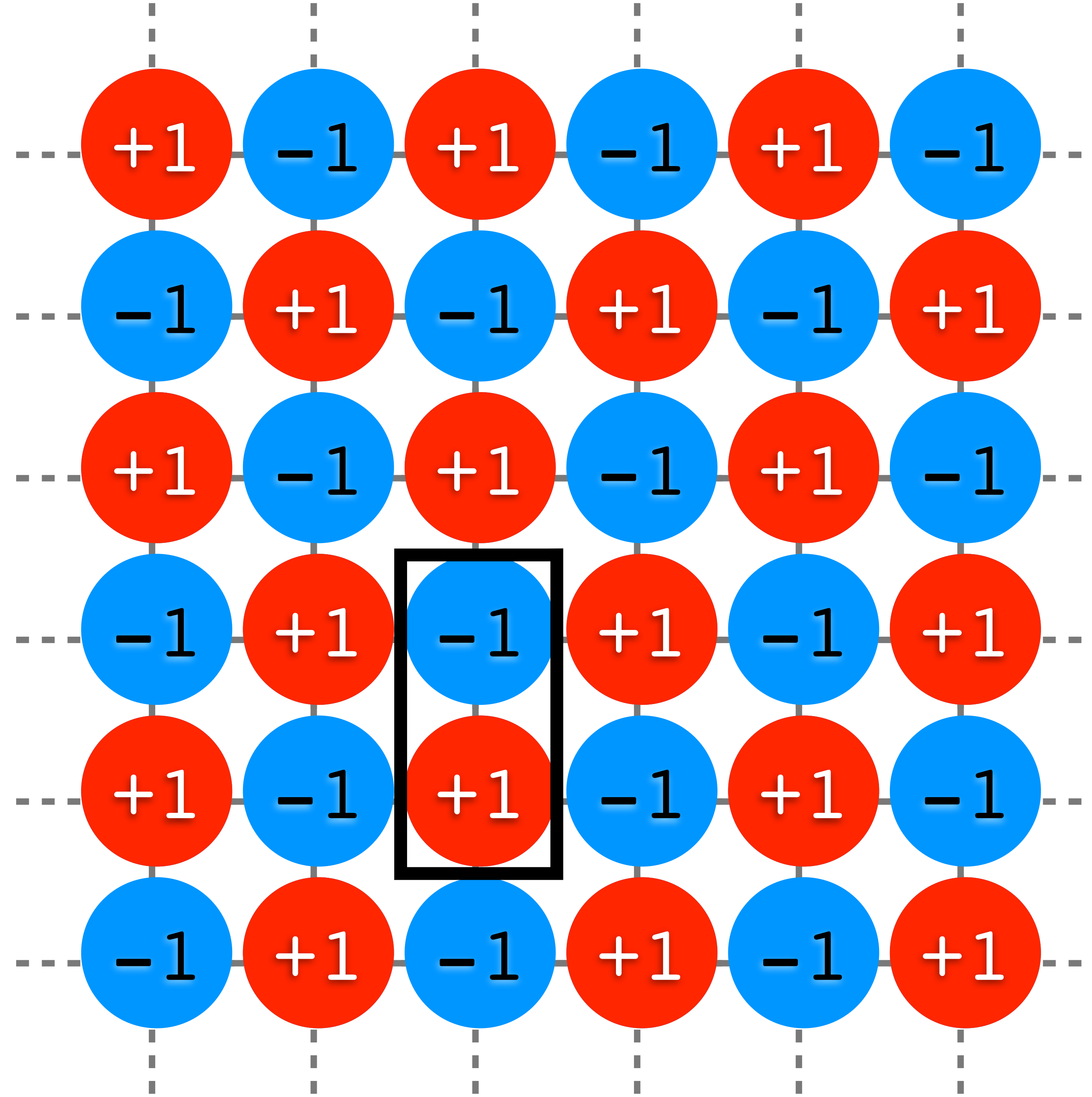

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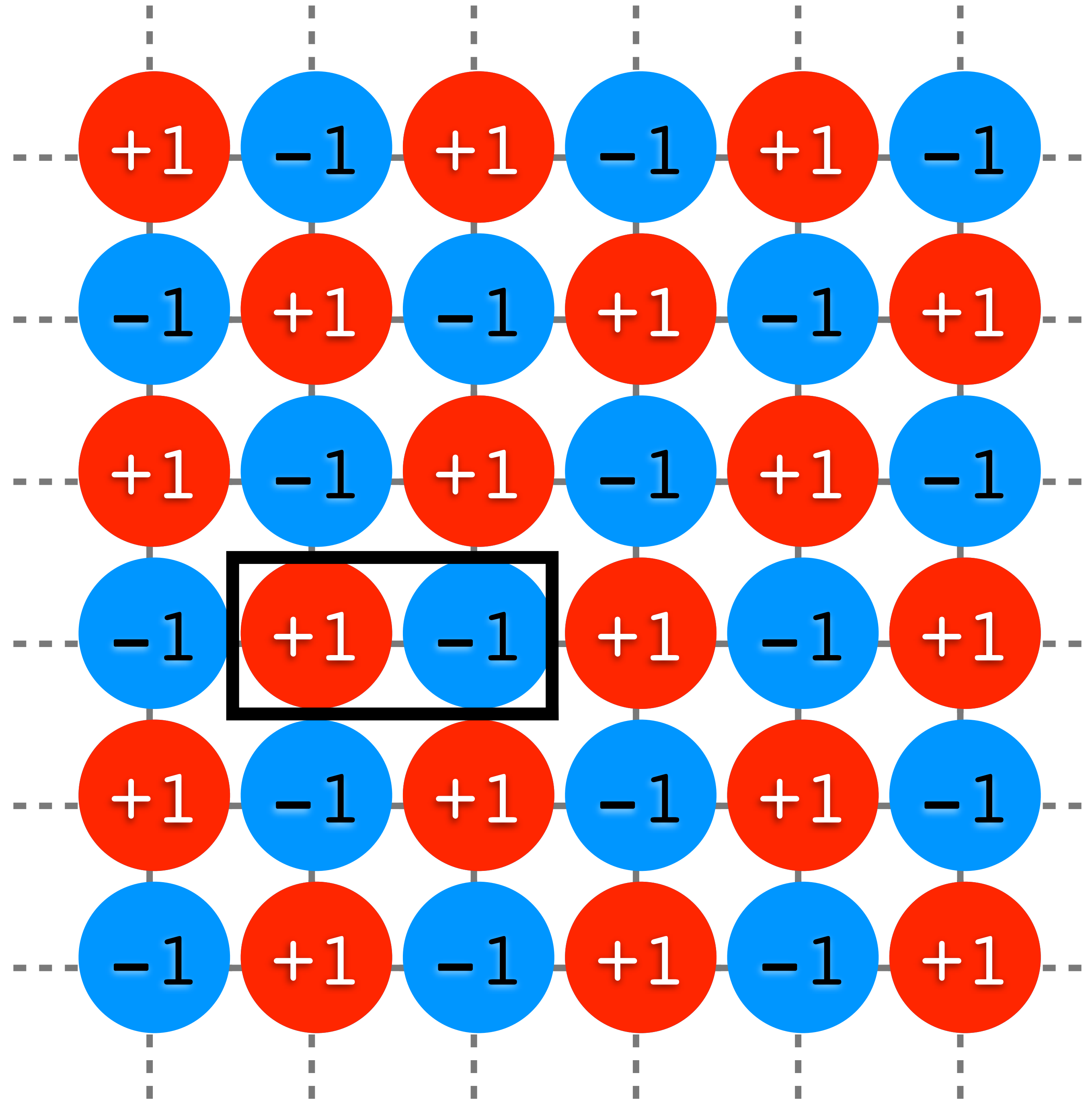

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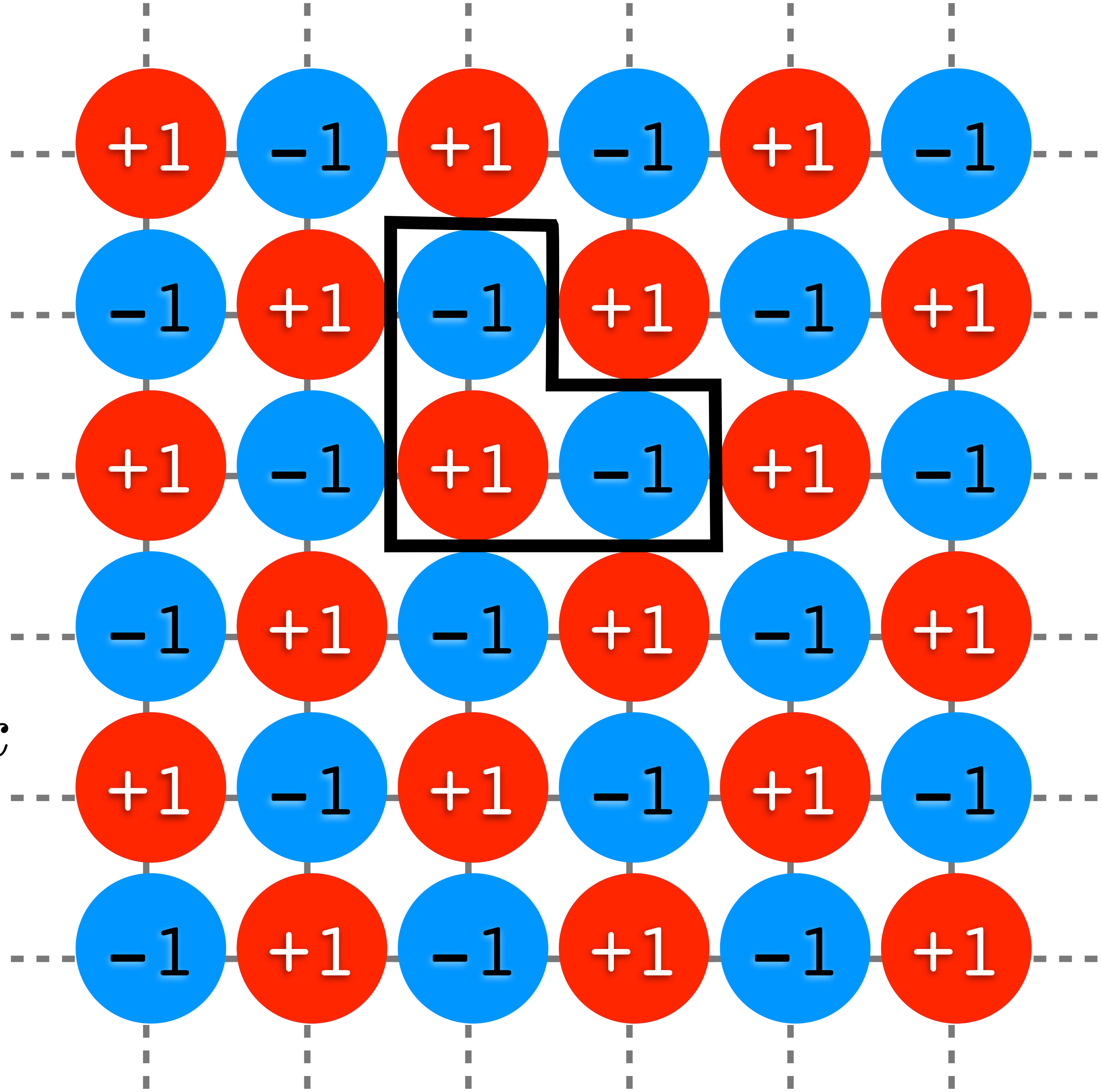

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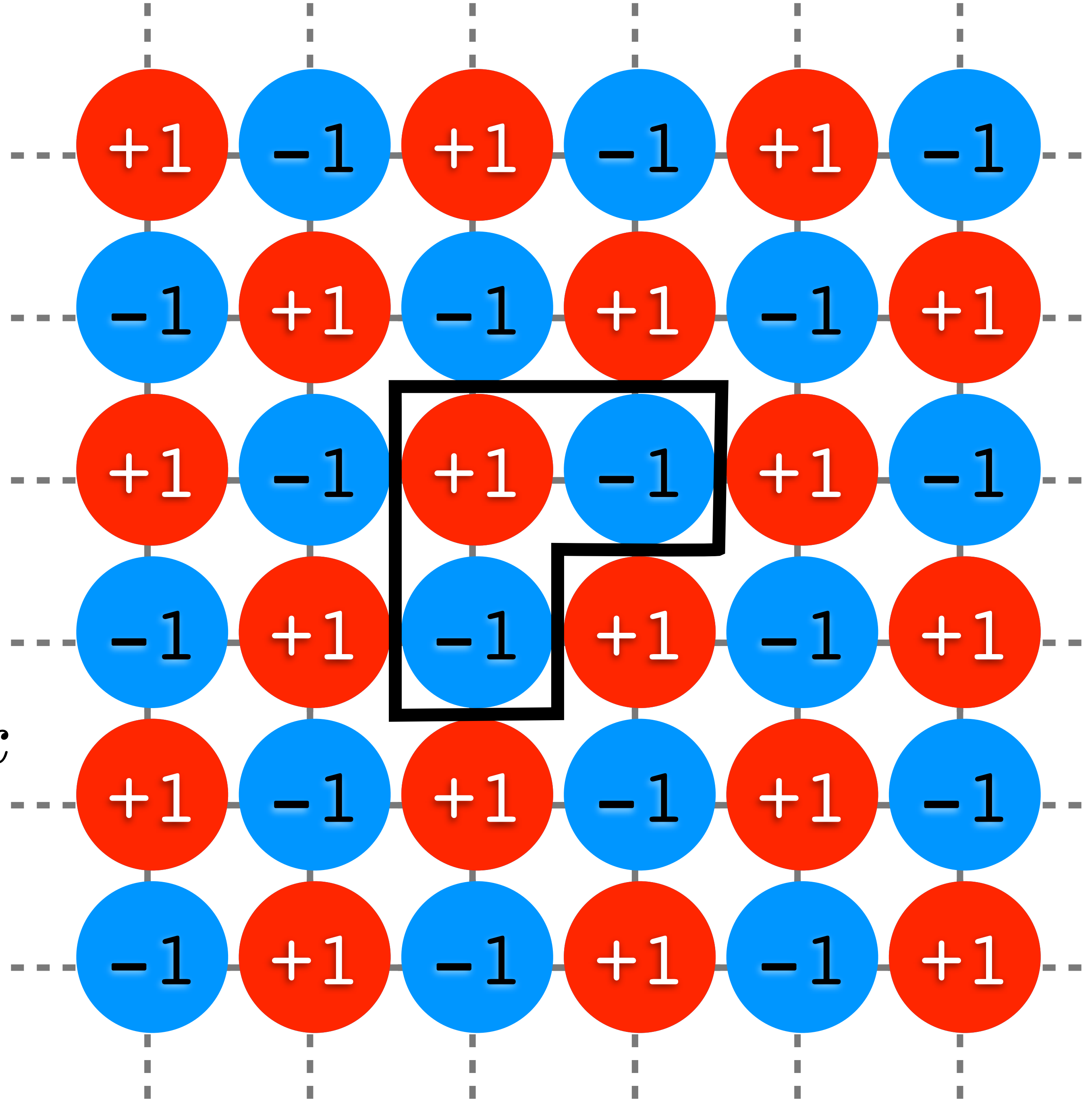

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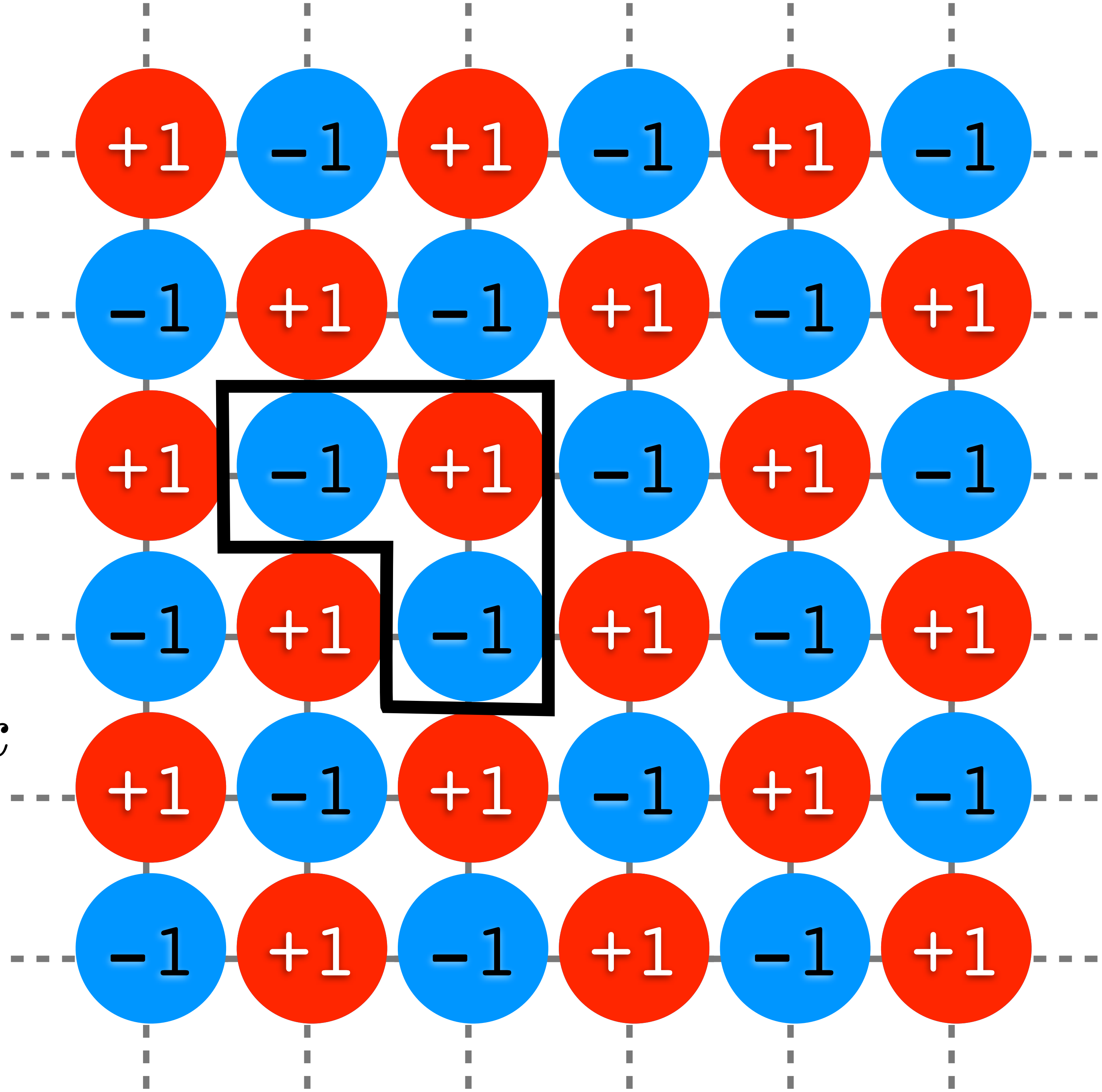

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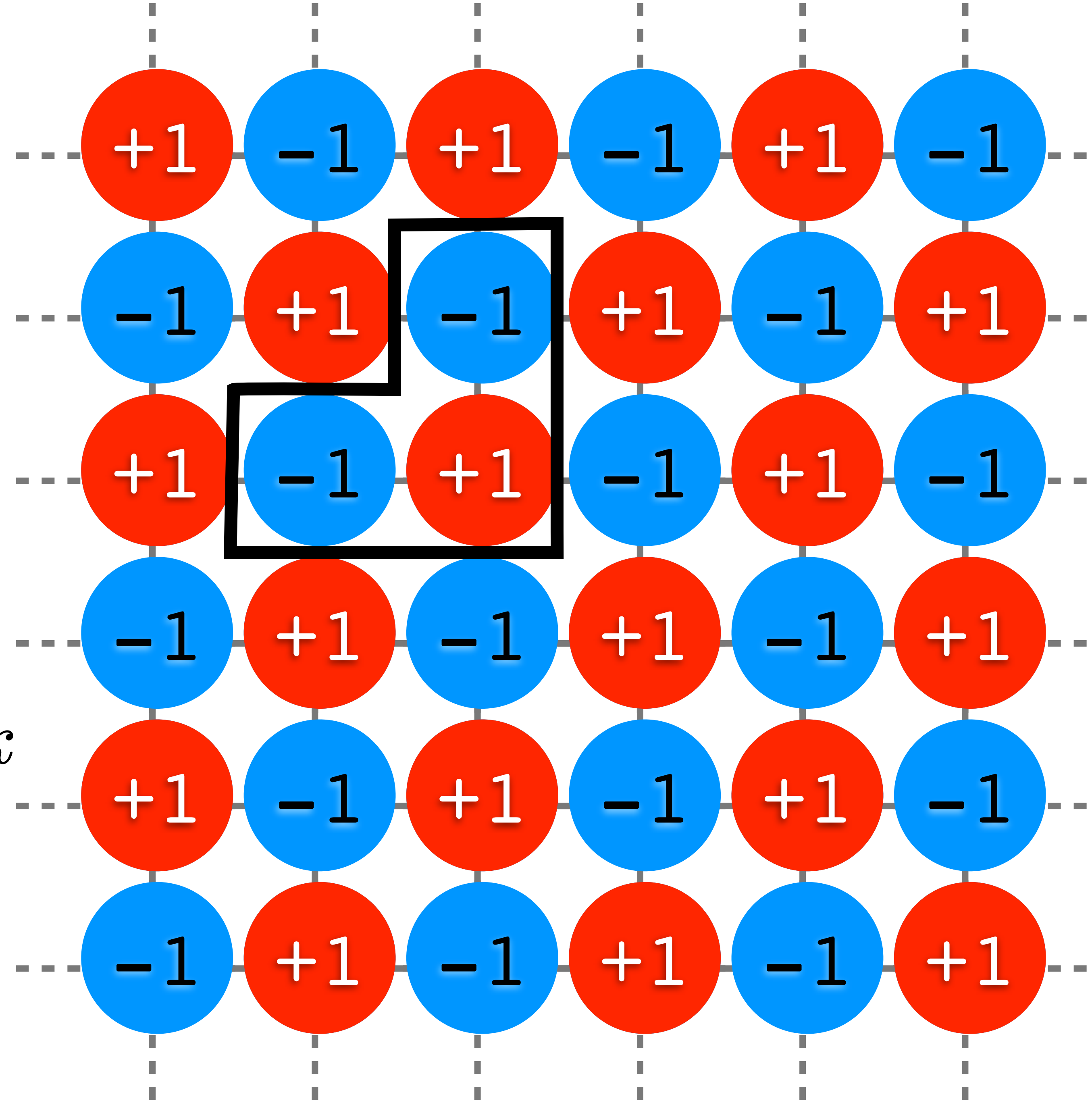

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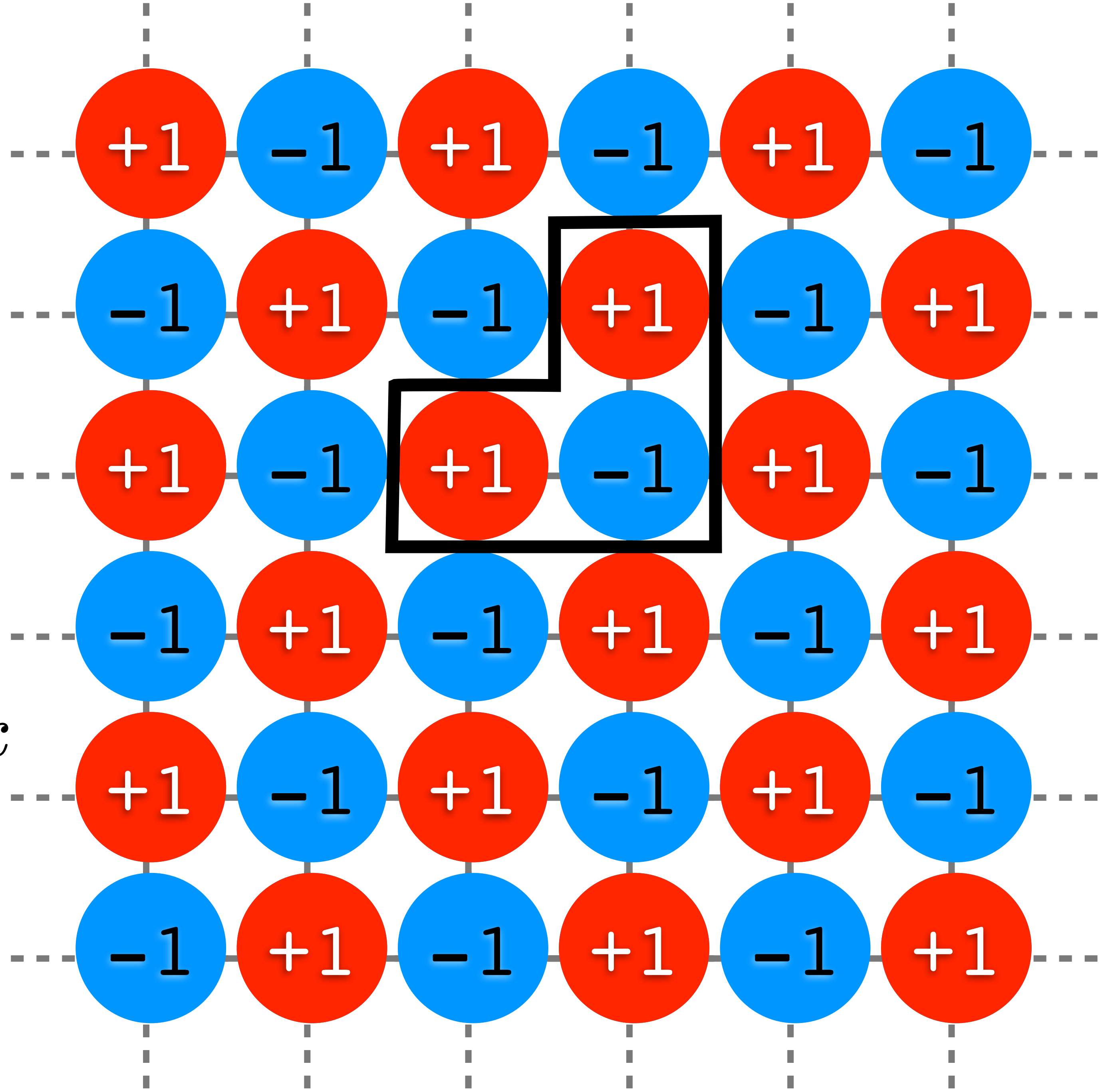

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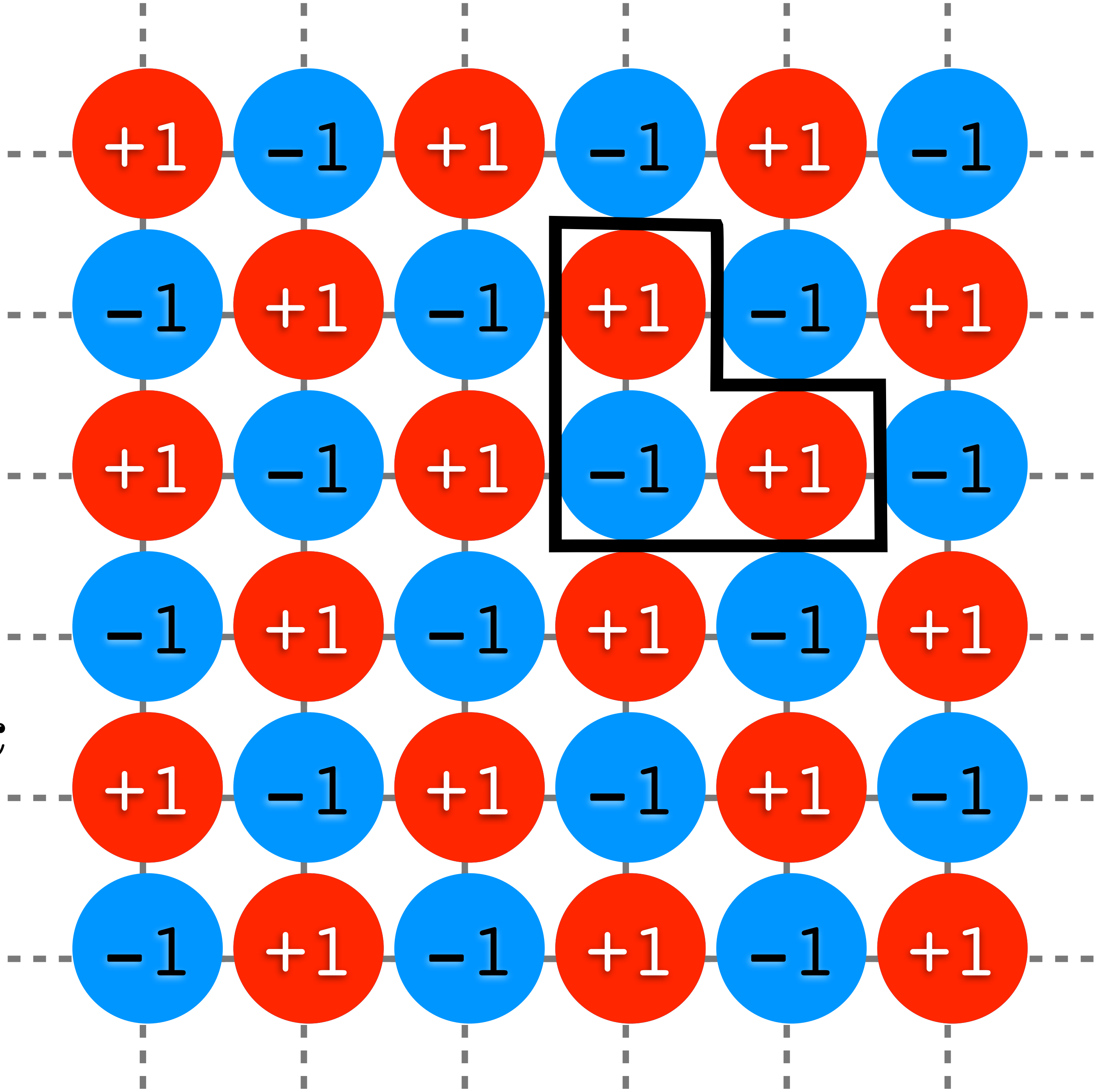

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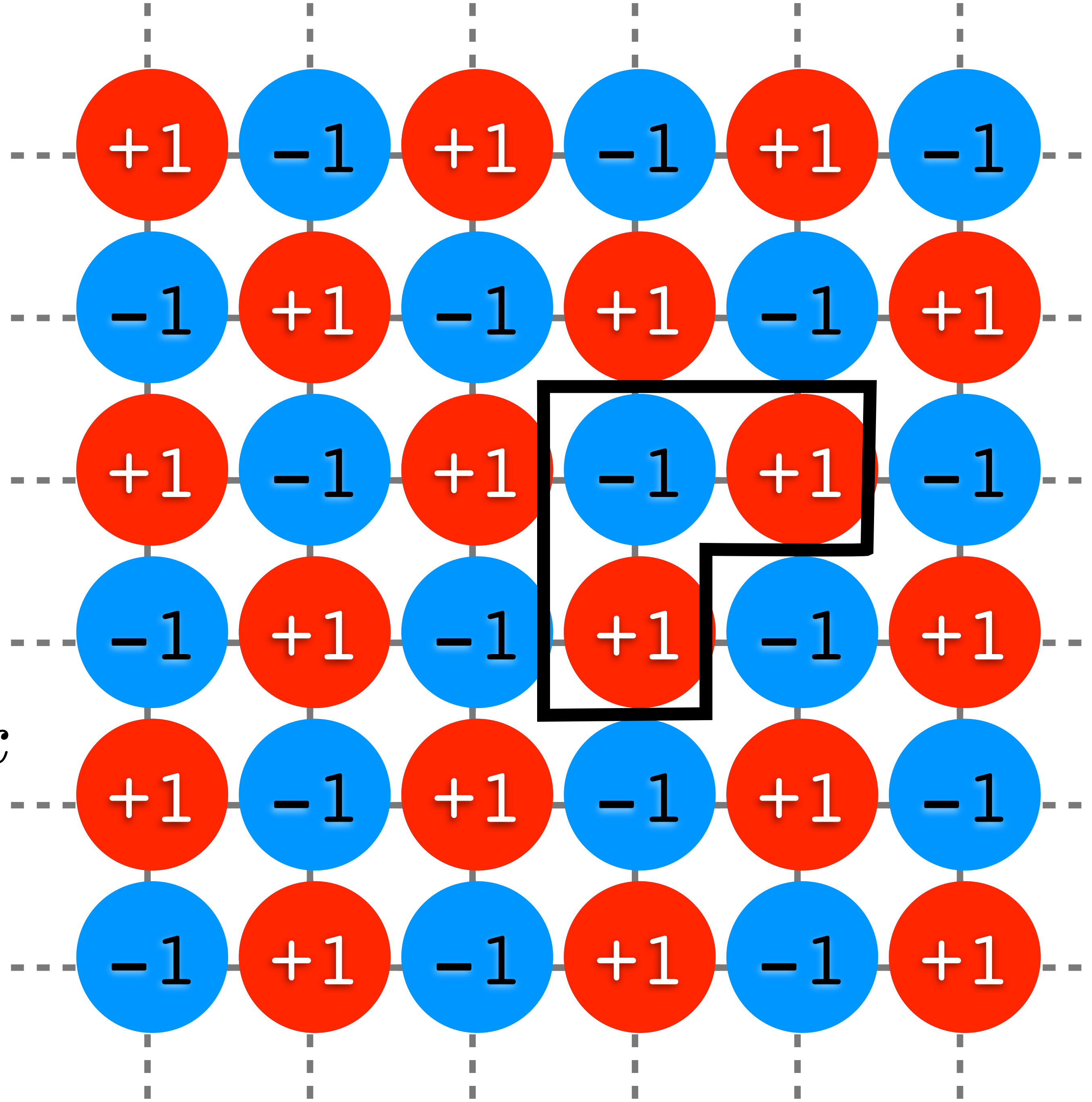
$$? = \frac{1}{N} \sum_{<i,j,k>_{\mathrm{N.N.}}}^{\text{lattice}} S_i S_j S_k$$



?

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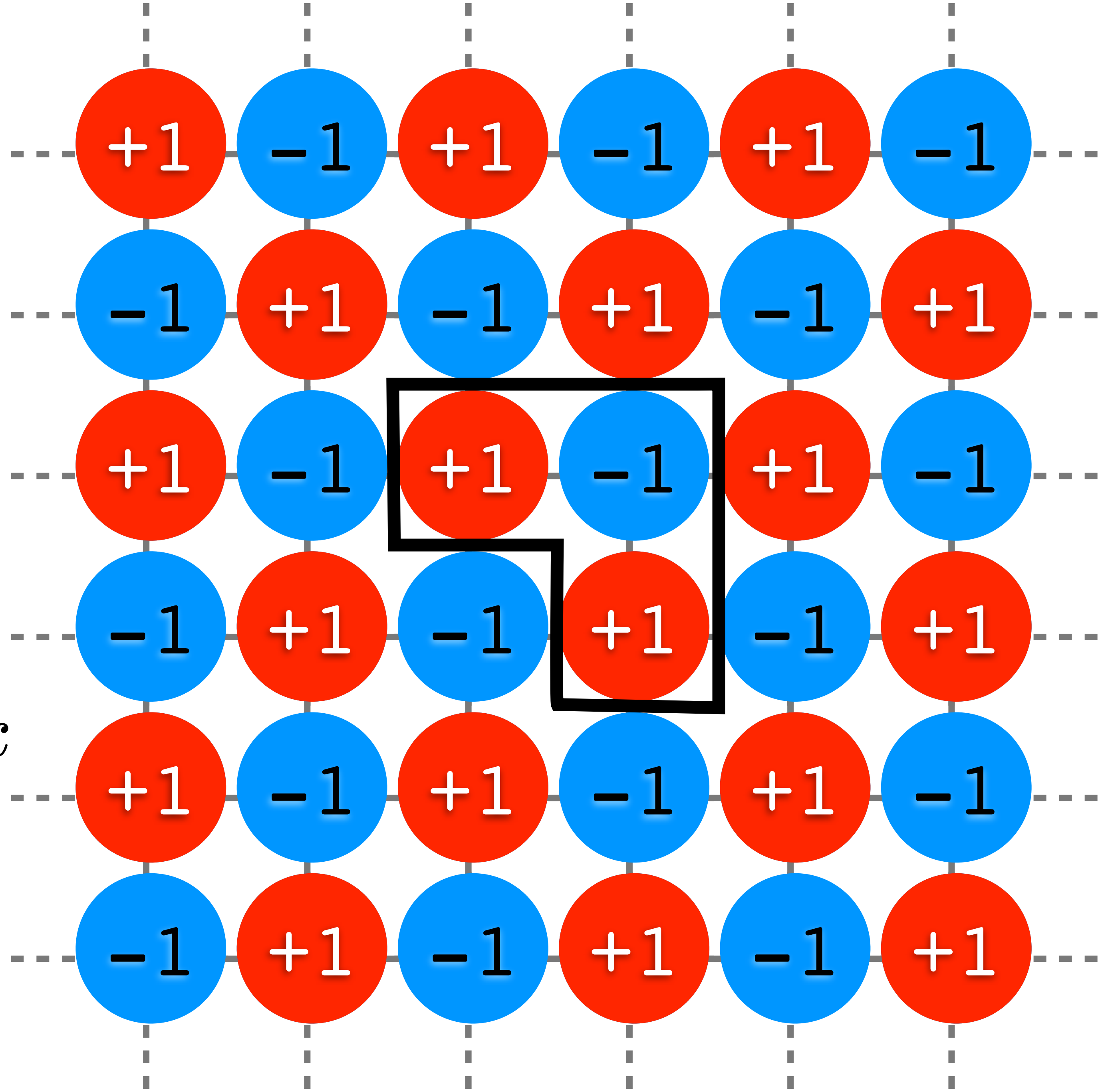
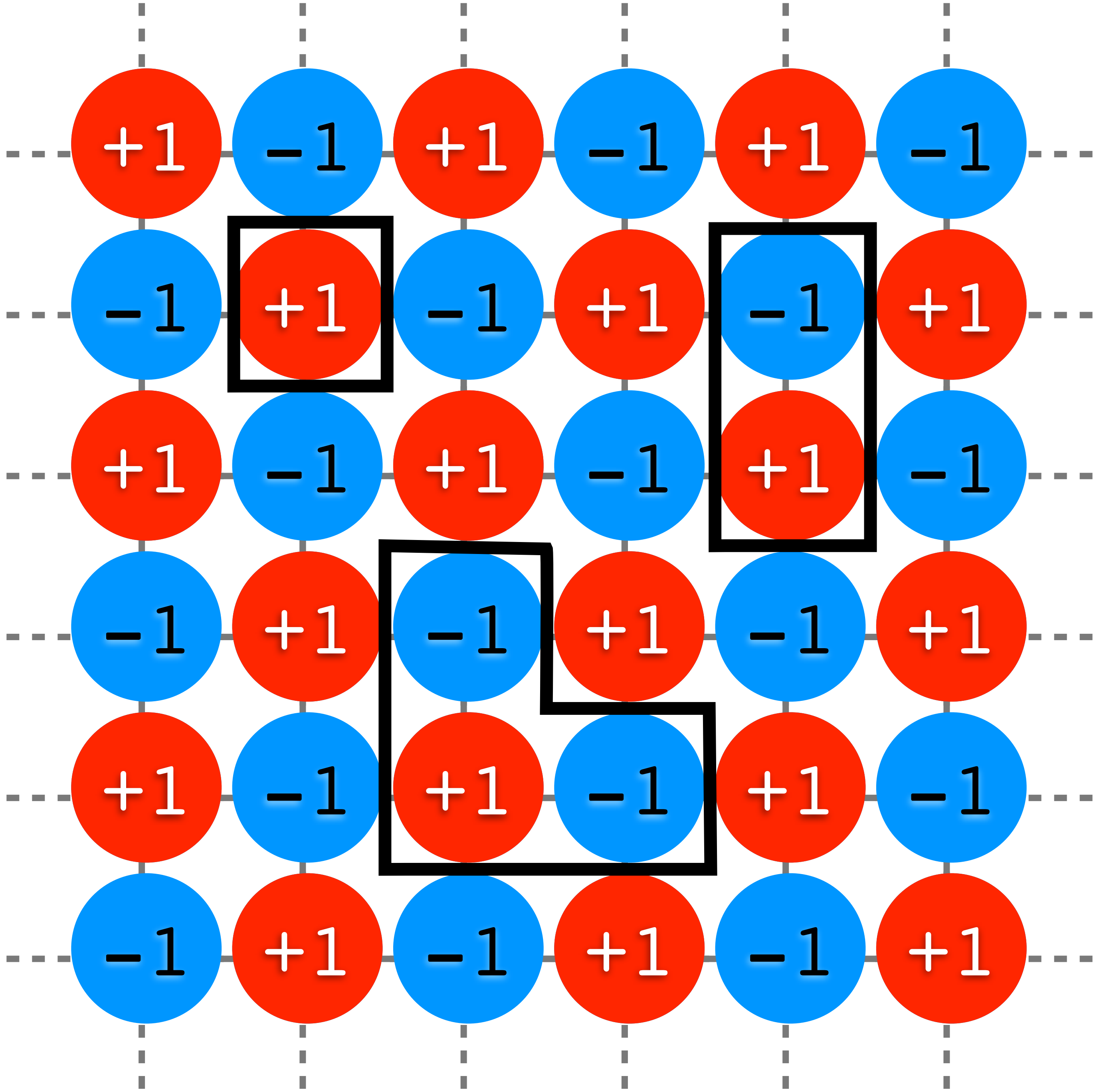
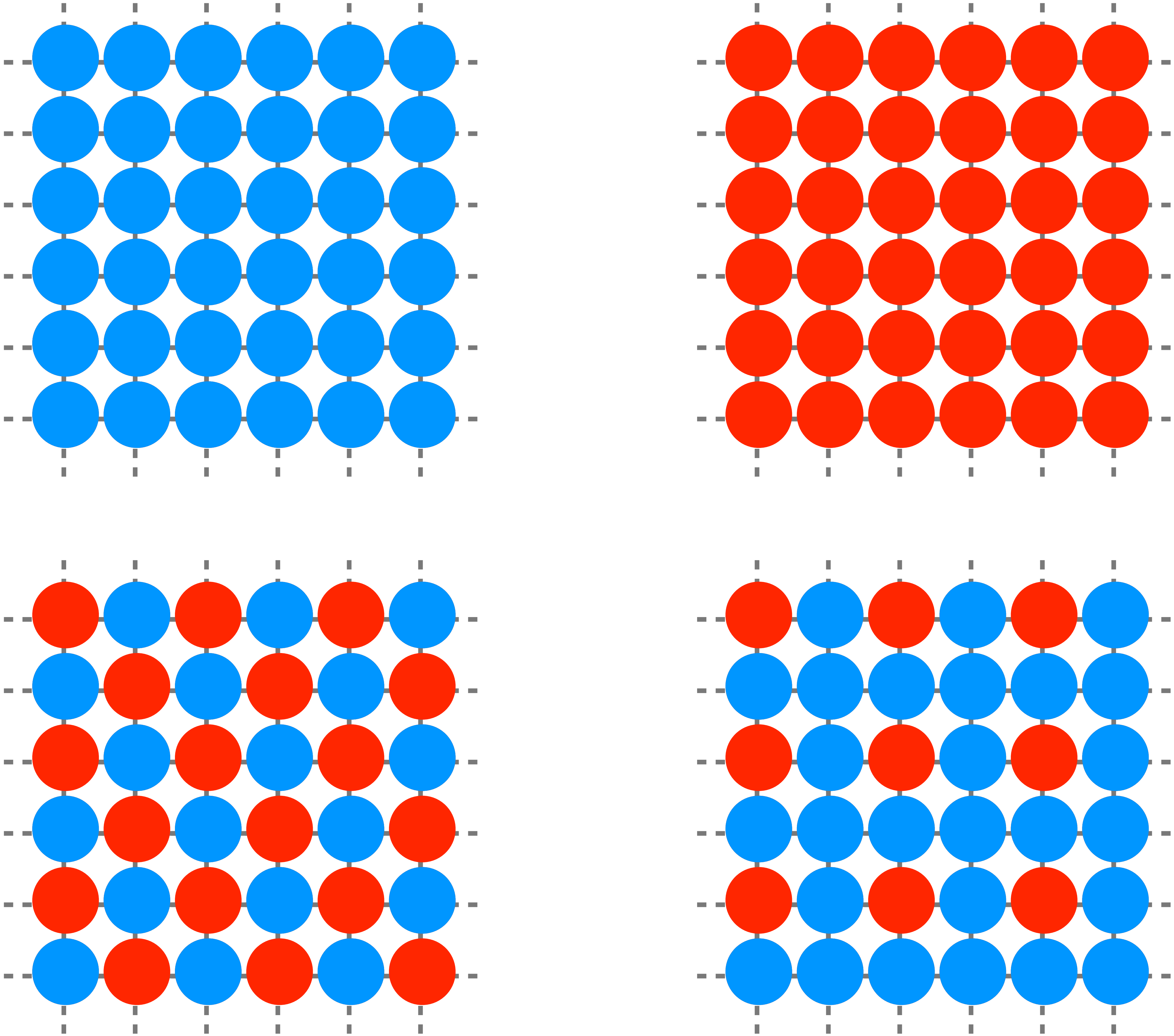
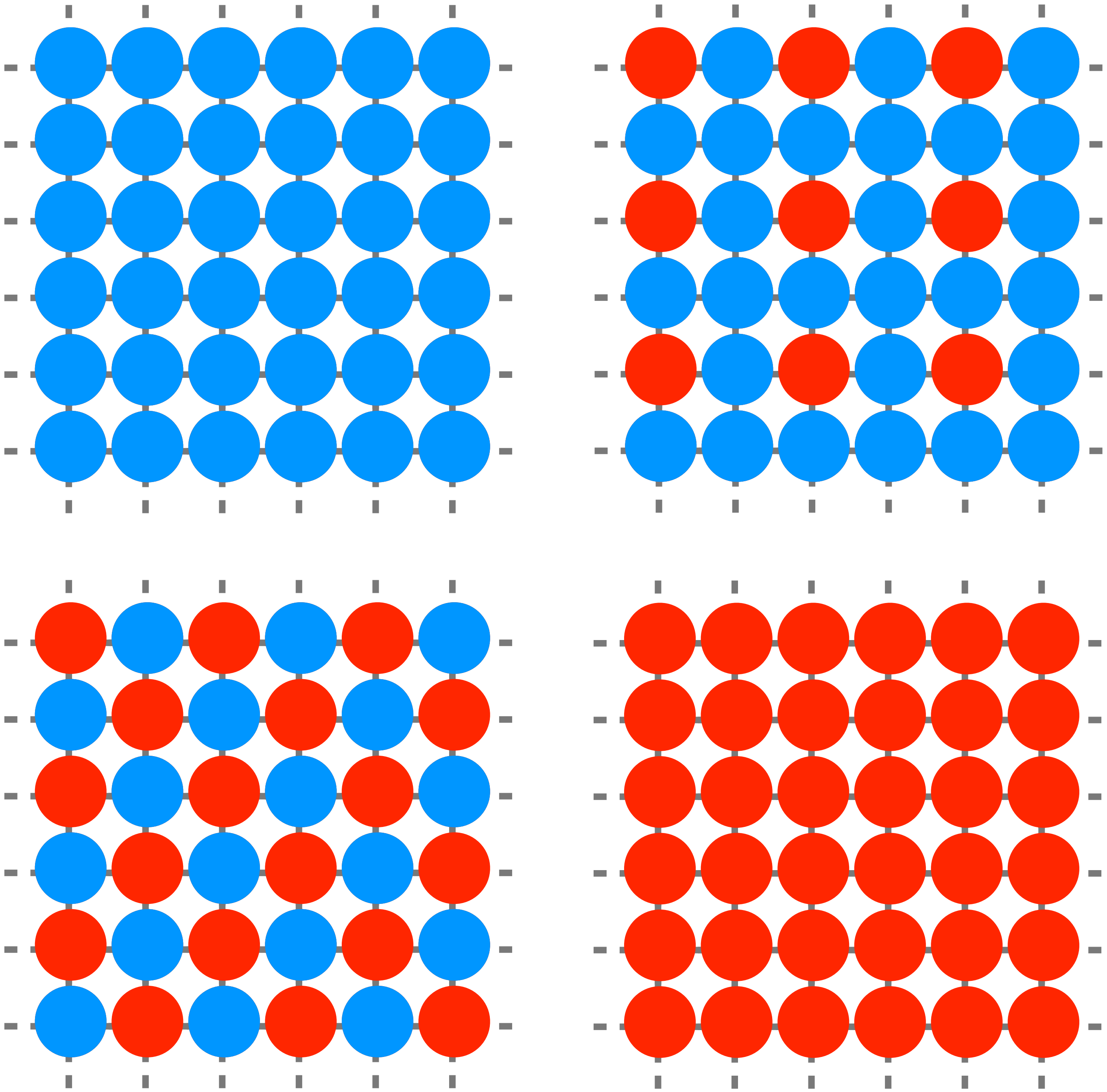


?



$$(\bar{\Pi}_0, \bar{\Pi}_1, \bar{\Pi}_2, \bar{\Pi}_3) = (1, 0, -1, 0)$$





$$\begin{pmatrix} \vdots & \vdots & \vdots & \vdots \\ 1 & 0 & -1 & 0 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

Problem I *(20 min.)*

$$\begin{pmatrix} E_1 \\ E_2 \\ E_3 \\ E_4 \end{pmatrix} = \begin{pmatrix} \Pi_{1,1} & \Pi_{1,2} & \Pi_{1,3} & \Pi_{1,4} \\ \Pi_{2,1} & \Pi_{2,2} & \Pi_{2,3} & \Pi_{2,4} \\ \Pi_{3,1} & \Pi_{3,2} & \Pi_{3,3} & \Pi_{3,4} \\ \Pi_{4,1} & \Pi_{4,2} & \Pi_{4,3} & \Pi_{4,4} \end{pmatrix} \begin{pmatrix} J_1 \\ J_2 \\ J_3 \\ J_4 \end{pmatrix}$$

$$\Downarrow$$

$$\begin{pmatrix} J_1 \\ J_2 \\ J_3 \\ J_4 \end{pmatrix} = \begin{pmatrix} \Pi_{1,1} & \Pi_{1,2} & \Pi_{1,3} & \Pi_{1,4} \\ \Pi_{2,1} & \Pi_{2,2} & \Pi_{2,3} & \Pi_{2,4} \\ \Pi_{3,1} & \Pi_{3,2} & \Pi_{3,3} & \Pi_{3,4} \\ \Pi_{4,1} & \Pi_{4,2} & \Pi_{4,3} & \Pi_{4,4} \end{pmatrix}^{-1} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \\ E_4 \end{pmatrix}$$

Problem I *(20 min.)*

$$\begin{pmatrix} E_1 \\ E_2 \\ E_3 \\ E_4 \end{pmatrix} = \begin{pmatrix} \Pi_{1,1} & \Pi_{1,2} & \Pi_{1,3} & \Pi_{1,4} \\ \Pi_{2,1} & \Pi_{2,2} & \Pi_{2,3} & \Pi_{2,4} \\ \Pi_{3,1} & \Pi_{3,2} & \Pi_{3,3} & \Pi_{3,4} \\ \Pi_{4,1} & \Pi_{4,2} & \Pi_{4,3} & \Pi_{4,4} \end{pmatrix} \begin{pmatrix} J_1 \\ J_2 \\ J_3 \\ J_4 \end{pmatrix}$$

$$\Downarrow$$

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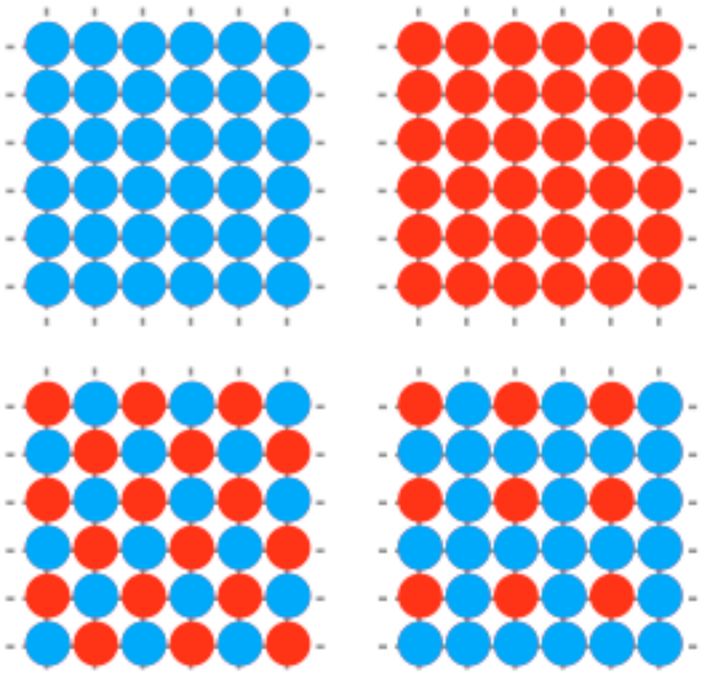
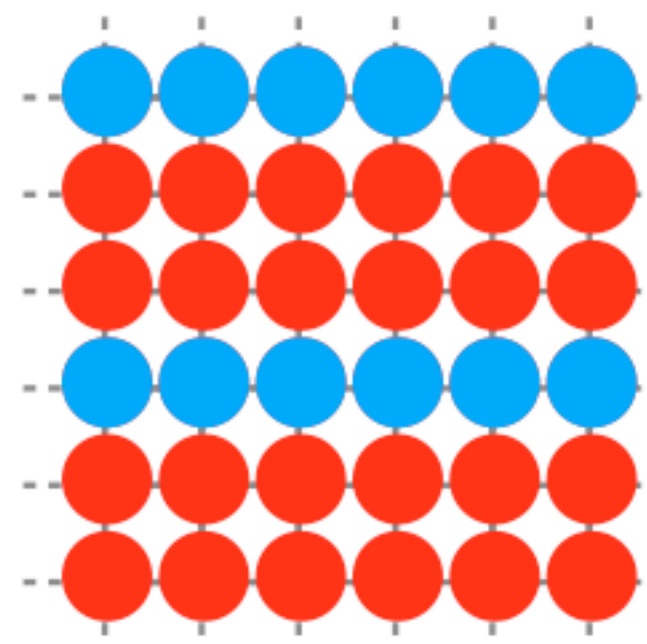


$$\begin{pmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ 1 & 0 & -1 & 0 \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

→ invert and predict by hand



Problem II *(20 min.)*

Problem II *(20 min.)*

... now do the same problem again but using UNCLE

Problem II *(20 min.)*

... now do the same problem again but using UNCLE
- and predict all structures up to four atoms

Problem II *(20 min.)*

... now do the same problem again but using UNCLE
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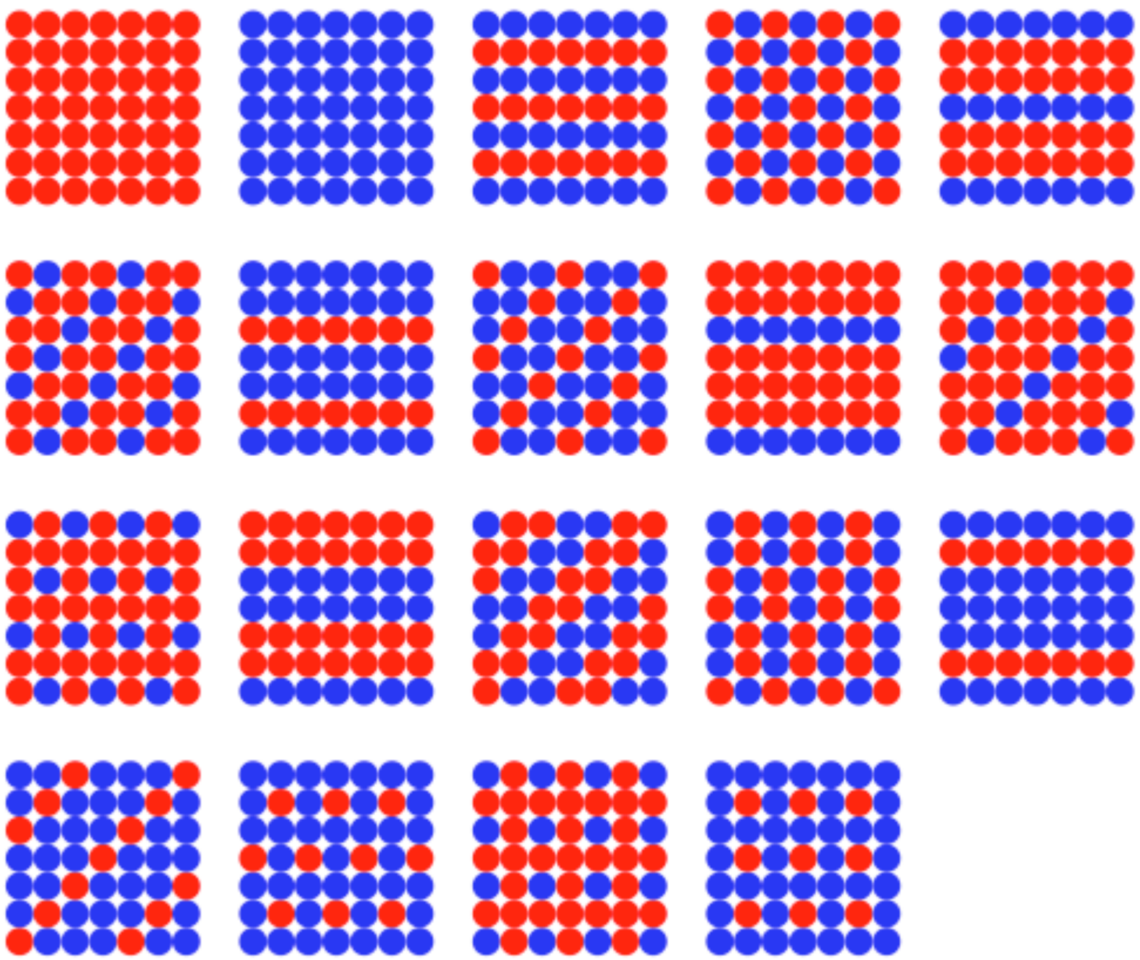

Problem II *(20 min.)*

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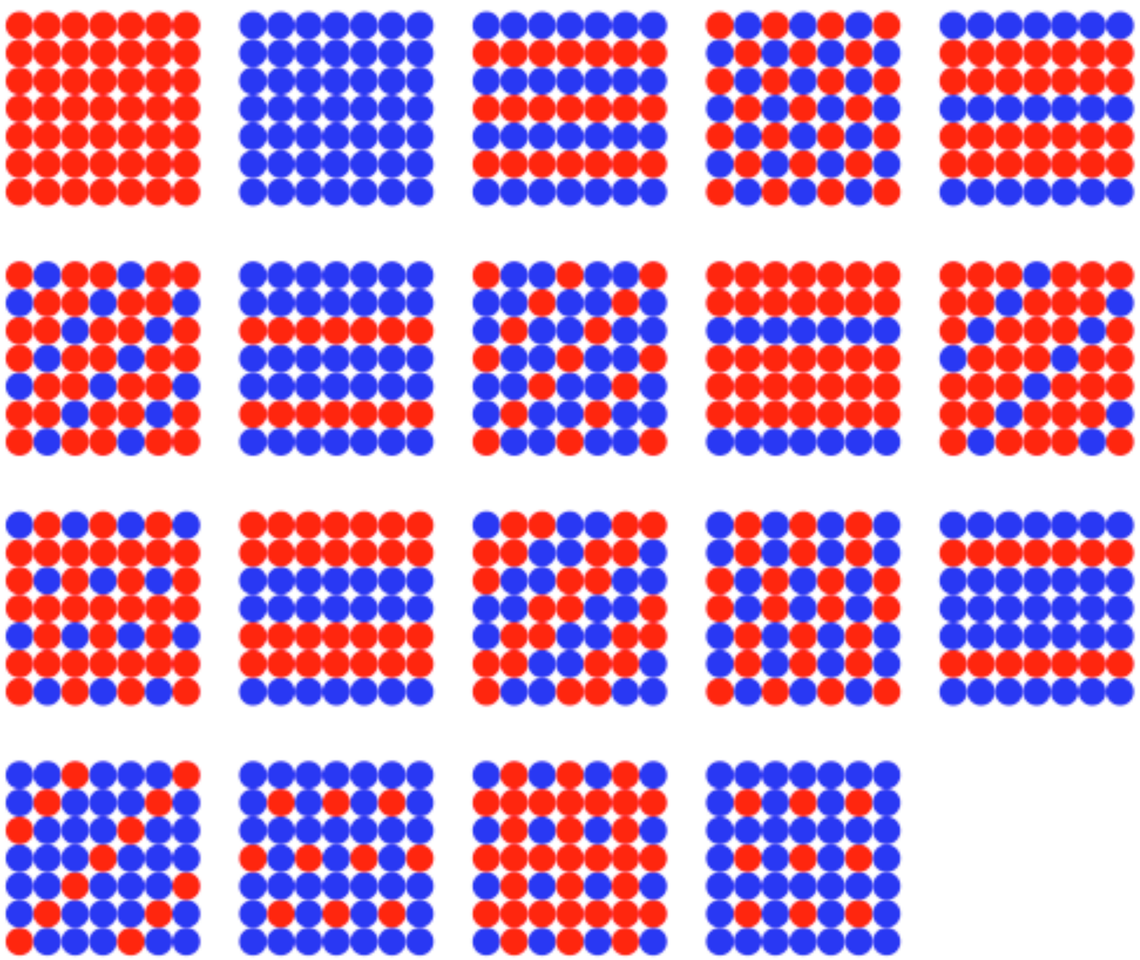

Matrix of $\overline{\Pi}$'s

1.000000	1.000000	1.000000	1.000000
1.000000	0.500000	0.500000	0.000000
1.000000	0.500000	0.000000	0.500000
1.000000	0.500000	0.000000	0.000000
1.000000	0.500000	0.000000	0.000000
1.000000	0.333333	0.333333	-0.333333
1.000000	0.333333	-0.333333	0.333333
1.000000	0.000000	0.500000	0.000000
1.000000	0.000000	0.000000	-1.000000
1.000000	0.000000	0.000000	0.000000
1.000000	0.000000	-0.500000	0.000000
1.000000	0.000000	-1.000000	1.000000
1.000000	-0.333333	0.333333	-0.333333
1.000000	-0.333333	-0.333333	0.333333
1.000000	-0.500000	0.500000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.500000
1.000000	-1.000000	1.000000	1.000000

Problem II *(20 min.)*

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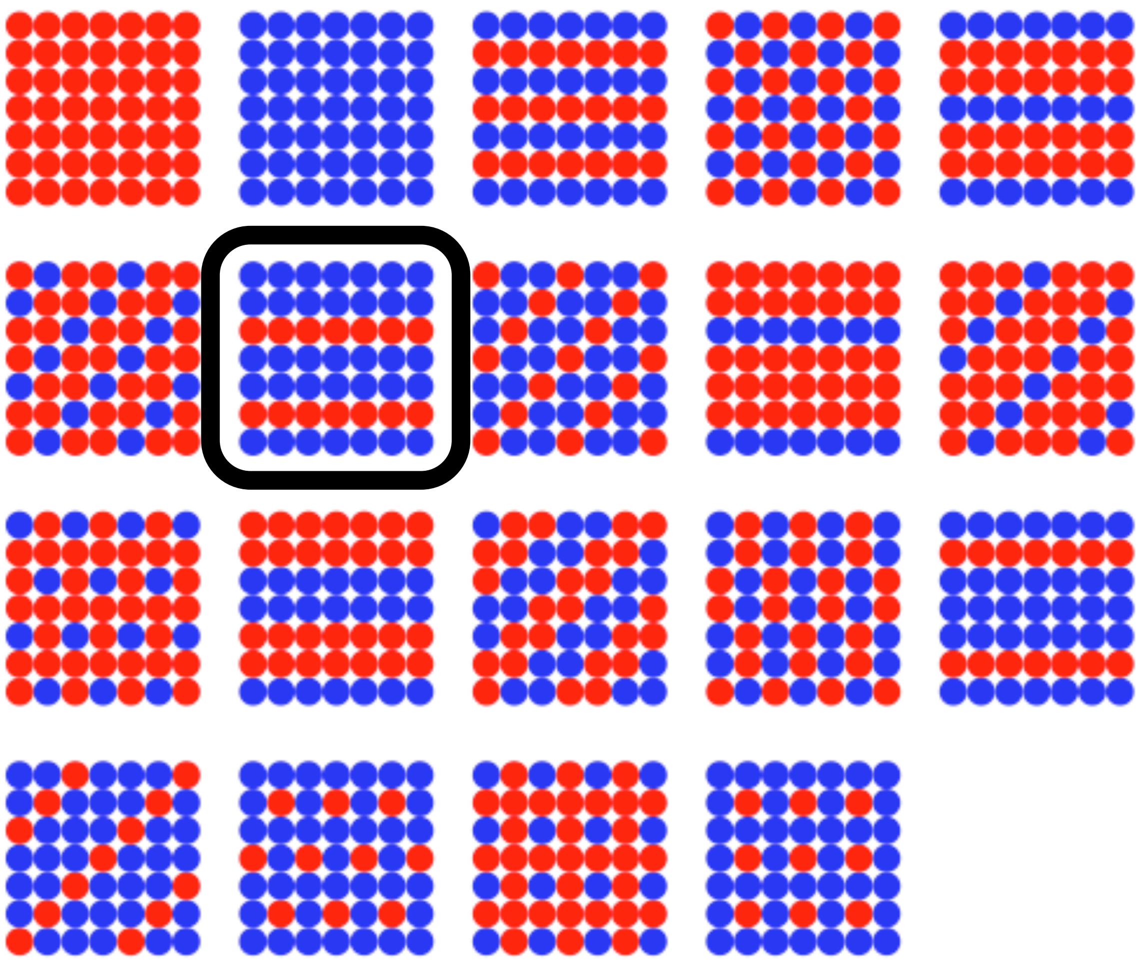

Matrix of $\overline{\Pi}$'s

1.000000	1.000000	1.000000	1.000000
1.000000	0.500000	0.500000	0.000000
1.000000	0.500000	0.000000	0.500000
1.000000	0.500000	0.000000	0.000000
1.000000	0.500000	0.000000	0.000000
1.000000	0.333333	0.333333	-0.333333
1.000000	0.333333	-0.333333	0.333333
1.000000	0.000000	0.500000	0.000000
1.000000	0.000000	0.000000	-1.000000
1.000000	0.000000	0.000000	0.000000
1.000000	0.000000	-0.500000	0.000000
1.000000	0.000000	-1.000000	1.000000
1.000000	-0.333333	0.333333	-0.333333
1.000000	-0.333333	-0.333333	0.333333
1.000000	-0.500000	0.500000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.500000
1.000000	-1.000000	1.000000	1.000000

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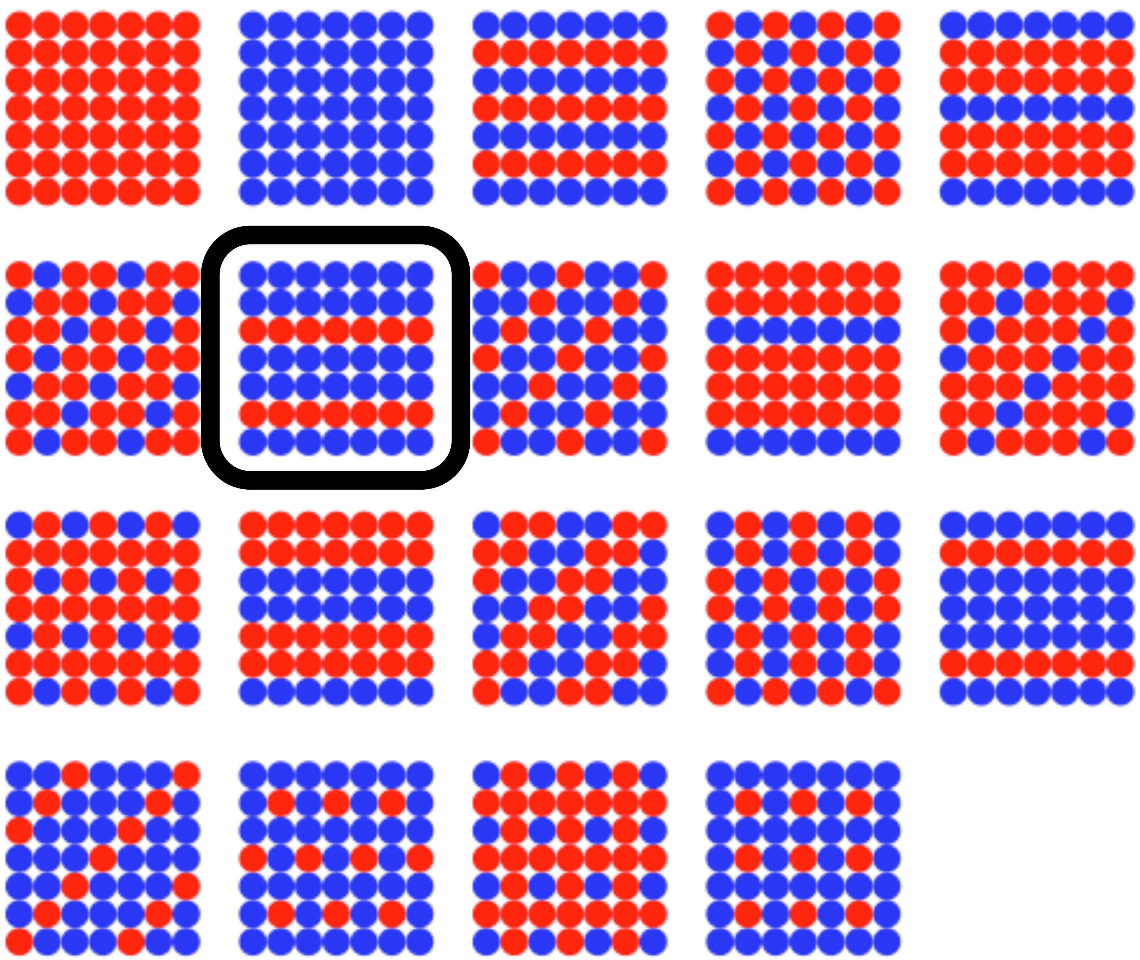
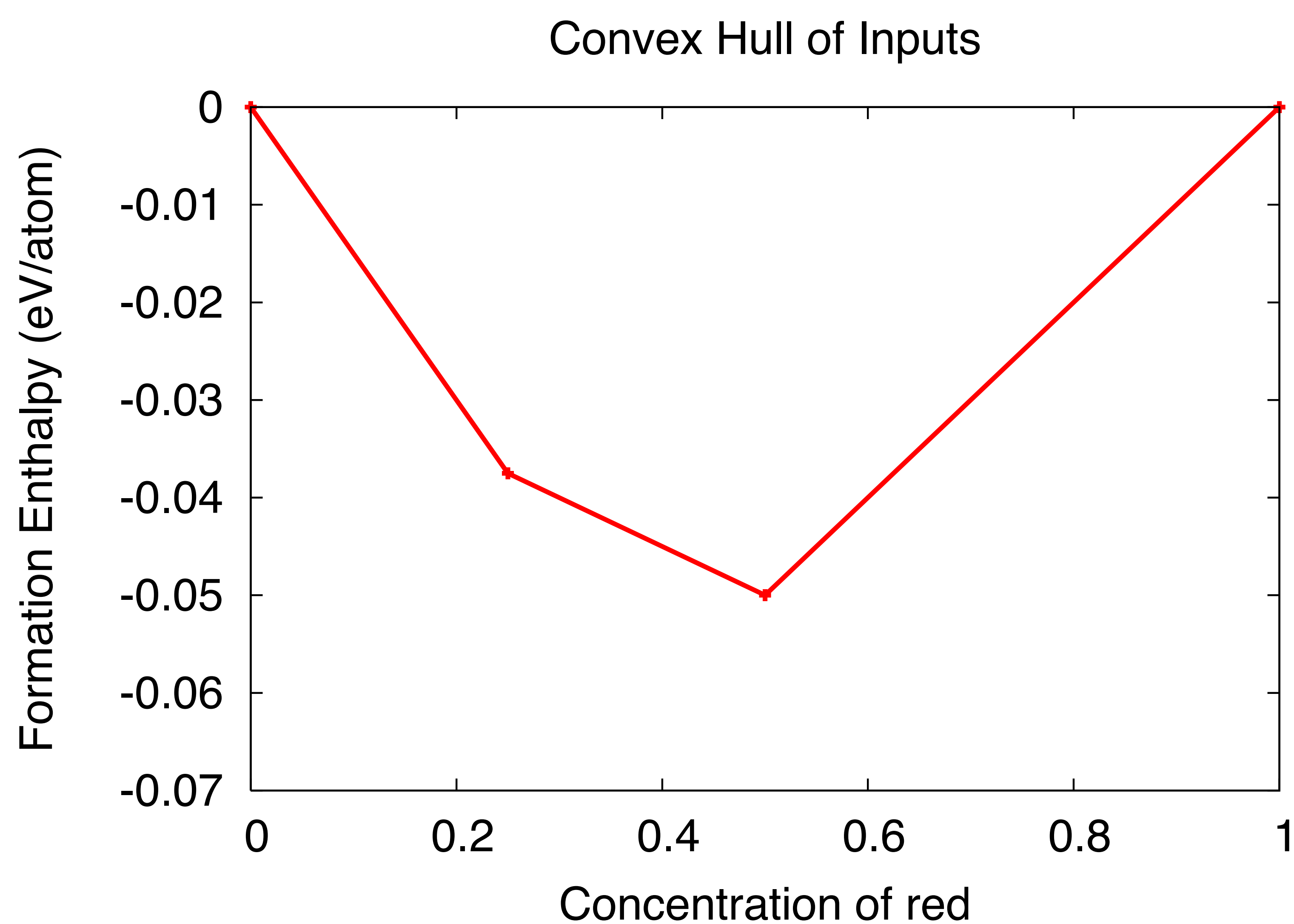


Matrix of $\overline{\Pi}$'s

1.000000	1.000000	1.000000	1.000000
1.000000	0.500000	0.500000	0.000000
1.000000	0.500000	0.000000	0.500000
1.000000	0.500000	0.000000	0.000000
1.000000	0.500000	0.000000	0.000000
1.000000	0.333333	0.333333	-0.333333
1.000000	**0.333333**	**-0.333333**	**0.333333**
1.000000	0.000000	0.500000	0.000000
1.000000	0.000000	0.000000	-1.000000
1.000000	0.000000	0.000000	0.000000
1.000000	0.000000	-0.500000	0.000000
1.000000	0.000000	-1.000000	1.000000
1.000000	-0.333333	0.333333	-0.333333
1.000000	-0.333333	-0.333333	0.333333
1.000000	-0.500000	0.500000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.000000
1.000000	-0.500000	0.000000	0.500000
1.000000	-1.000000	1.000000	1.000000

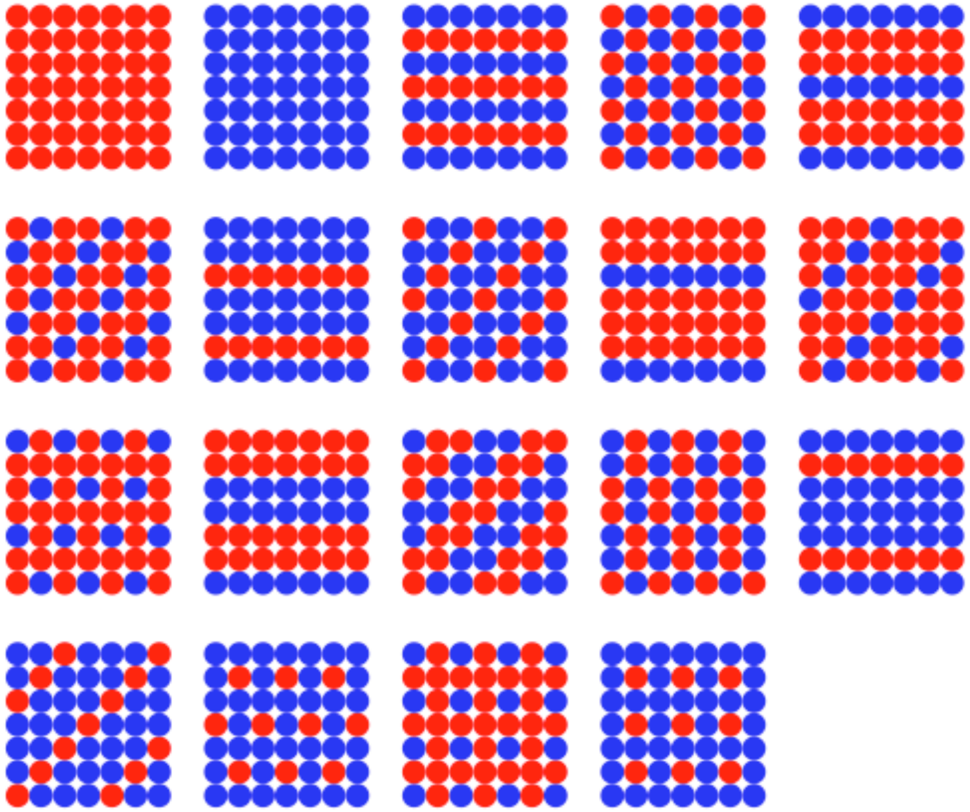
$$E = \vec{\overline{\Pi}} \cdot \vec{J}$$

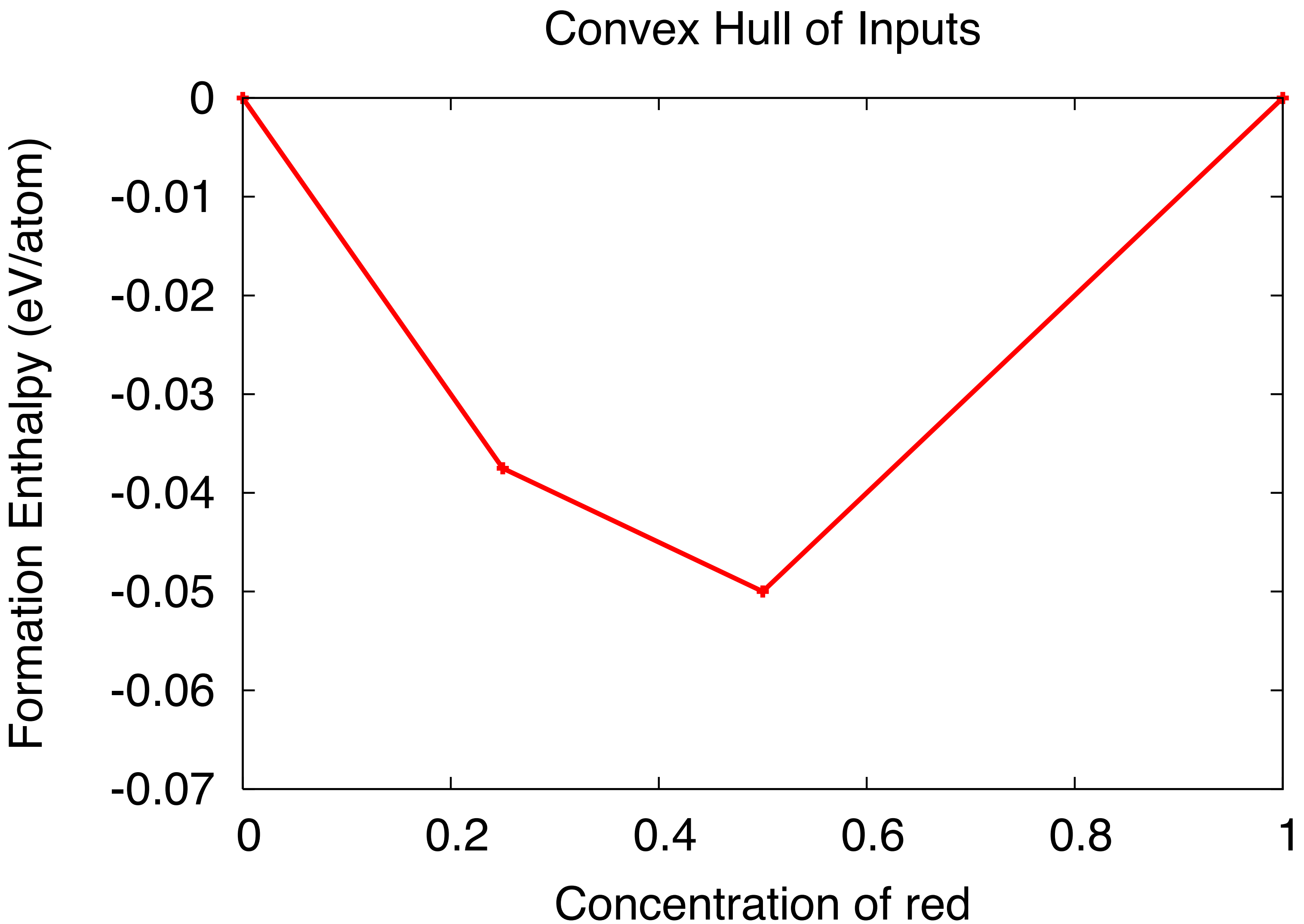
Problem II *(20 min.)*



Constructing the **convex hull** from the predictions

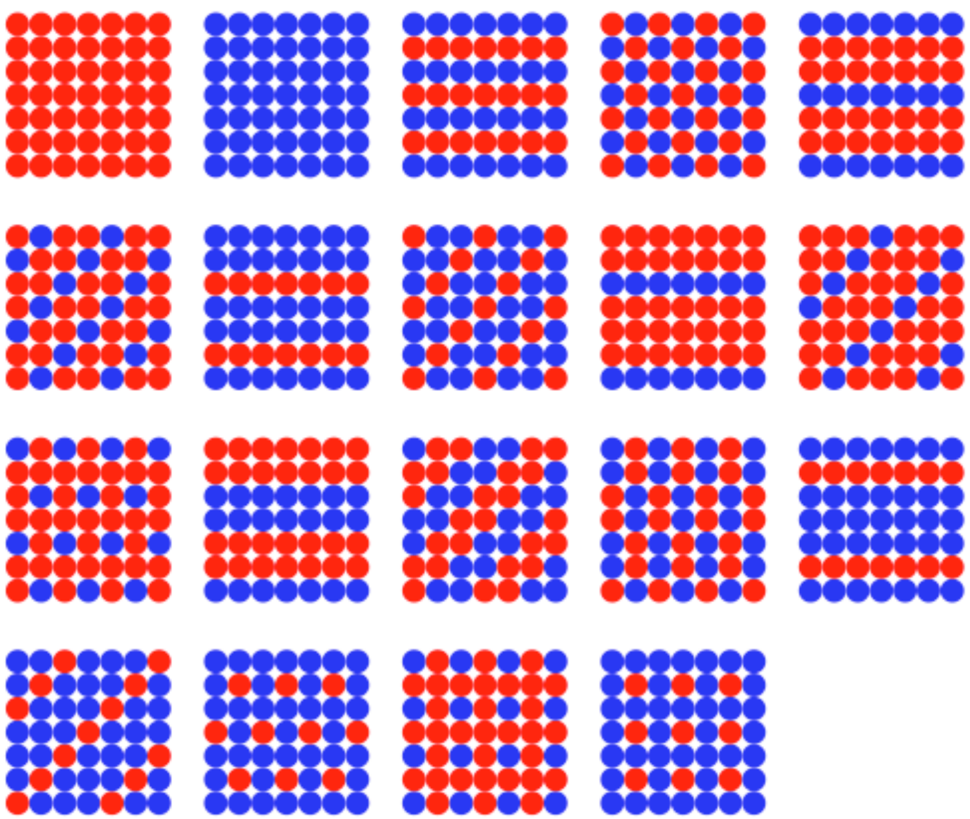
Problem II *(20 min.)*

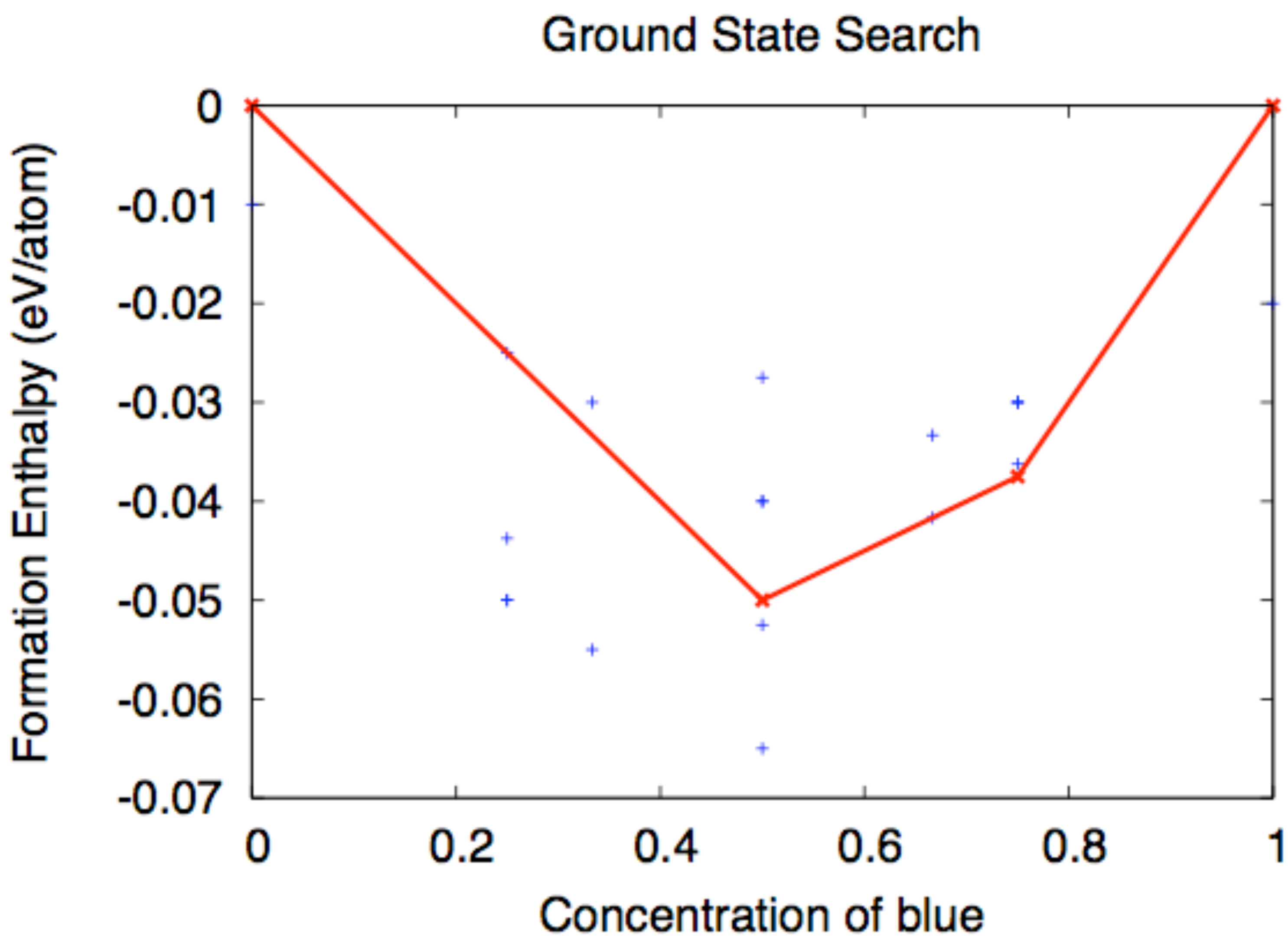




Constructing the **convex hull** from the predictions

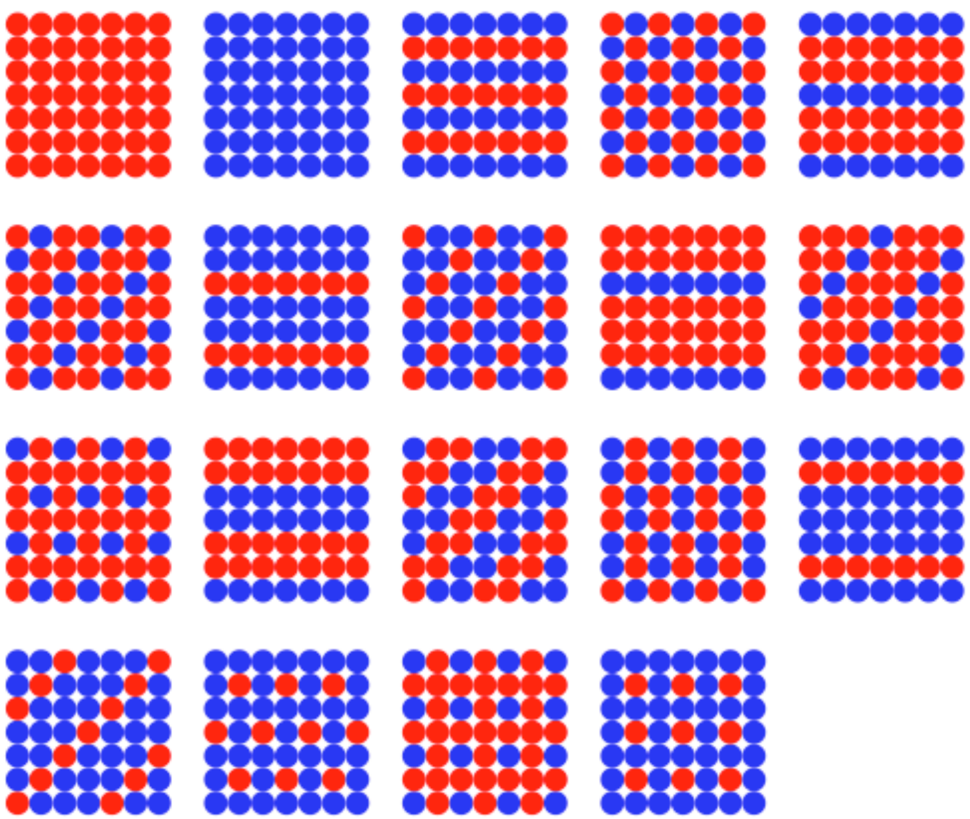
Problem II *(20 min.)*

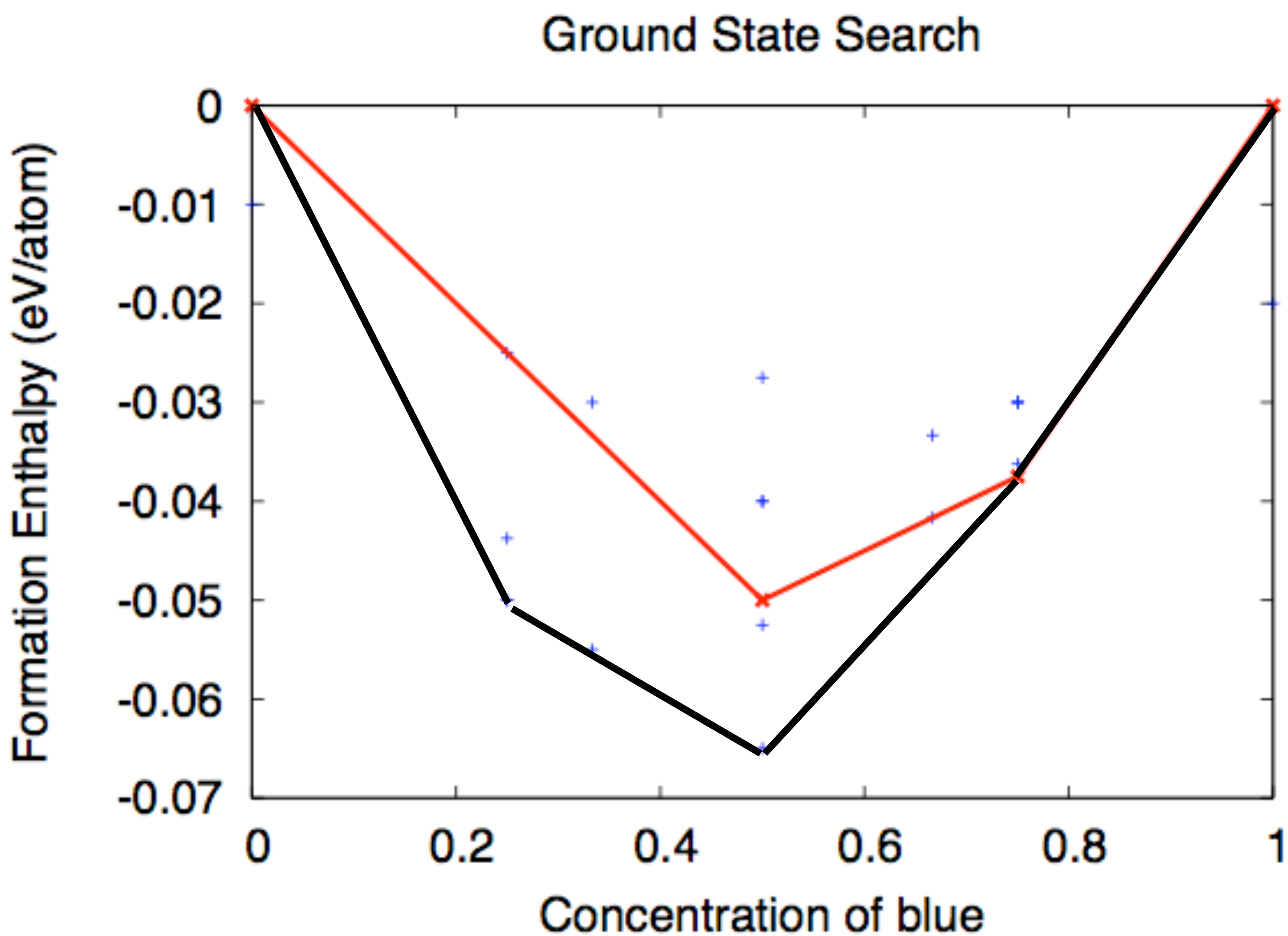




Constructing the **convex hull** from the predictions

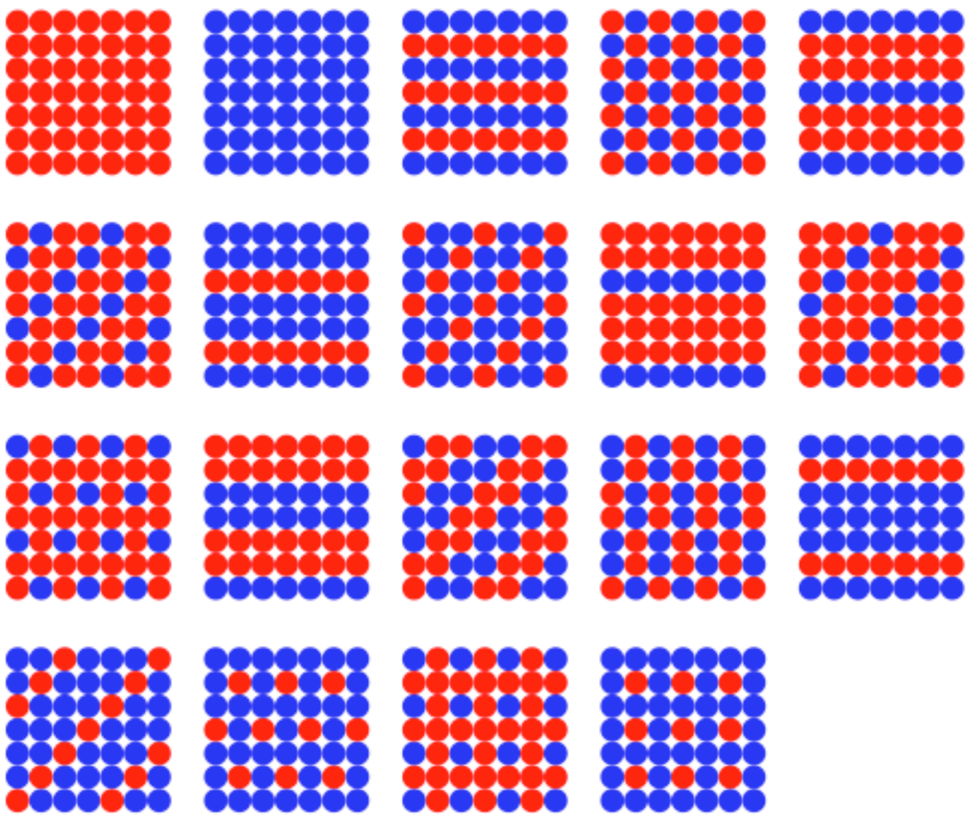
Problem II *(20 min.)*

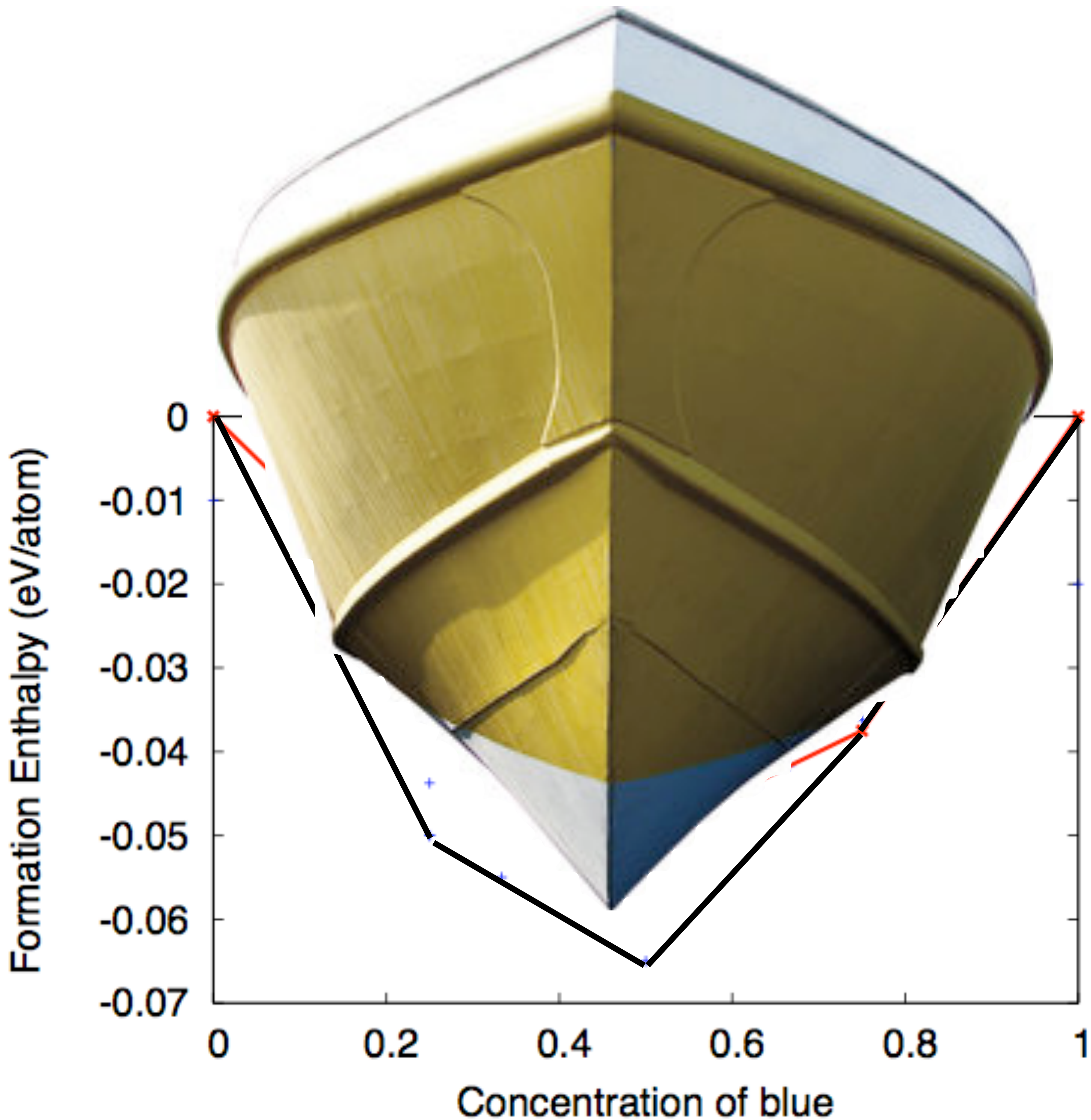




Constructing the **convex hull** from the predictions

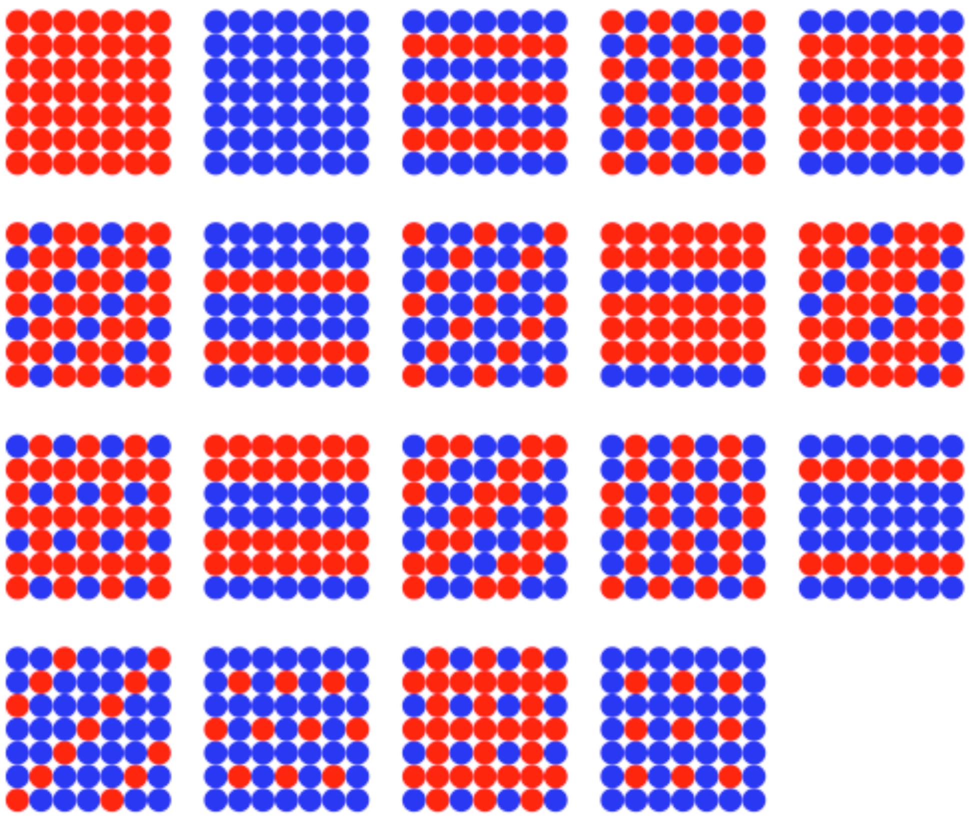
Problem II *(20 min.)*

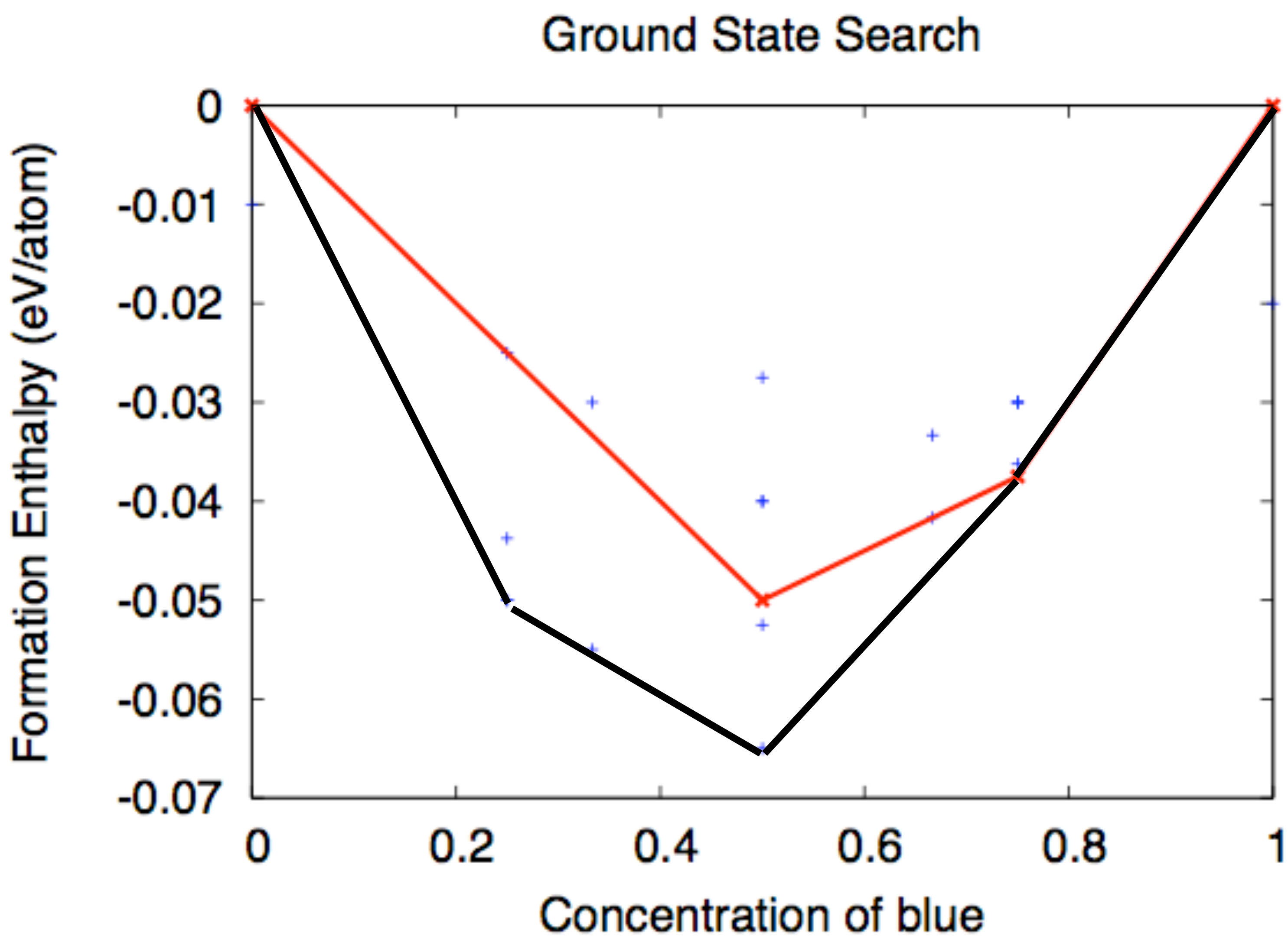




Constructing the **convex hull** from the predictions

Problem II *(20 min.)*





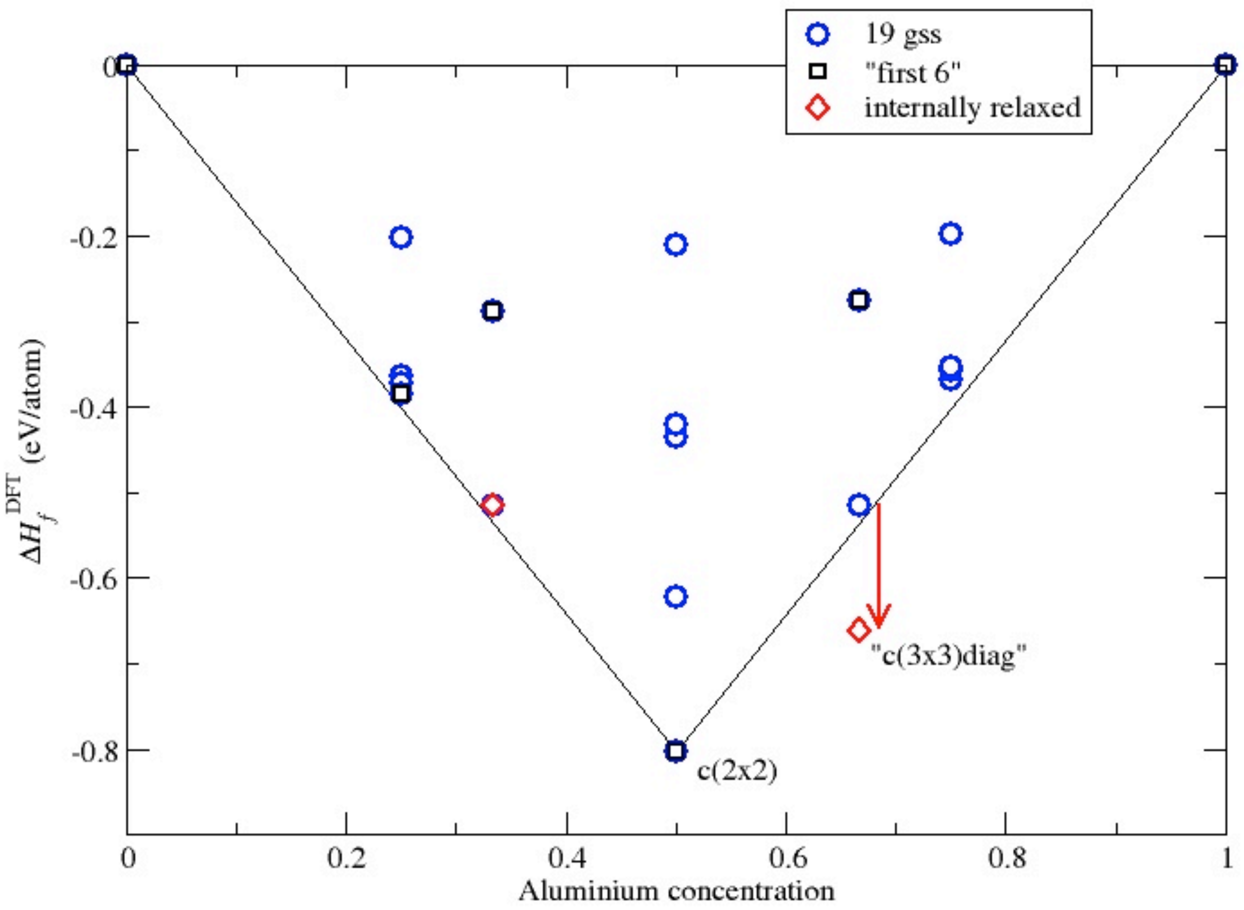
Constructing the **convex hull** from the predictions

Problem III *(60 min.)*

Repeat cluster expansion with real data

Predict ground state line, unrelaxed

Compute four DFT-LDA structures (3 atoms), relaxed!



Find optimum CE based on first 8 relaxed structures, predict remaining 19!

Problem V *(remaining time)*: Order-disorder transitions

Repeat two cluster expansions: nearest-neighbour only vs. optimum
(19 DFT input structures)

Predict ground states for both

Monte Carlo temperature schedules for both CE's,
different unit cells, 50 %:

Monte Carlo temperature schedules for both CE's,
different unit cells, 80% (Ni-rich):
Phase separation?

Monte Carlo modeling in a nutshell

Monte Carlo modeling in a nutshell

Use random numbers to...

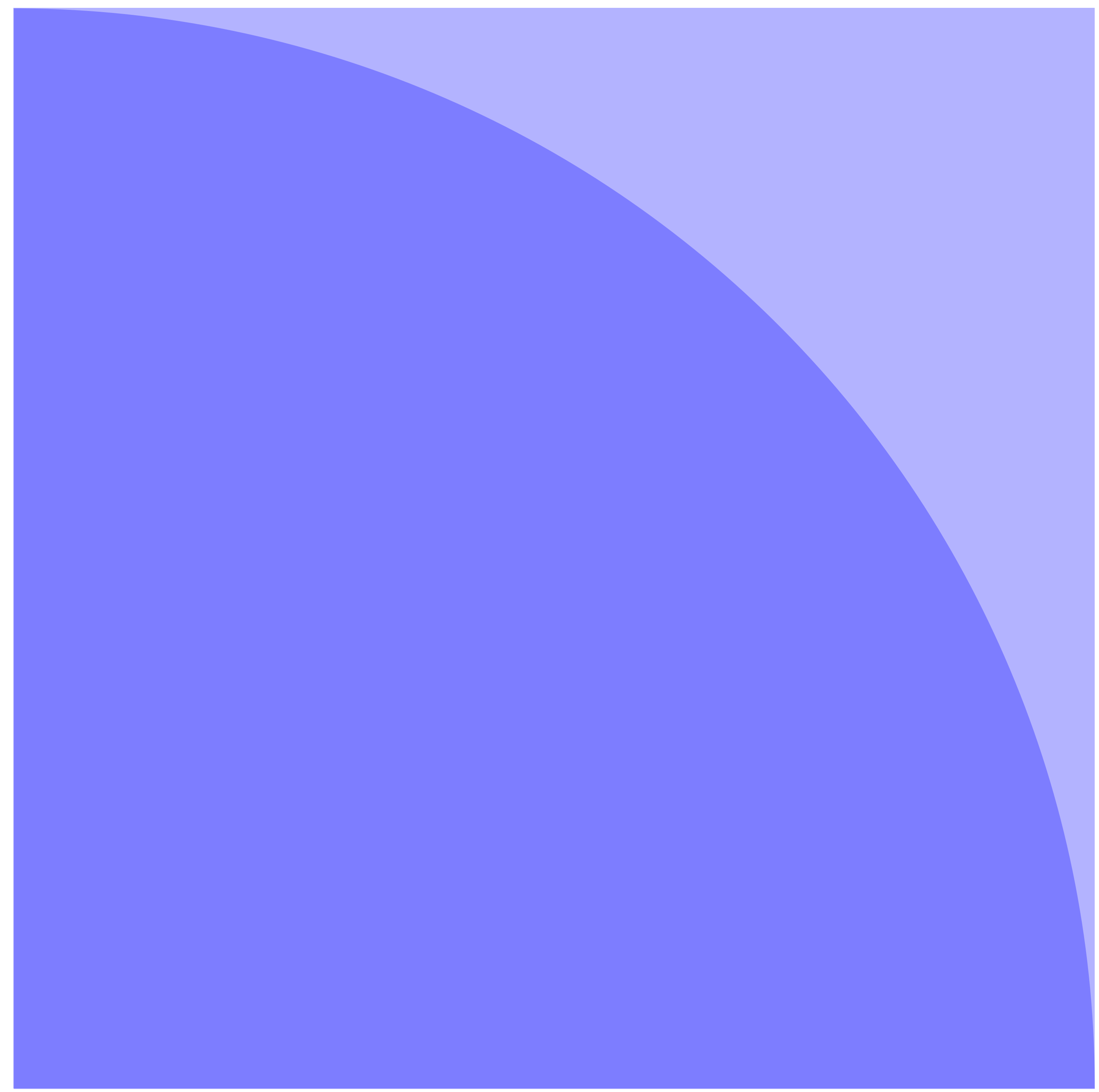
Find the thermodynamic equilibrium of a system as a function of temperature.

Monte Carlo modeling in a nutshell

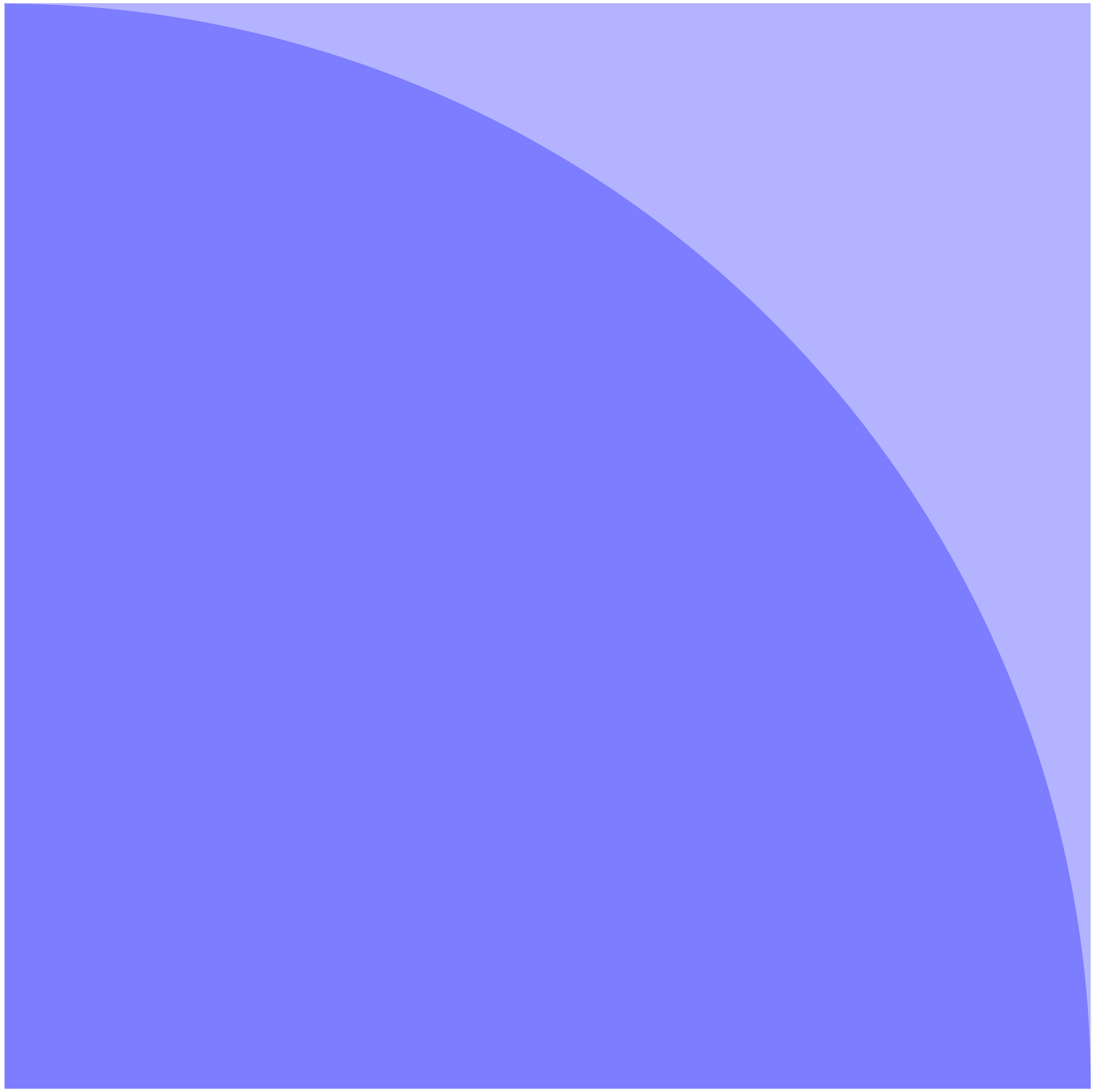
Use random numbers to...

Find the thermodynamic equilibrium of a system as a function of temperature.

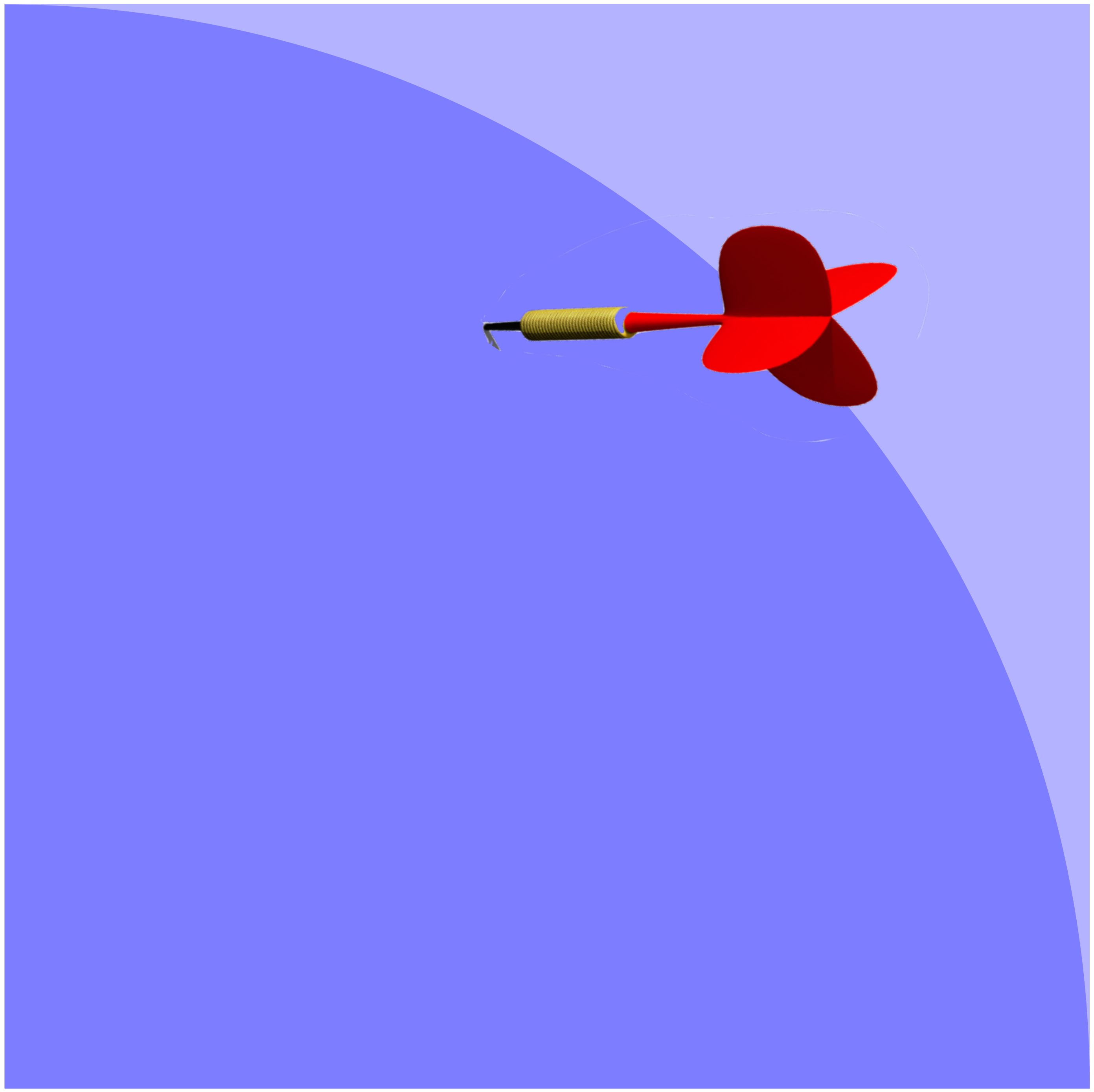
- Is a material magnetic at a given T?
- Is a material ordered (stronger) at a given T?



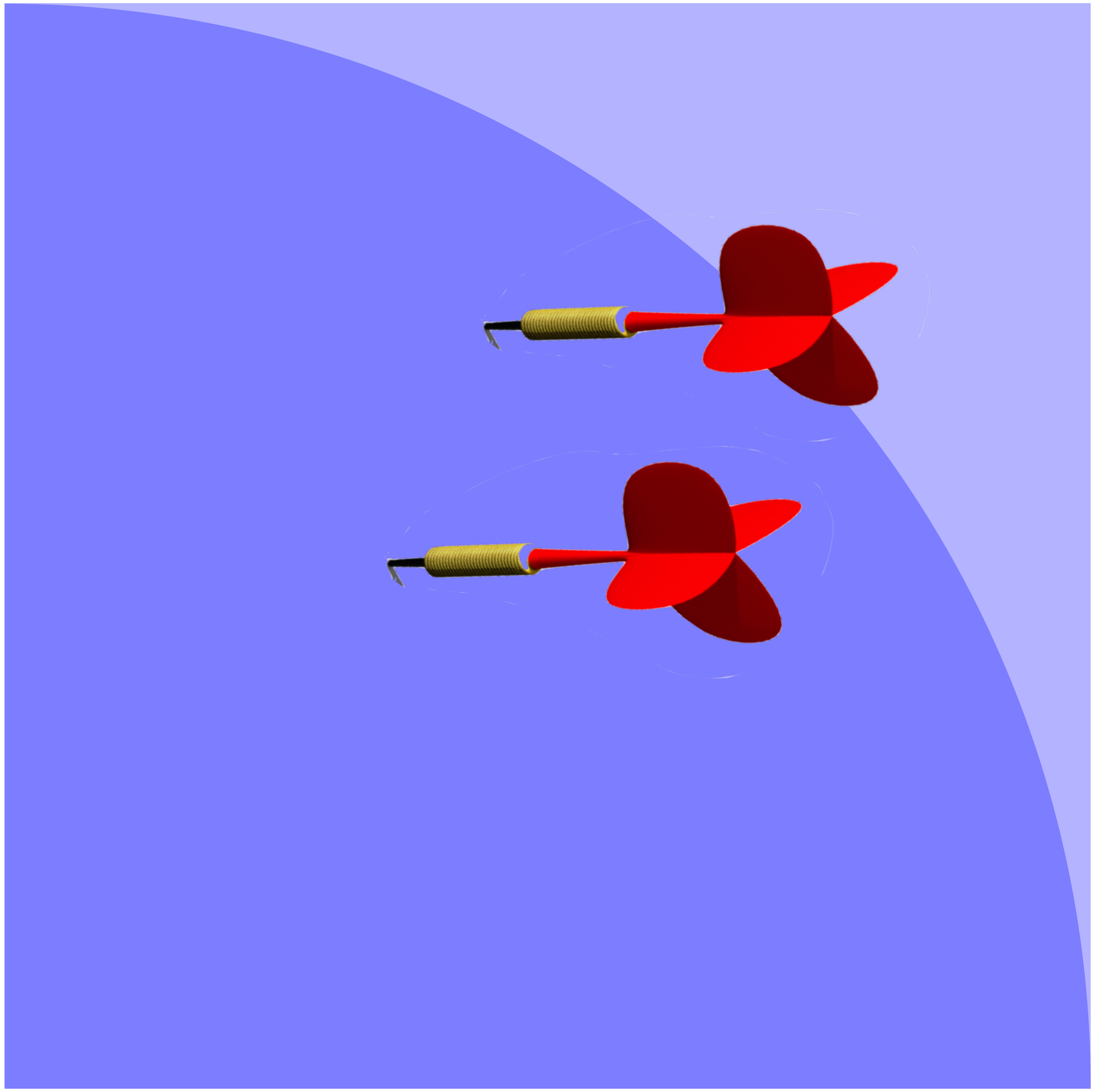
$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$



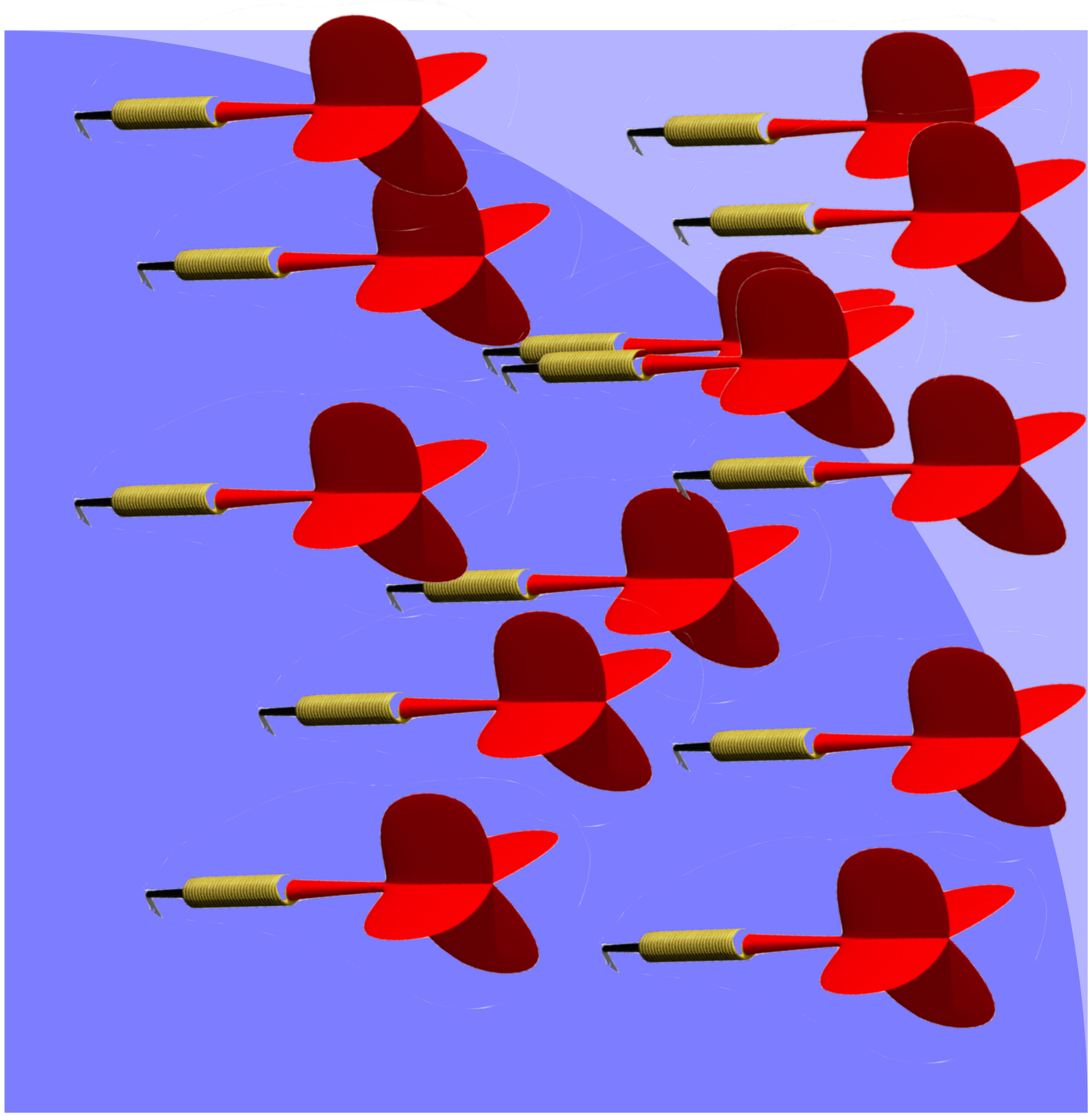
$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$



$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$

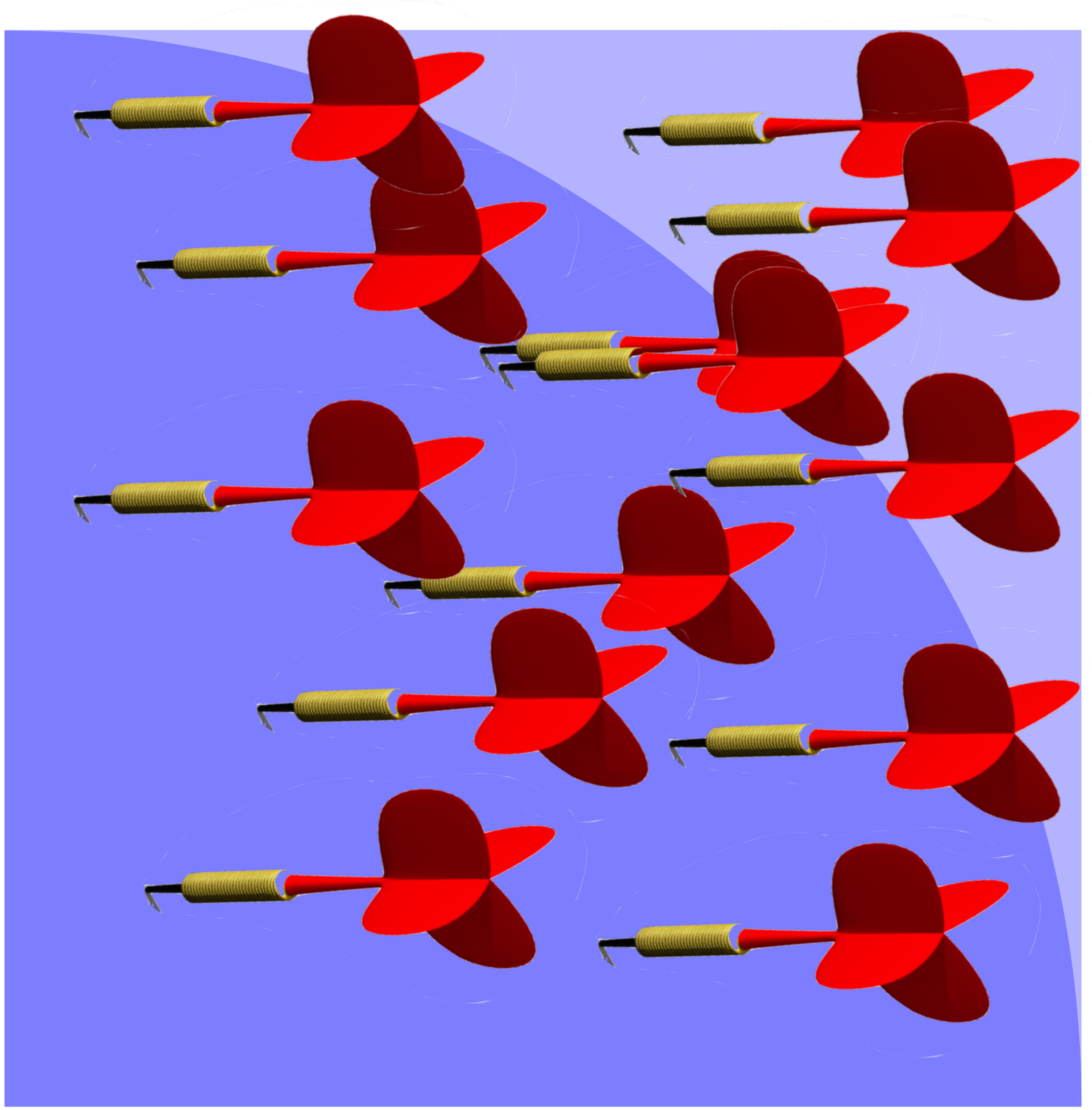


$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$



$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$

$$\frac{N_{\text{circle}}}{N_{\text{square}}} \approx \frac{\pi}{4}$$



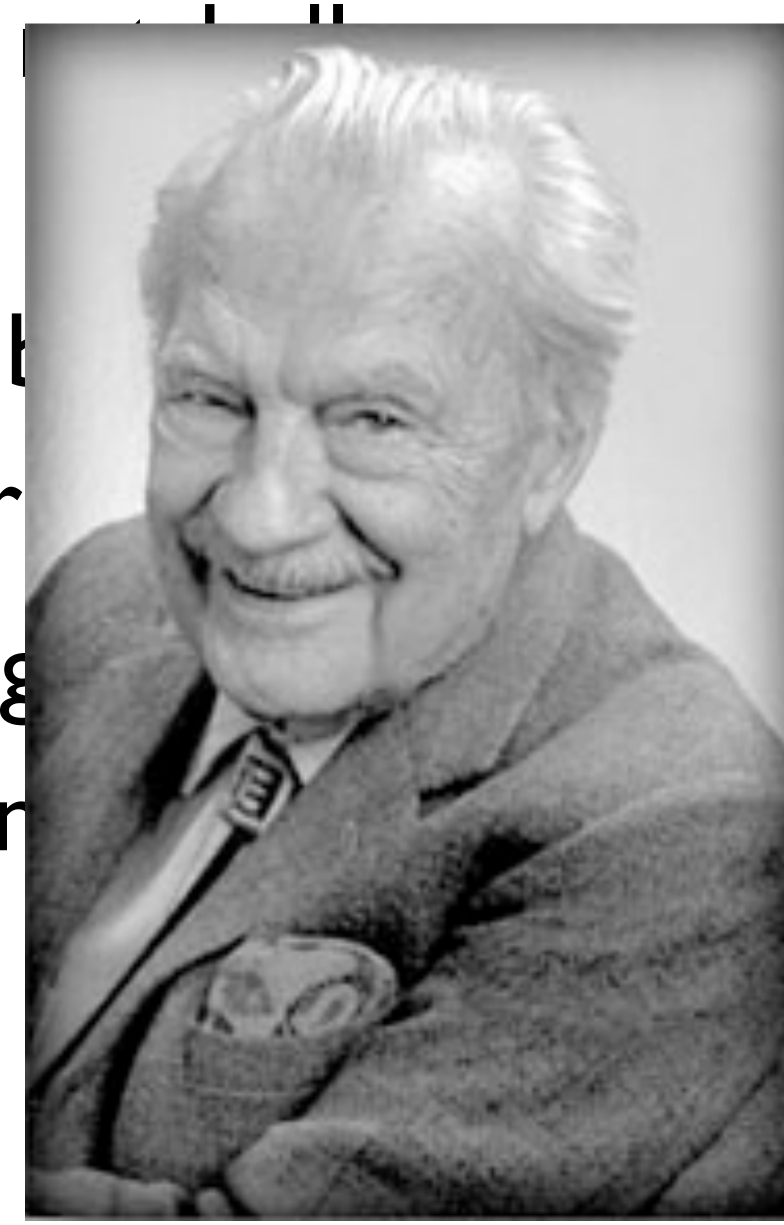
Monte Carlo modeling in a nutshell

Find the thermodynamic equilibrium of a system as a function of temperature.

- Is a material magnetic at a given *T*?
- Is a material ordered (stronger) at a given *T*?

Metropolis algorithm:

Monte Carlo modeling in a n

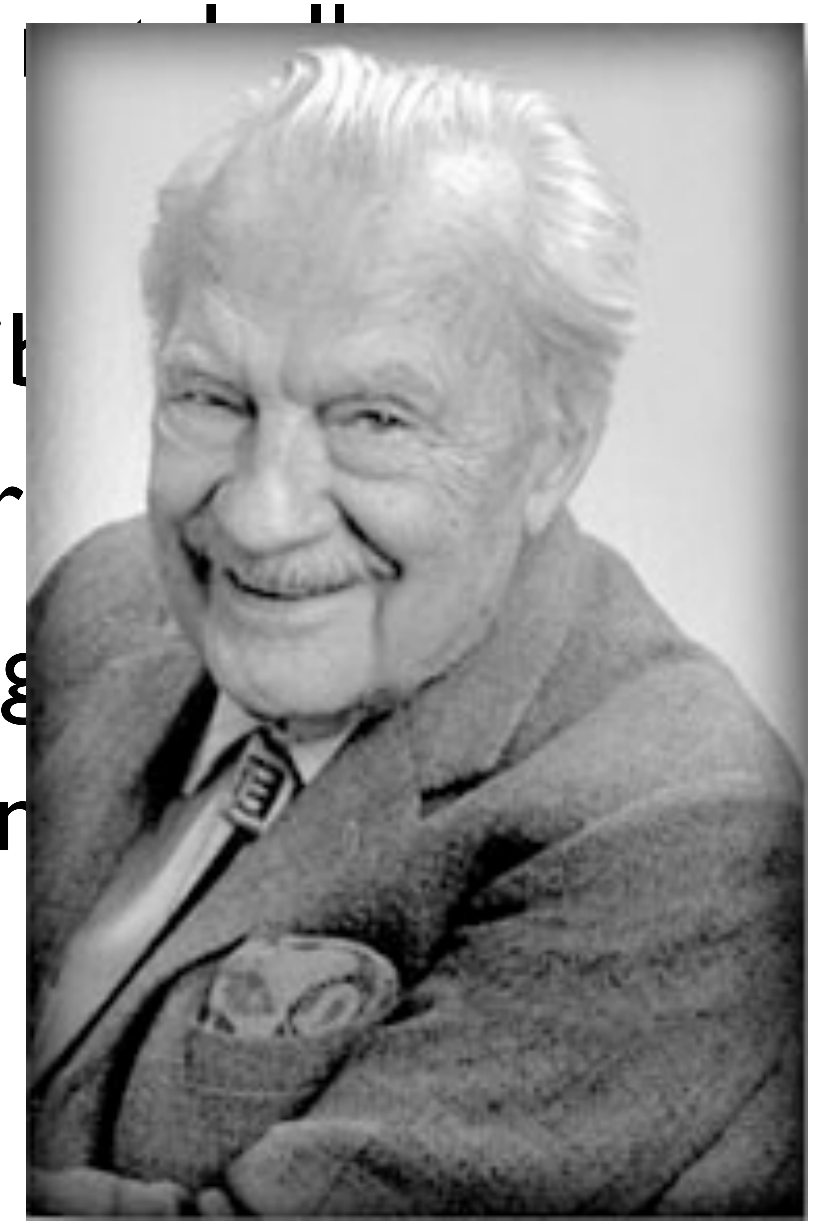


Find the thermodynamic equilib
system as a function of temper

- Is a material magnetic at a g
- Is a material ordered (stron

Metropolis algorithm:

Monte Carlo modeling in a



Find the thermodynamic equilib
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- Is a material magnetic at a g
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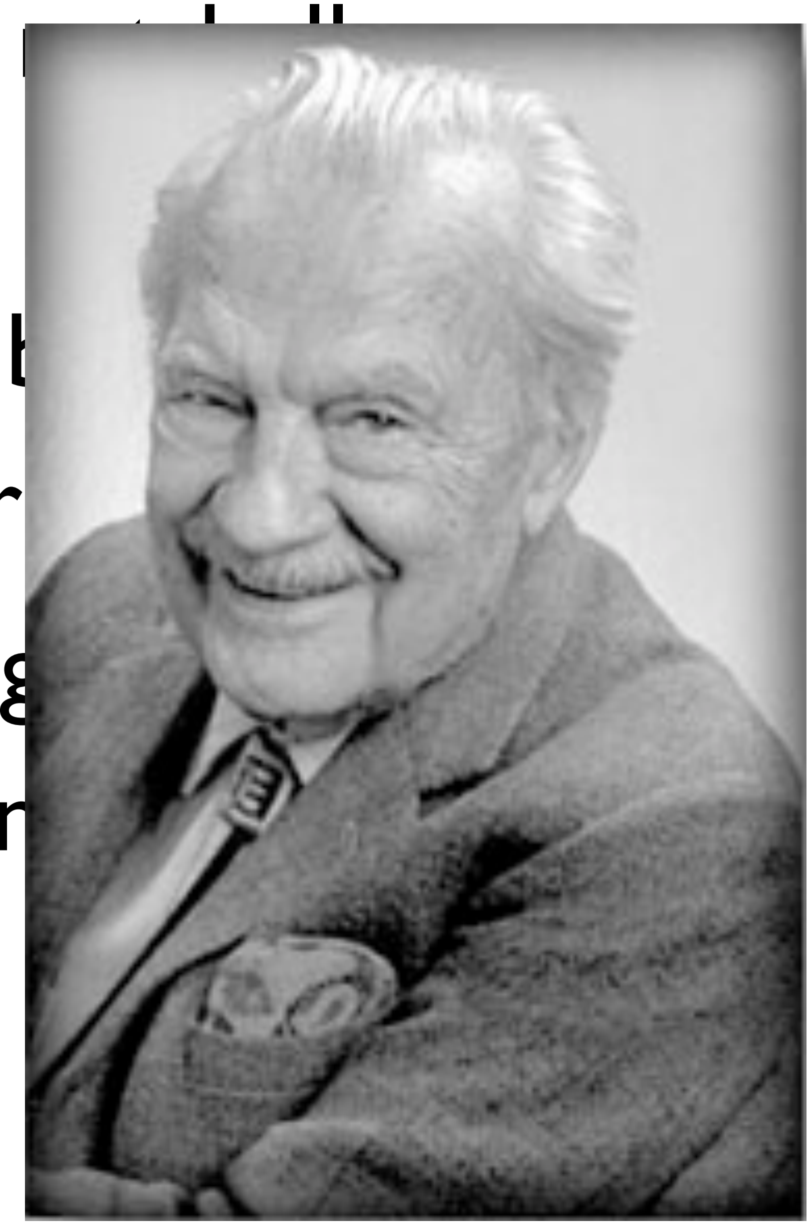
Metropolis algorithm:

- Choose a new configuration, compute ΔE
- If $\Delta E \leq 0$, keep it
- If $\Delta E > 0$, keep it only if $\exp \Delta E/kT > r$

Monte Carlo modeling in a



Find the thermodynamic equilib

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Metropolis algorithm:

At random

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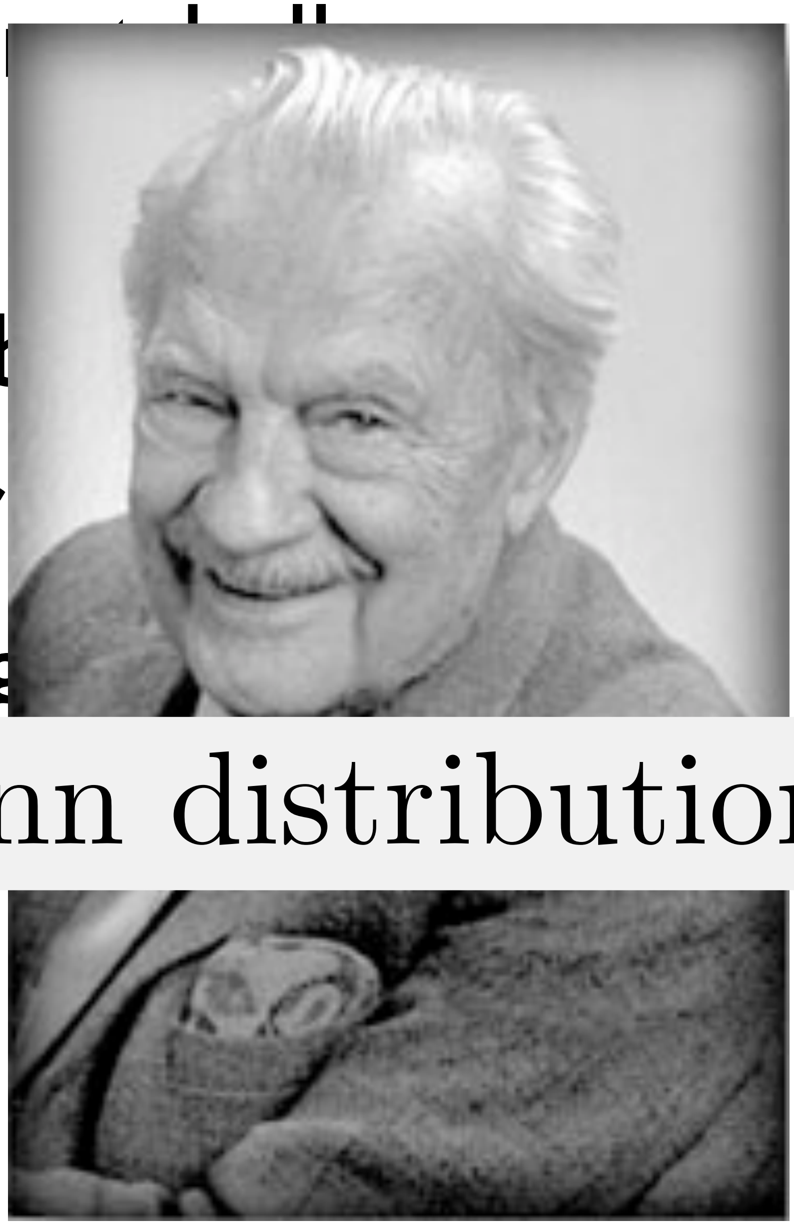
Monte Carlo modeling in a

Find the thermodynamic equilib

system as a function of temper

- Is a material magnetic at a g



Collection of states: Boltzmann distribution

Metropolis algorithm:

At random

- Choose a new configuration, compute ΔE
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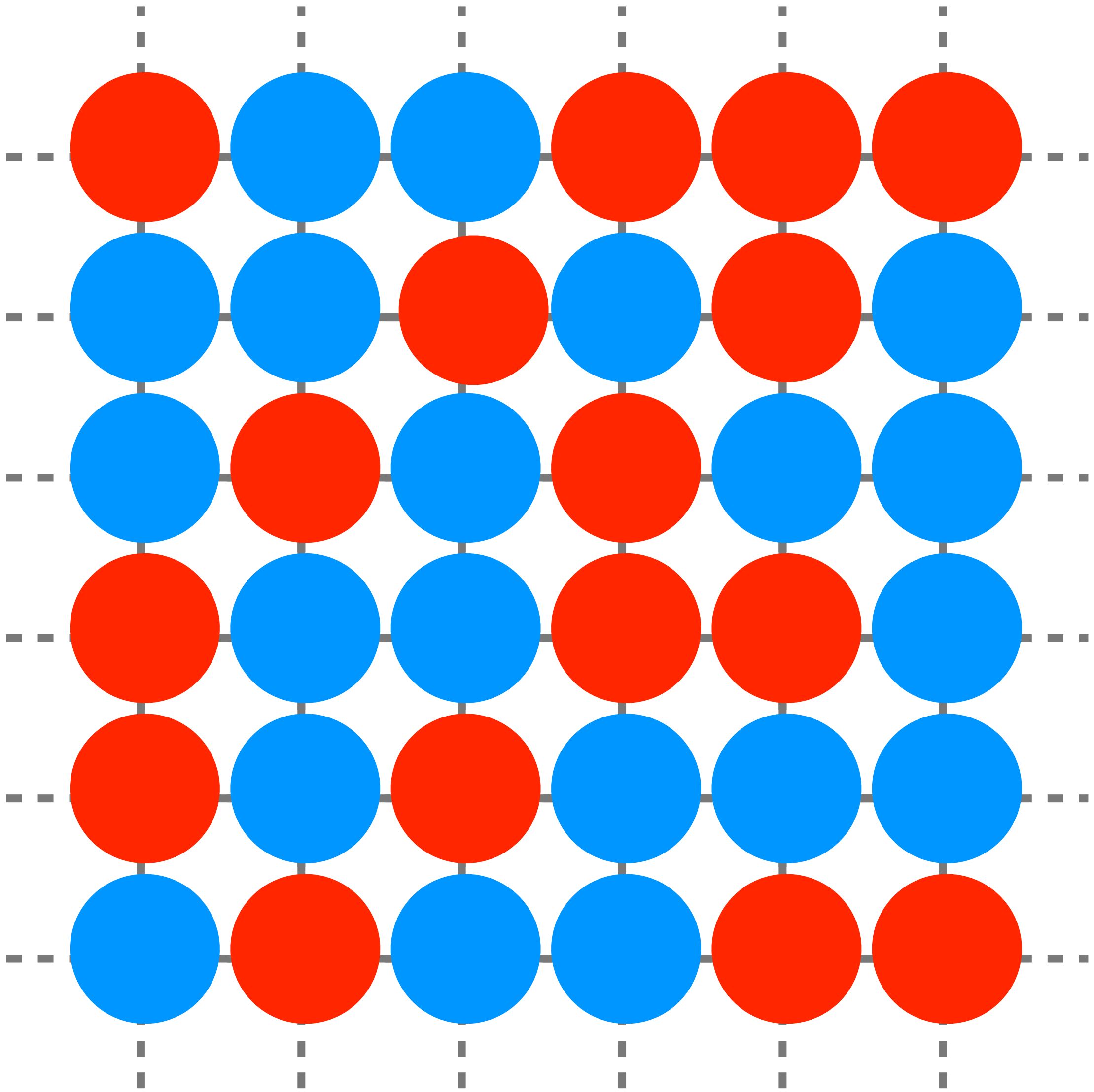

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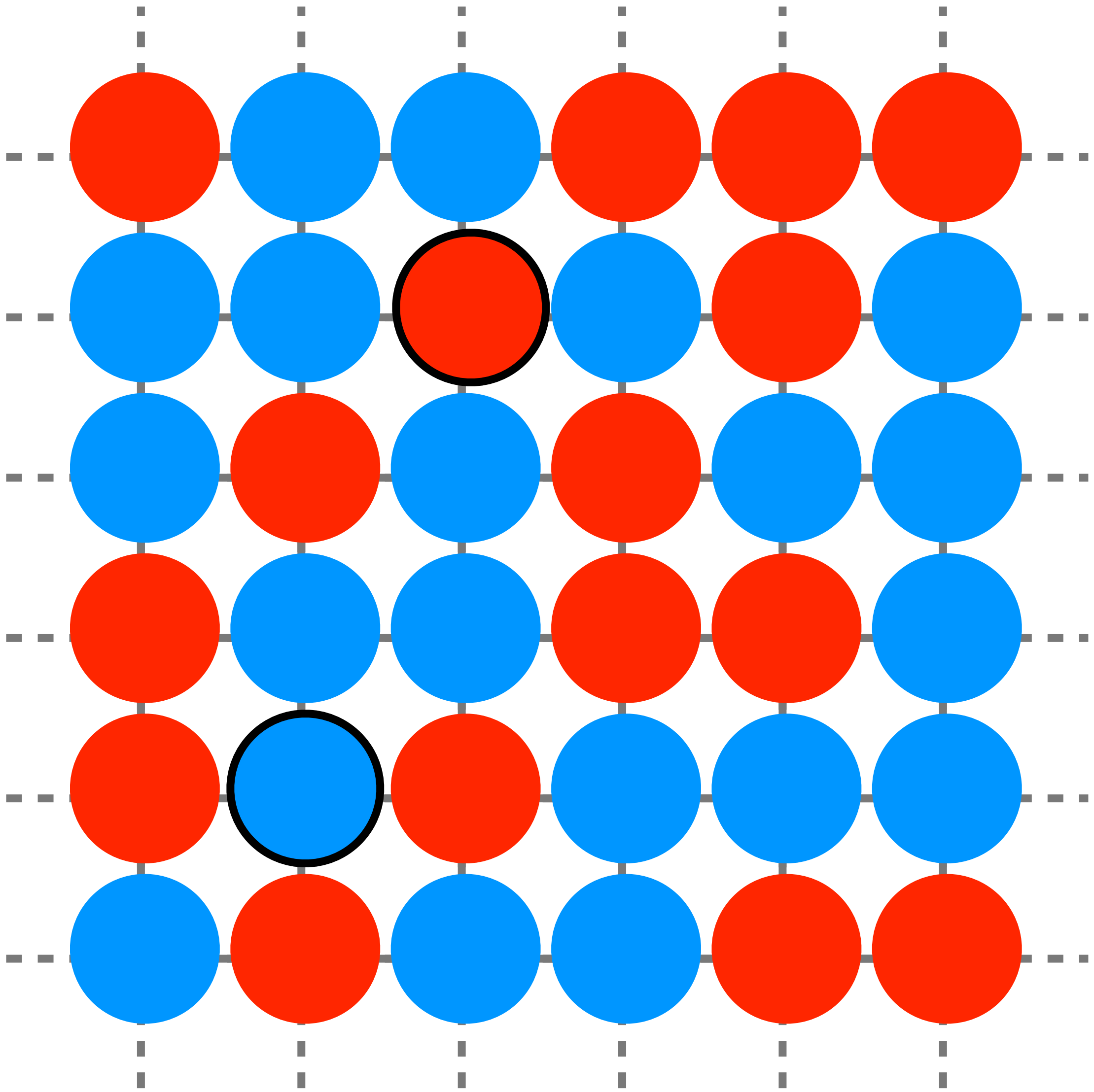

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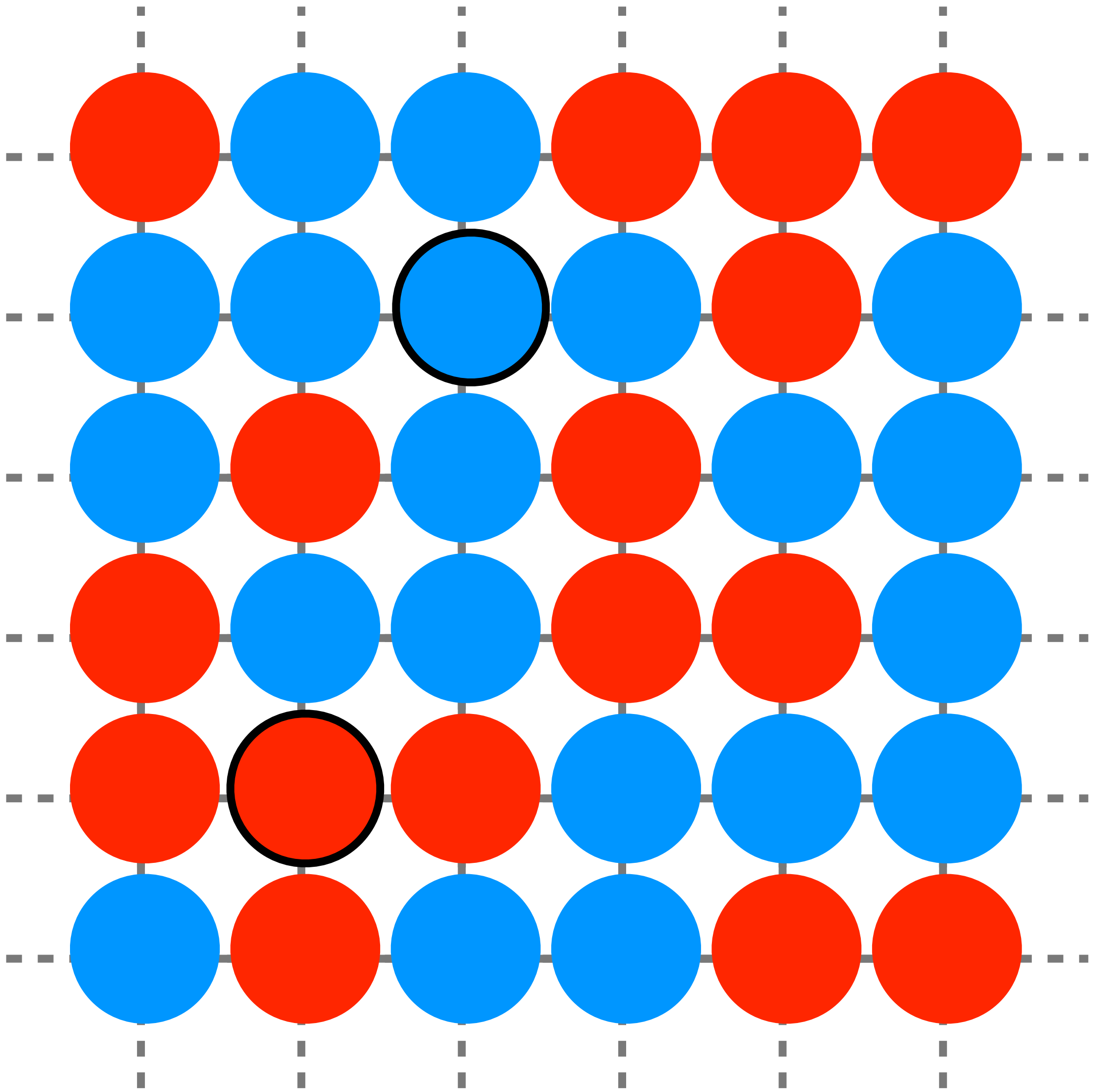

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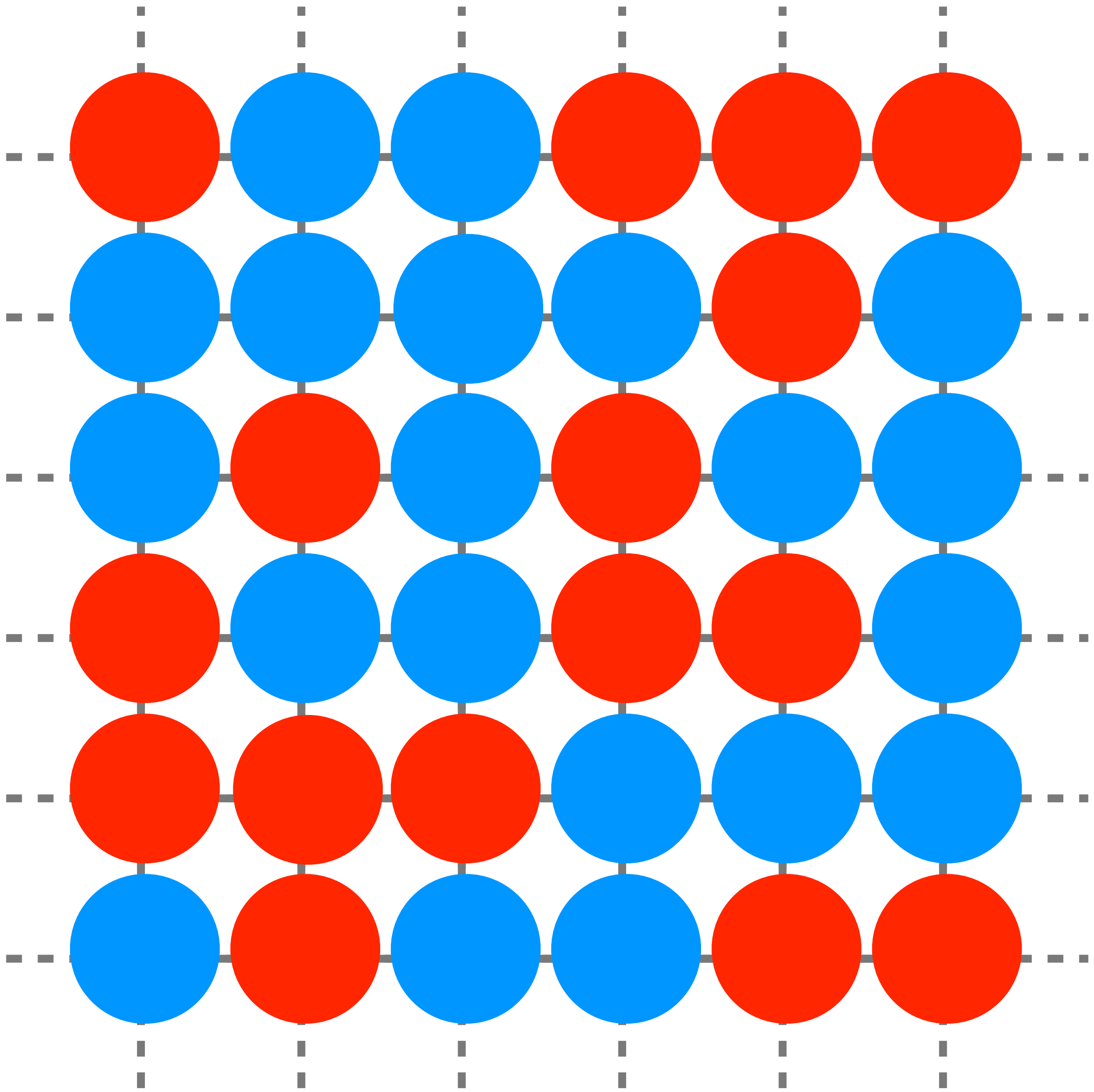

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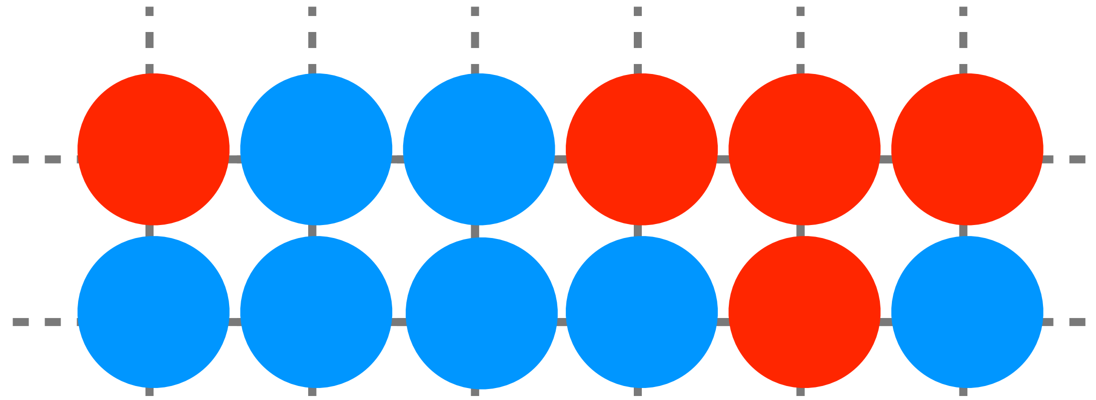
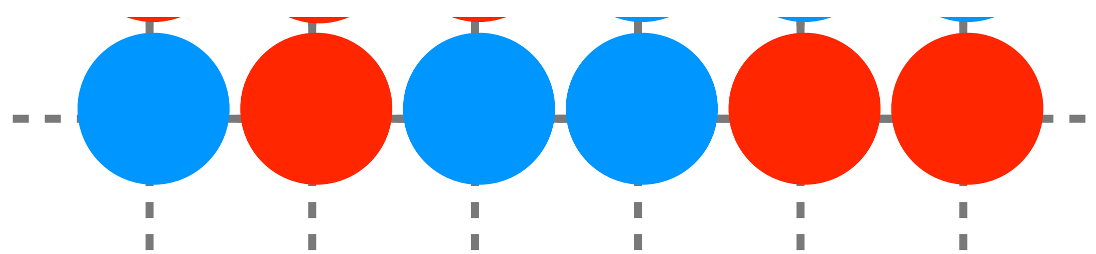
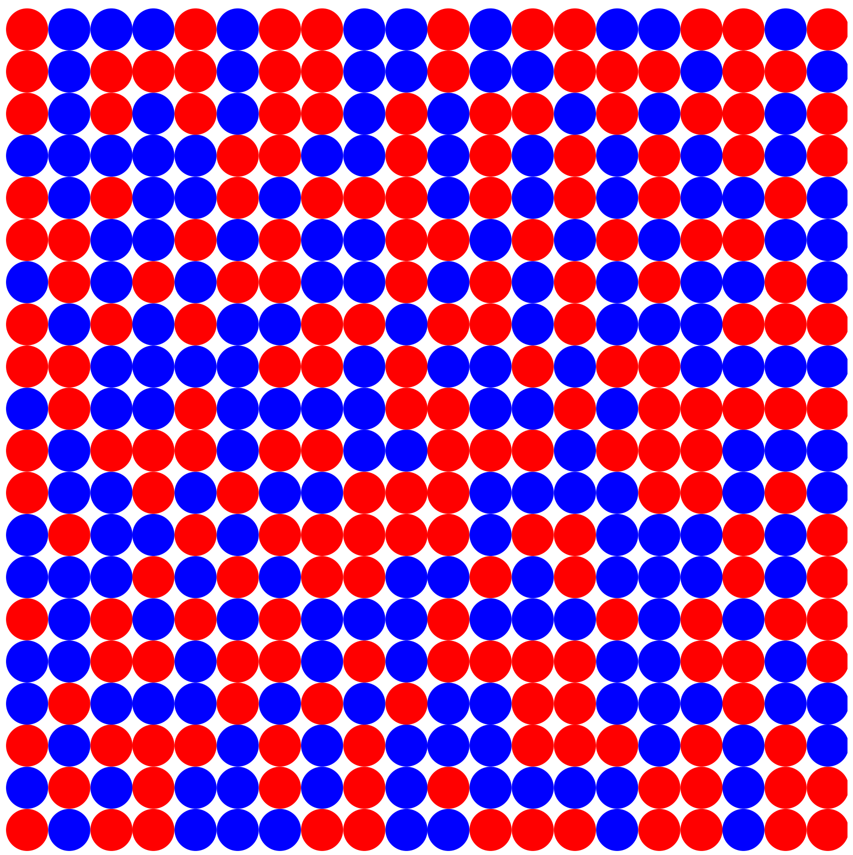


$$F = U - TS$$

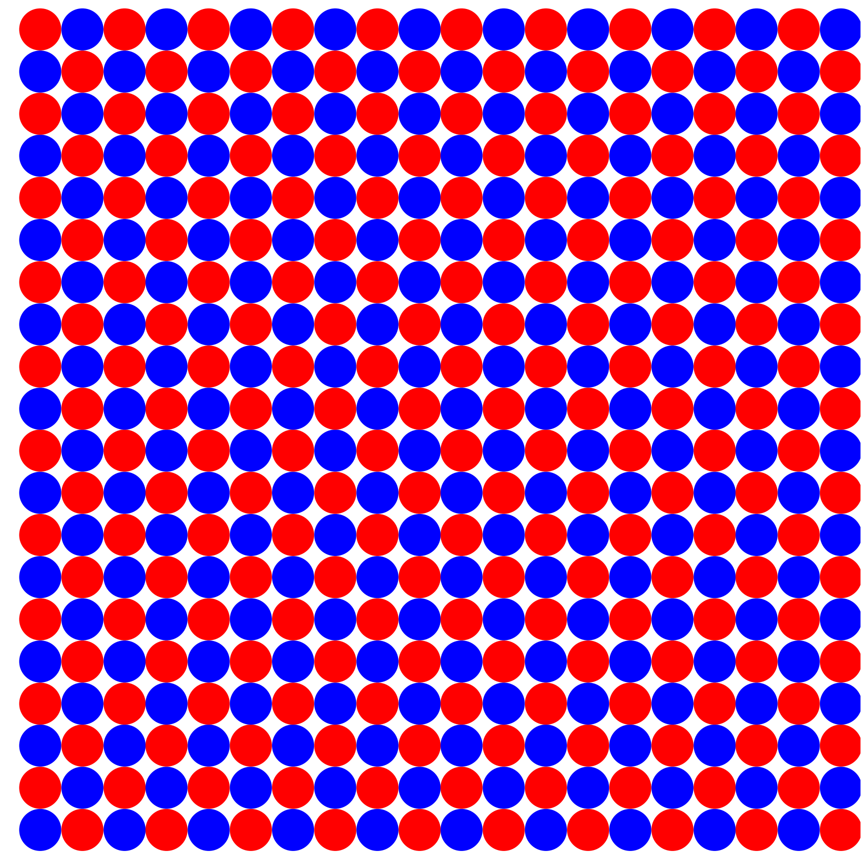


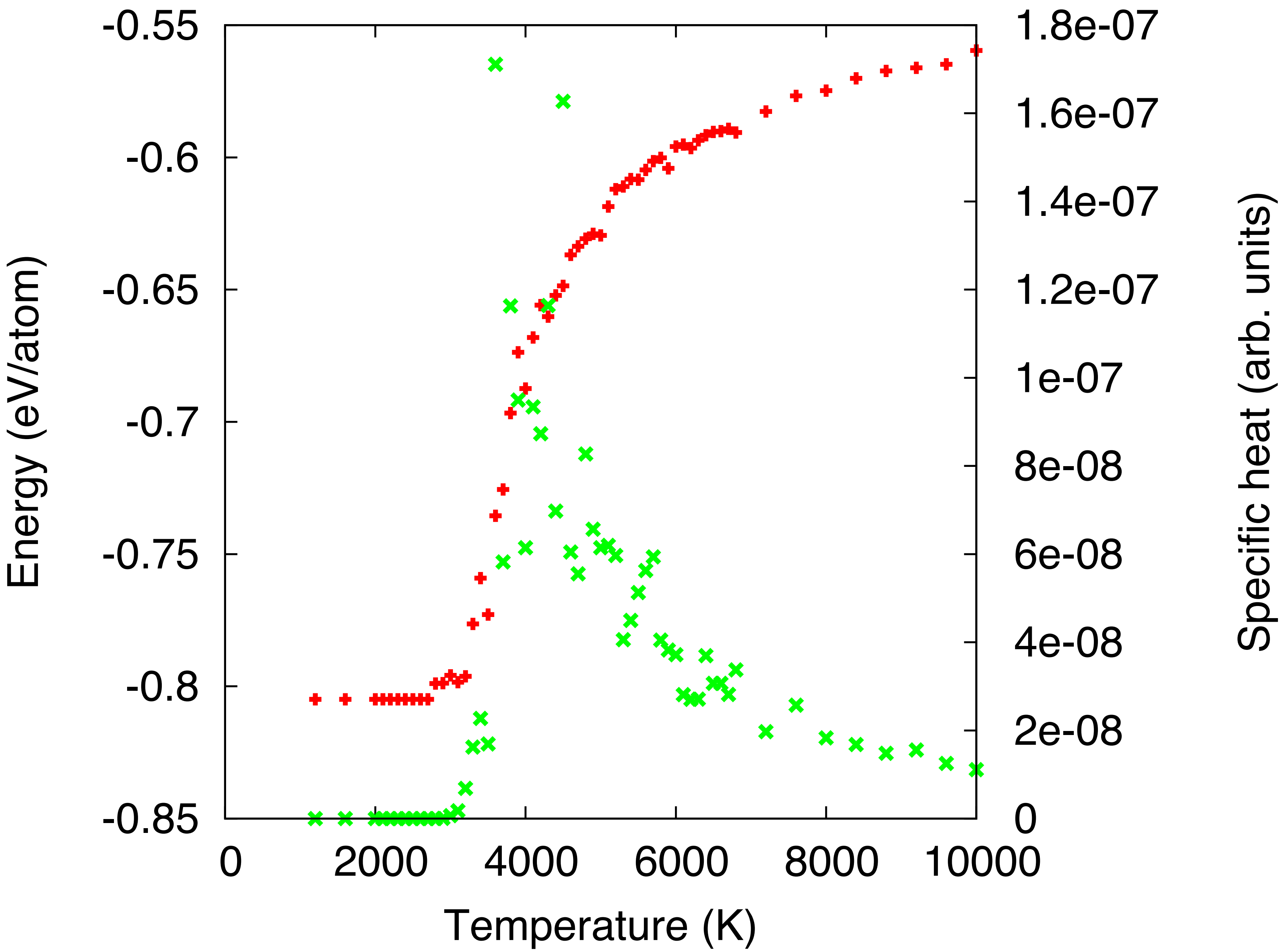
- Choose a new configuration, compute ΔE
- If $\Delta E \leq 0$, keep it
- If $\Delta E > 0$, keep it only if $\exp \Delta E / kT > r$

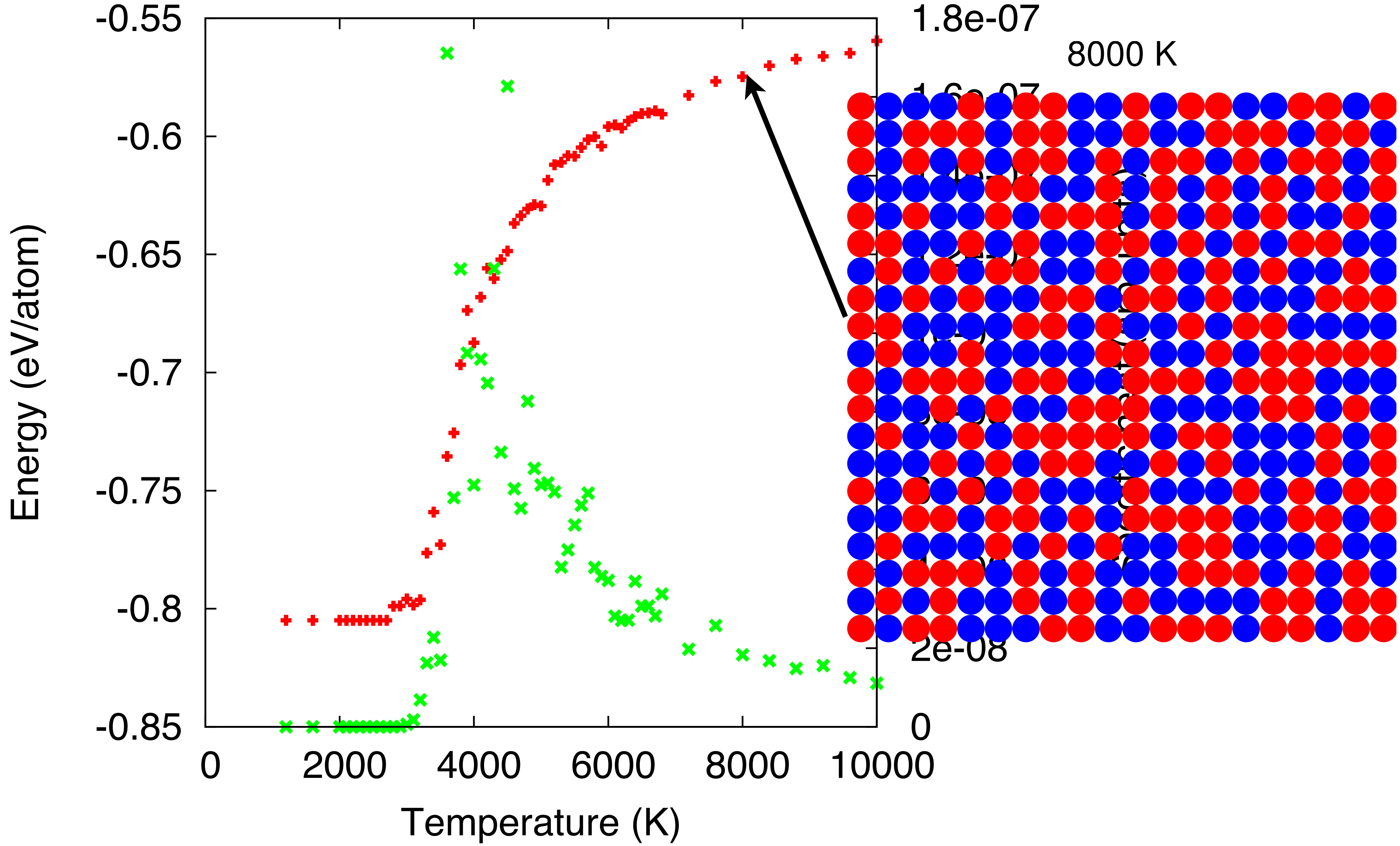
8000 K

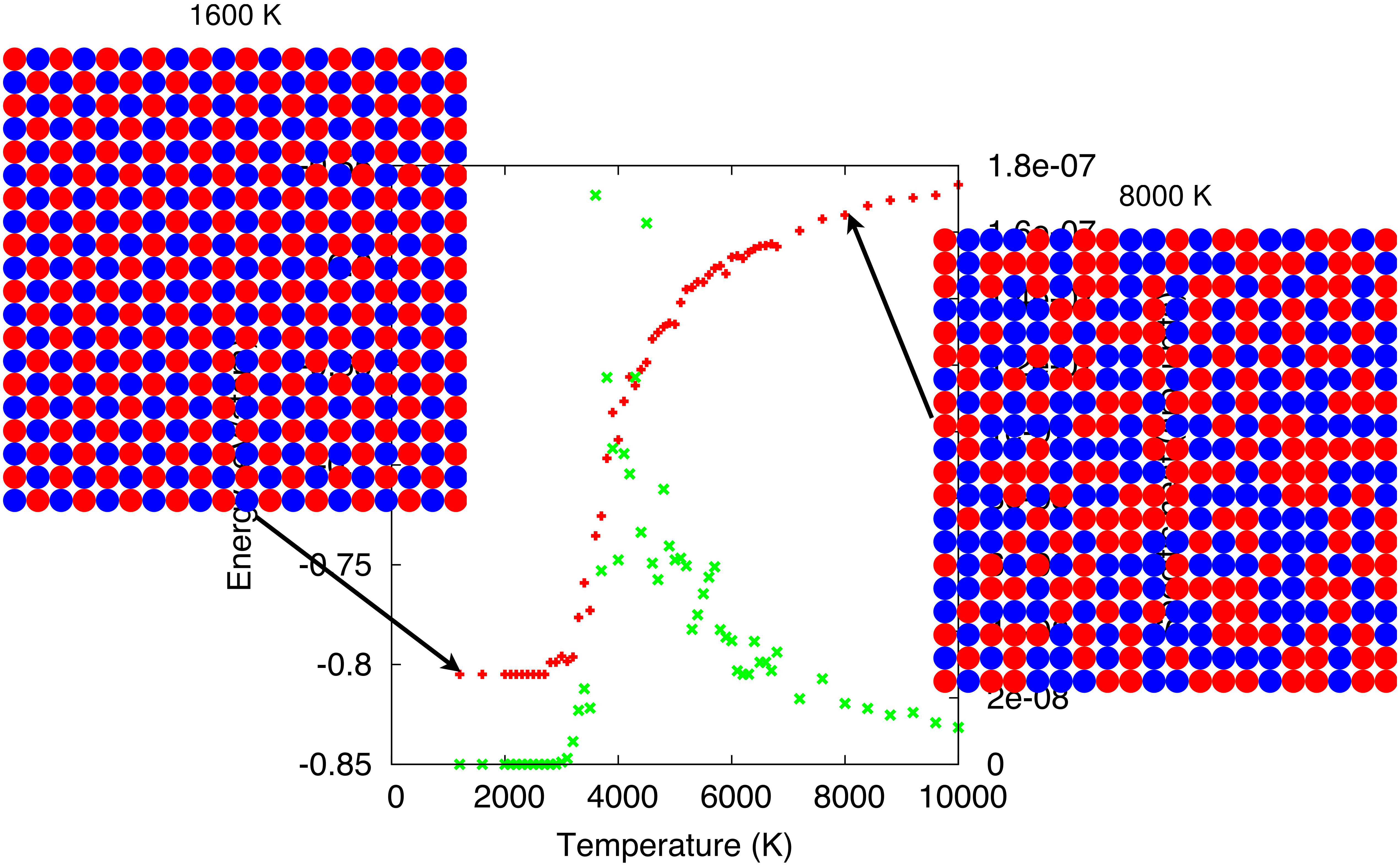


1600 K




-0.55
-0.6
-0.65
-0.7
-0.75
-0.8
-0.85
Energy (eV/atom)
1.8e-07
1.6e-07
1.4e-07
1.2e-07
1e-07
8e-08
6e-08
4e-08
2e-08
0
Specific heat (arb. units)
0
2000
4000
6000
8000
10000
Temperature (K)


-0.55
-0.6
-0.65
-0.7
-0.75
-0.8
-0.85
1.8e-07
2e-08
0
8000 K
Energy (eV/atom)
0
2000
4000
6000
8000
10000
Temperature (K)


1600 K
8000 K
1.8e-07
2e-08
0
-0.75
-0.8
-0.85
0
2000
4000
6000
8000
10000
Temperature (K)