Multiscale modelling of configurational energetics
- The first-principles cluster expansion method -

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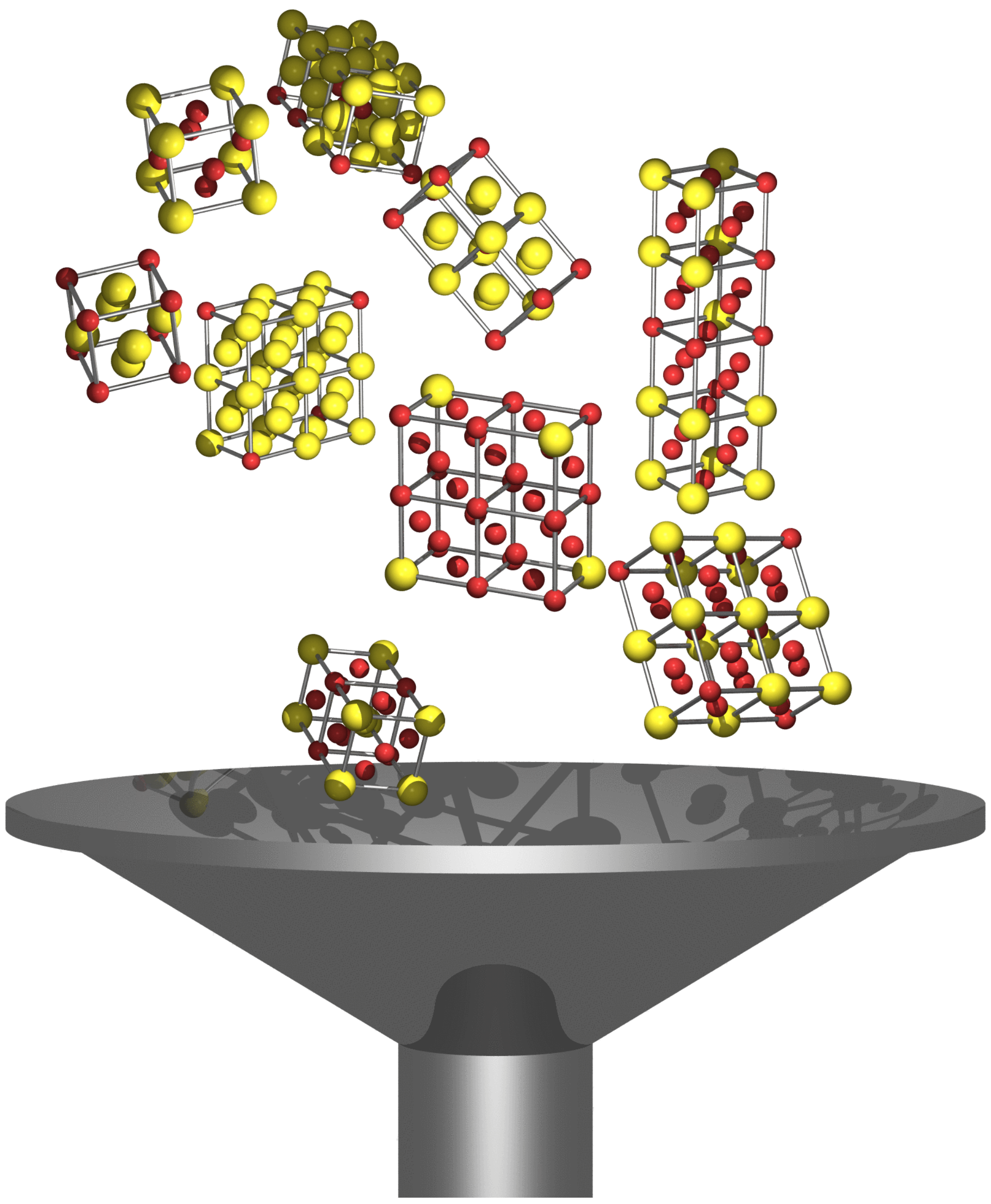


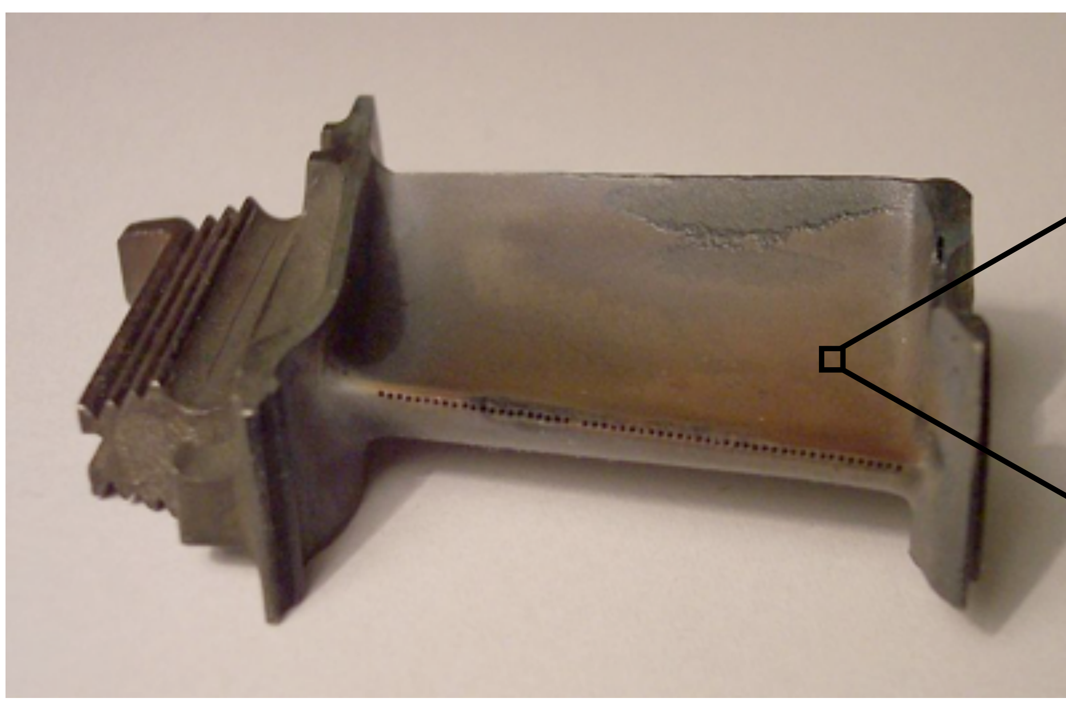
Figure by Ralf Drautz

A feasible first step

A completely general, simple analytic form for

$$E \equiv E^{\text{gs}}_{\text{BO}}(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_M)$$

is most likely not feasible.
But what if we know something about the problem?

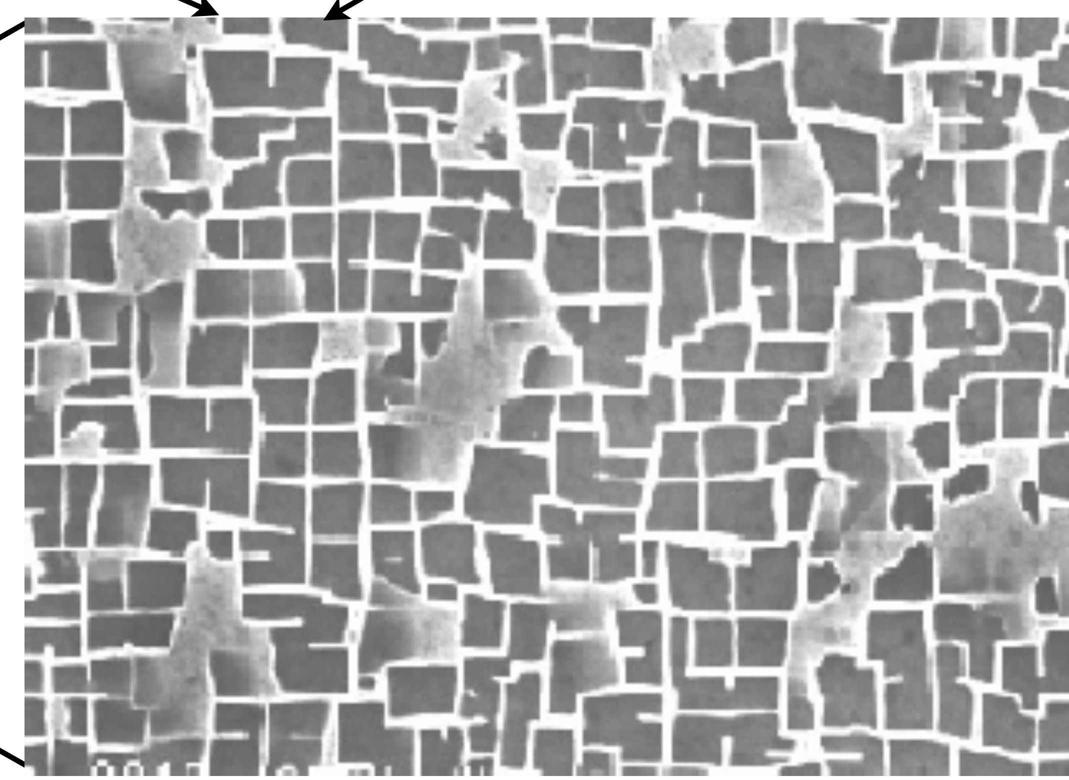


Nickel superalloy jet engine turbine blade

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

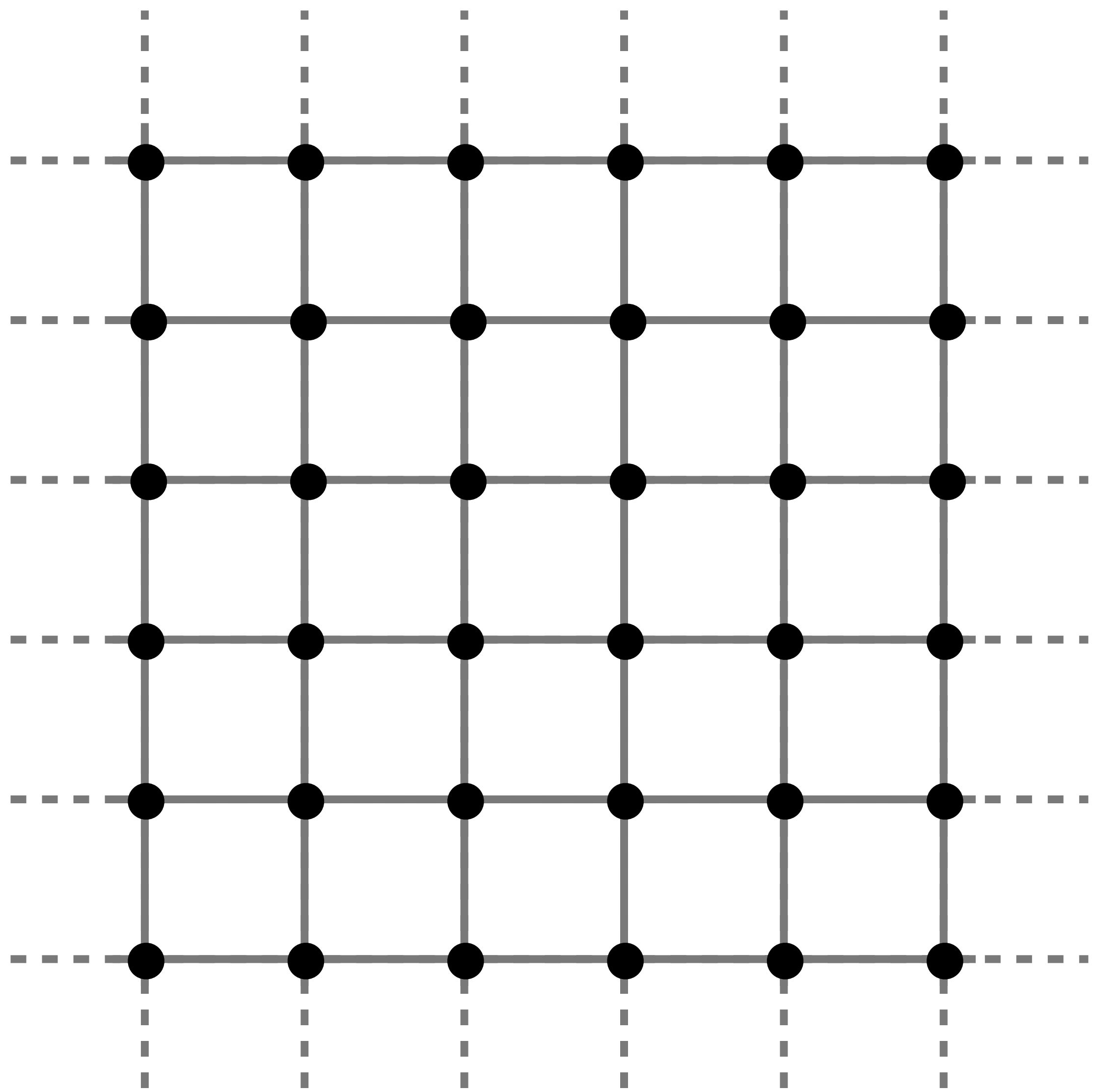
disordered fcc Ni+(Co,Cr,Mo,W,...)

ordered Ni_3(Al,Ti)

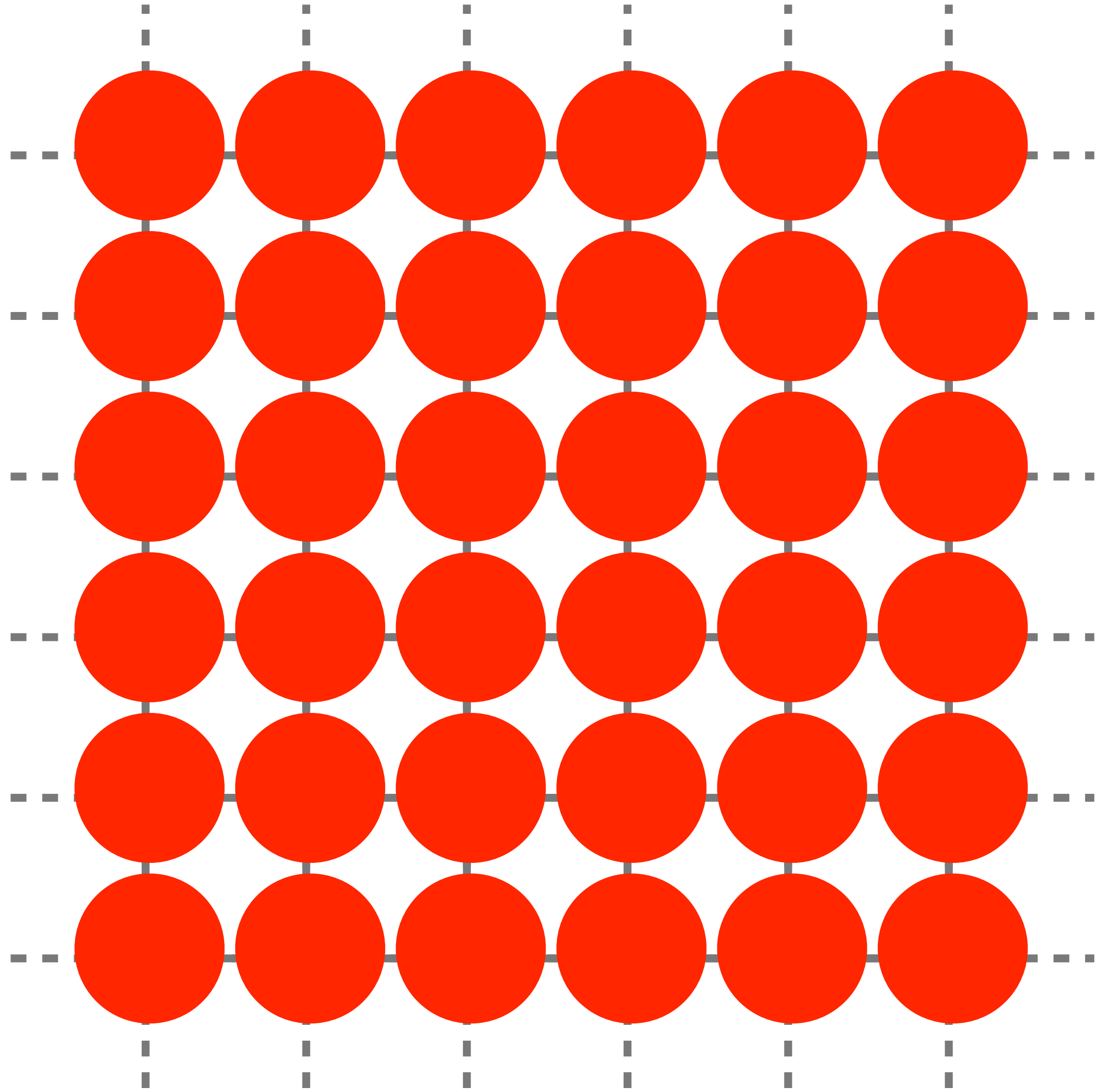


http://www.tms.org/meetings/specialty/superalloys2000/superalloyshistory.html

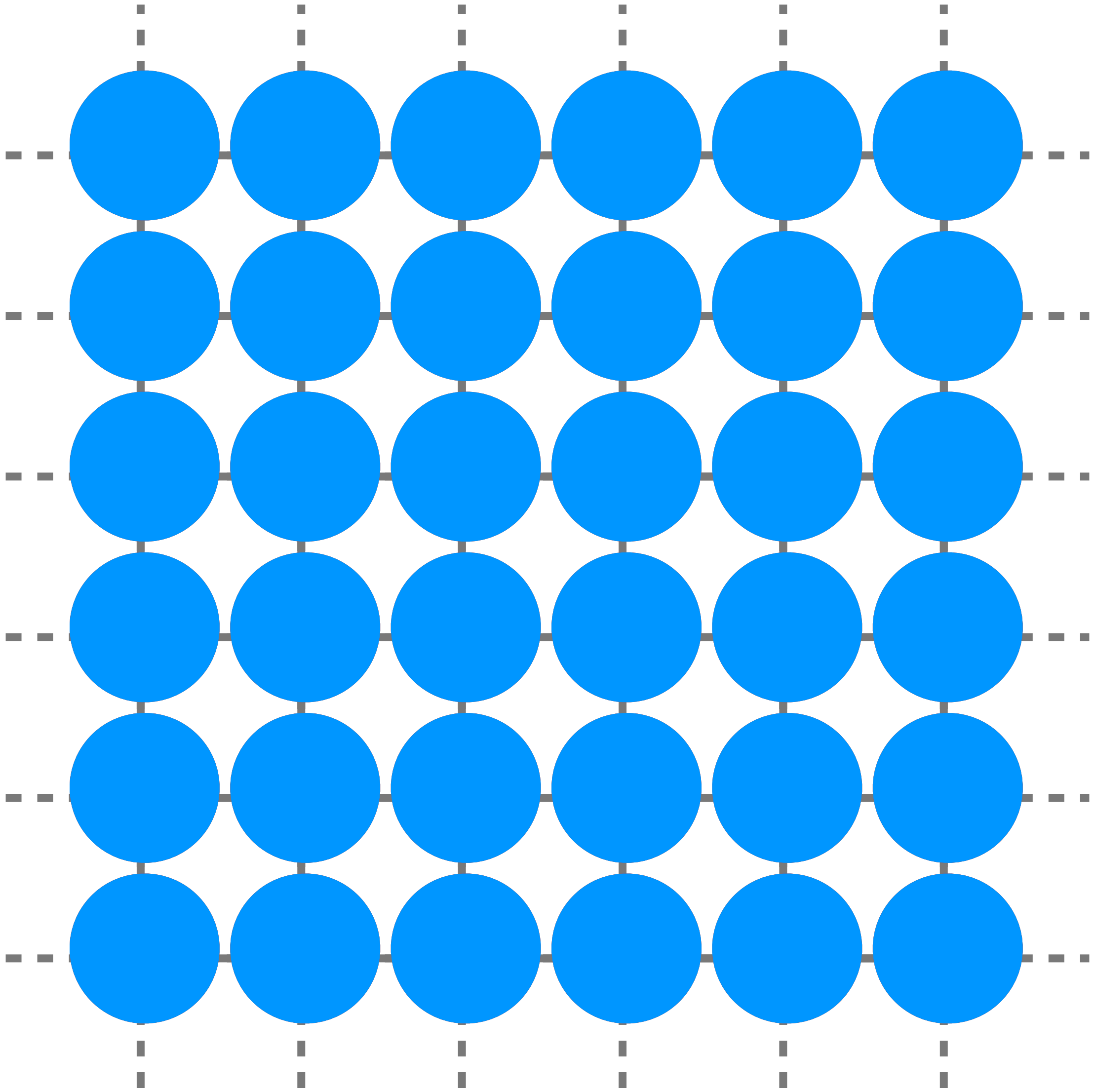
Configurations on a lattice

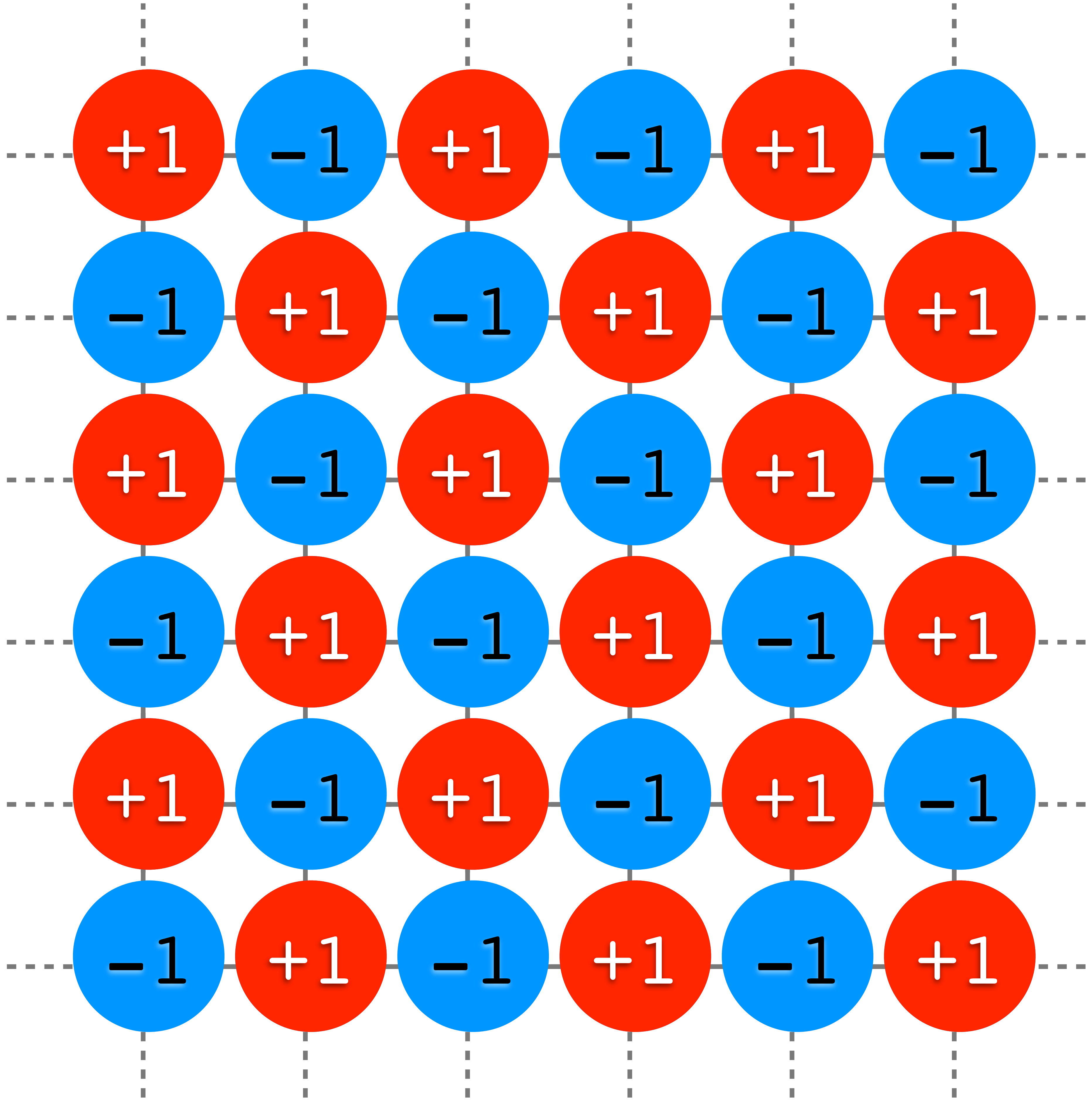


Configurations on a lattice



Configurations on a lattice




+1 −1 +1 −1 +1 −1
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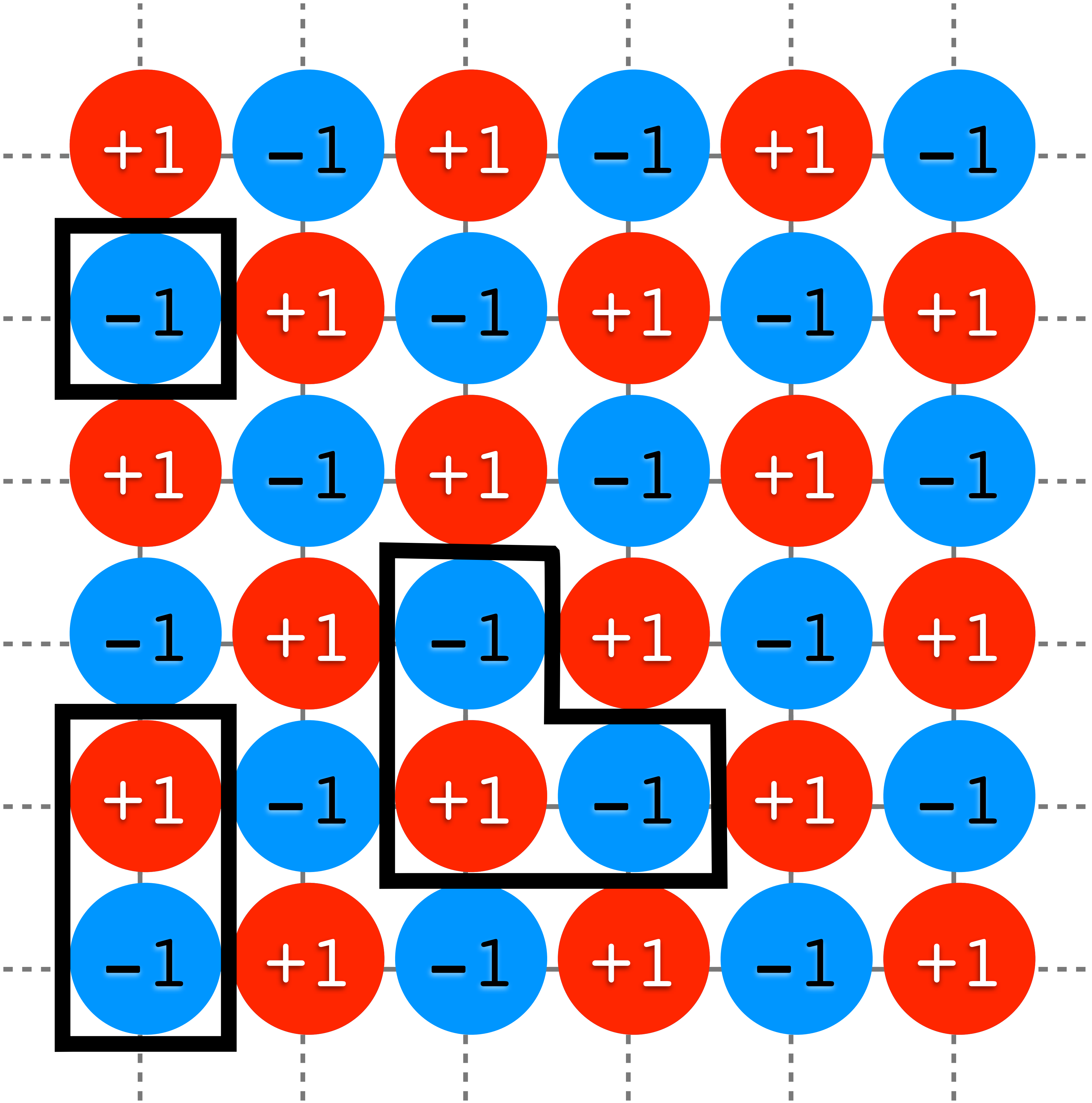
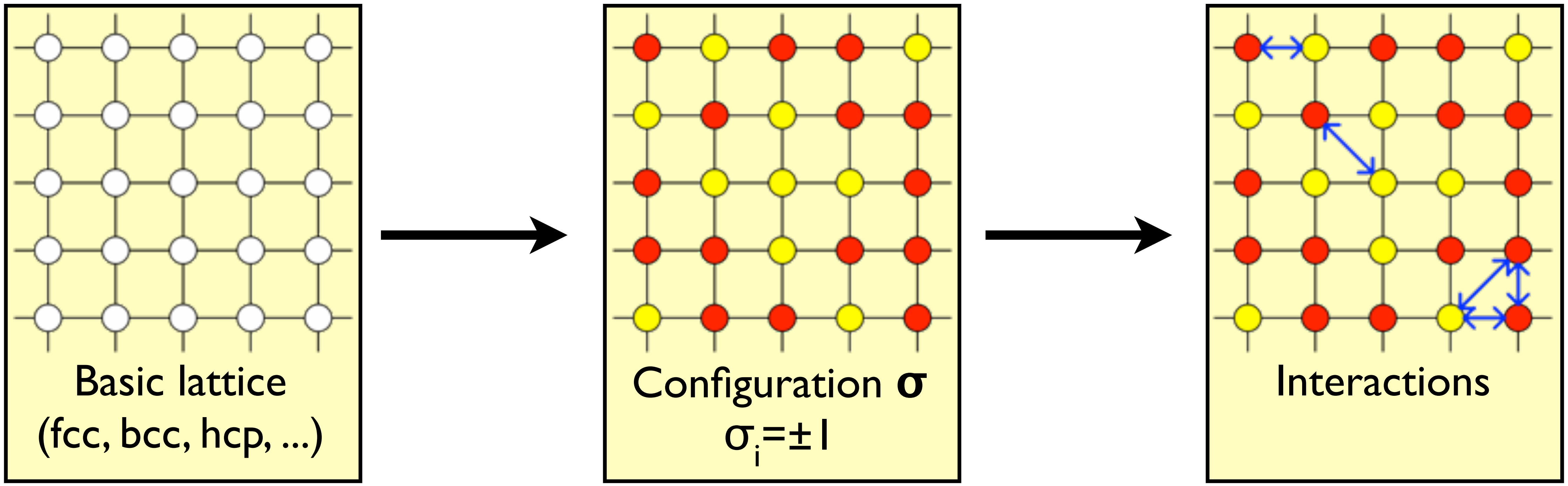
−1 +1 −1 +1 −1 +1

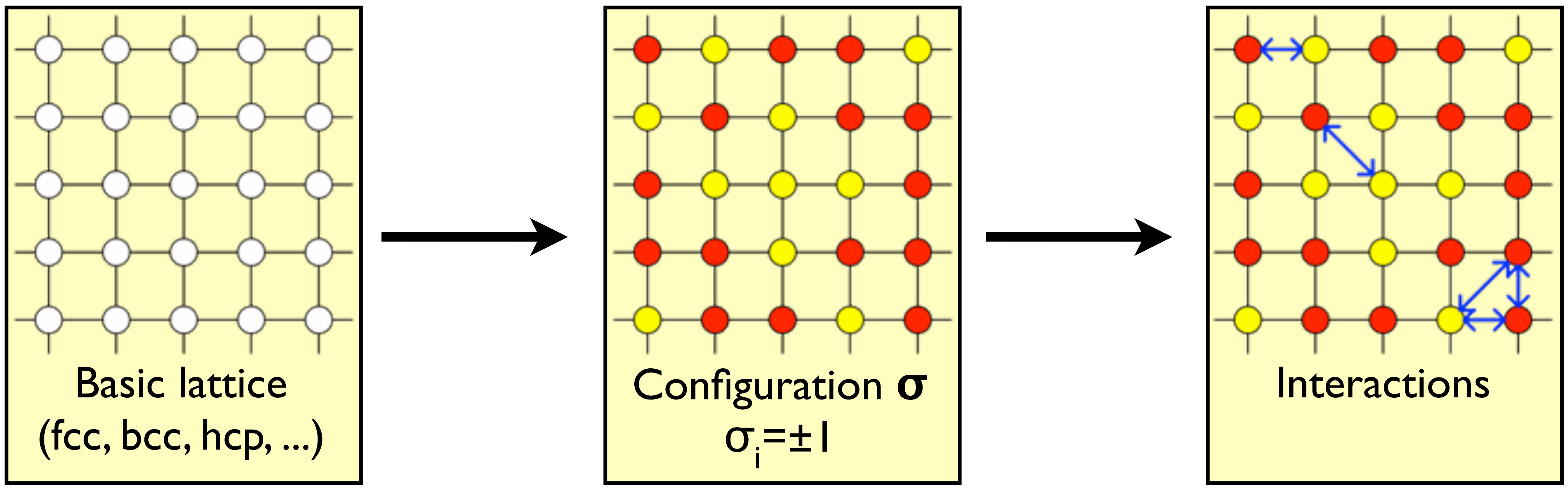

+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1

First-principles cluster expansion



$$E(\sigma) = J_0 + \sum_i \sigma_i J_i + \sum_{i,j} J_{ij}\sigma_i\sigma_j + \sum_{ijk} J_{ijk}\sigma_i\sigma_j\sigma_k + \ldots$$

First-principles cluster expansion



$$E(\sigma) = J_0 + \sum_i \sigma_i J_i + \sum_{i,j} J_{ij}\sigma_i\sigma_j + \sum_{ijk} J_{ijk}\sigma_i\sigma_j\sigma_k + \ldots$$

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

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

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

This tutorial

Ni-Al (superalloy poster child)

FHI-aims for DFT-LDA

UNCLE cluster expansion code (learn as we go along)

Problem I: A 2D cluster expansion fit by hand

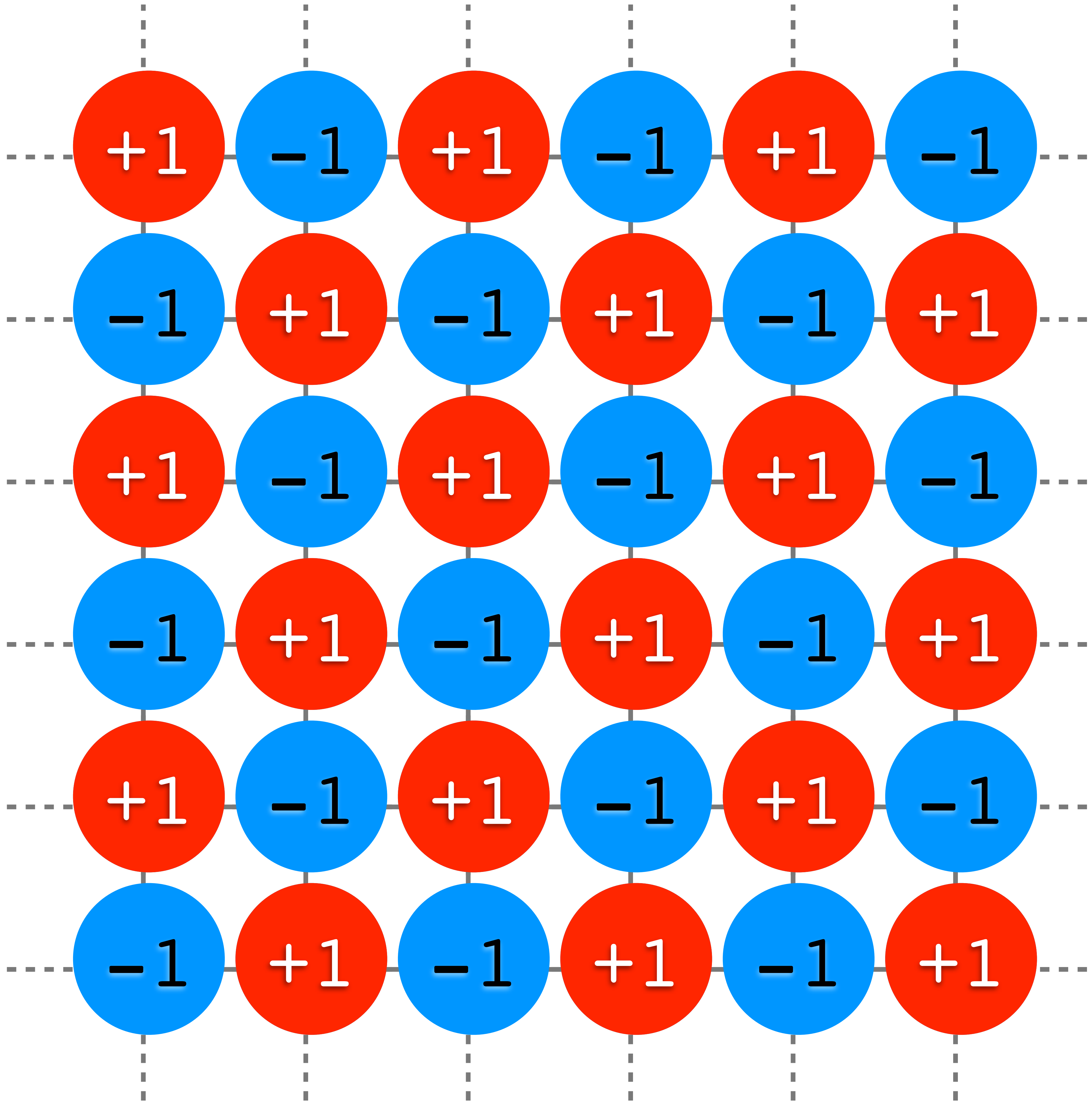
Problem II: Using the cluster expansion code

Problem III: Input energies: Ni-Al on a square lattice

Problem IV: Minimal cluster expansion for 2d Ni-Al ... and some predictions

Problem V: Order-disorder transitions

Bonus from here on



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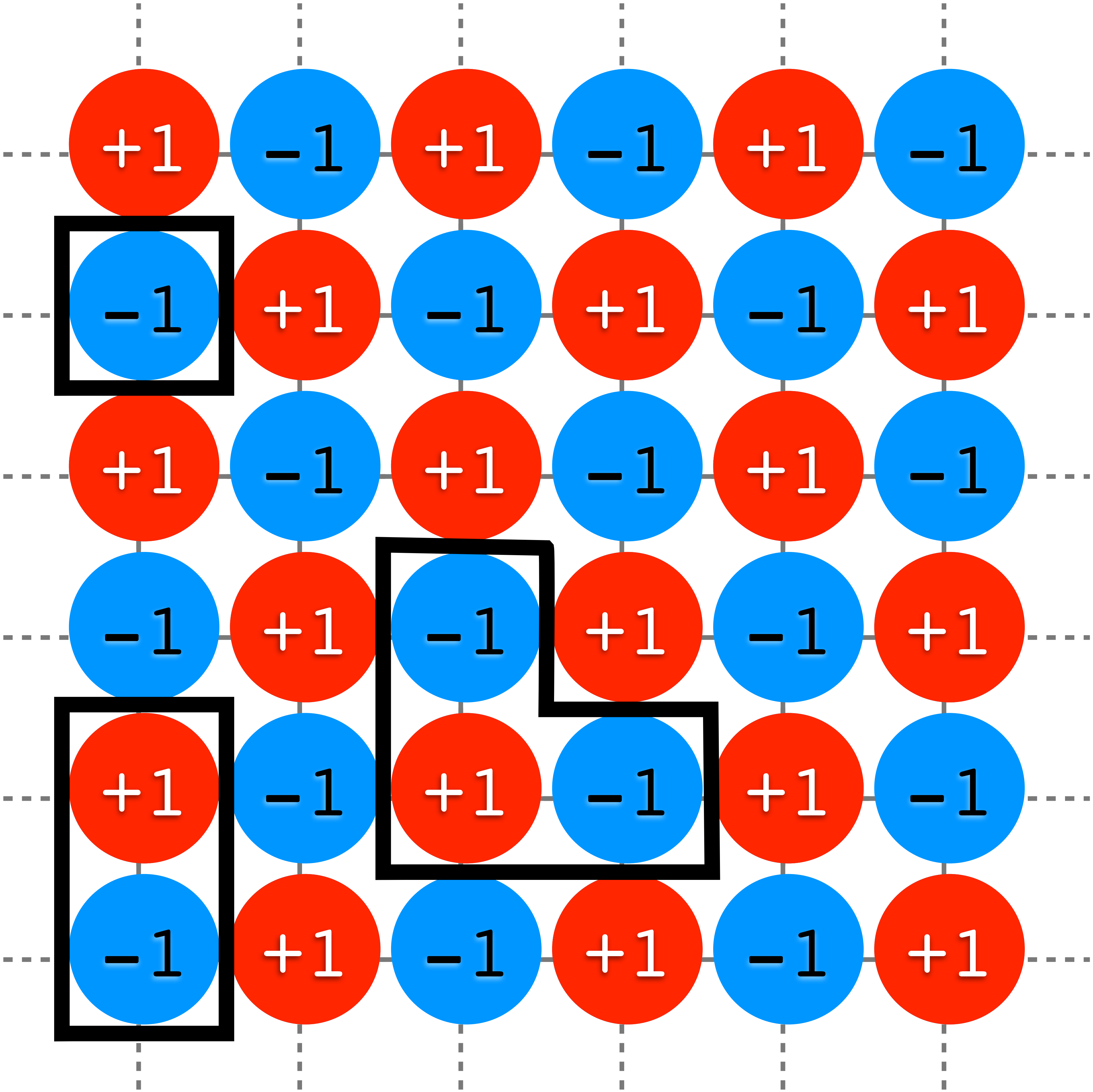
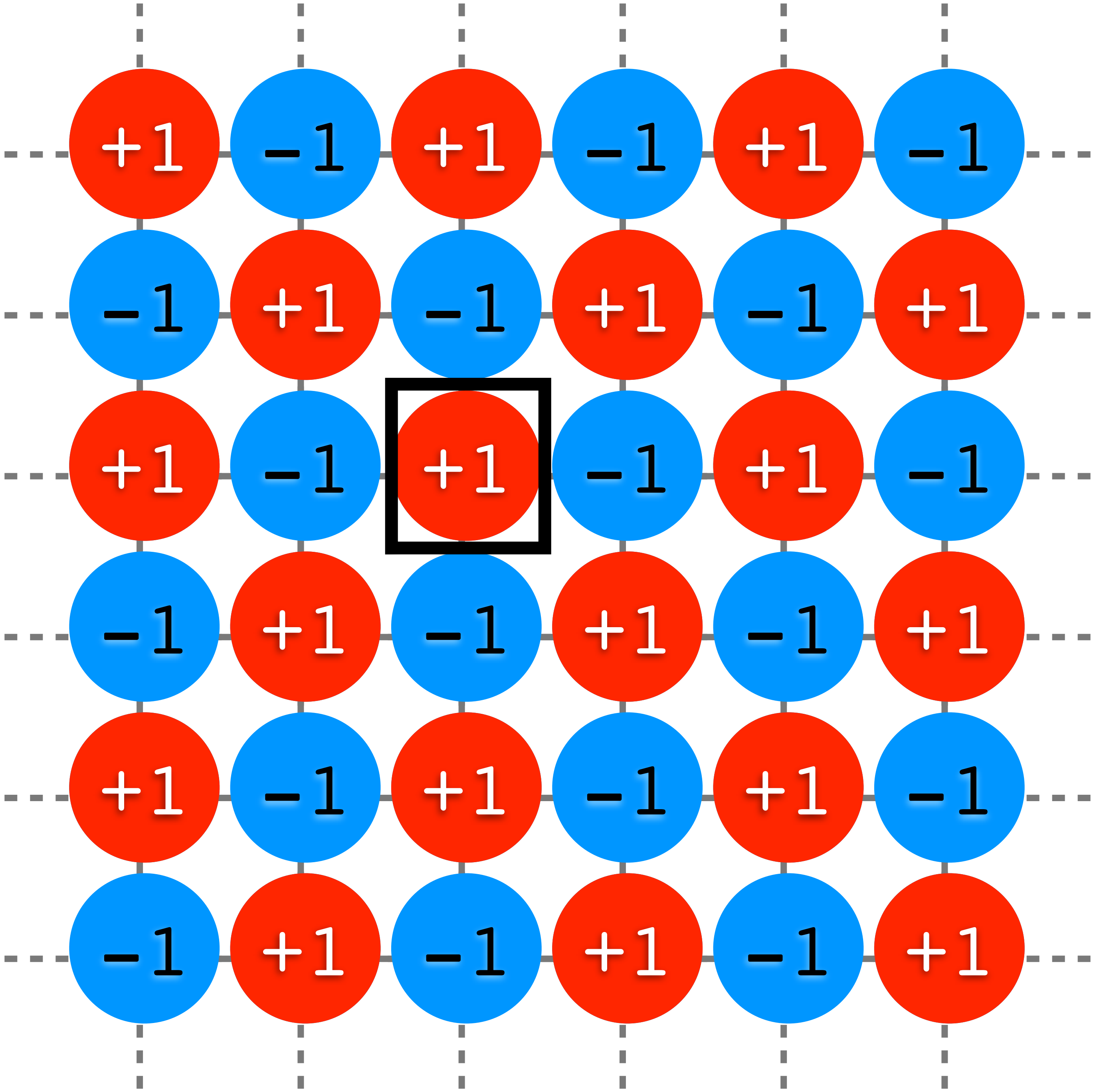


+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1
+1 −1 +1 −1 +1 −1
−1 +1 −1 +1 −1 +1

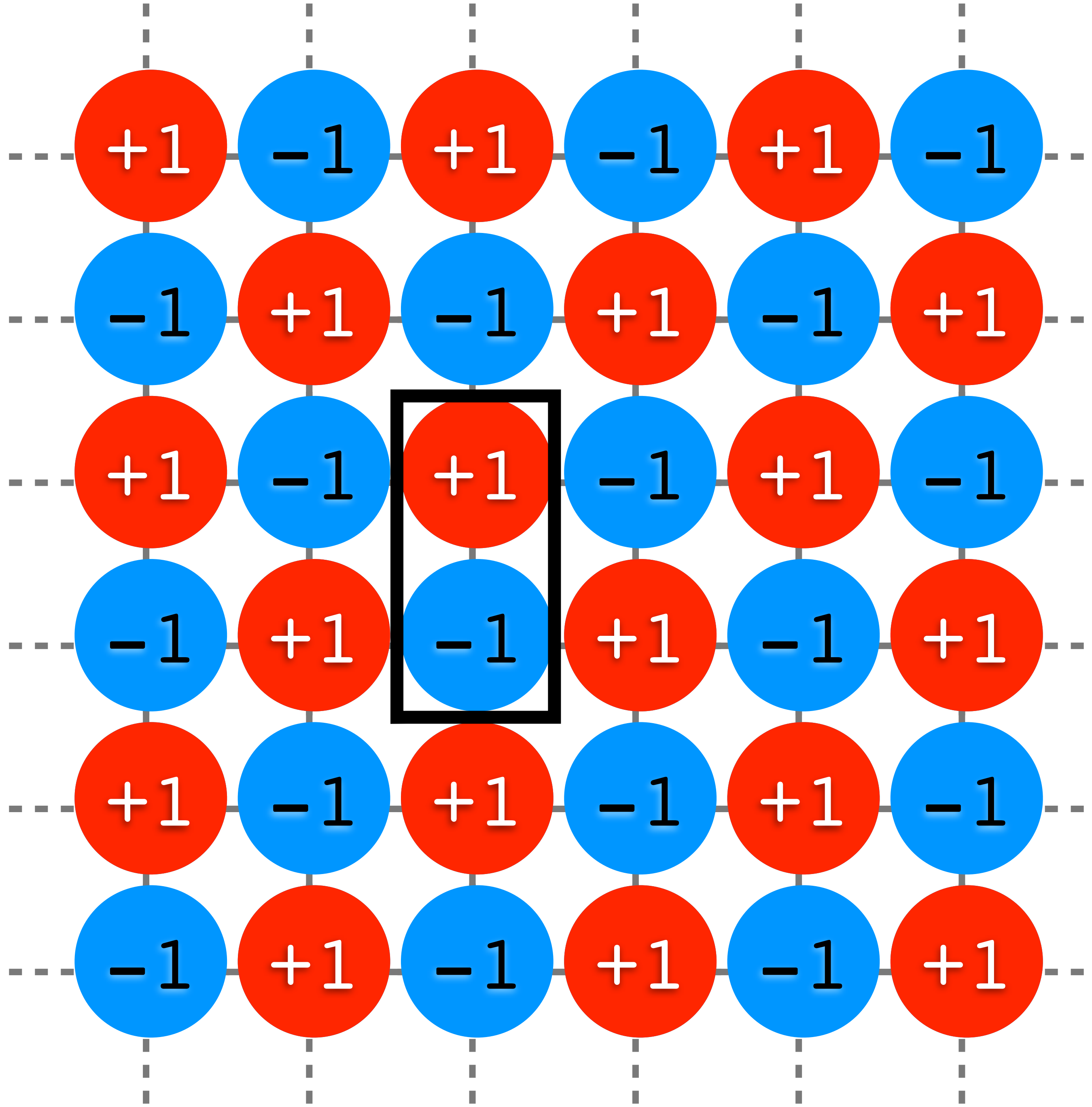
Now the exercise

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



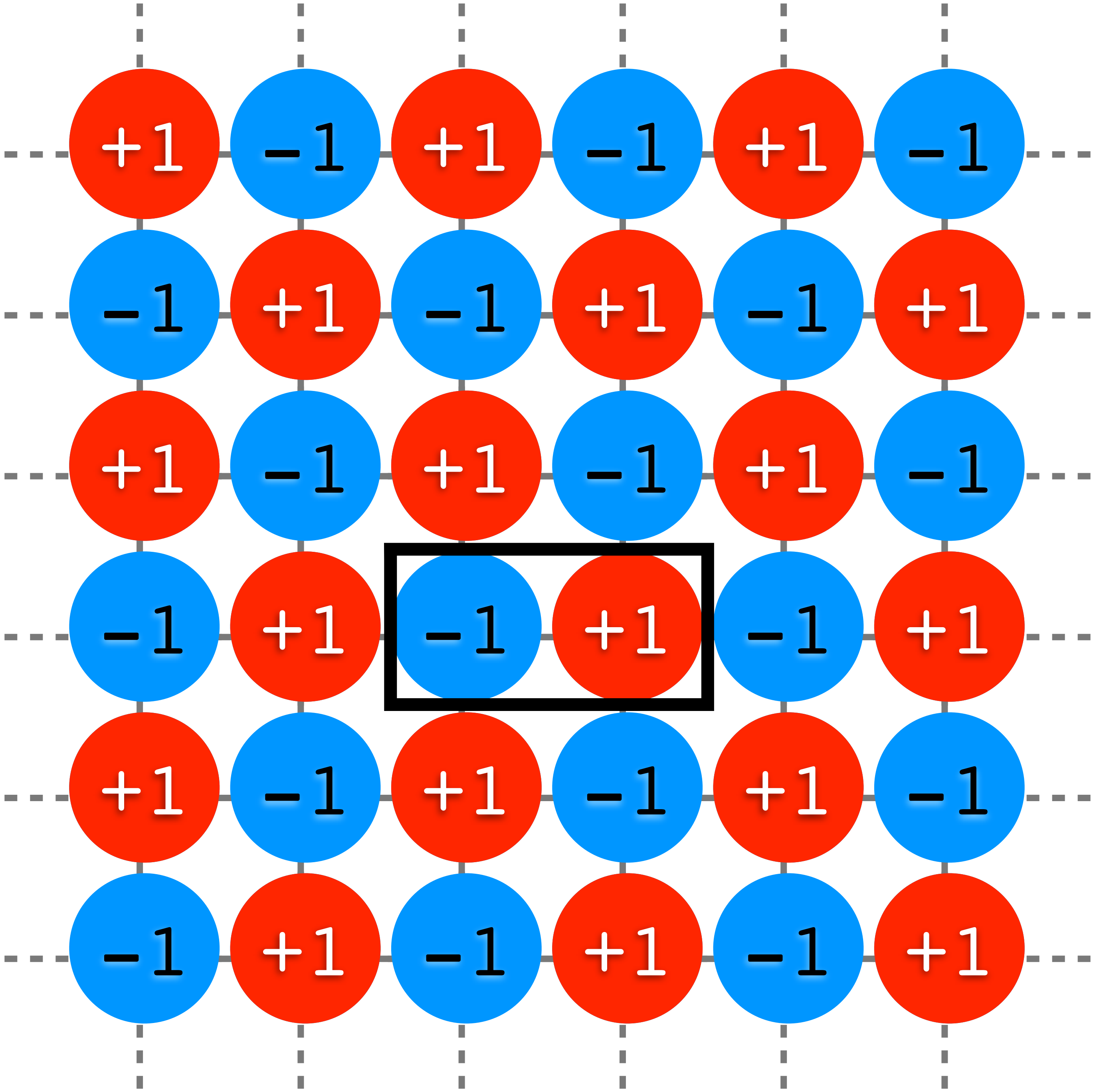
$$0 = (-1) + (+1) + (-1) + (+1) + \cdots$$

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



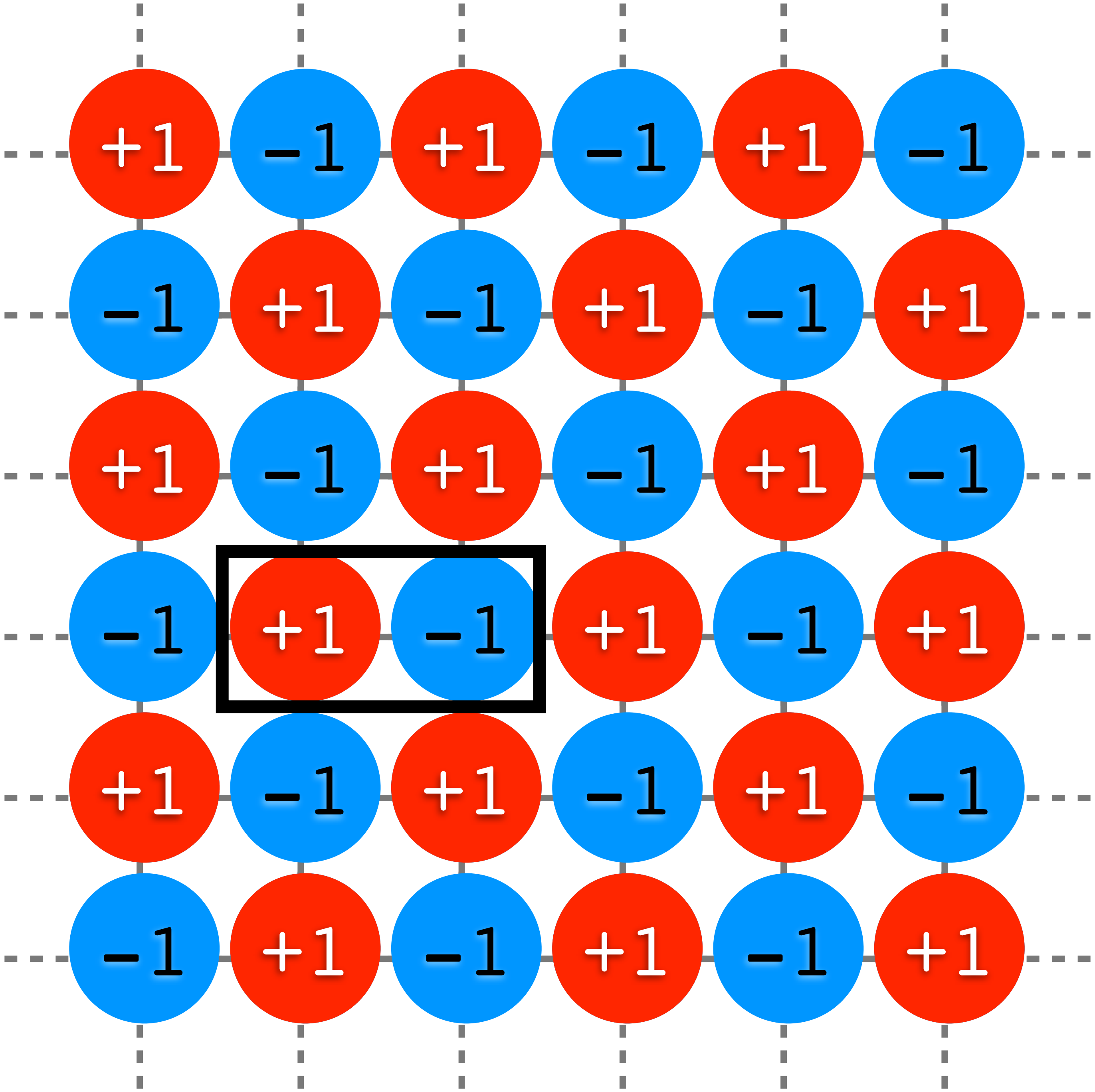
$$-1 = \frac{1}{8}[(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)]$$

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



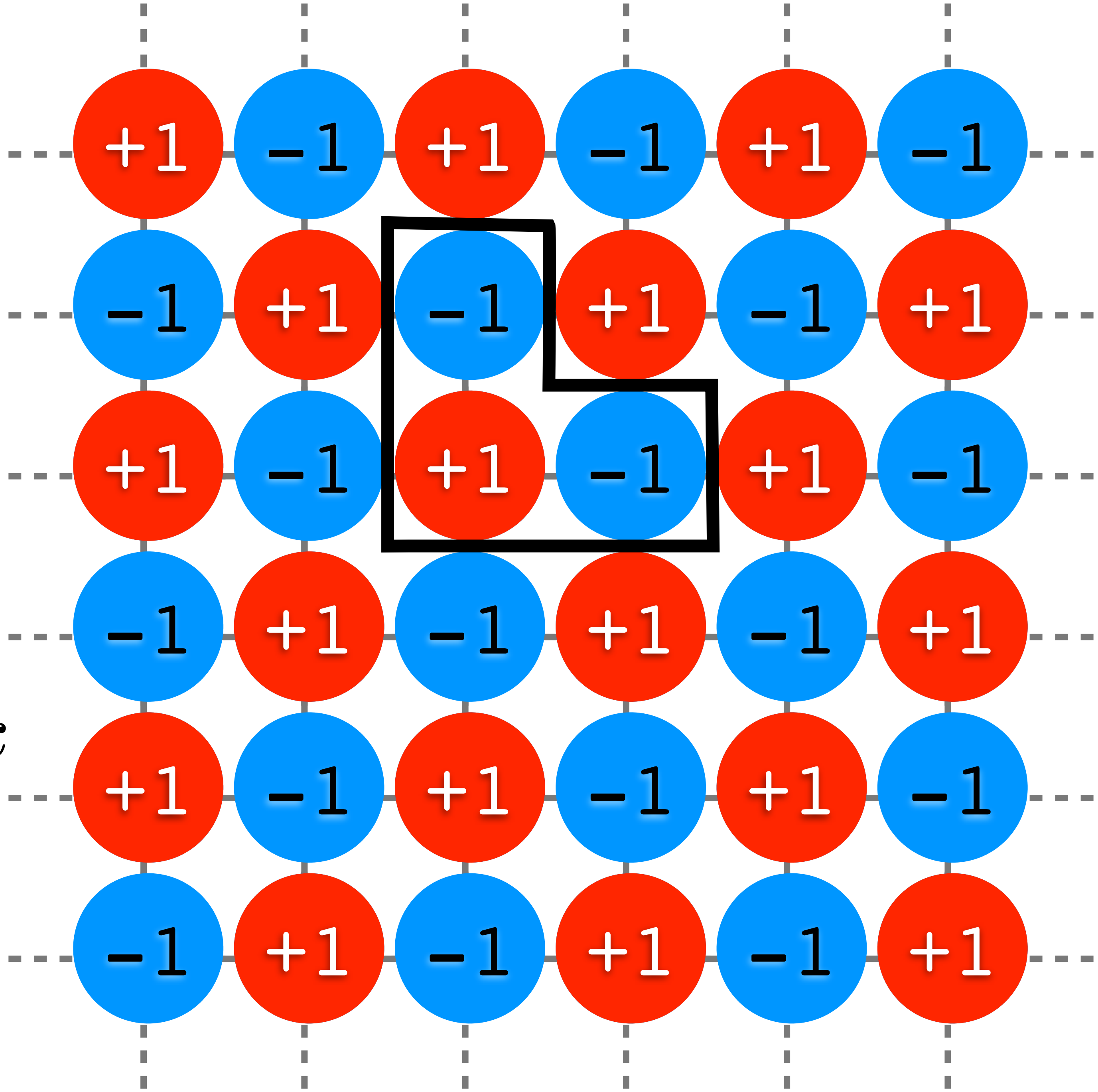
$$-1 = \frac{1}{8}[(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)]$$

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



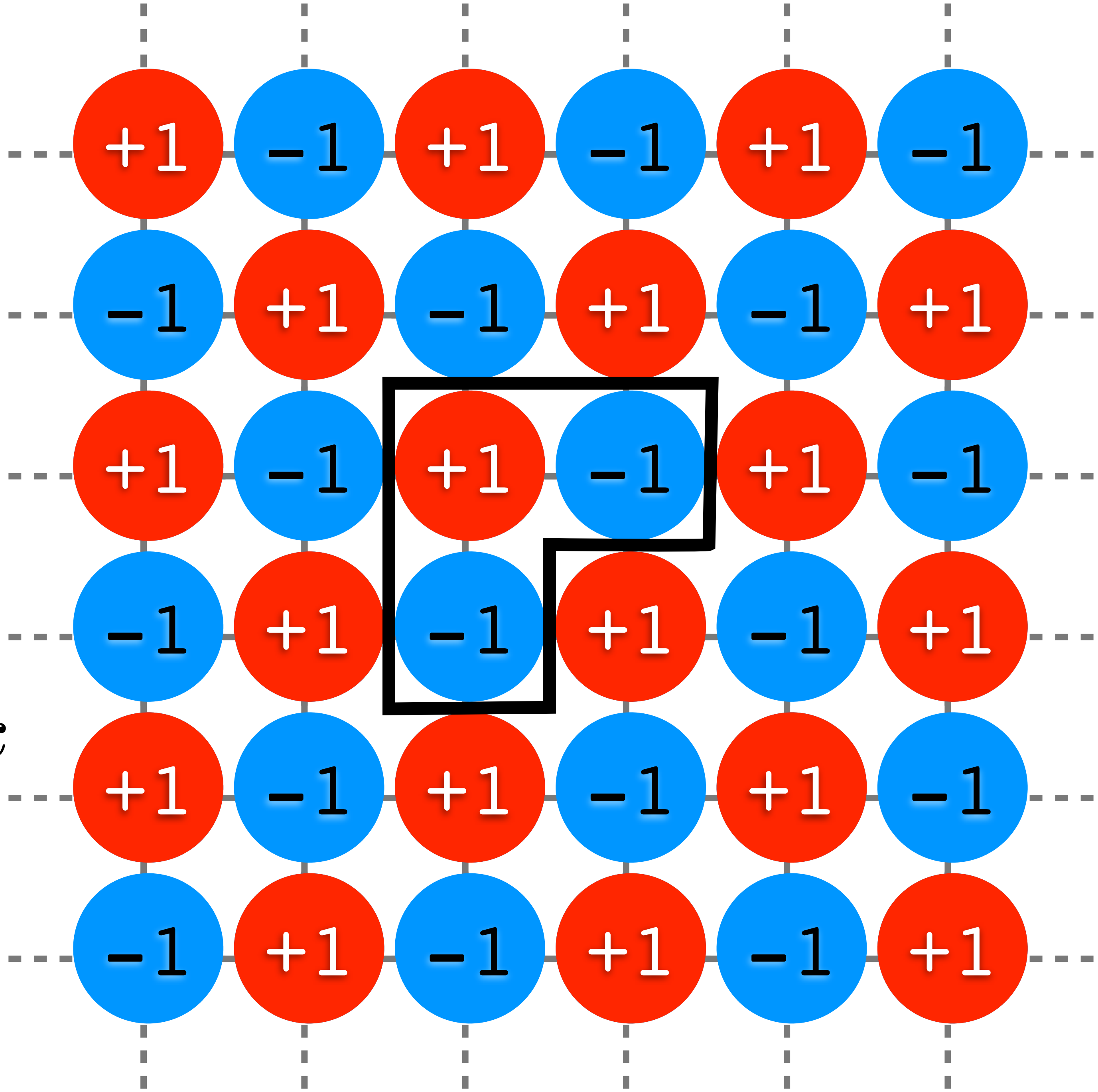
$$-1 \quad = \quad \frac{1}{8}[(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)$$
$$+(-1)(+1) + (-1)(+1) + (-1)(+1) + (-1)(+1)]$$

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



?

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



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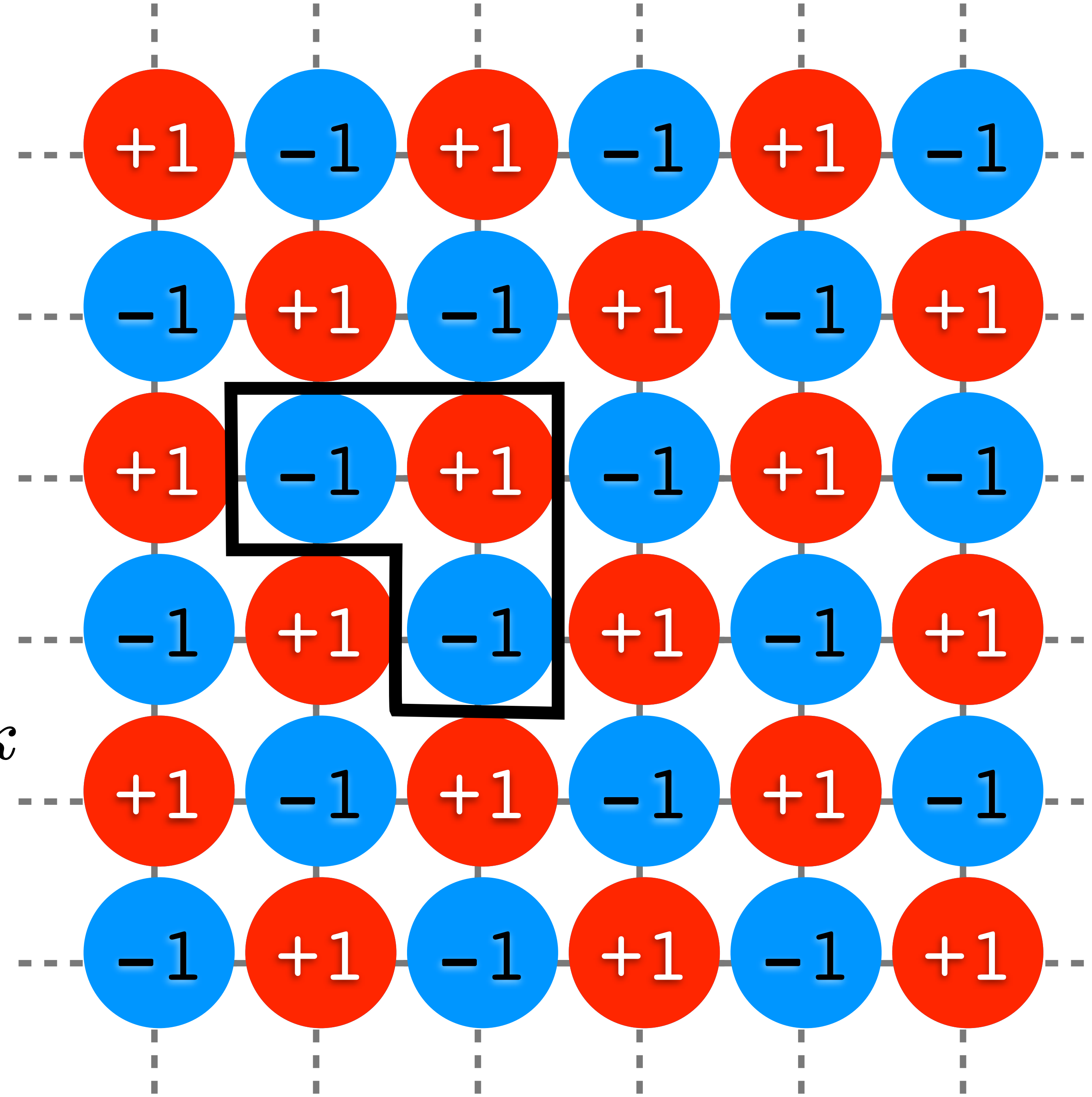
$$? = \frac{1}{N} \sum_{<i,j,k>_{\mathrm{N.N.}}}^{\mathrm{lattice}} S_i S_j S_k$$



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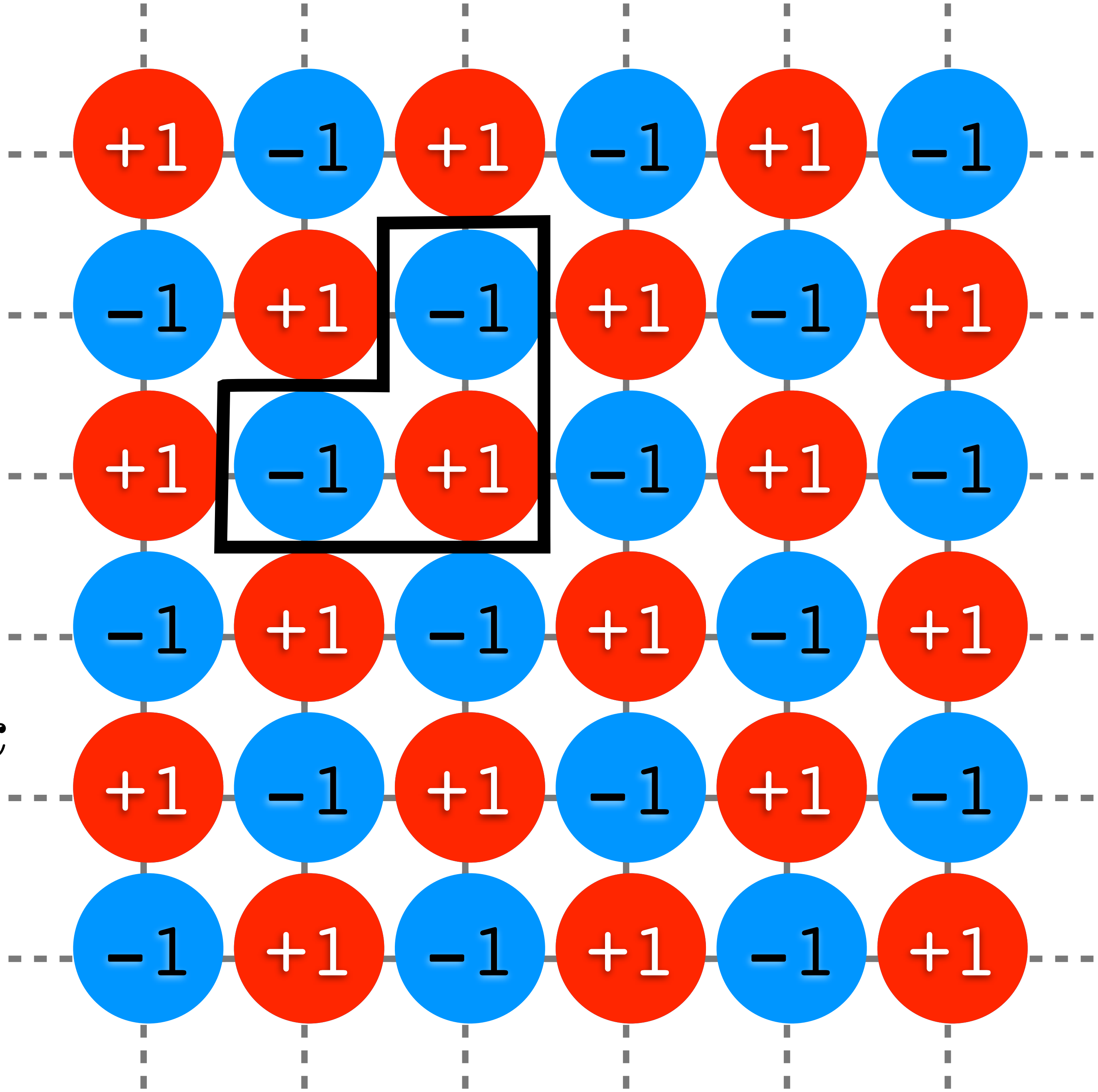

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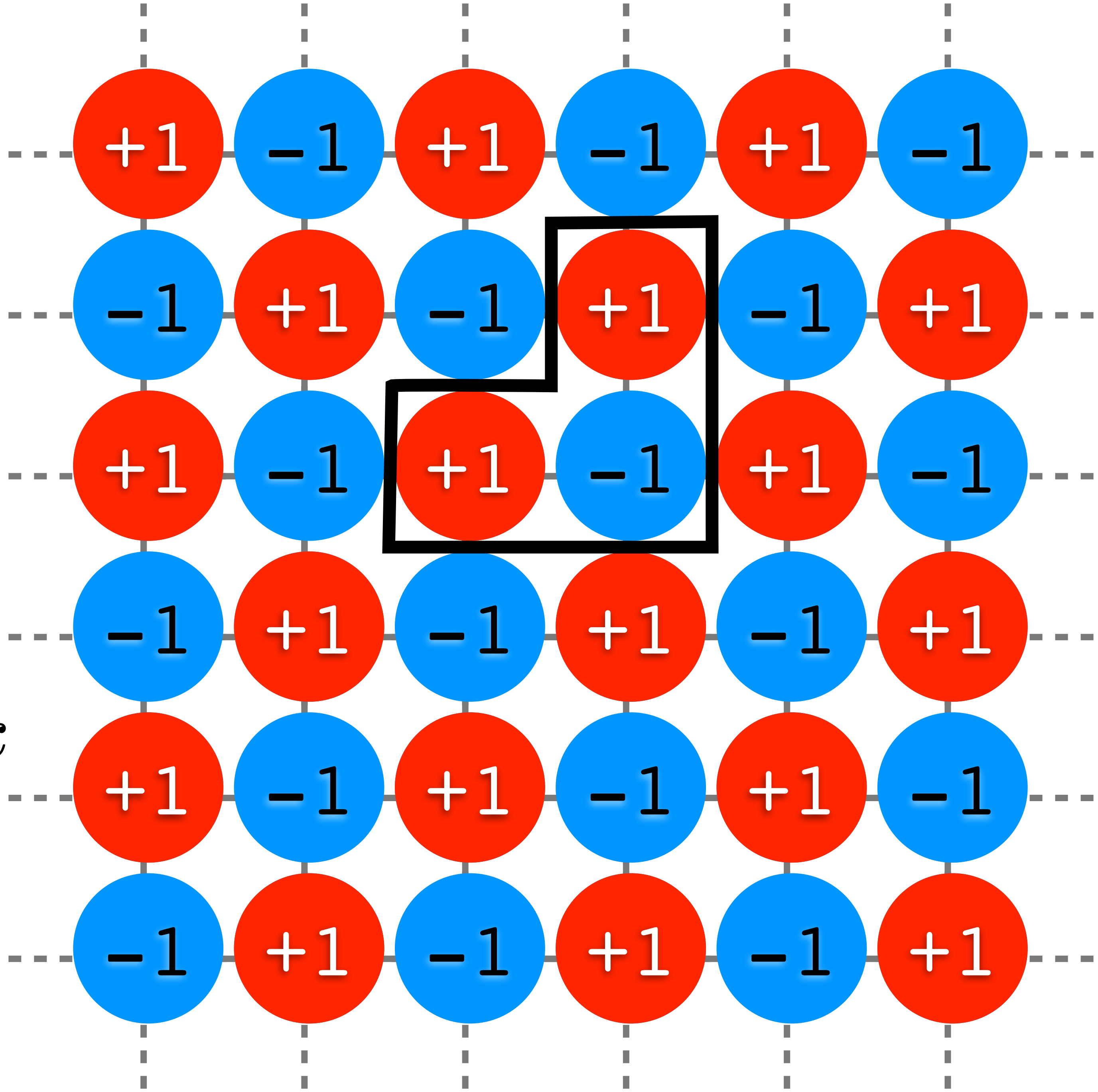
$$? = \frac{1}{N} \sum_{<i,j,k>_{\mathrm{N.N.}}}^{\mathrm{lattice}} S_i S_j S_k$$



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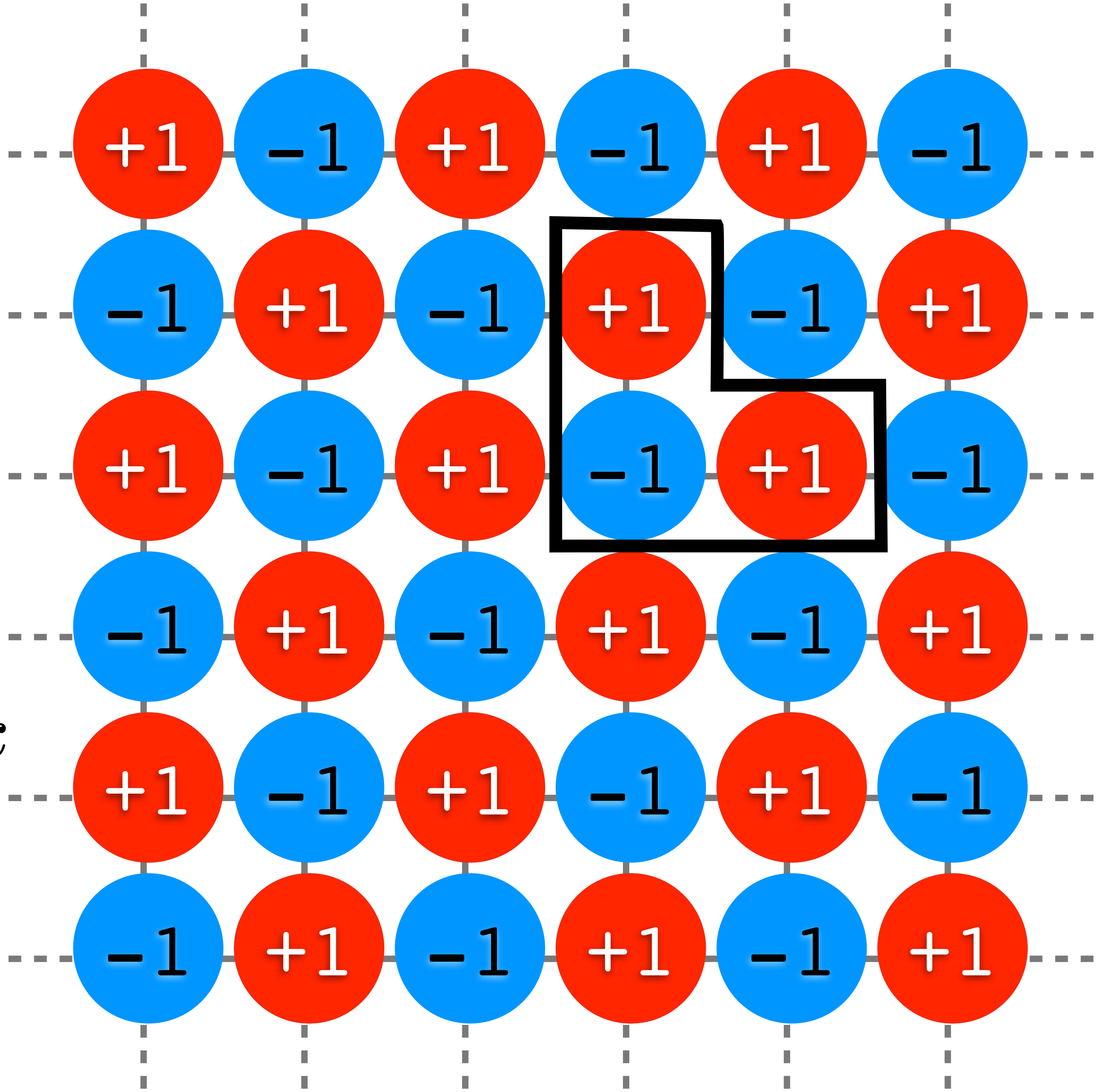

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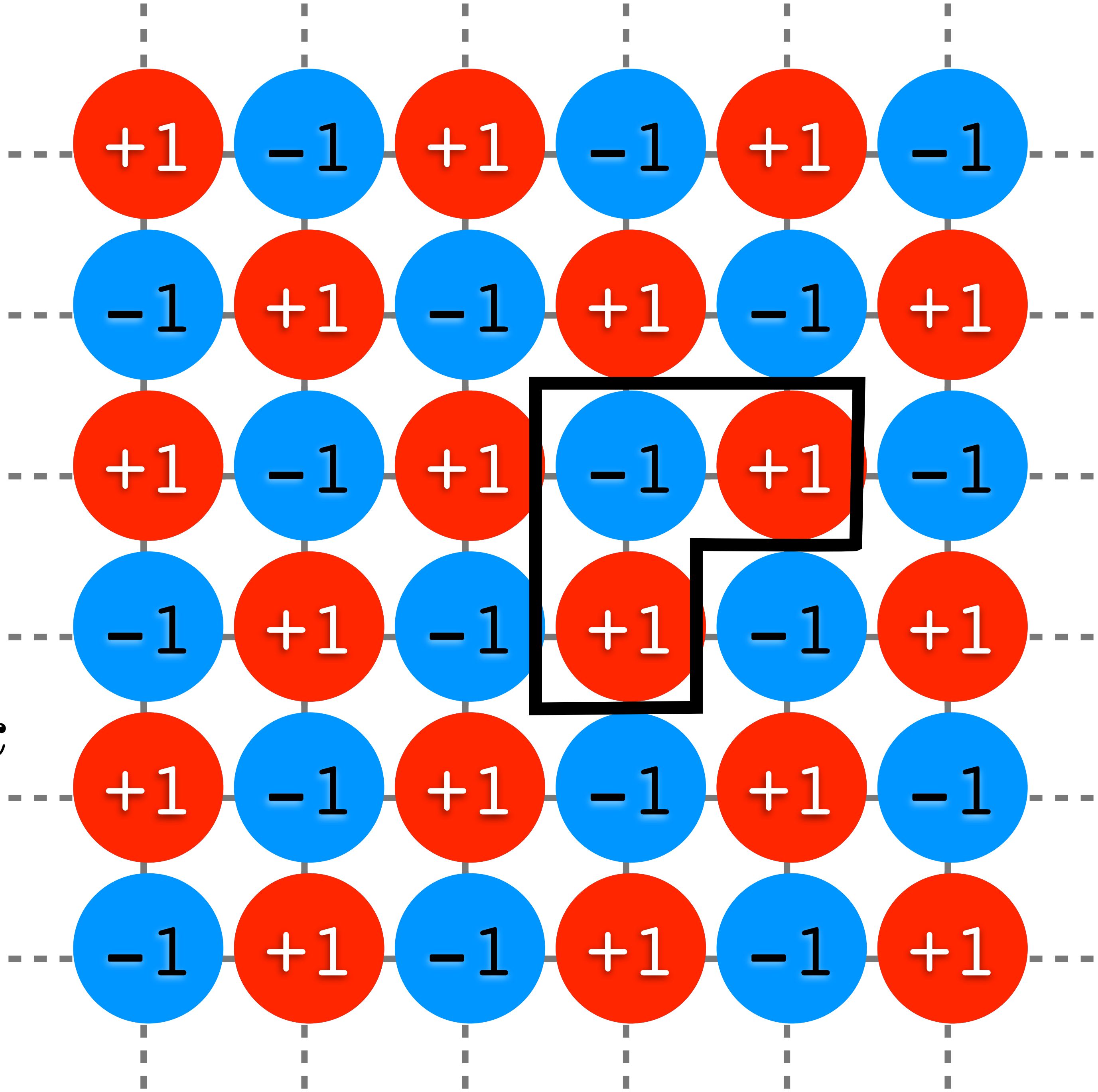

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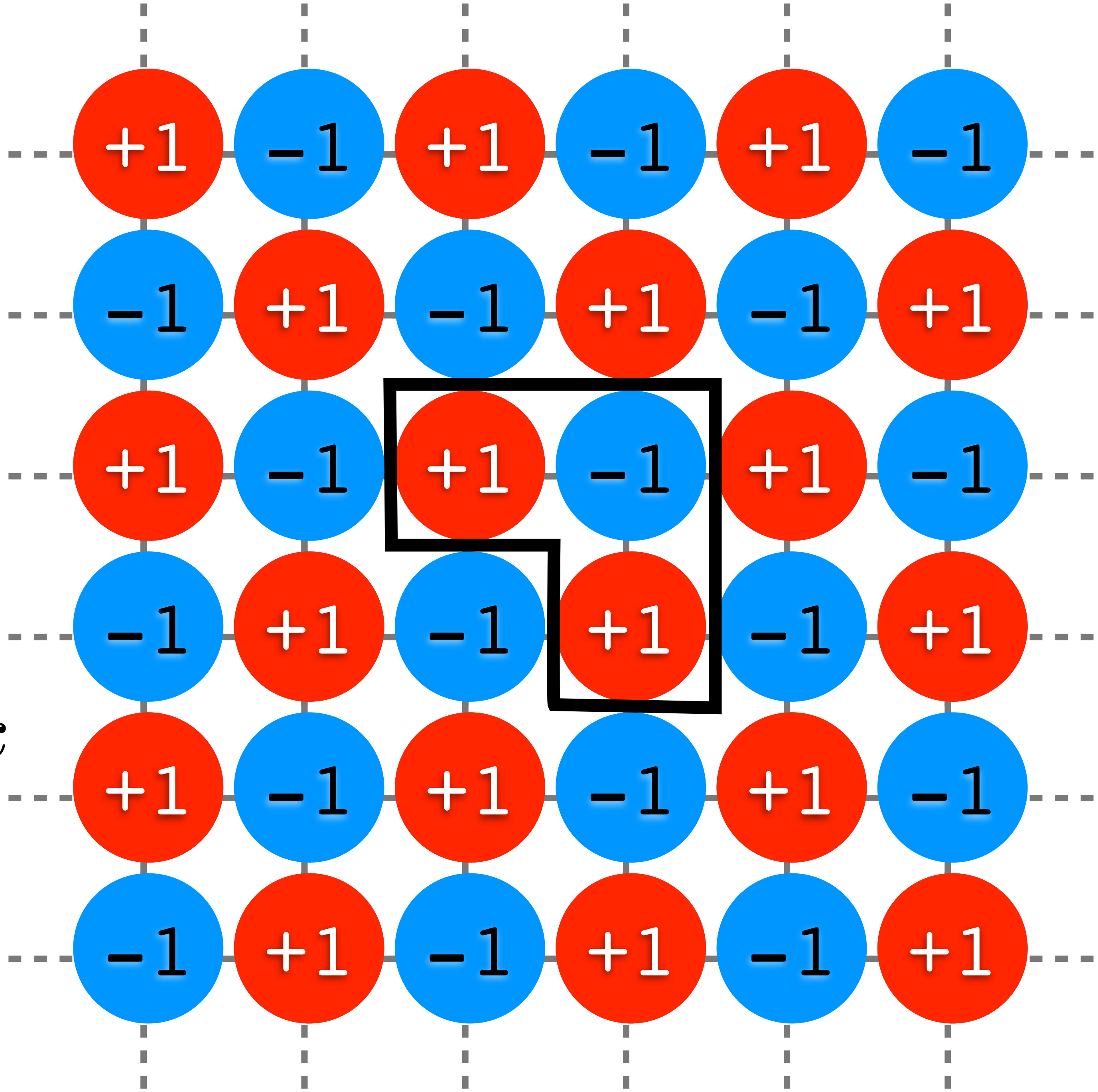
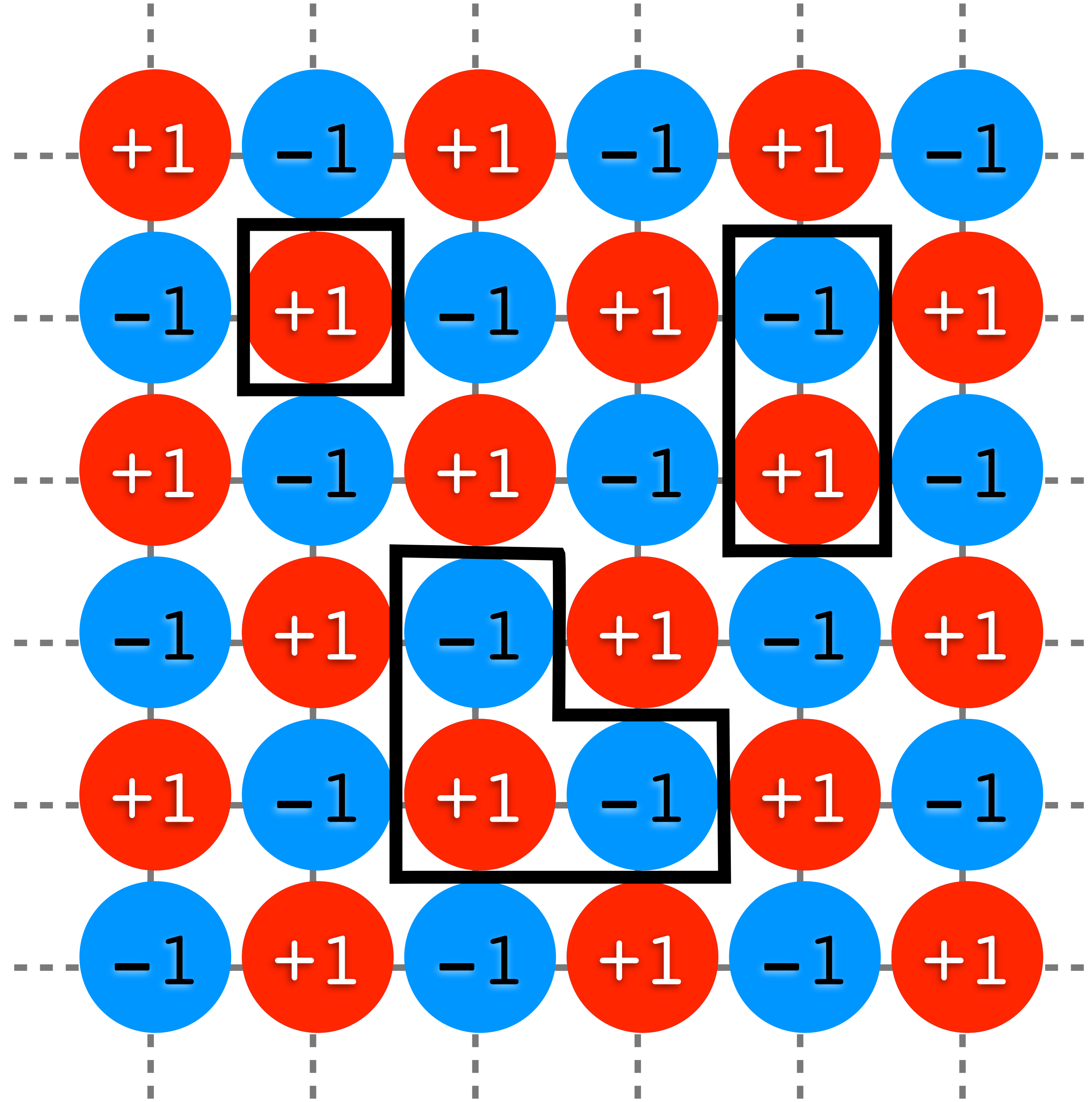
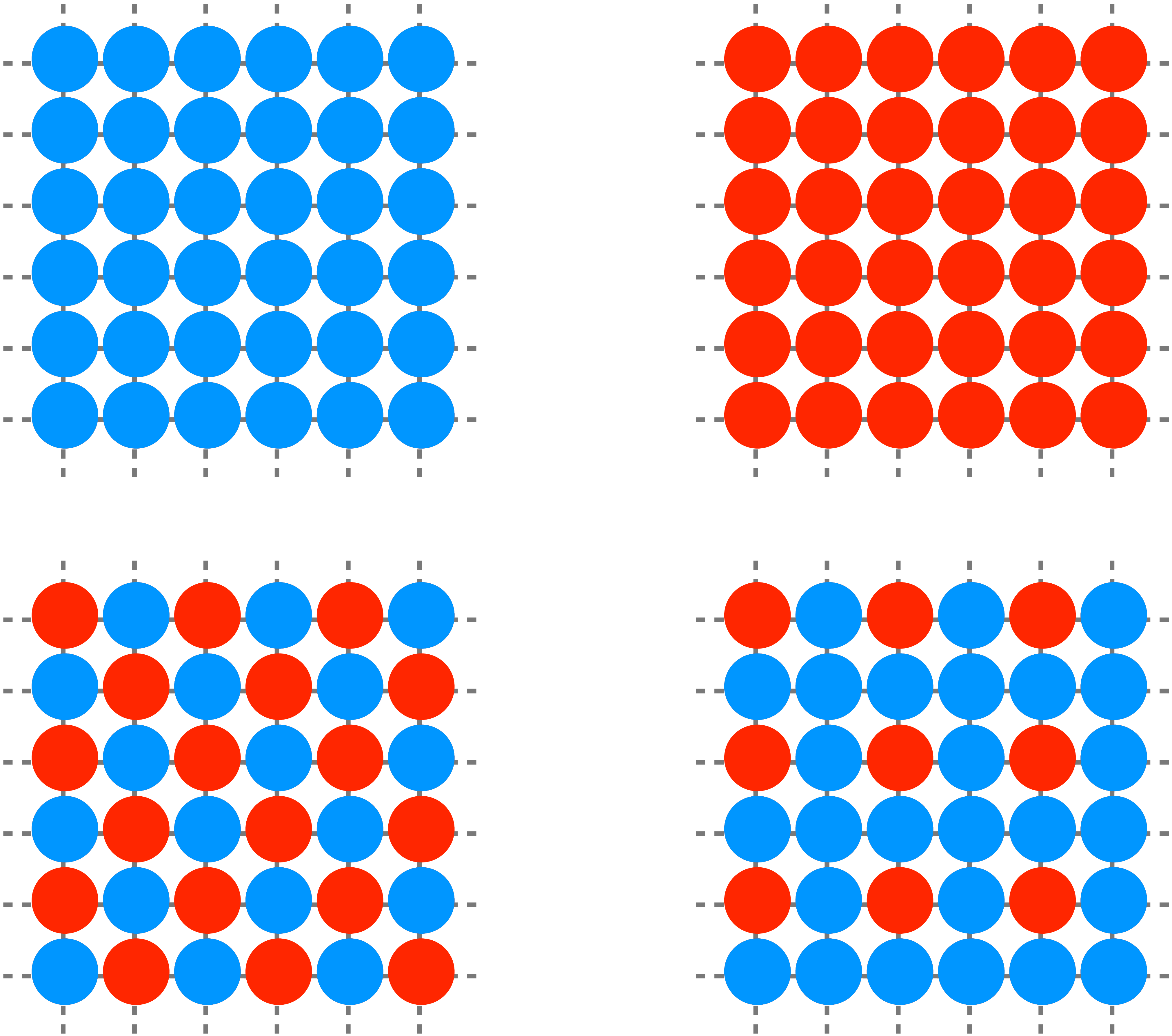
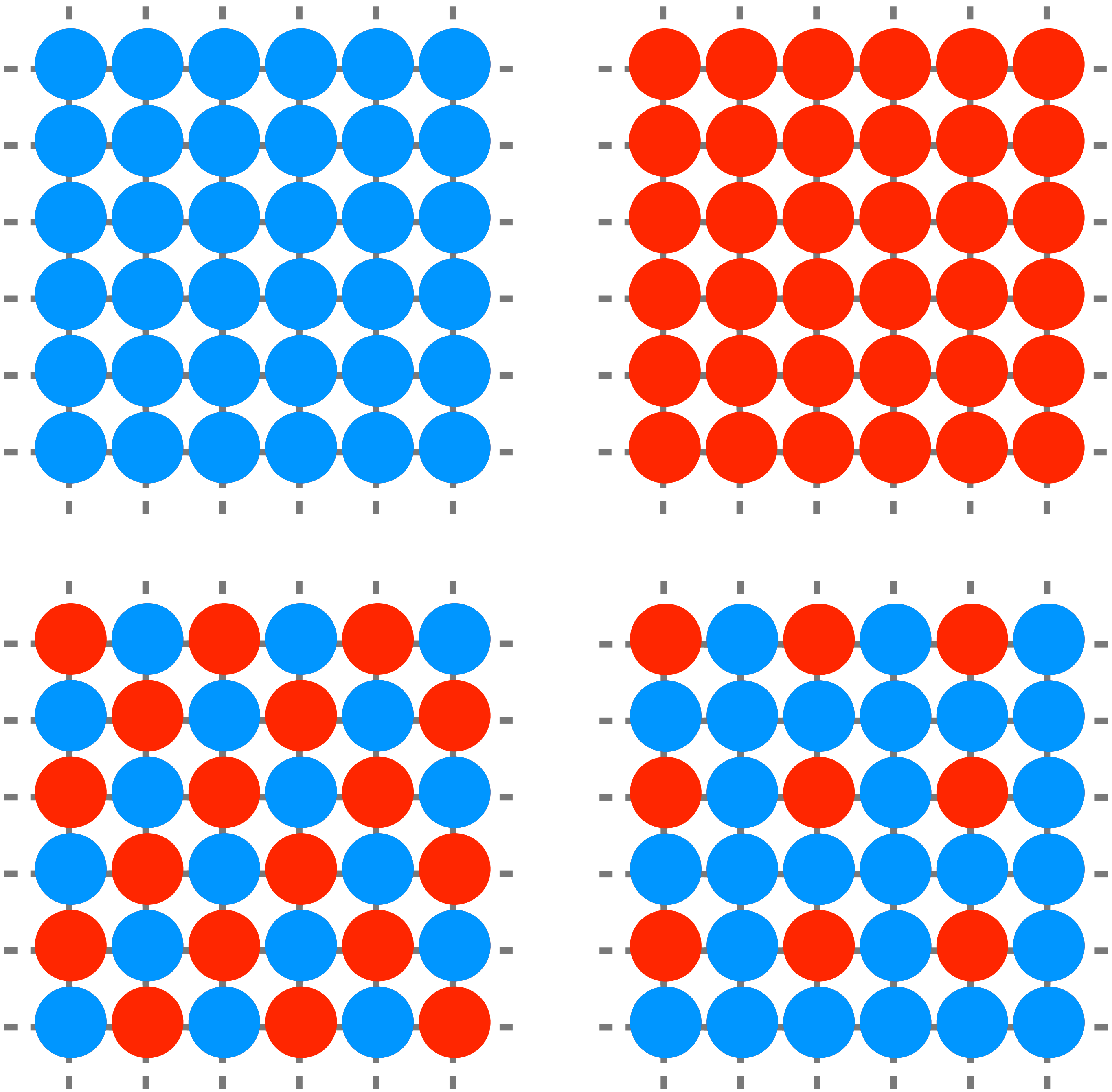


?



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





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

Problem 1 *(20 min.)*

$$E(\boldsymbol{\sigma}) = E^{\mathrm{CE}}(\boldsymbol{\sigma}) = \sum_f J_f \Pi_f(\boldsymbol{\sigma})$$

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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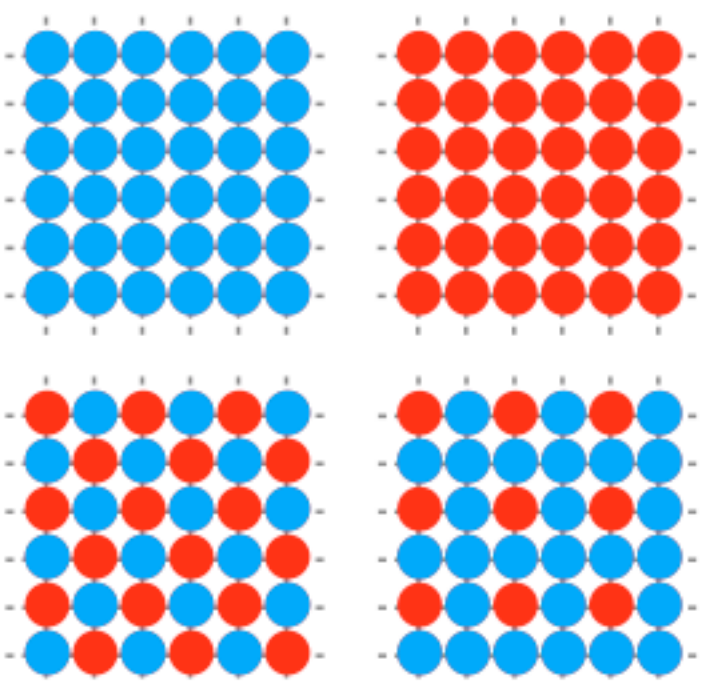
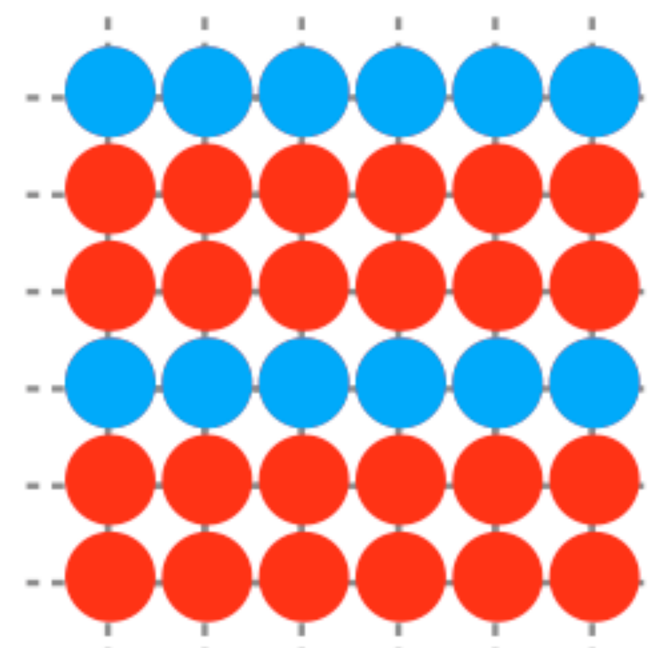


$$\begin{pmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ 1 & 0 & -1 & 0 \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

→ 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

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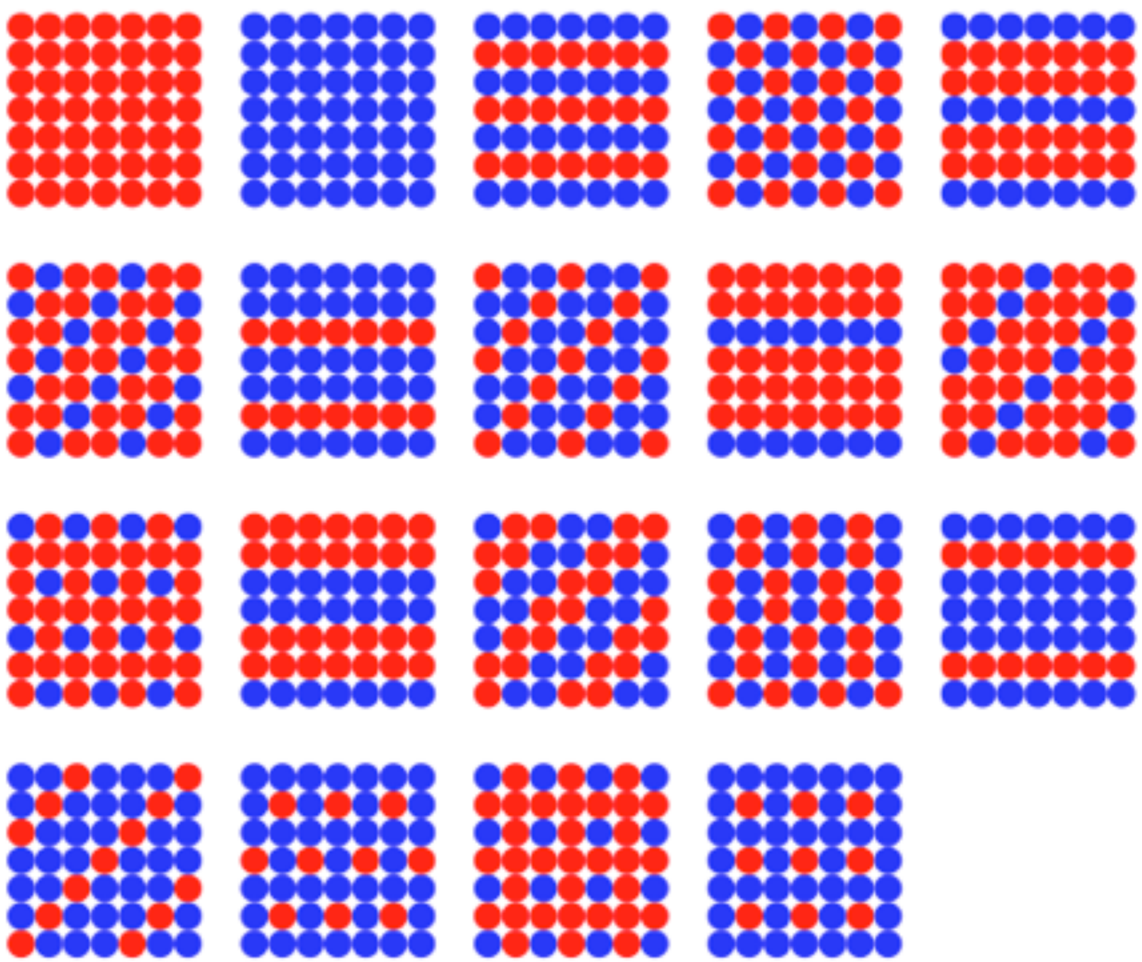

Problem II *(20 min.)*

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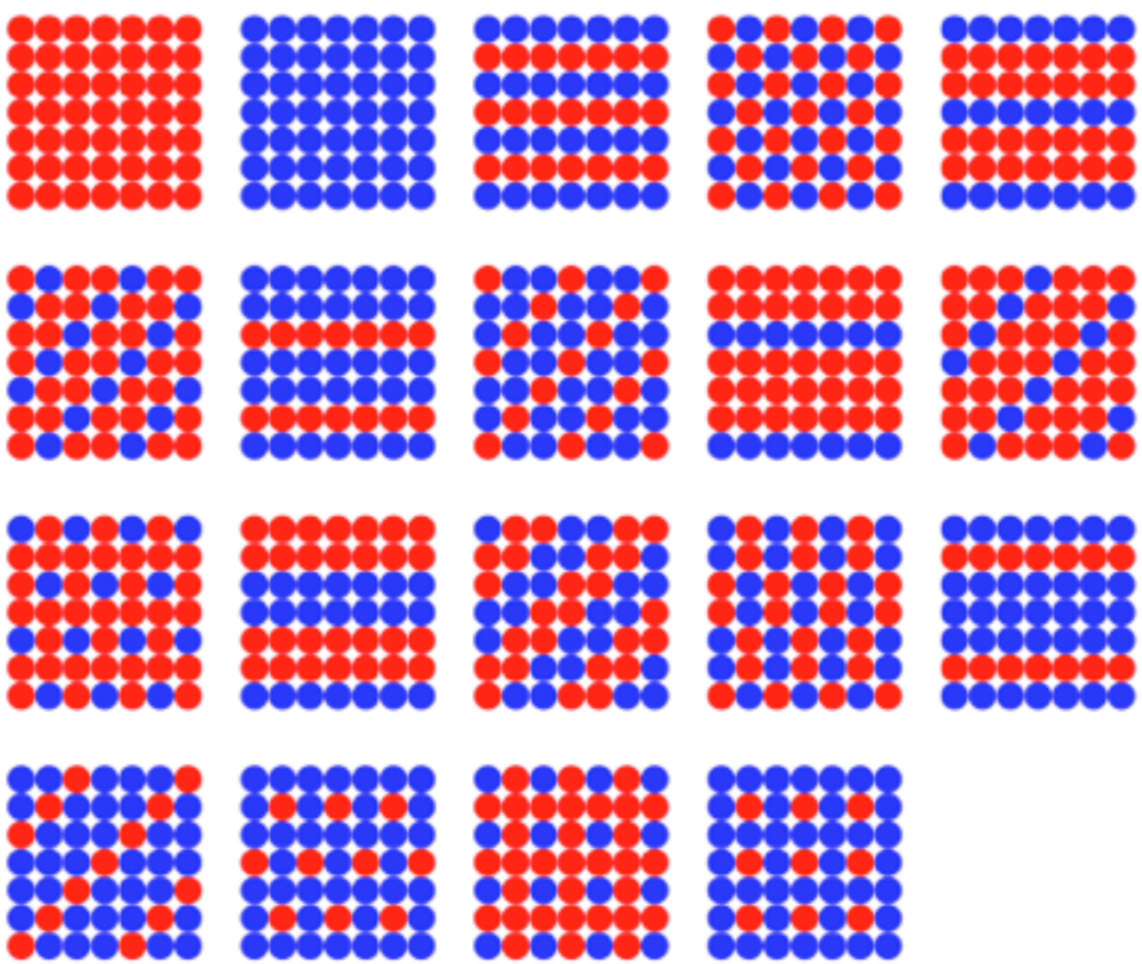

Matrix of $\overline{\Pi}$'s

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.)*

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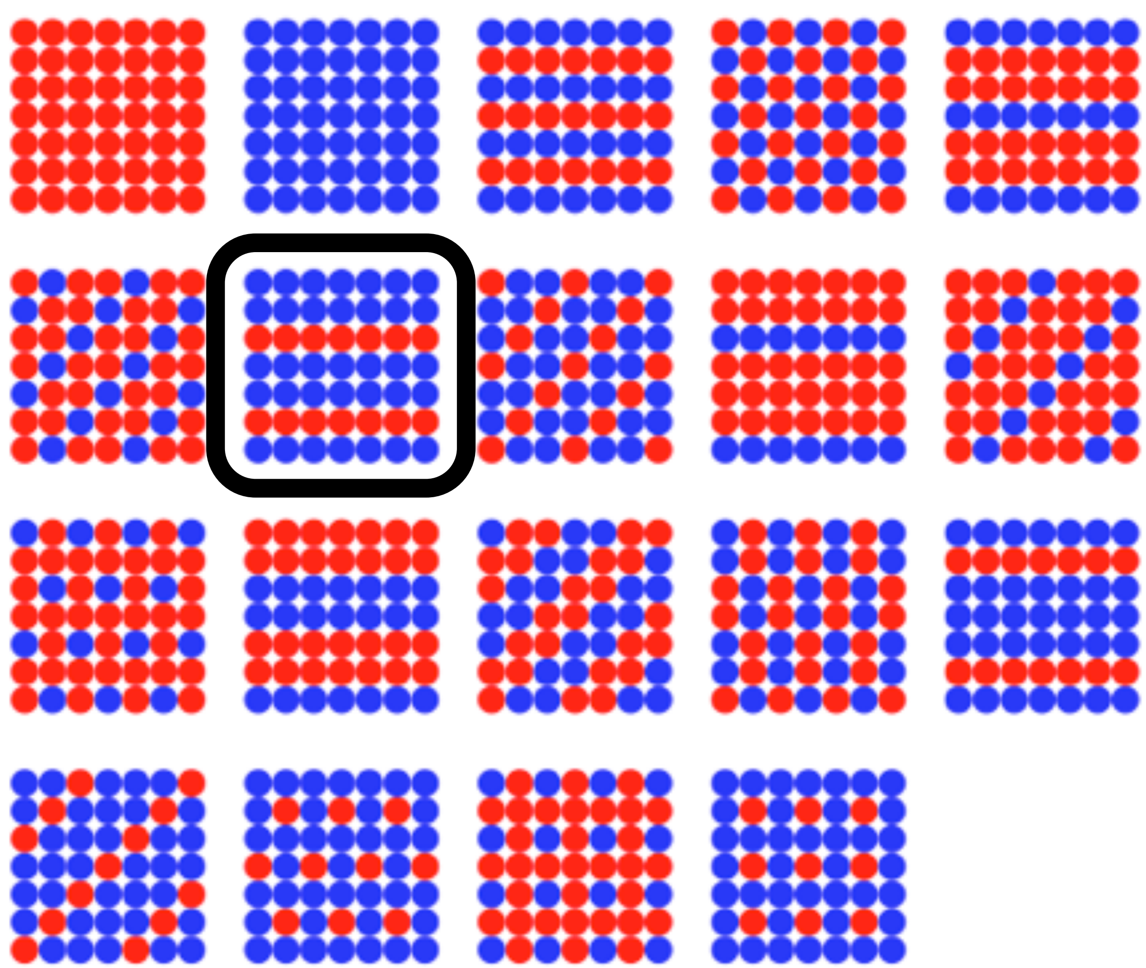

Matrix of $\overline{\Pi}$'s

1.000000	1.000000	1.000000	1.000000
1.000000	0.500000	0.500000	0.000000
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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
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Problem II *(20 min.)*

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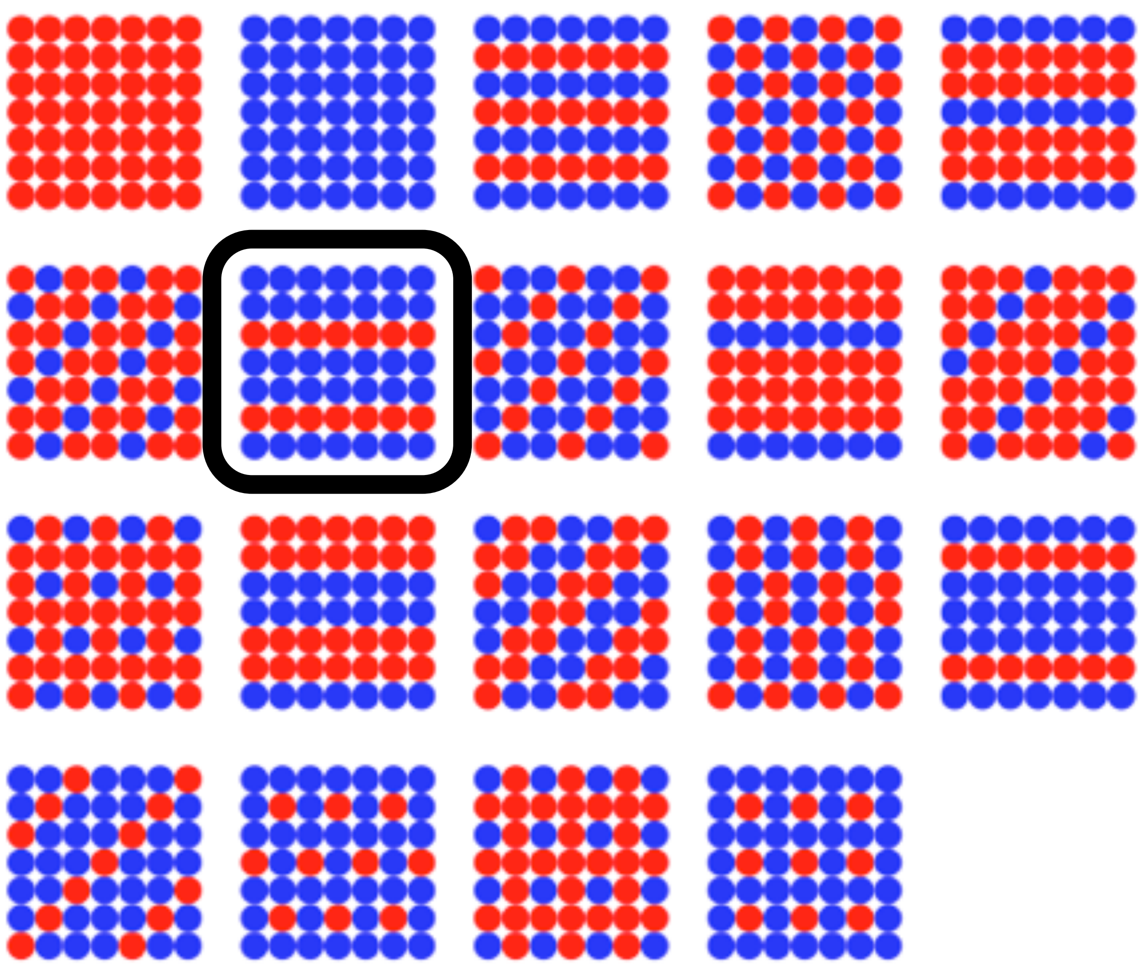

Matrix of $\overline{\Pi}$'s

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1.000000	0.333333	-0.333333	0.333333
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1.000000	-0.333333	-0.333333	0.333333
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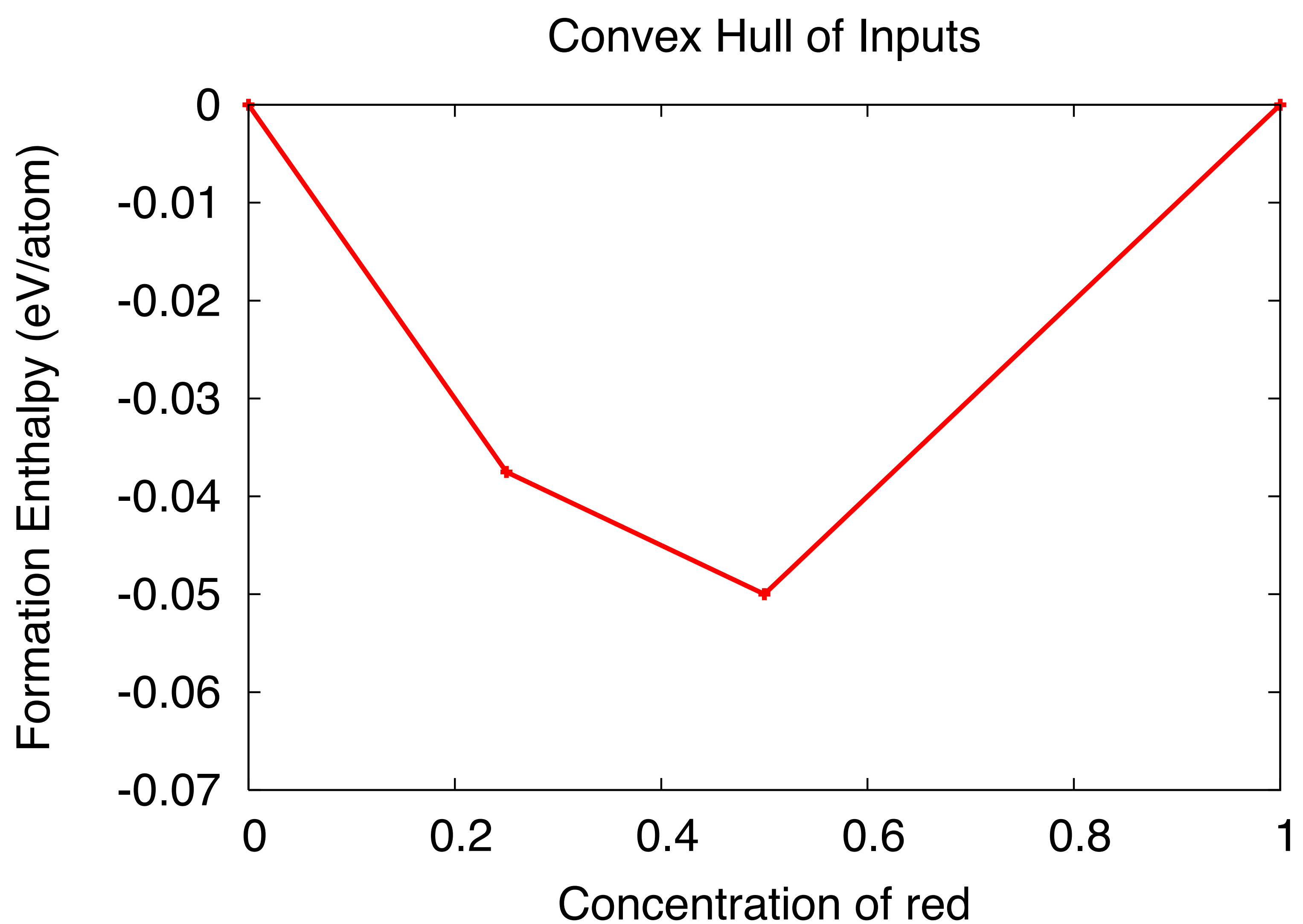
1.000000	-1.000000	1.000000	1.000000

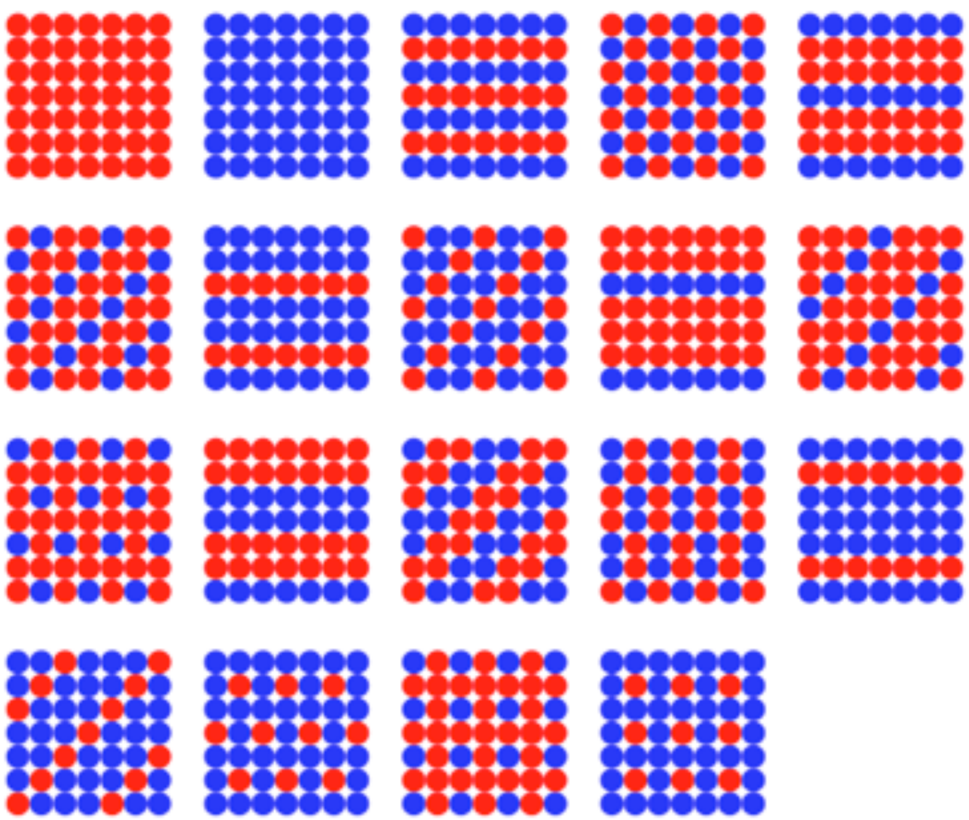
$$E = \overline{\vec{\Pi}} \cdot \vec{J}$$

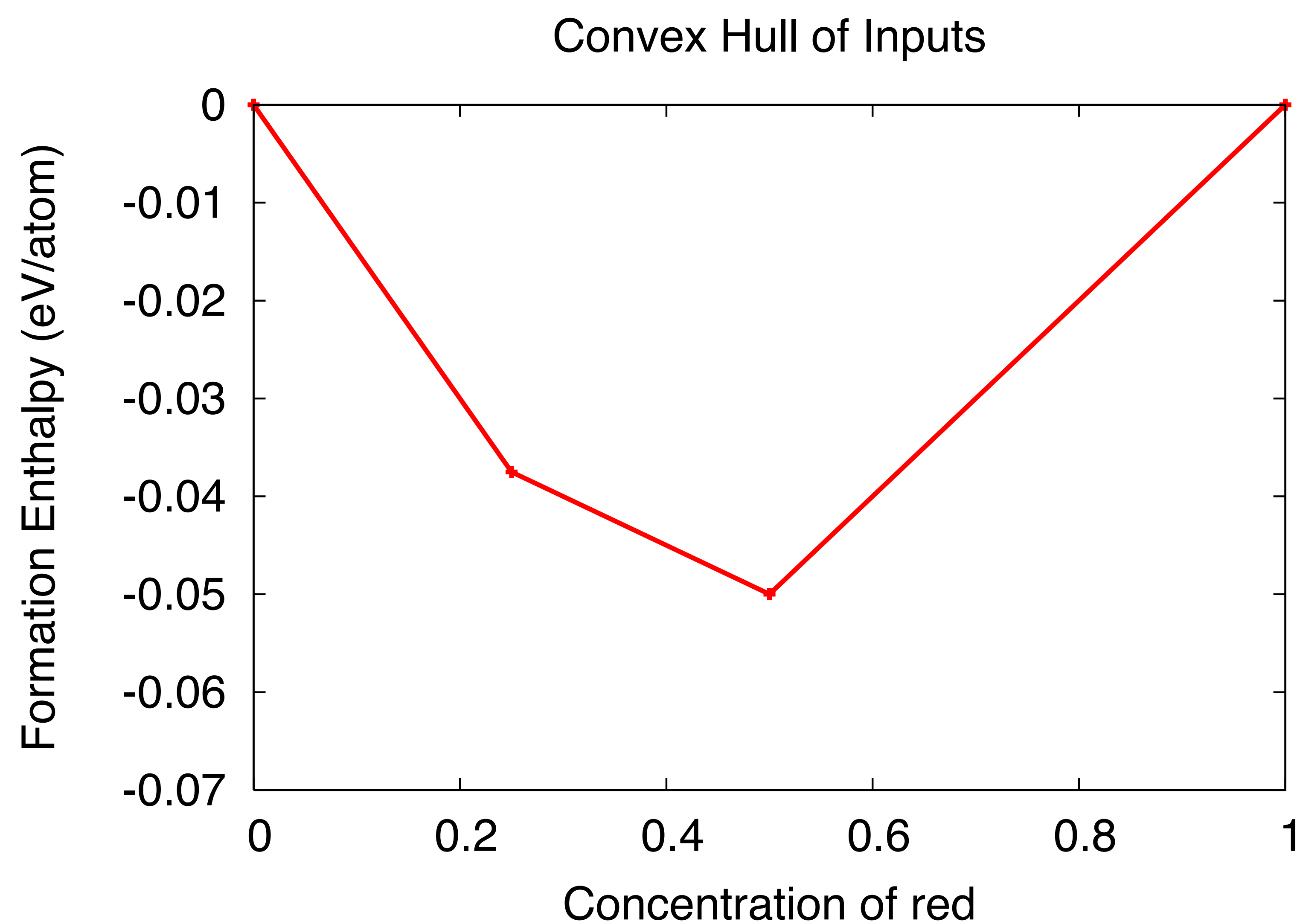
Problem II *(20 min.)*



Constructing the **convex hull** from the predictions

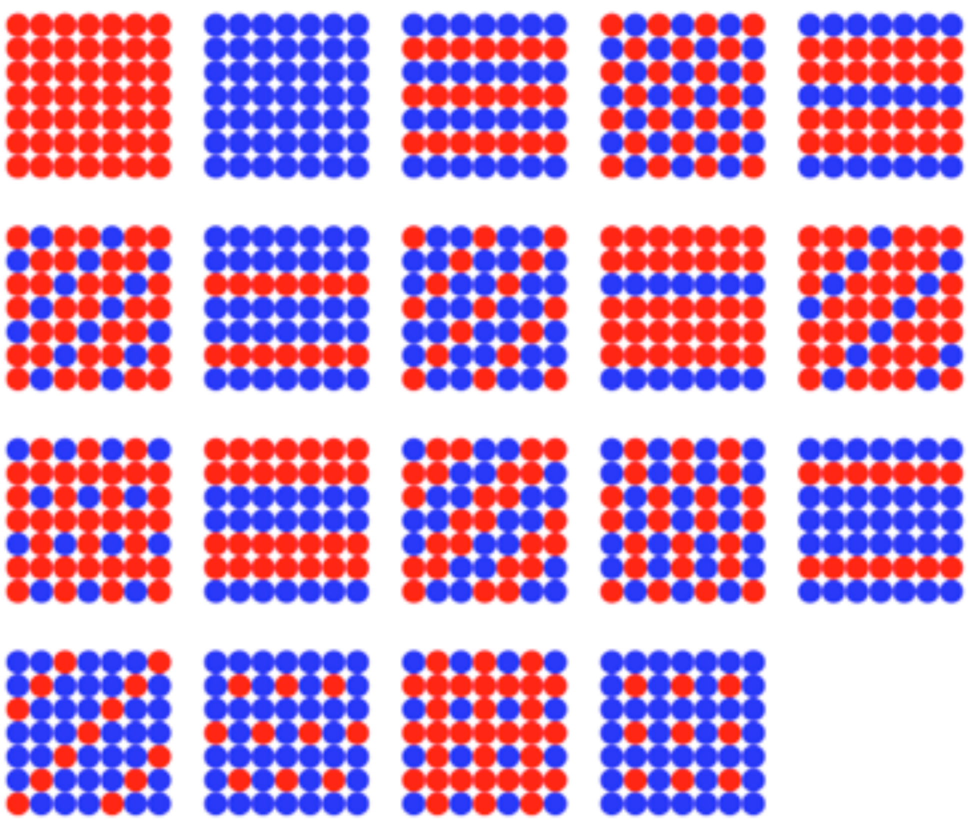
Problem II *(20 min.)*

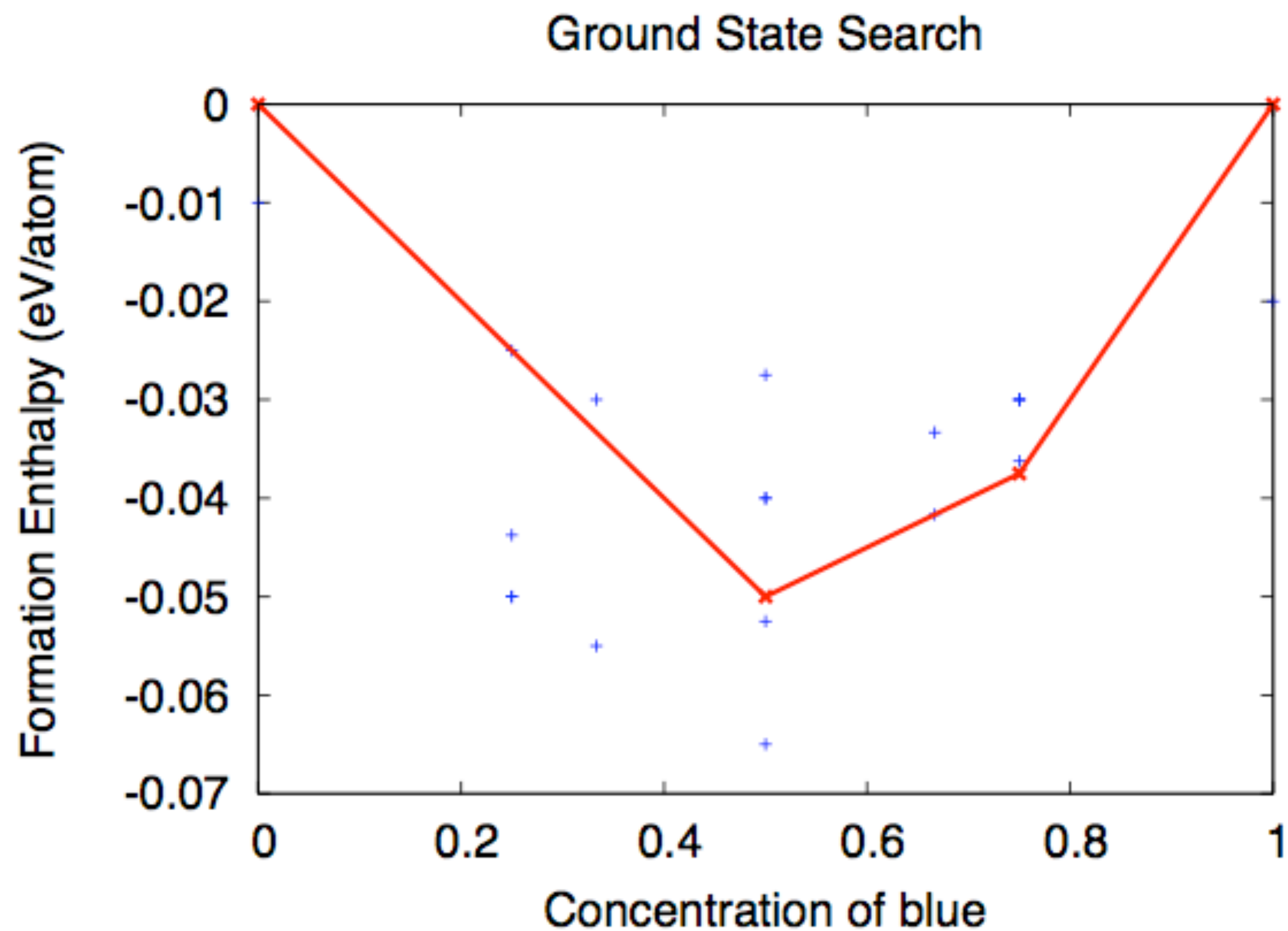




Constructing the **convex hull** from the predictions

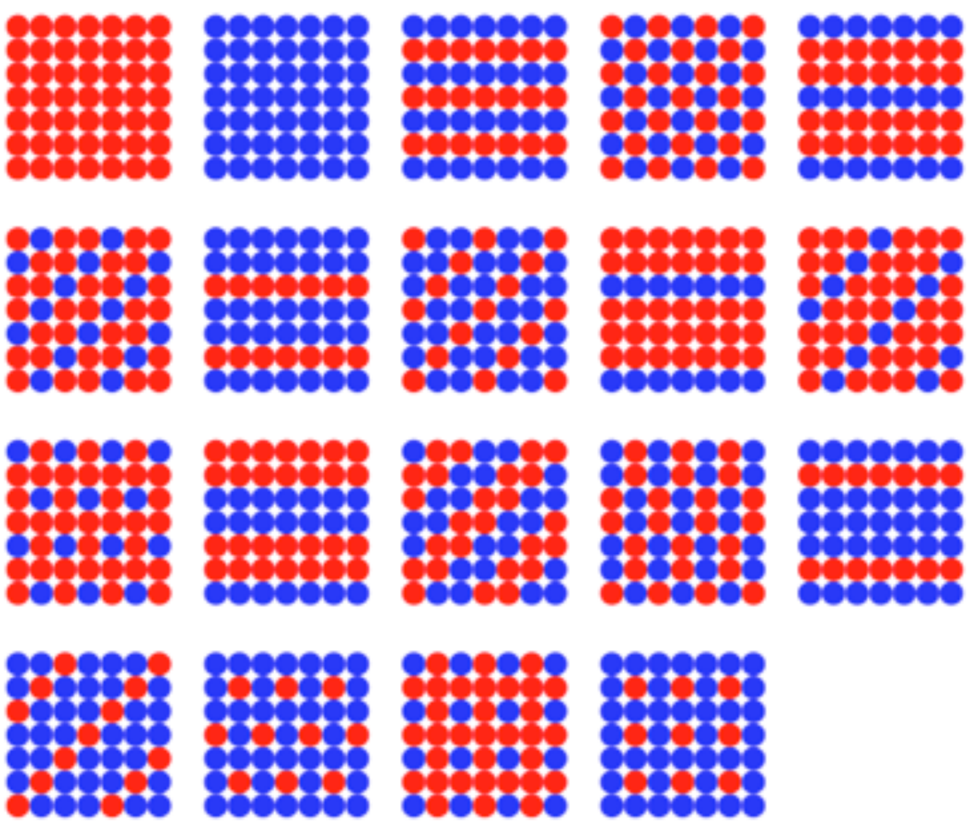
Problem II *(20 min.)*

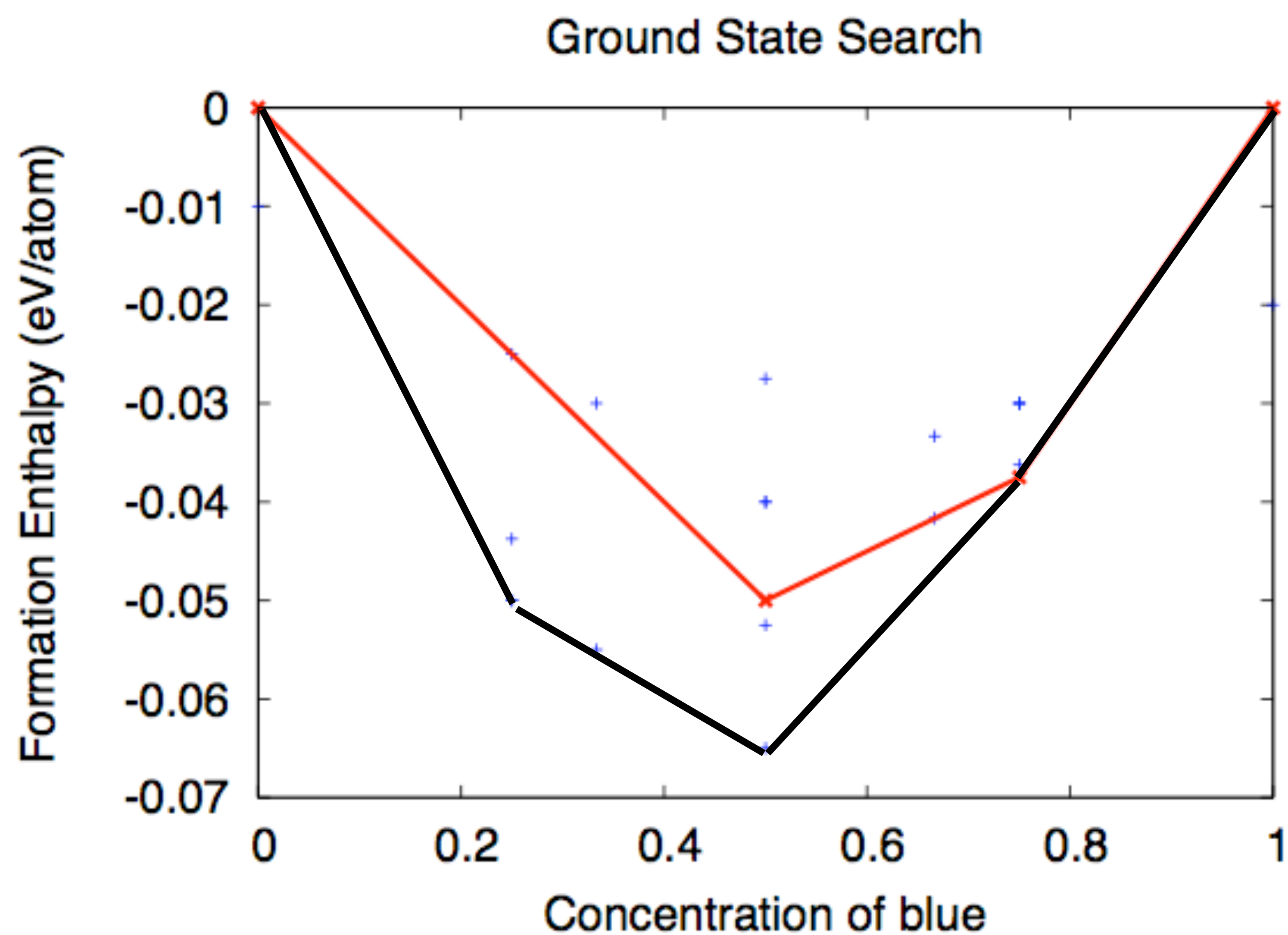




Constructing the **convex hull** from the predictions

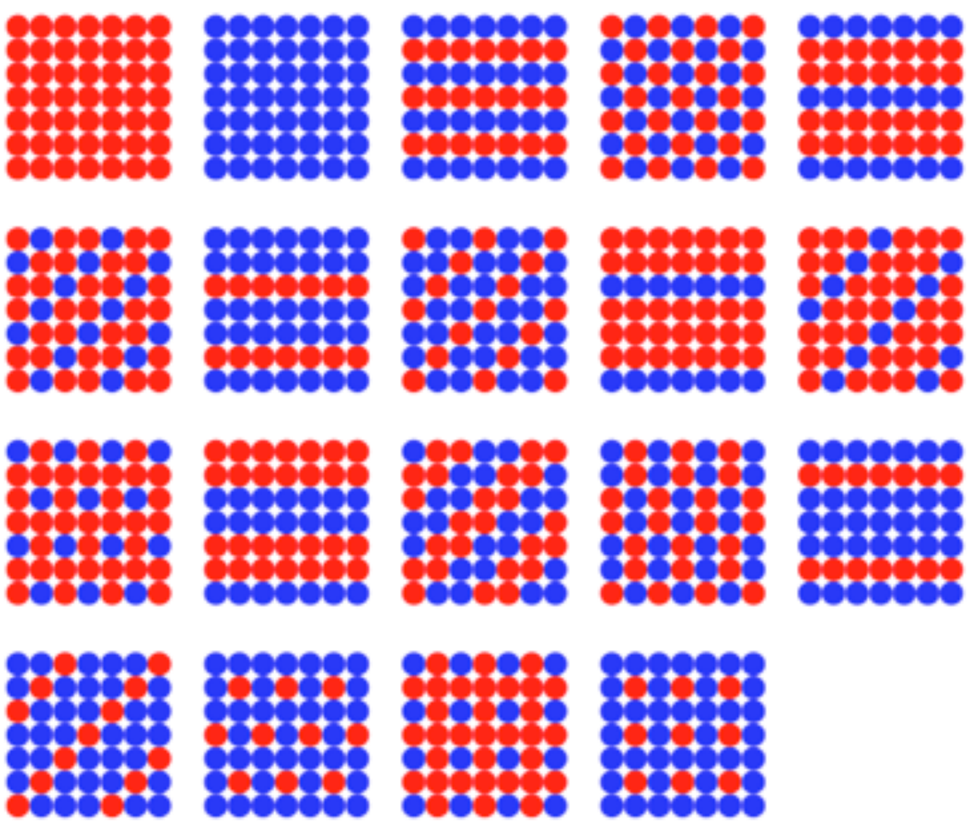
Problem II *(20 min.)*

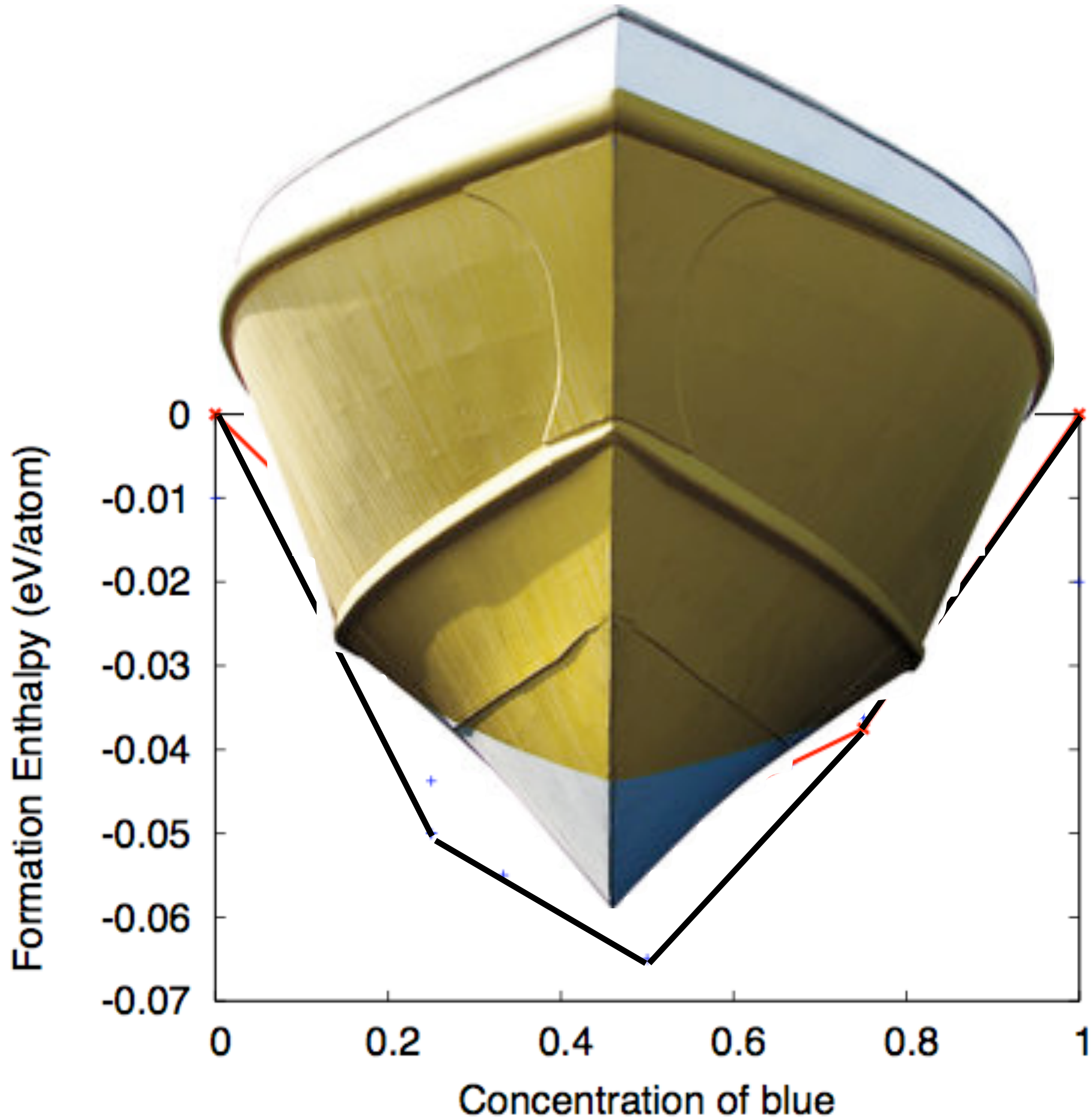




Constructing the **convex hull** from the predictions

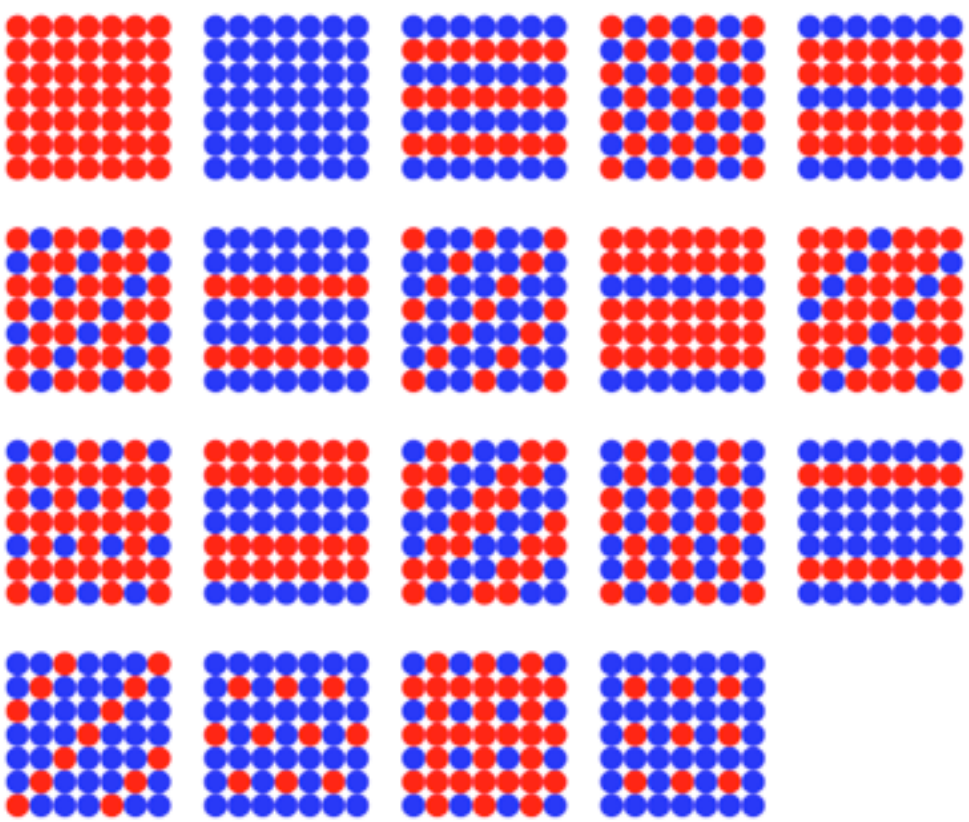
Problem II *(20 min.)*

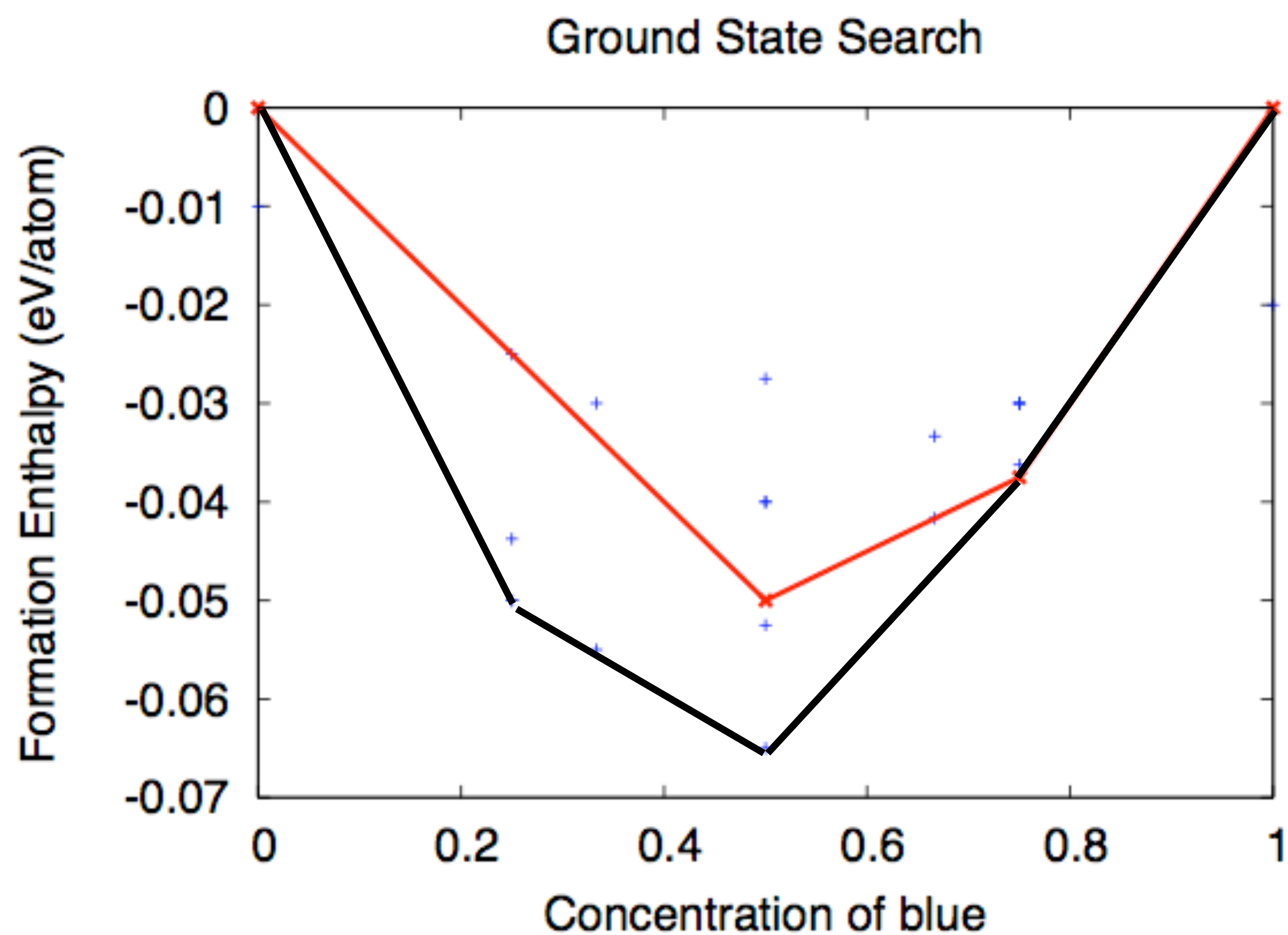




Constructing the **convex hull** from the predictions

Problem II *(20 min.)*





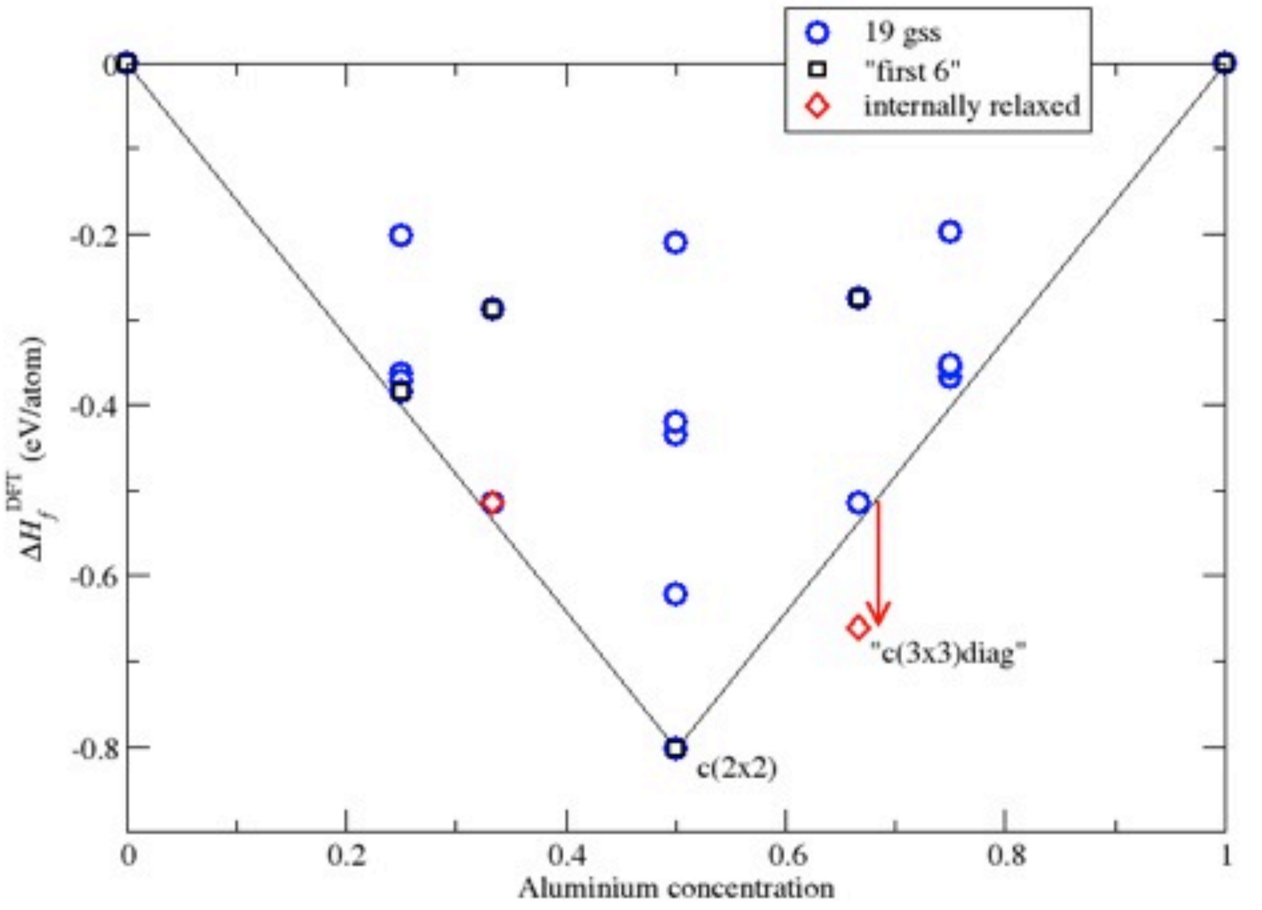
Constructing the **convex hull** from the predictions

Problem IV *(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.

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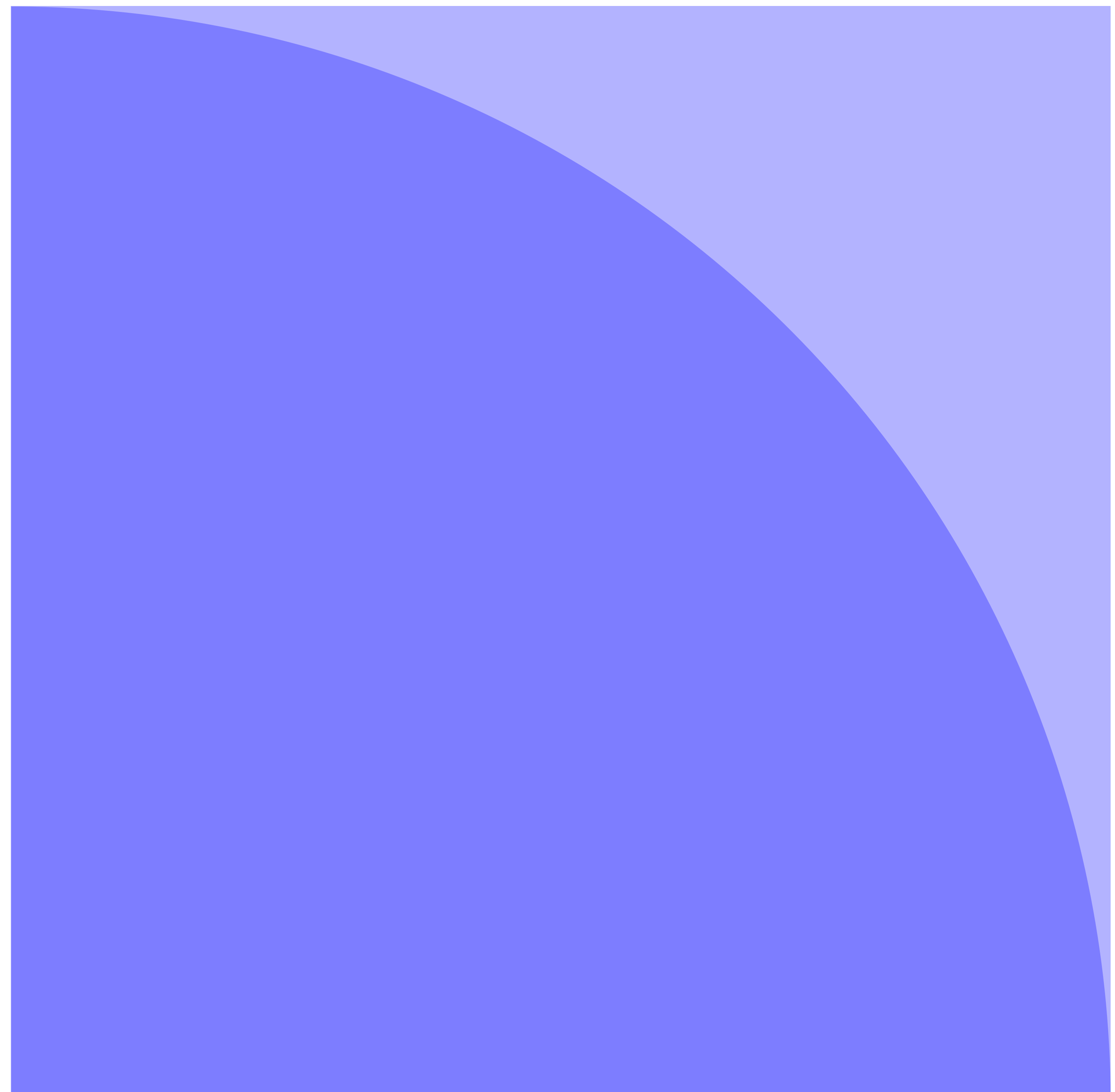
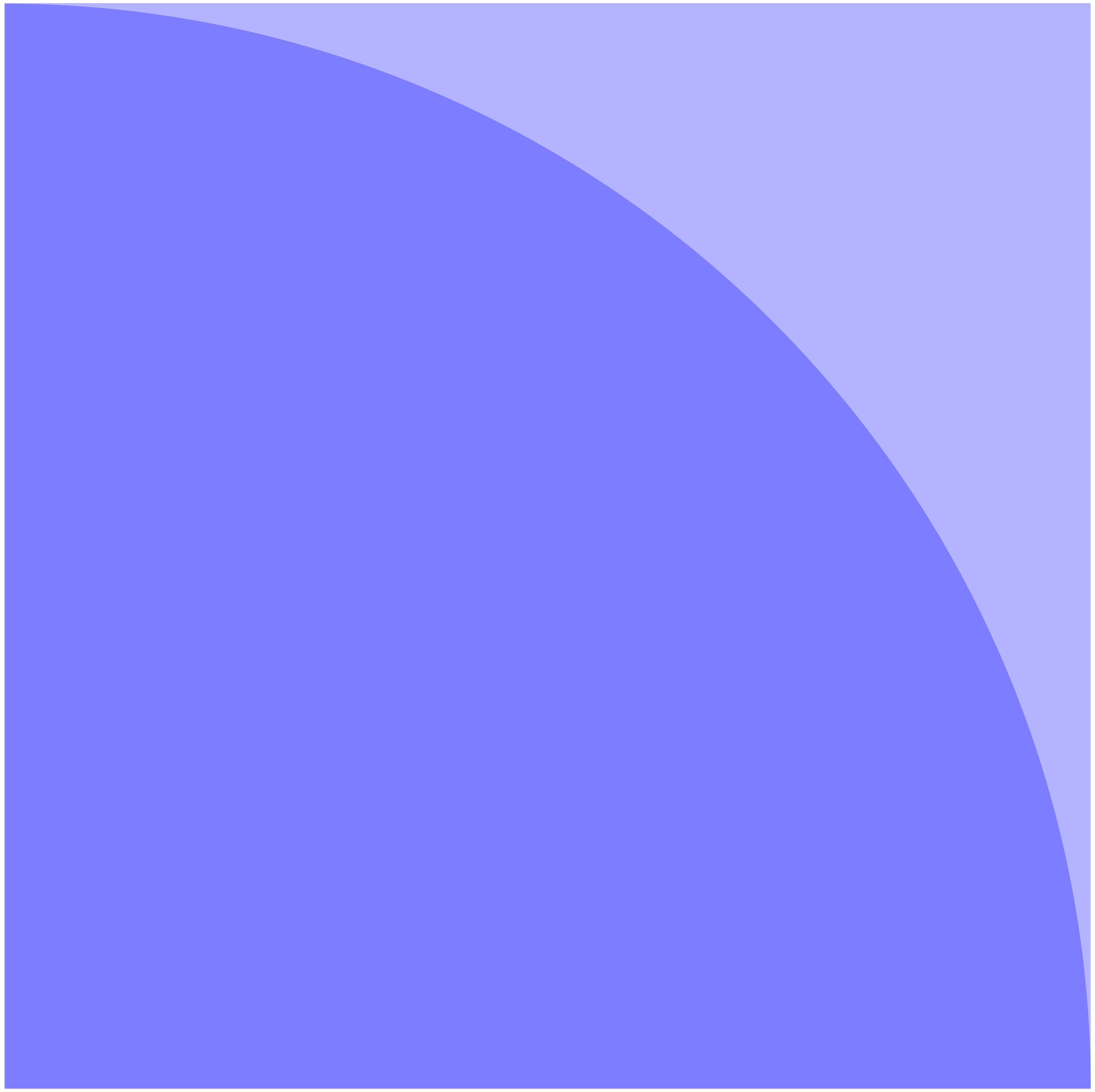
Find the thermodynamic equilibrium of a system as a function of temperature.

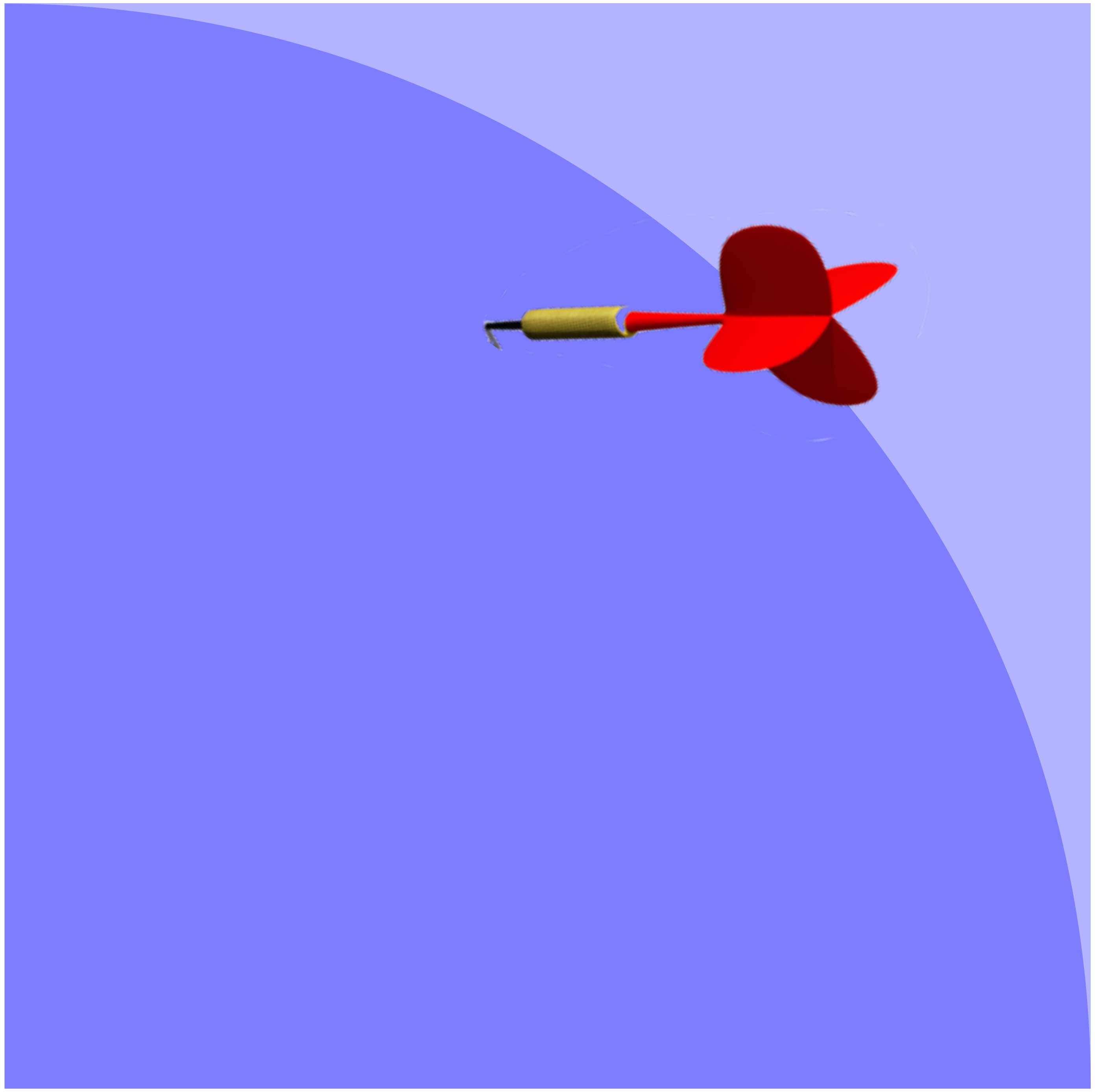
- Is a material magnetic at a given *T*?
- Is a material ordered (stronger) at a given *T*?



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



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



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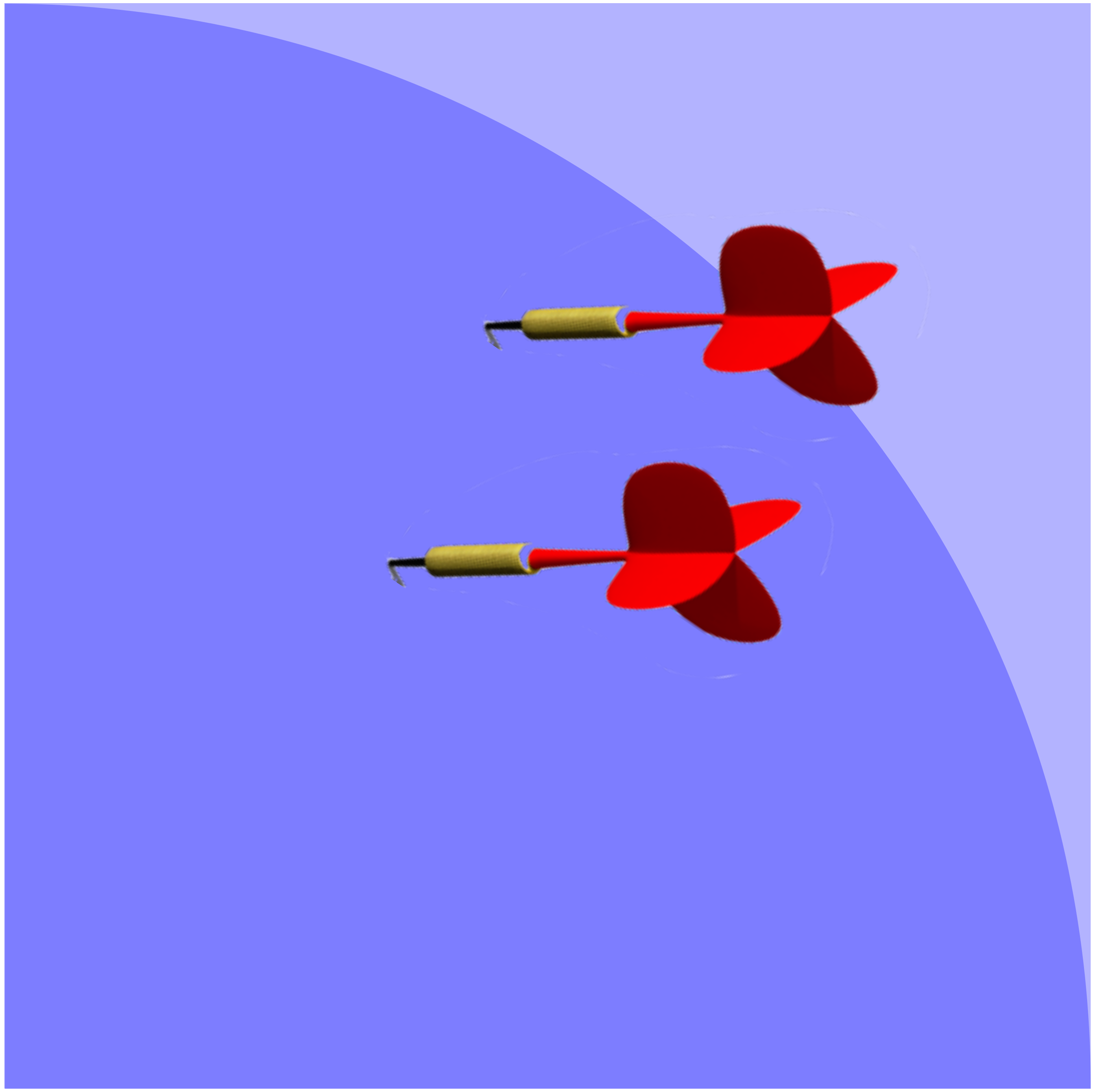
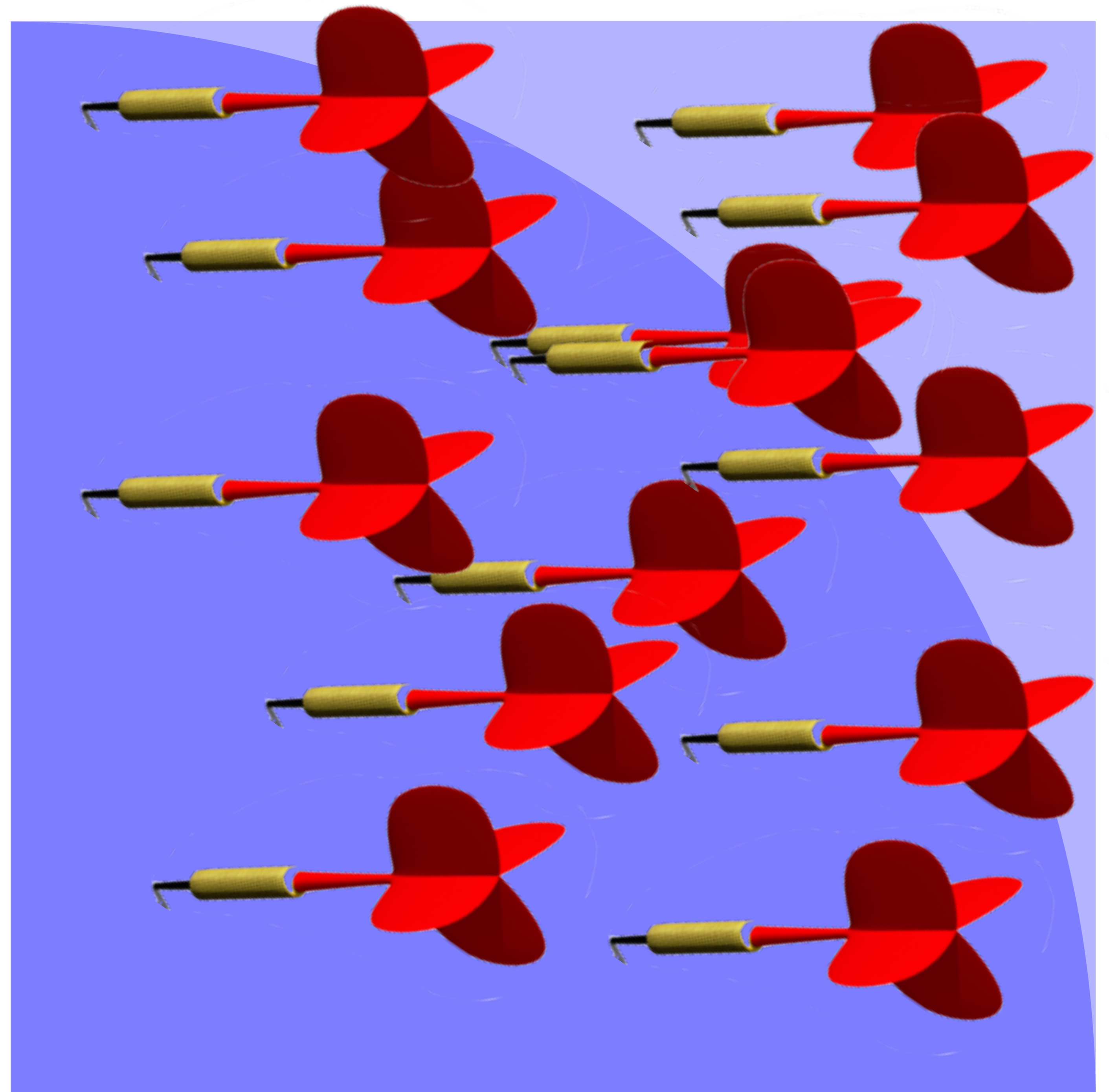
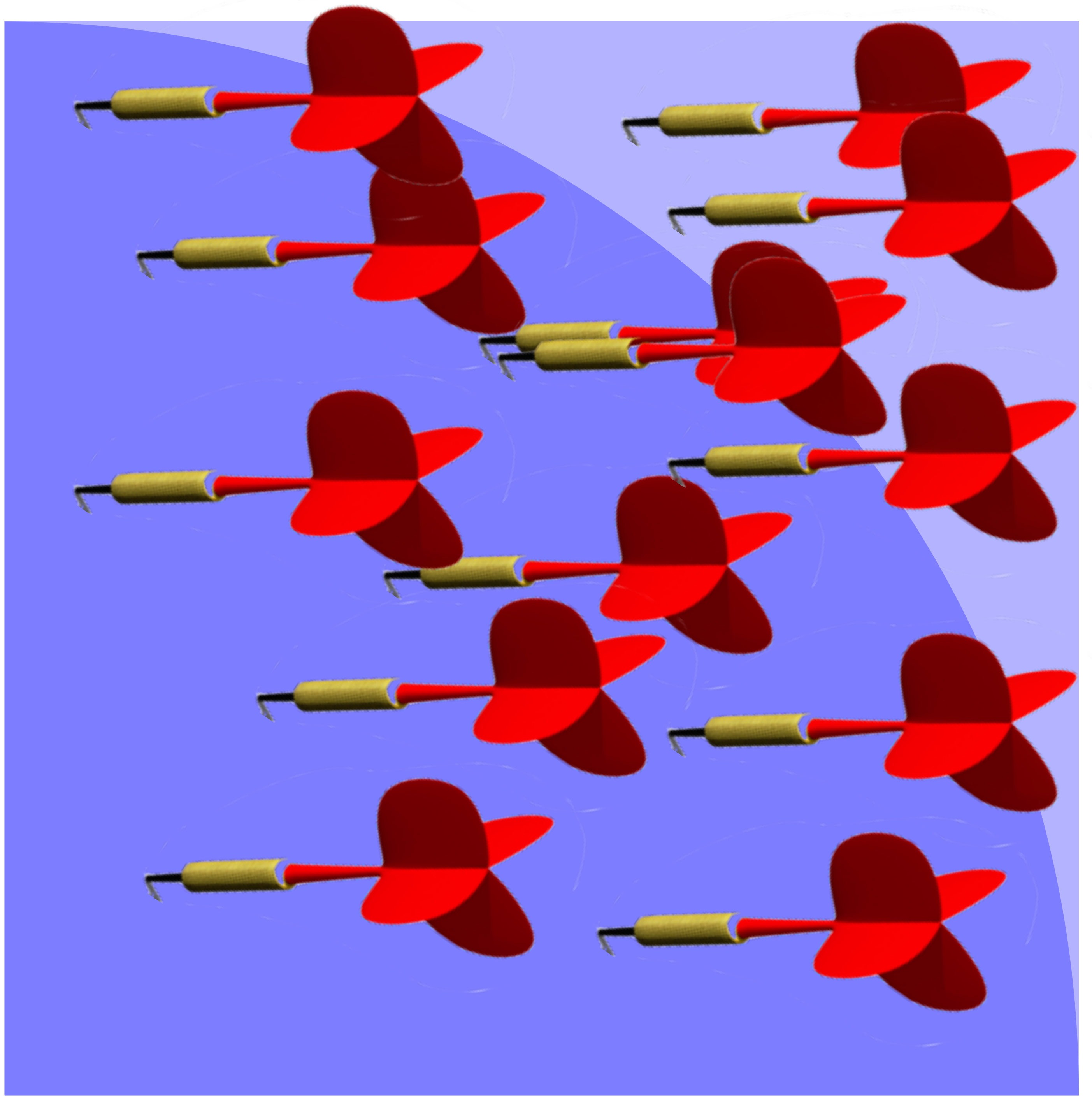


$$\frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$



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

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



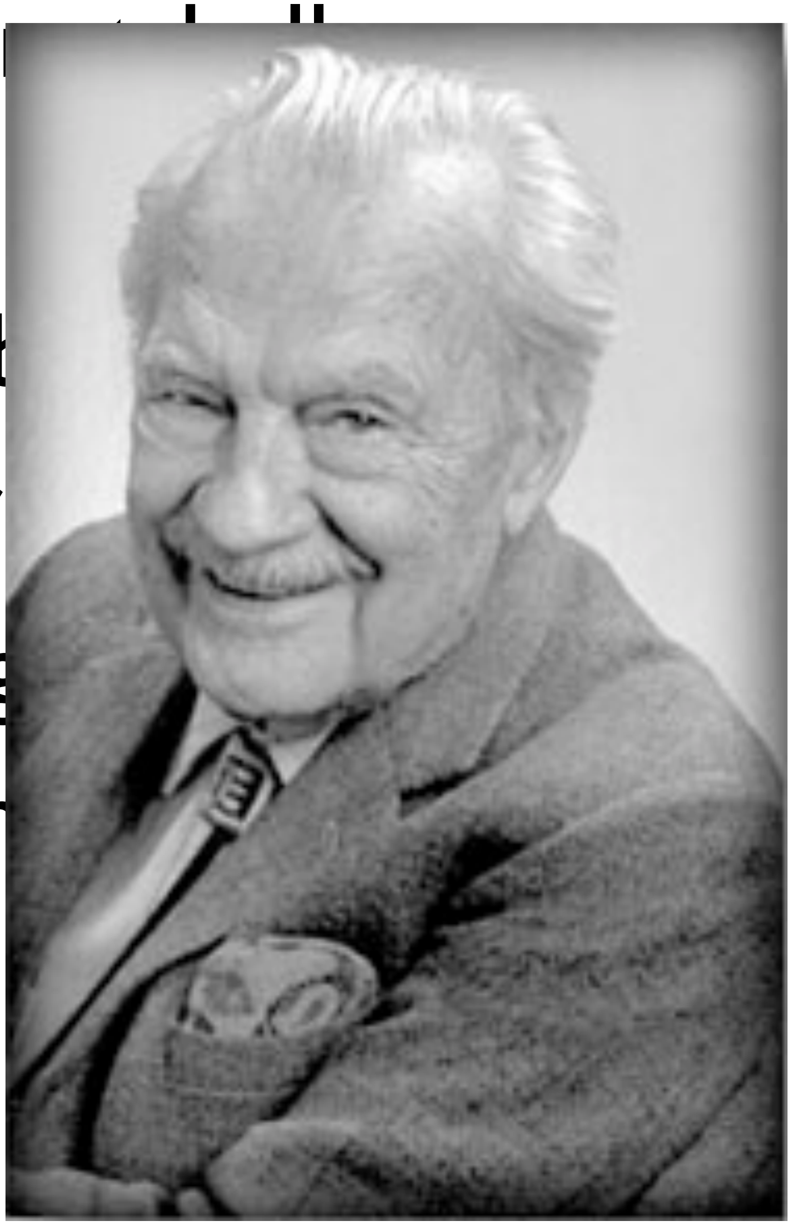
Monte Carlo modeling in a nutshell

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

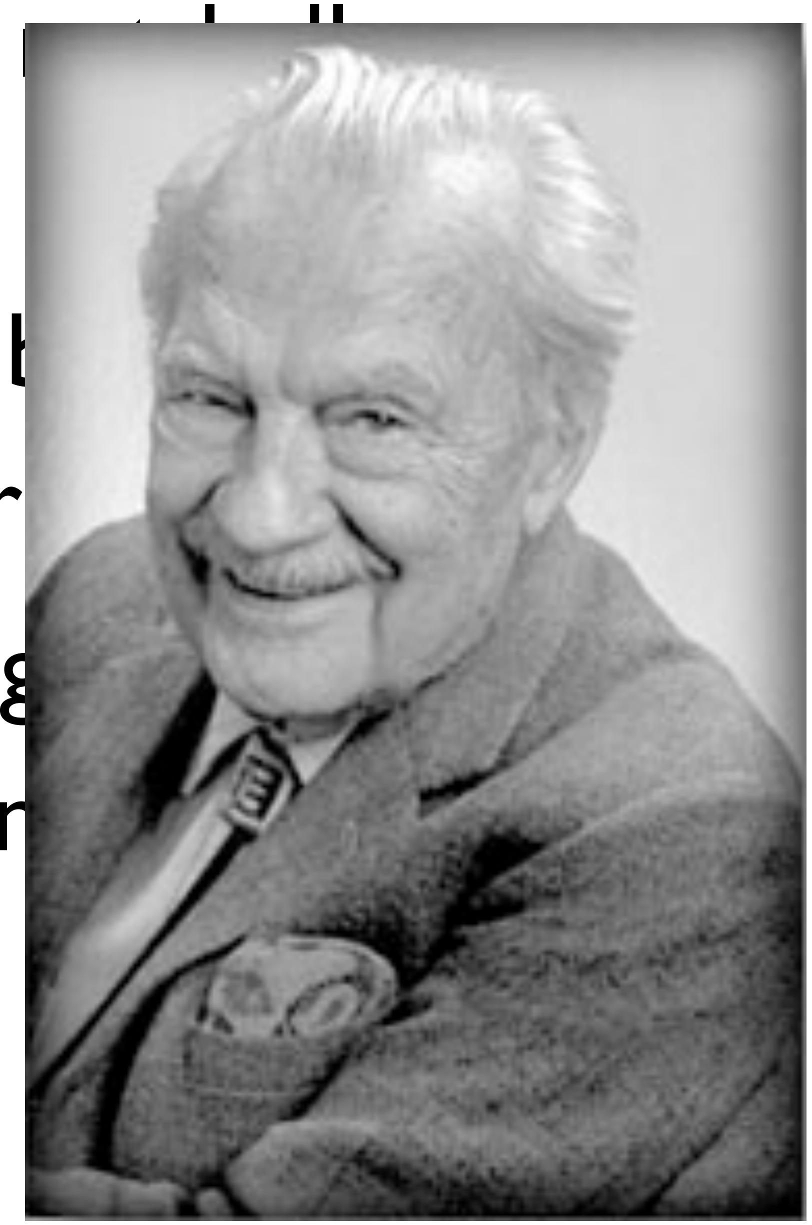


Find the thermodynamic equilib
system as a function of temper

- 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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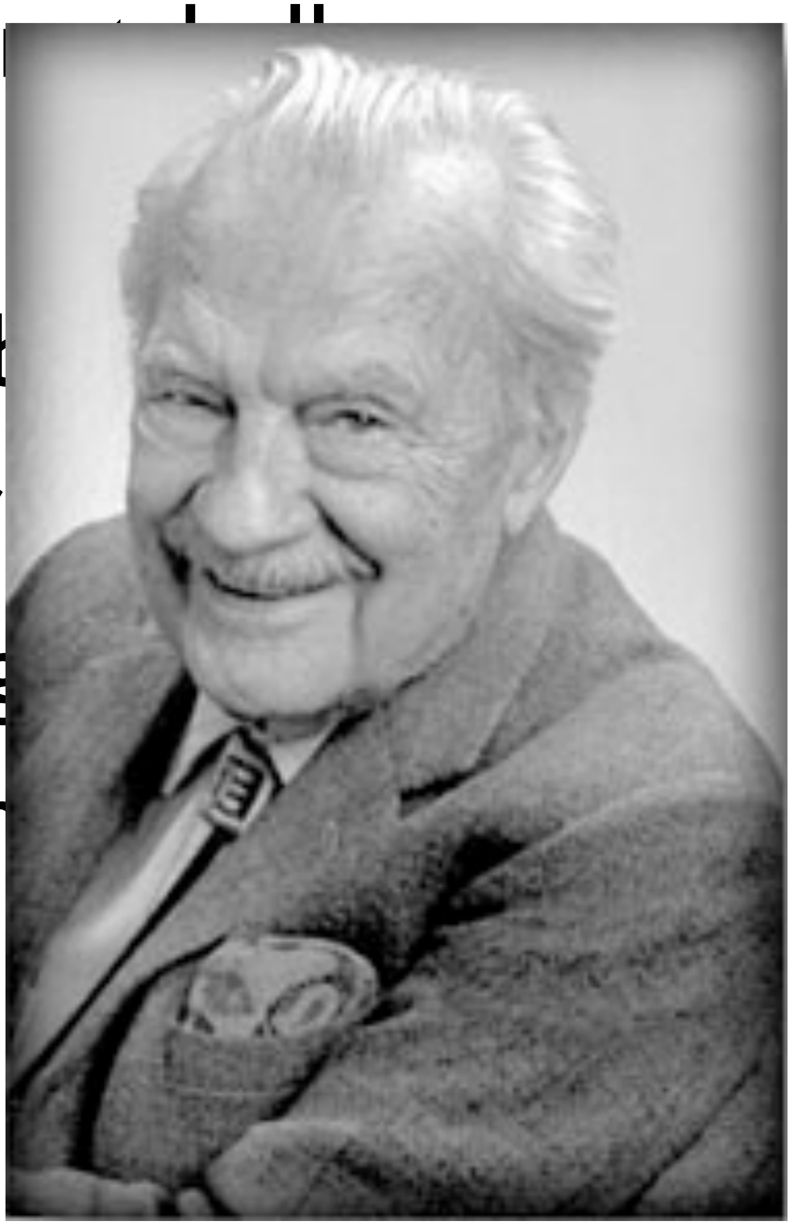
Metropolis algorithm:

- 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



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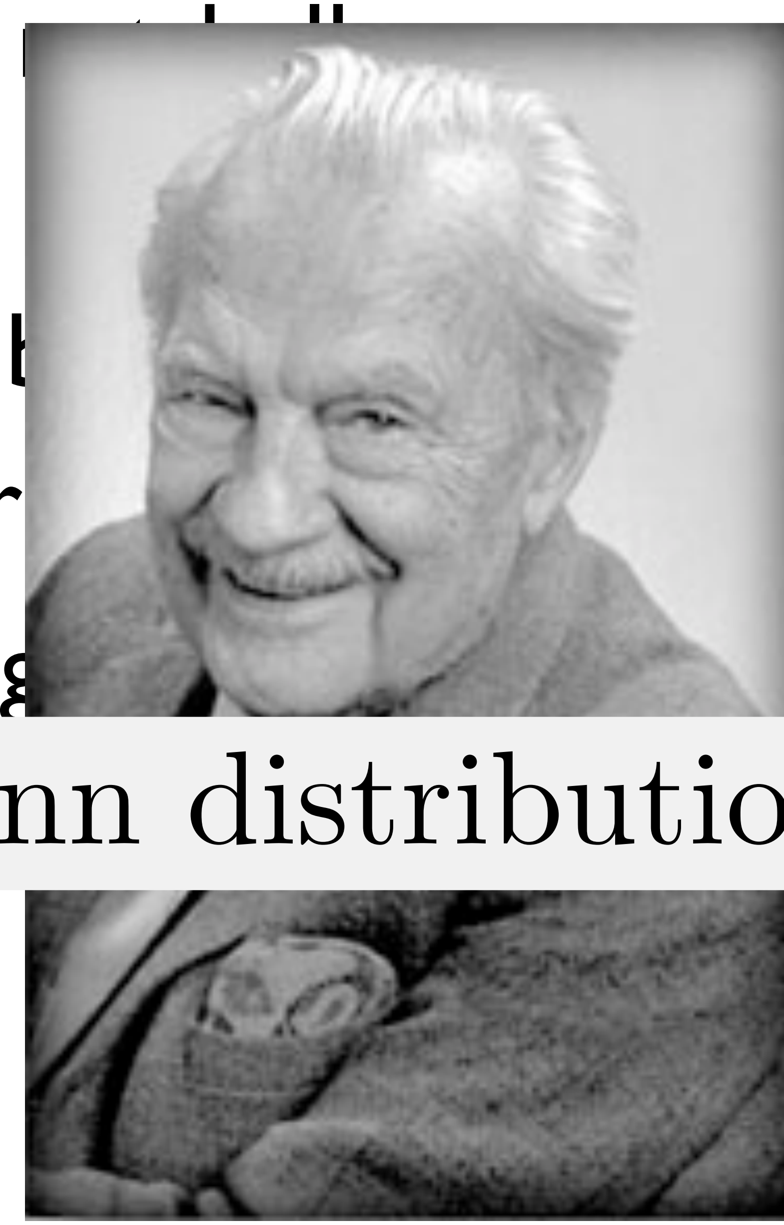

Collection of states: Boltzmann distribution

Metropolis algorithm:

At random

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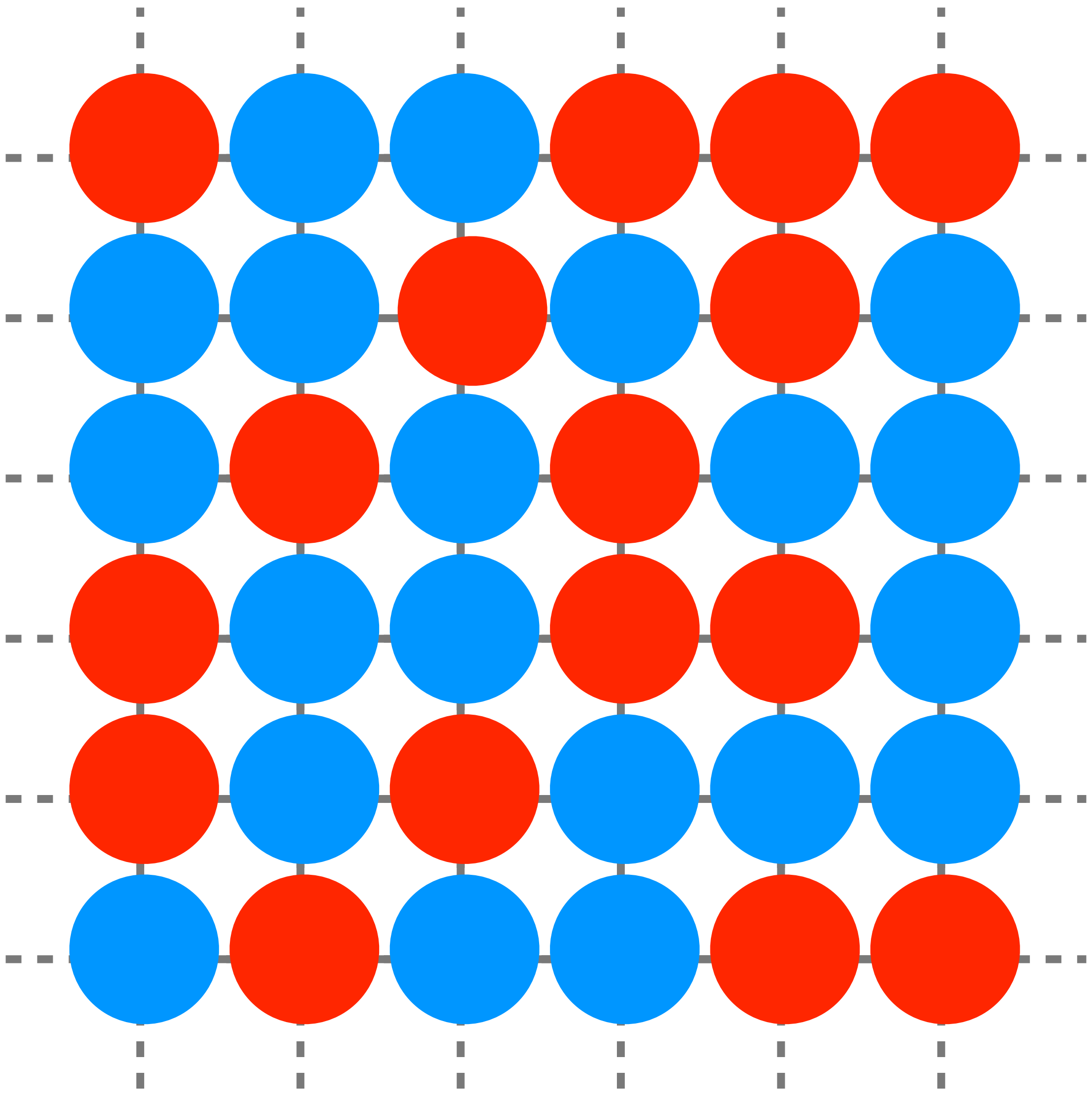

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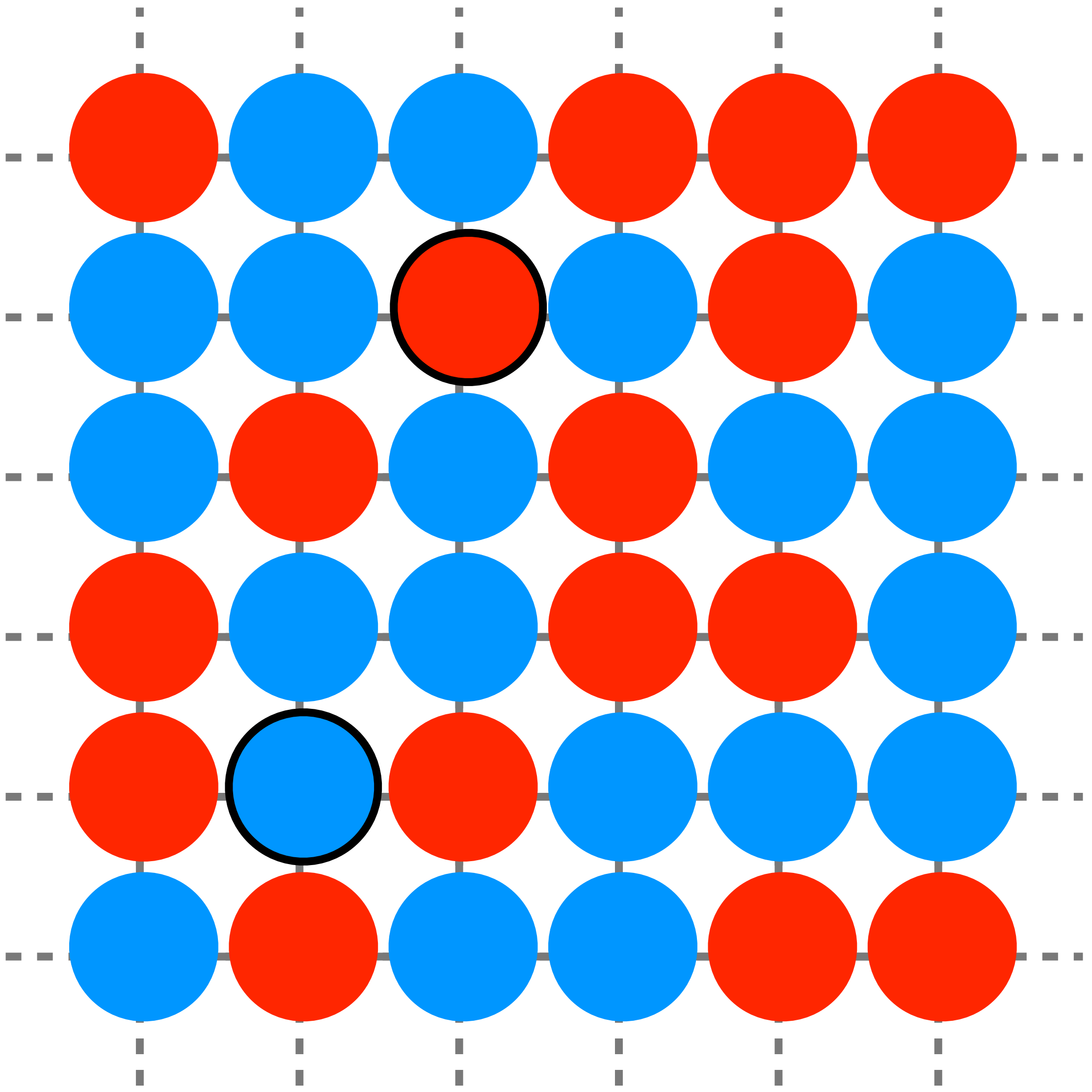

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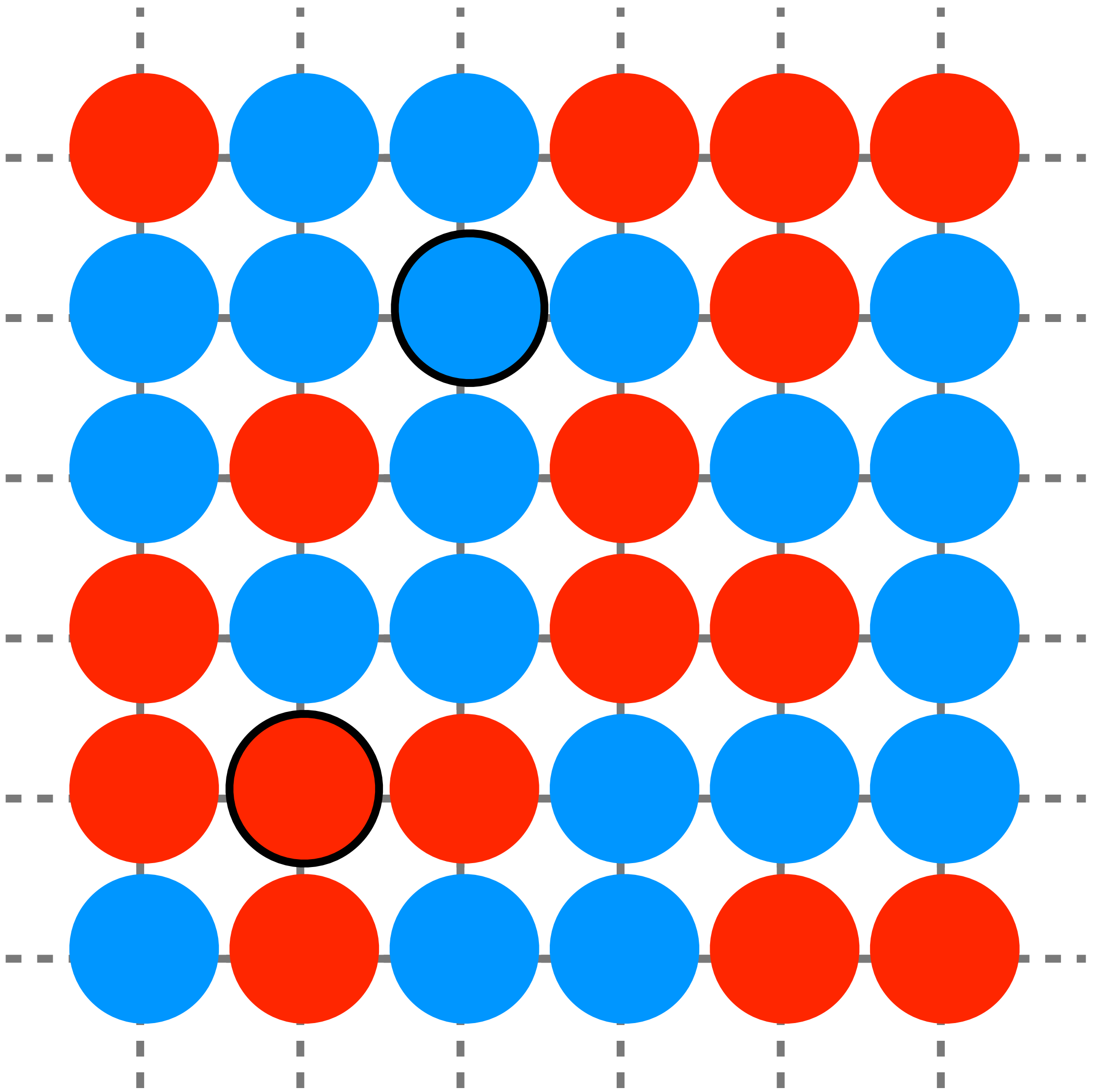

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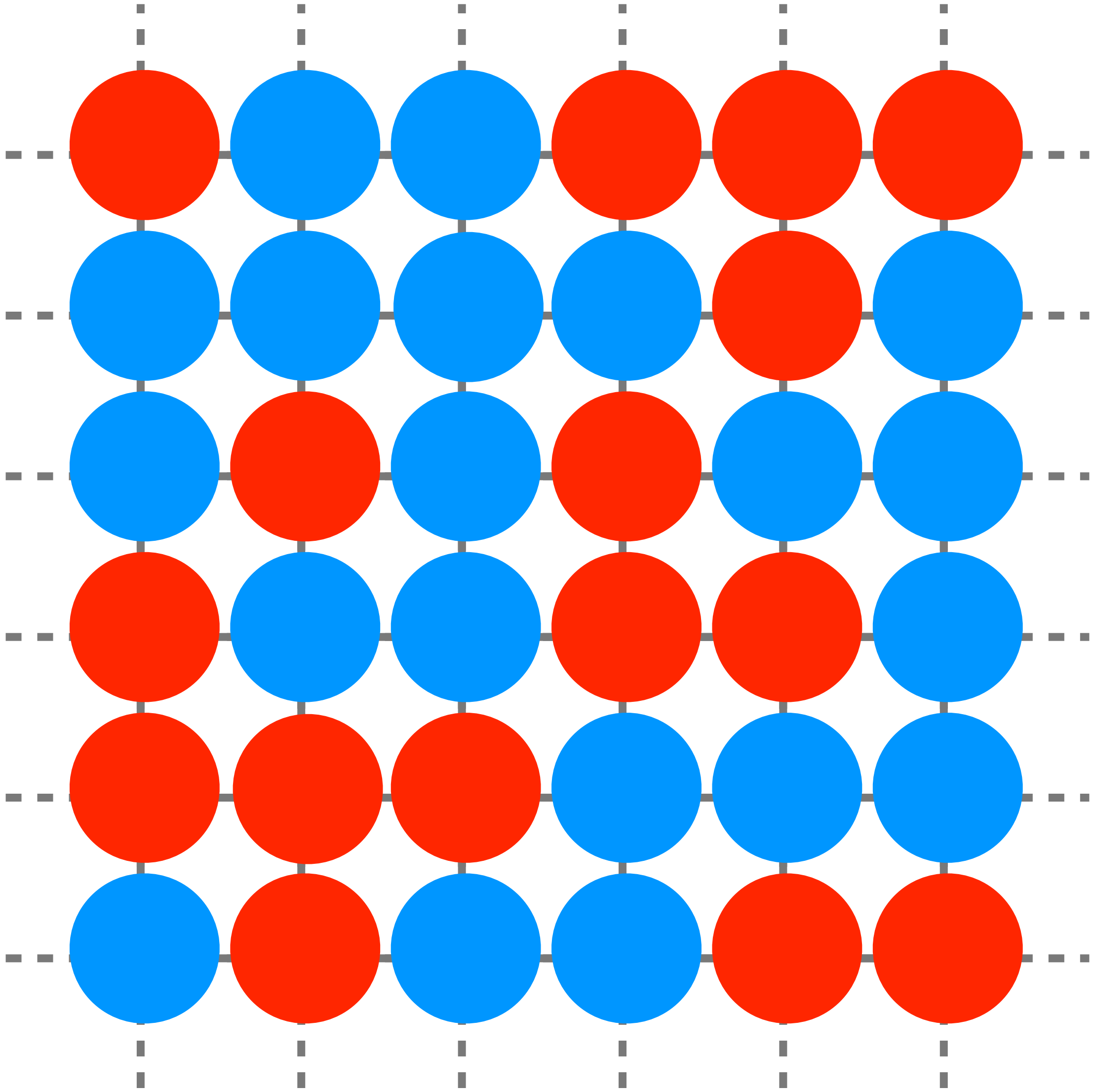

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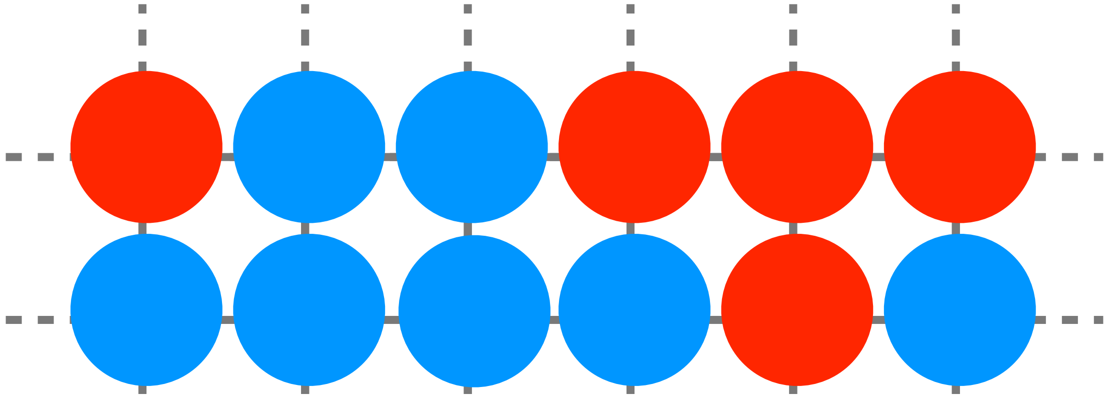
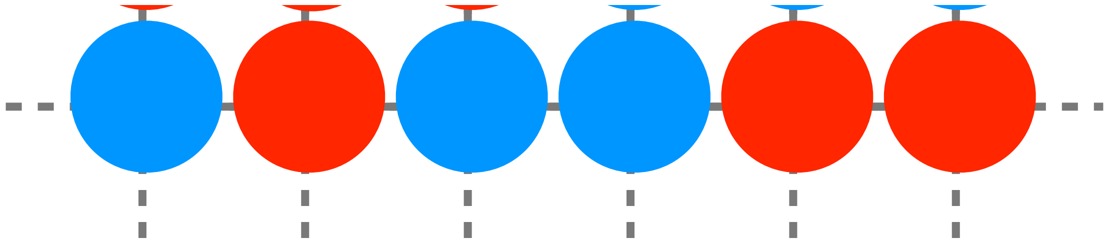


$$F = U - TS$$



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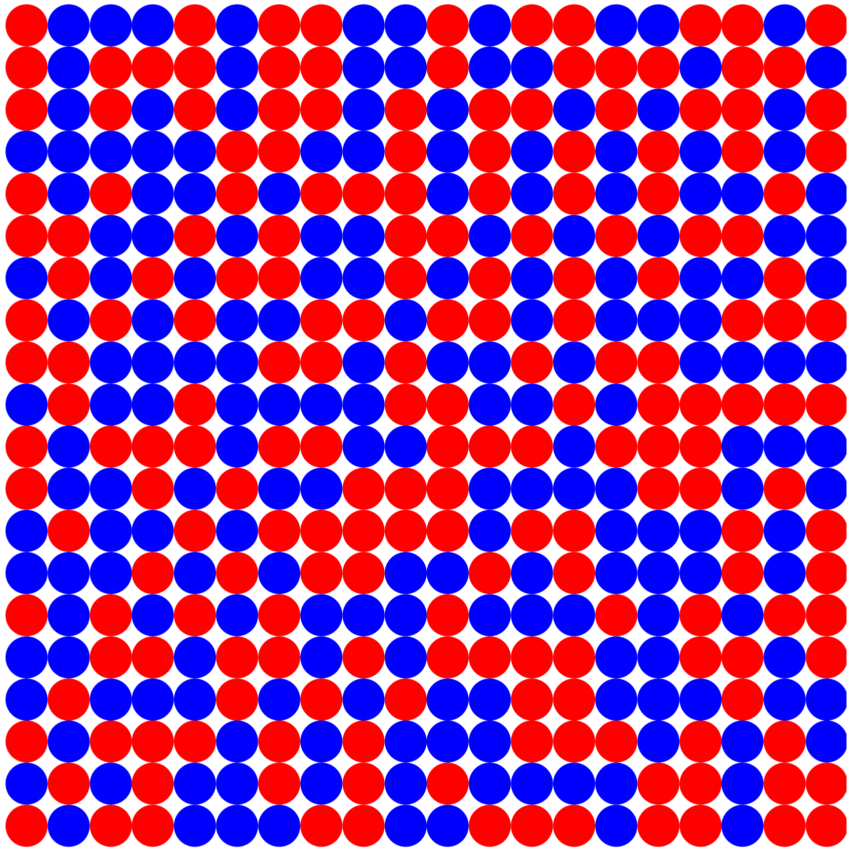
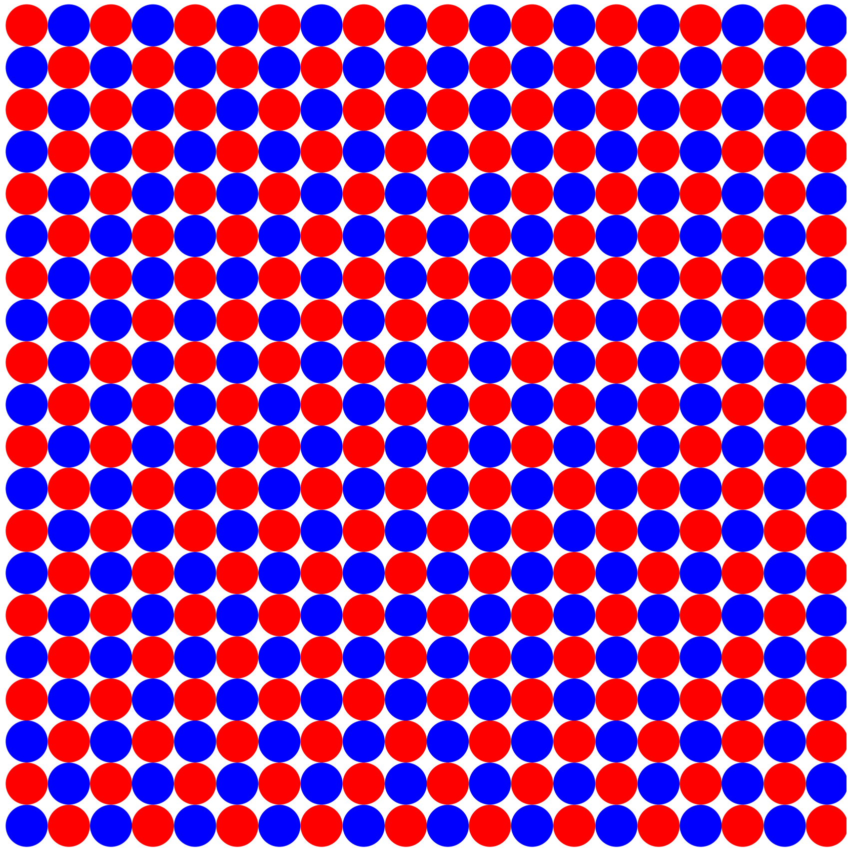
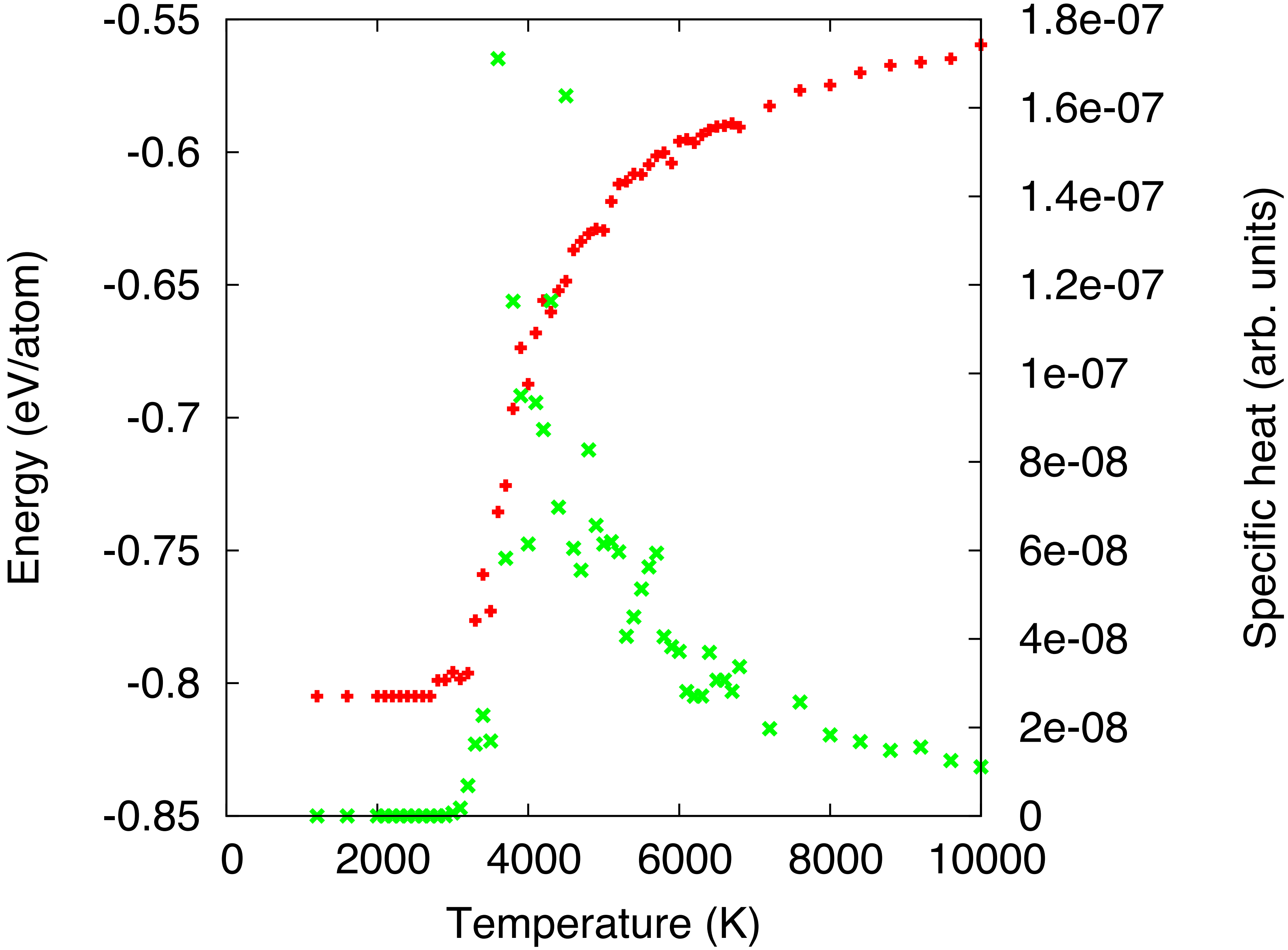
8000 K

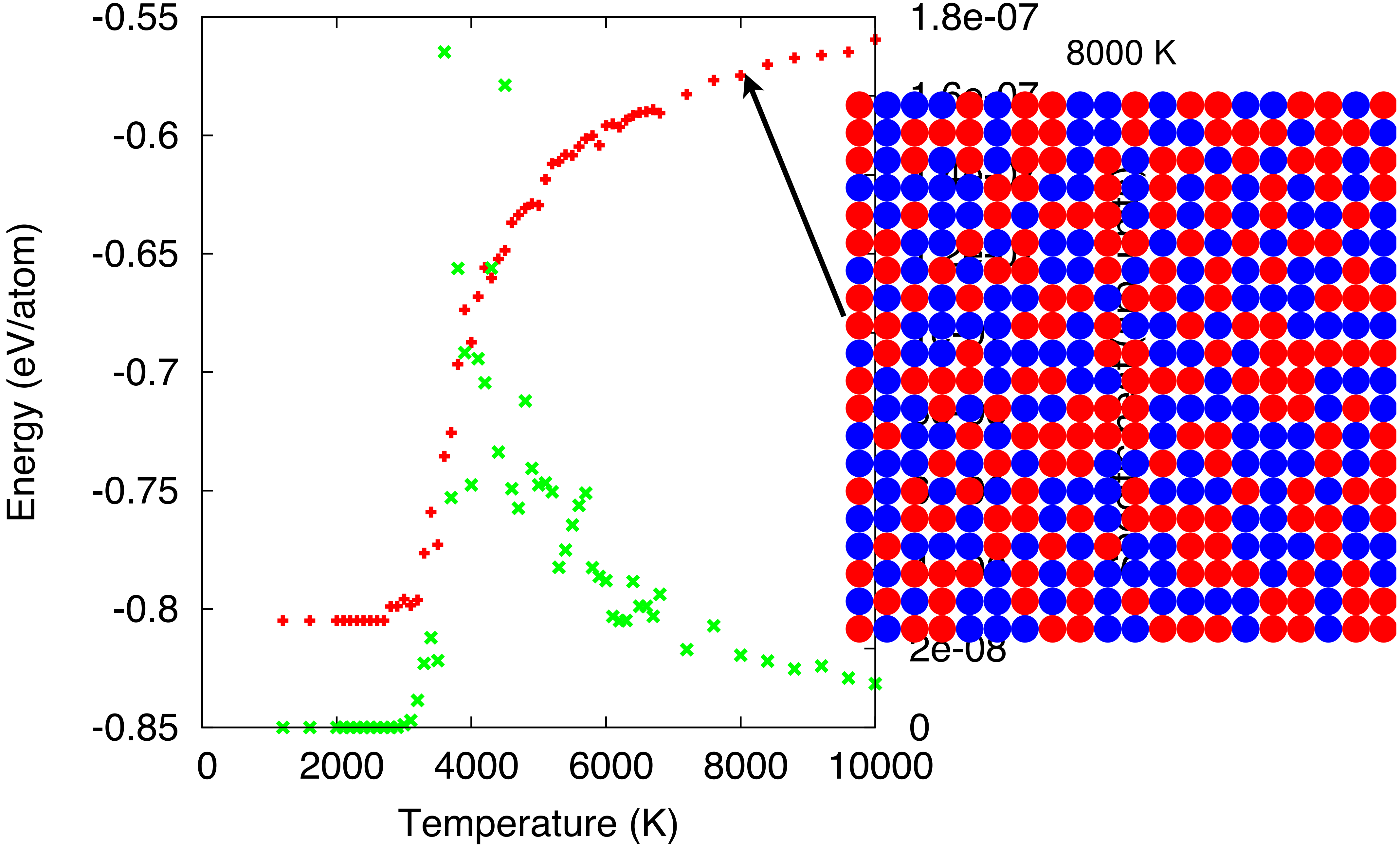


1600 K





-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)



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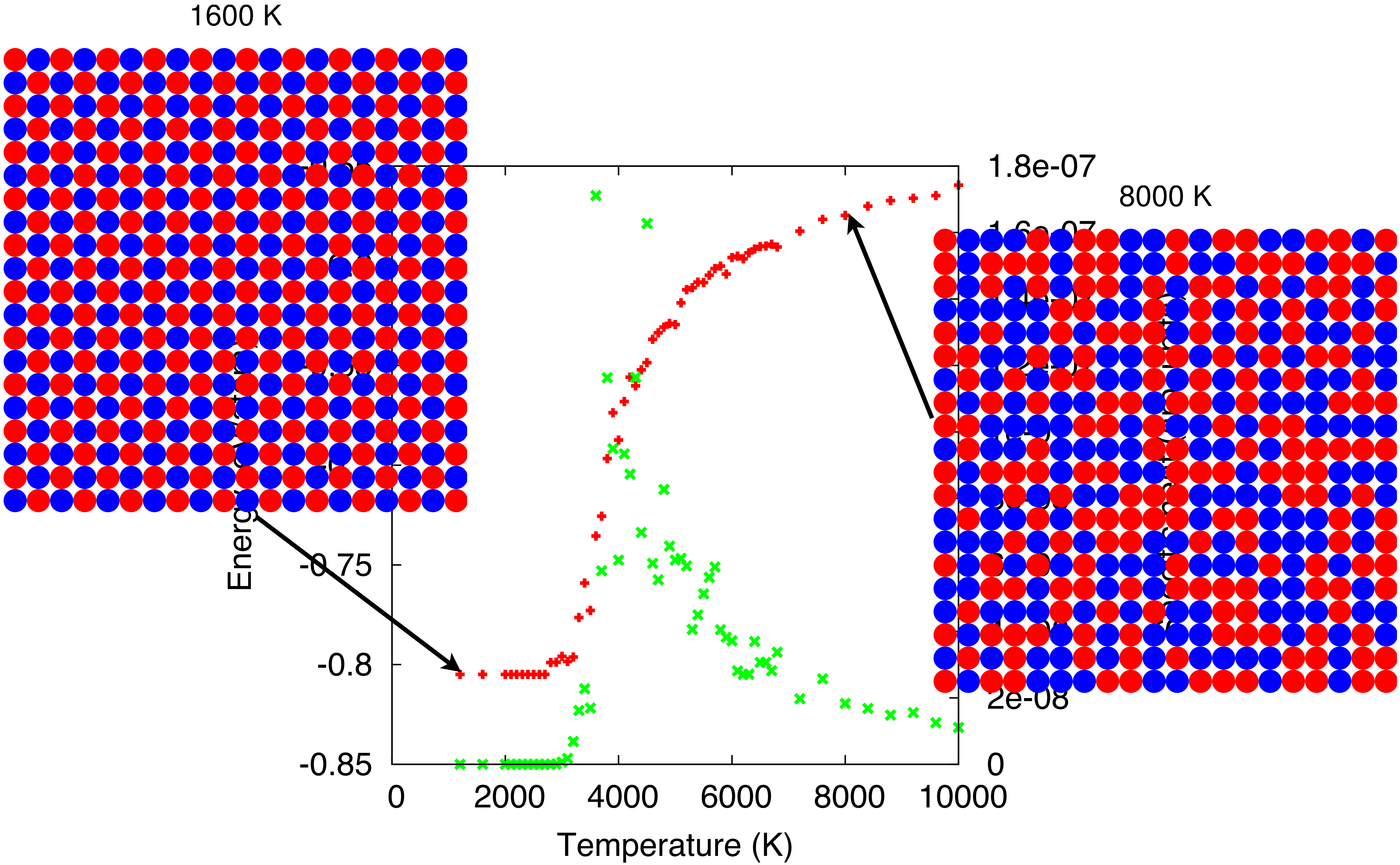
1600 K
8000 K
-0.75
-0.8
-0.85
Energ
1.8e-07
2e-08
0
0
2000
4000
6000
8000
10000
Temperature (K)