Order Disorder & Order *by* Disorder

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OSSA Lecture Series – Aug. 30th, 2022

University of Windsor

Three questions:

1. What is **order**?

2. What is **disorder**?

3. How can **disorder** lead to **order**?

Three questions:

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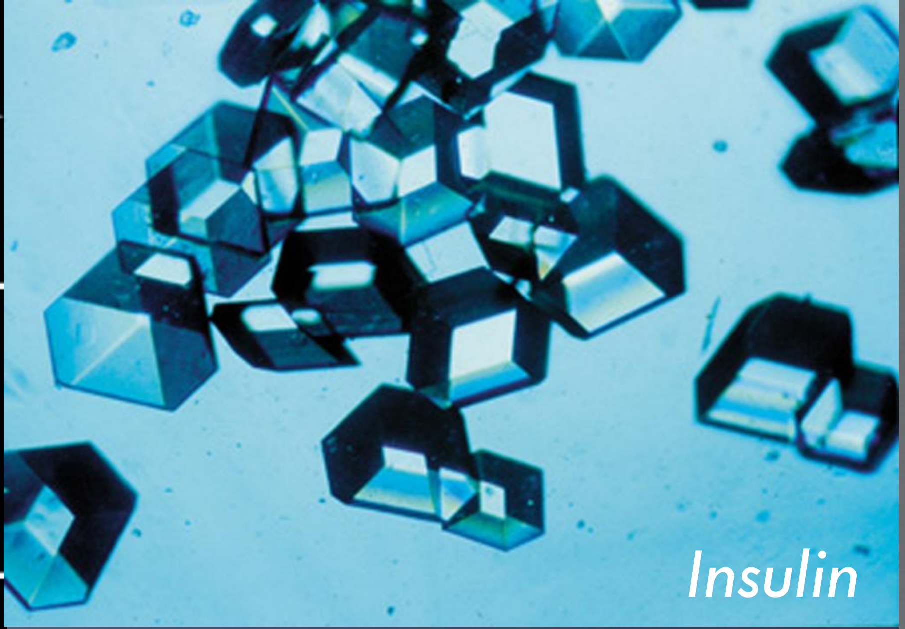
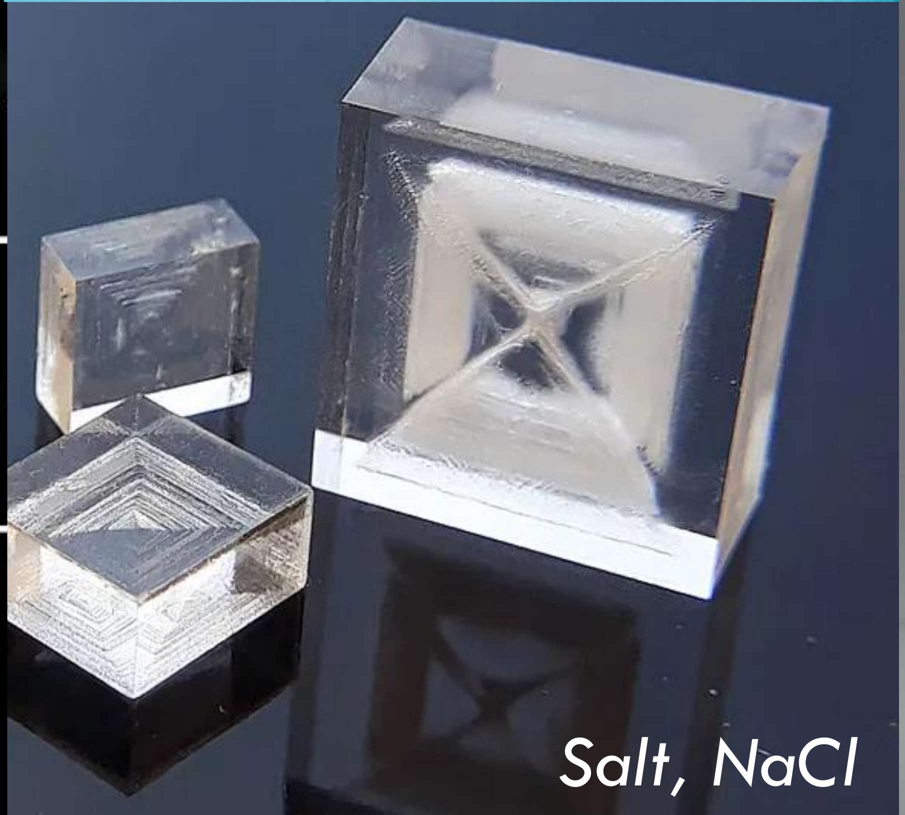
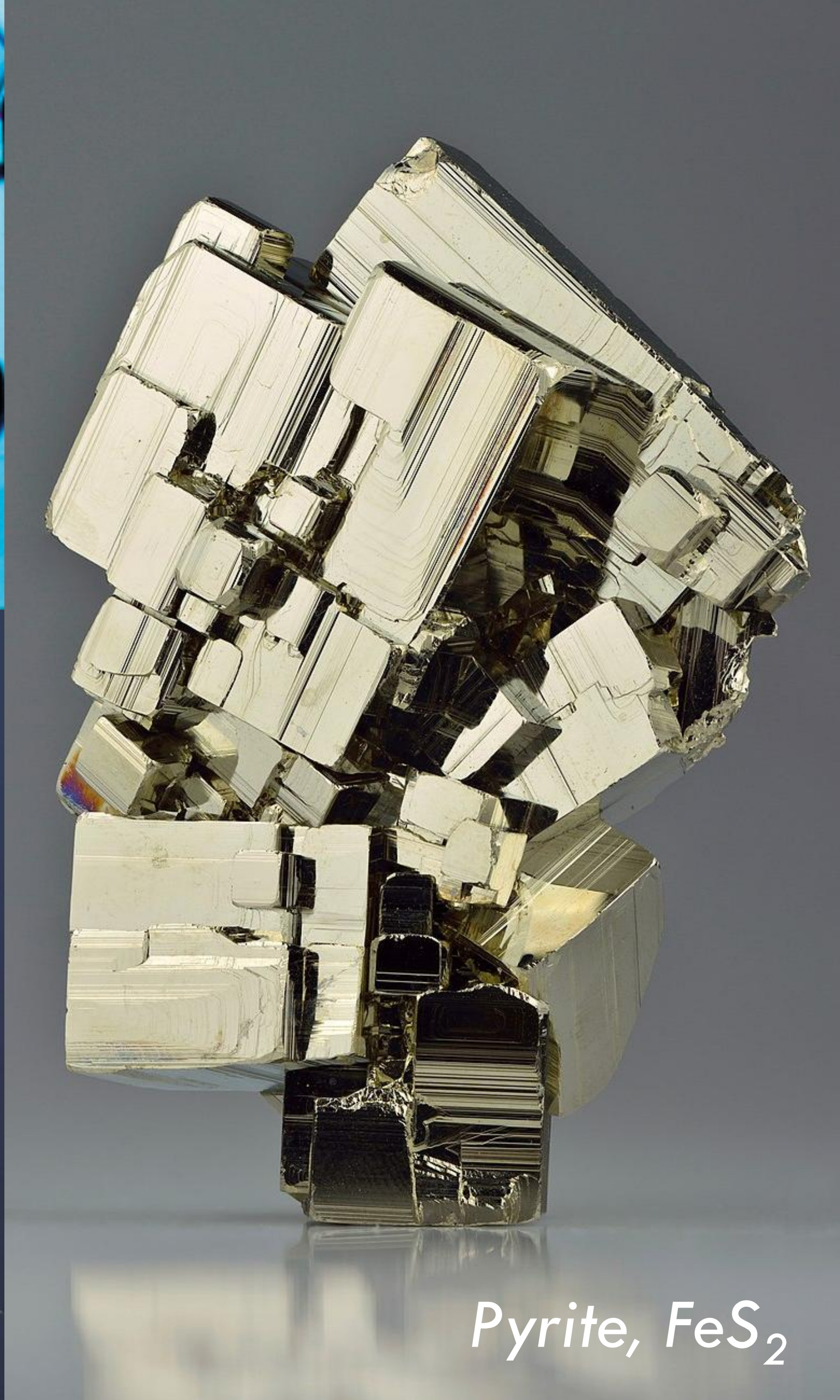
Ice


Insulin


Salt, NaCl

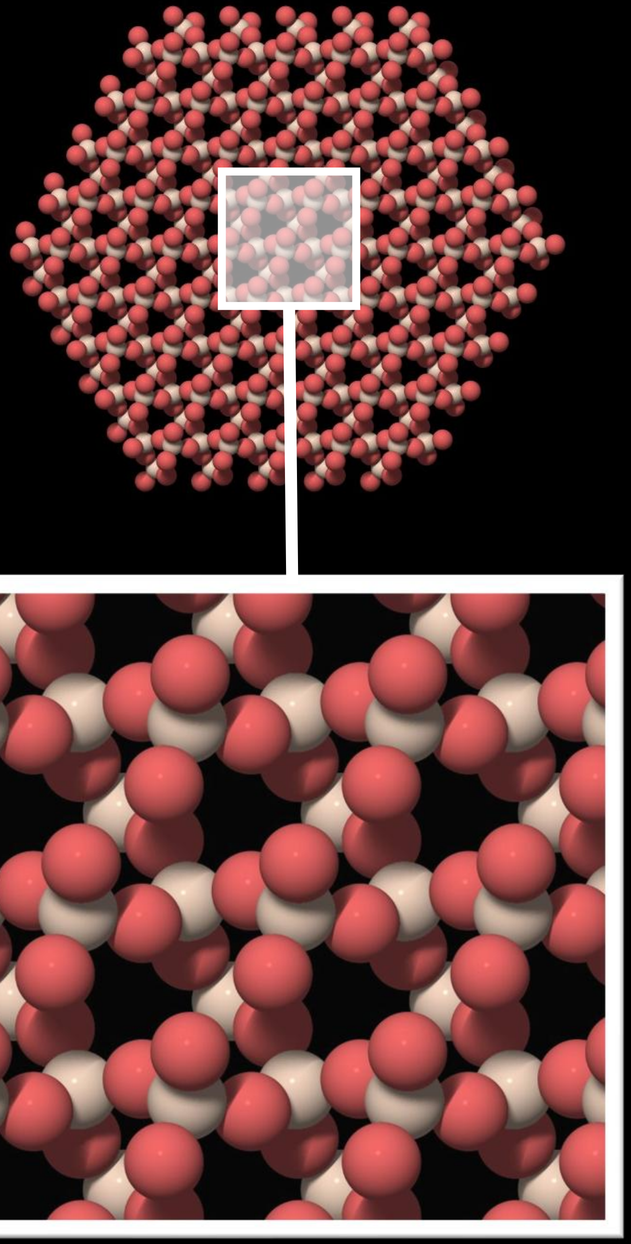

Pyrite, FeS2

“Cave of the Crystals”, Mexico

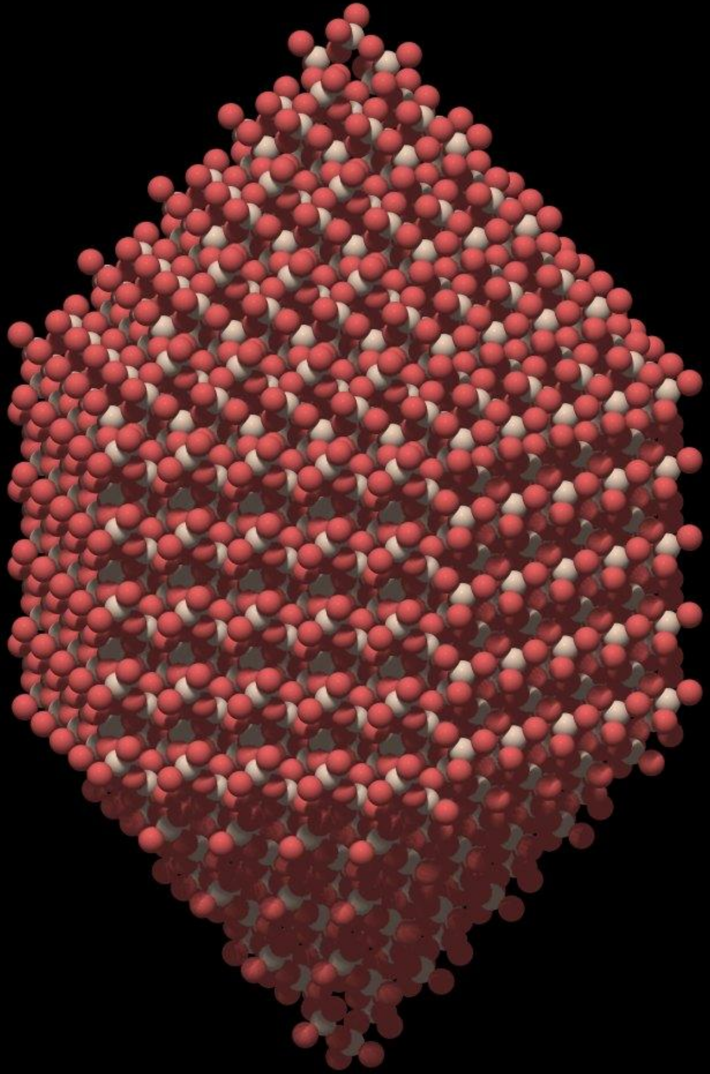
Gypsum, $CaSO_4 \cdot 2H_2O$

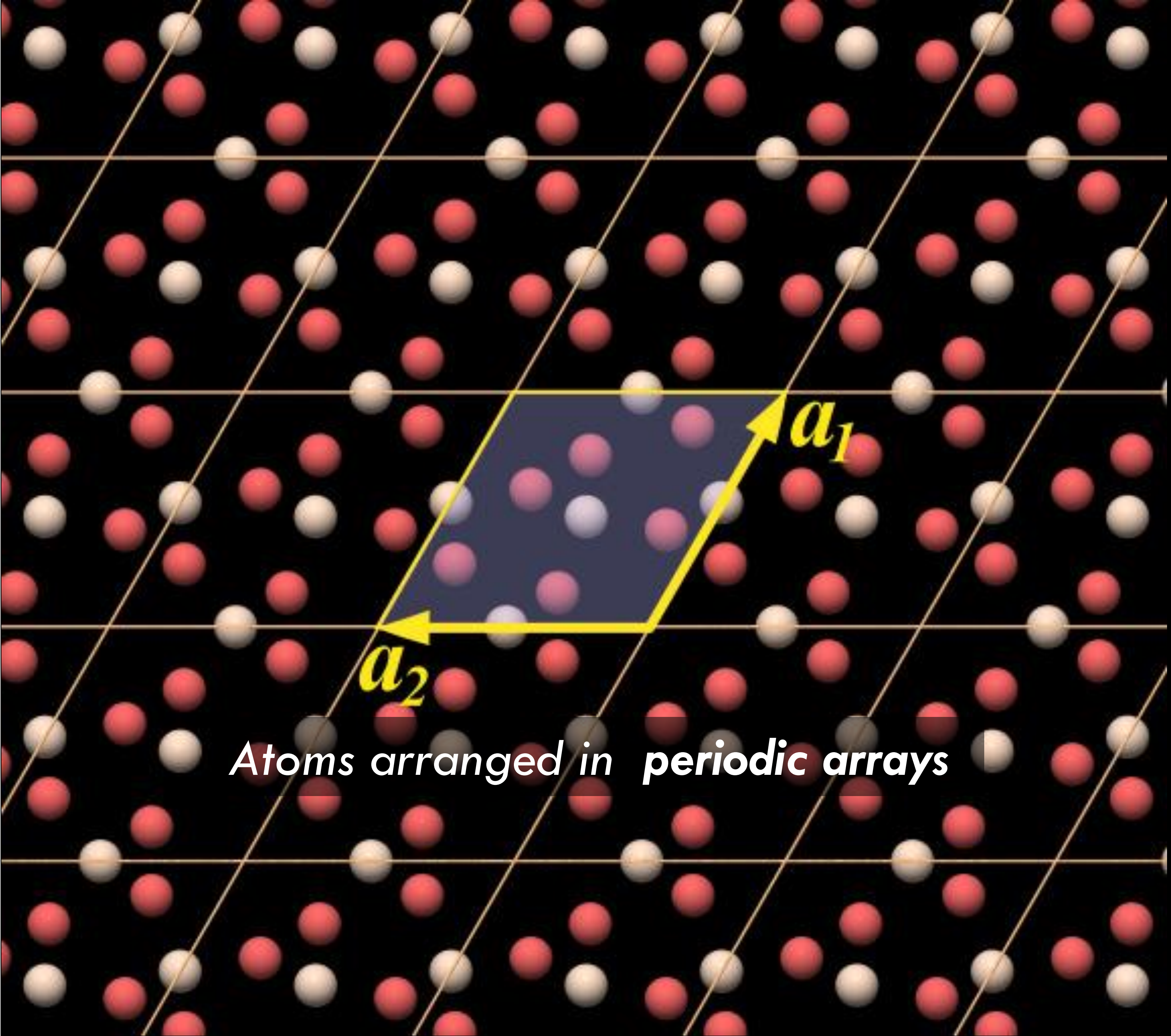
Quartz, SiO_2

Cut through middle

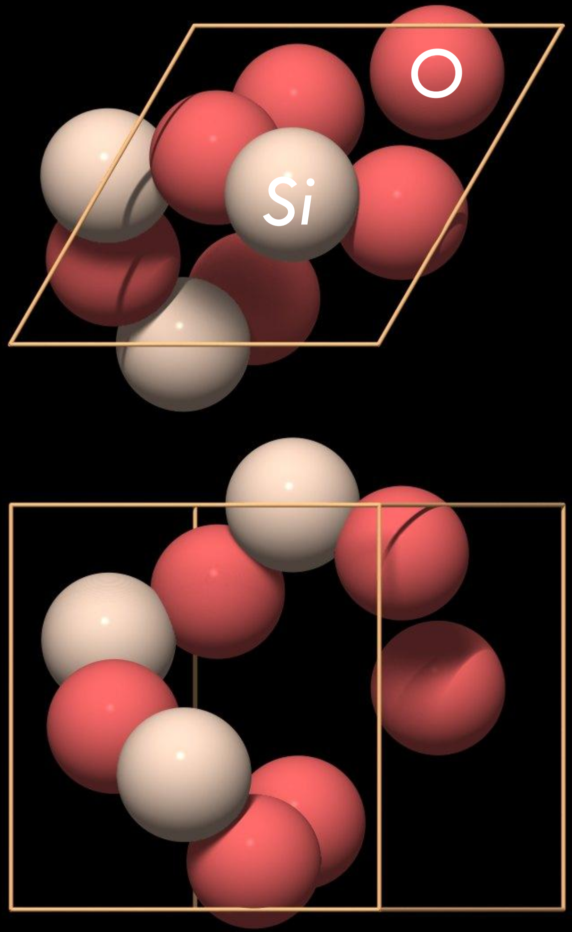


quartzpage.de

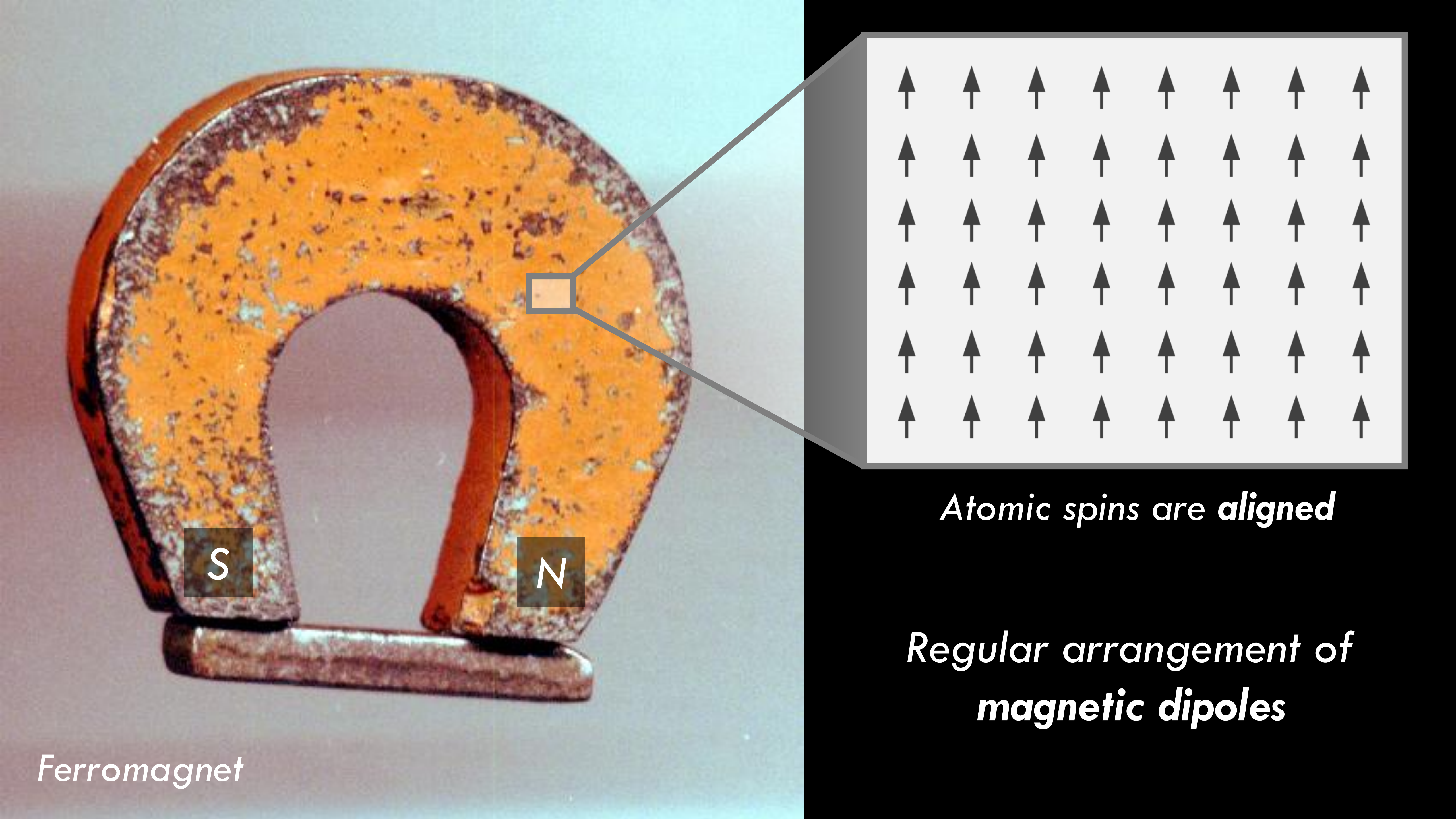


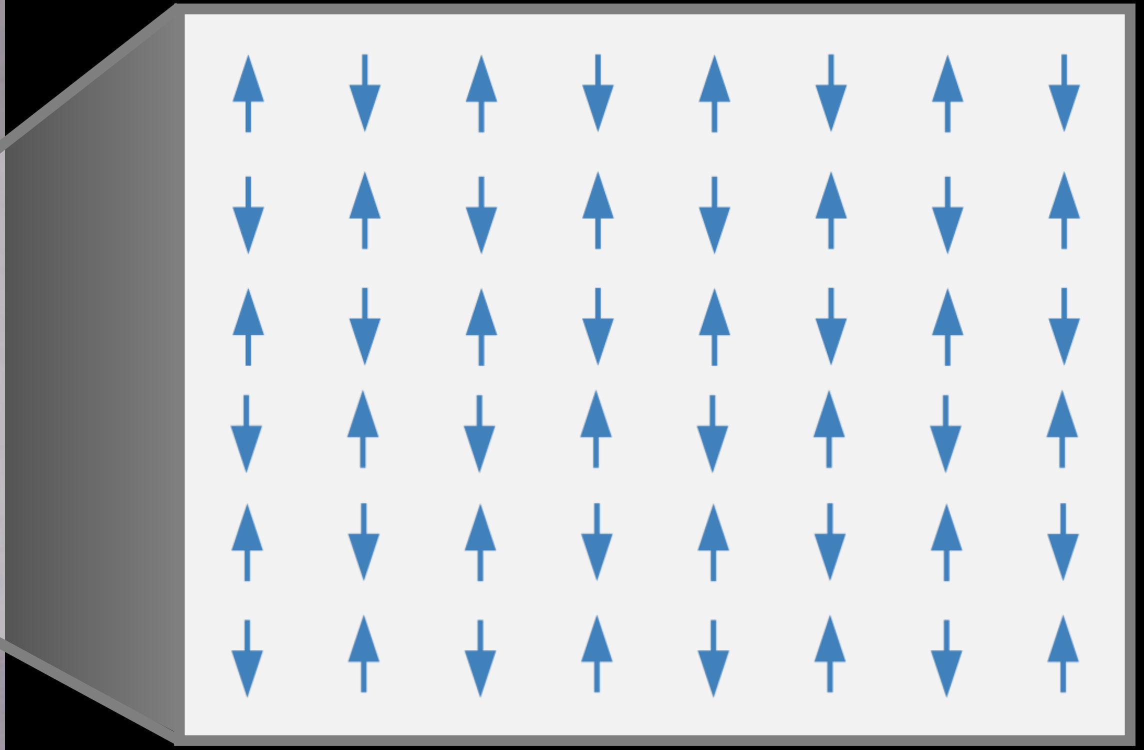


Atoms arranged in ***periodic arrays***



Repeating "unit" of the crystal


S
N
Ferromagnet
Atomic spins are aligned
Regular arrangement of magnetic dipoles



Atoms ***alternate between aligned and anti-aligned***

Still ***regular*** *arrangement!*

So how do define “order”?

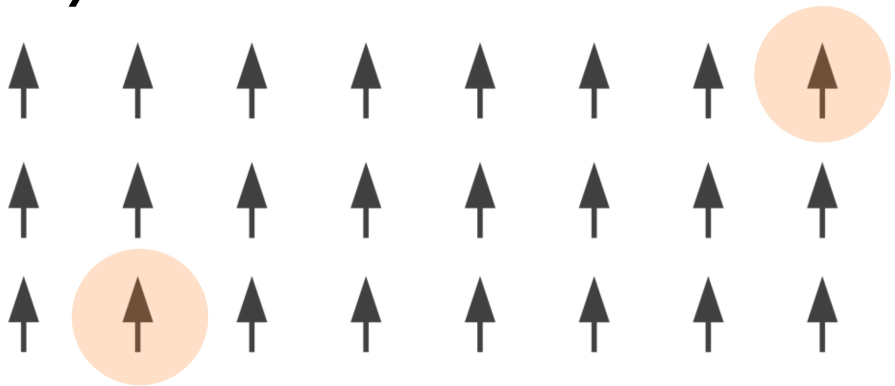
Local Observable? *Physical property in one place.*
E.g. Location of an atom, direction of a spin, …

Definition: A system has **(long-range) order** *if* some **local observable property** is **correlated** even at very **distant** locations

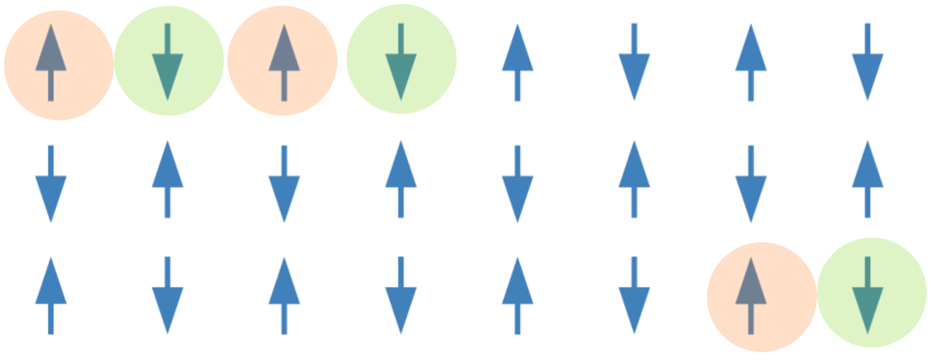
Distant? *Many, many atomic spacings apart*

Correlated? *We can (mostly) determine the value of one from the other*

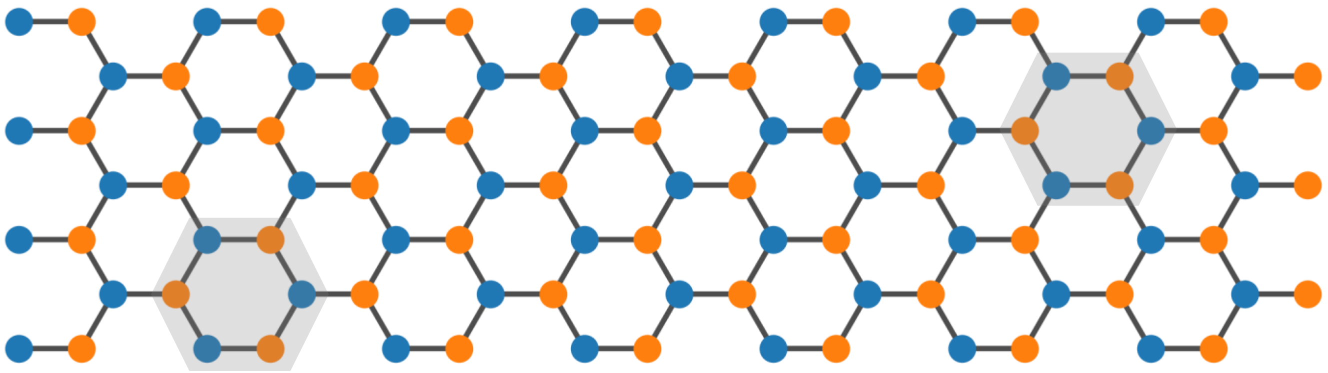
If you know this direction …



… you know this one too



(Same idea, just alternate direction)



Once you fix the first few atoms,
the ***pattern*** *fixes all the rest*

Why do we find order?

- At low temperatures, systems tend to states with **as little energy as possible**

  Cold removes all the energy it can from system

- Interactions between atoms typically **highly symmetric**

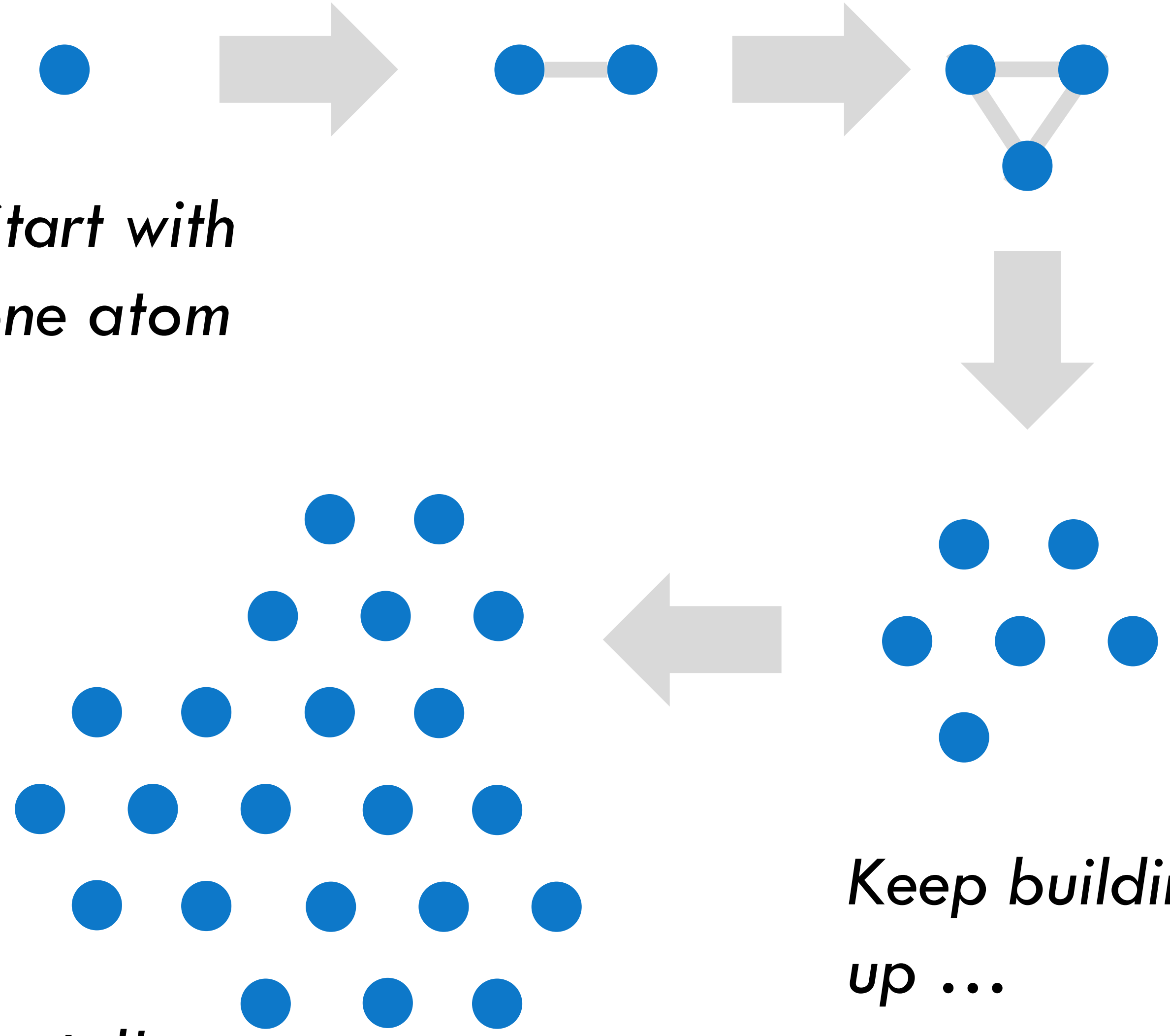
  Laws of Nature have high symmetry!

- Only* a **handful** of way to get the lowest possible energy

  ** Not always true: “Frustration”*

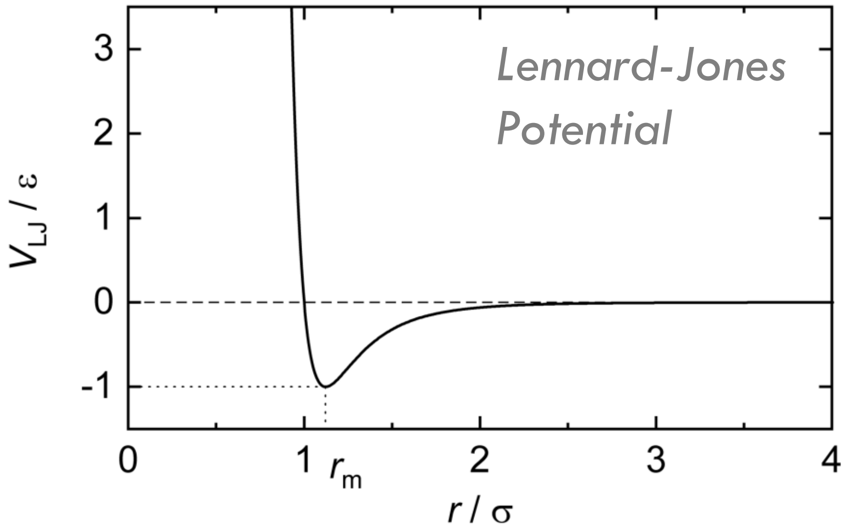
Start with one atom

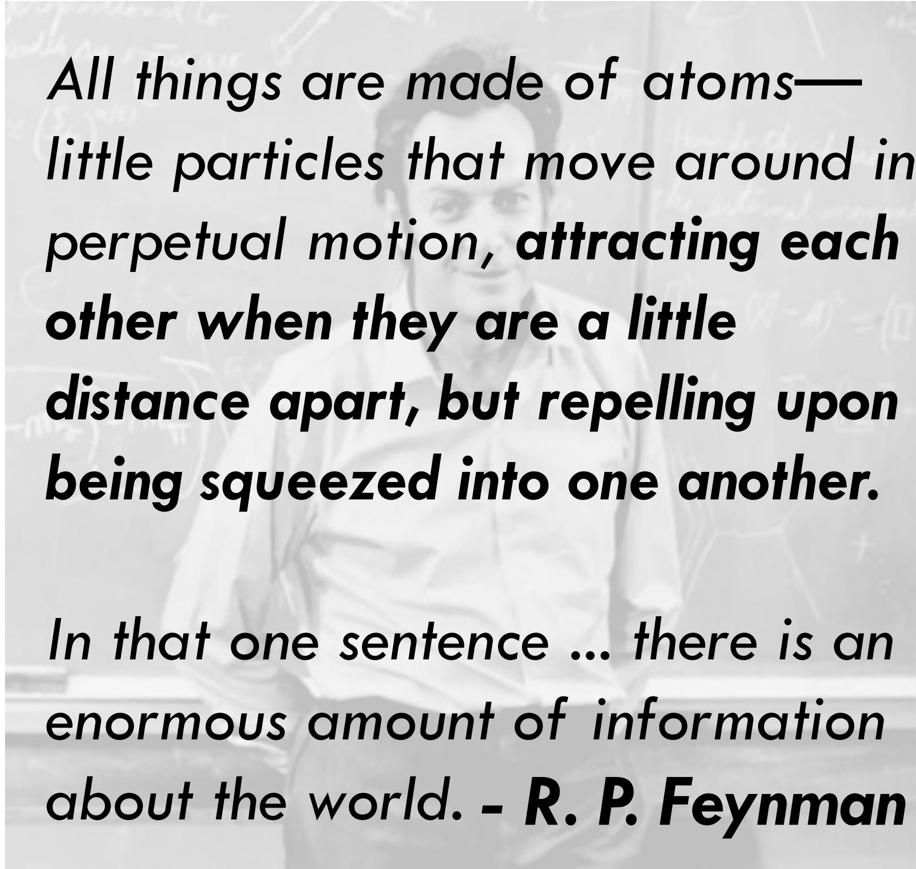
Get close, but not too close



Keep building it up …

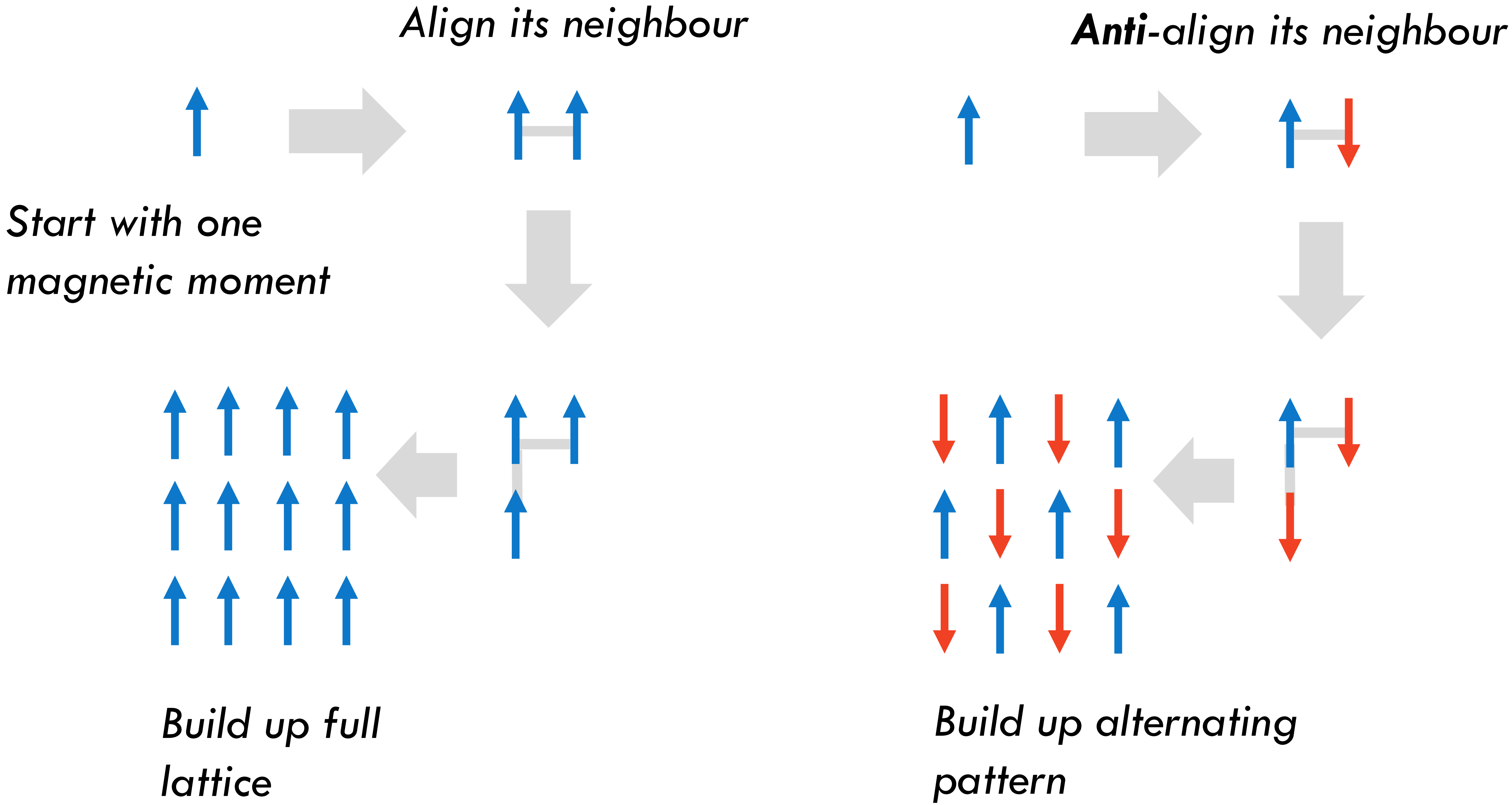
Crystal!





All things are made of atoms—little particles that move around in perpetual motion, ***attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.***

In that one sentence ... there is an enormous amount of information about the world. **- R. P. Feynman**

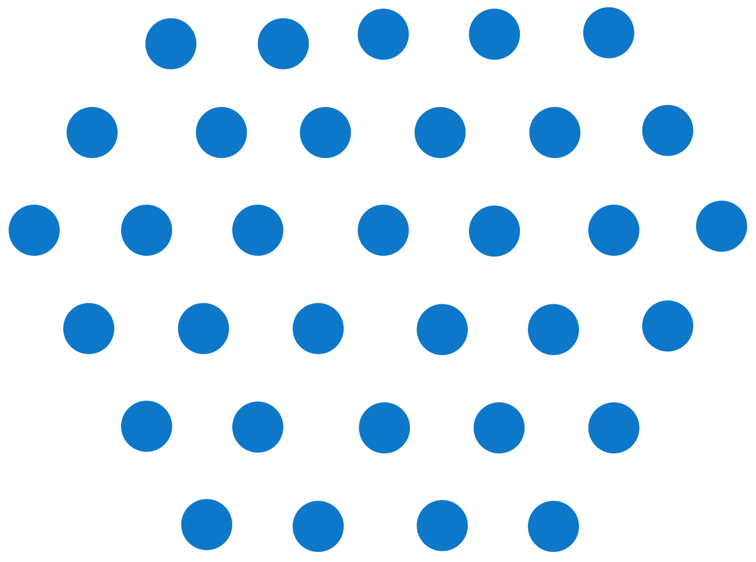

Align its neighbour
Anti-align its neighbour
Start with one magnetic moment
Build up full lattice
Build up alternating pattern

Three questions:

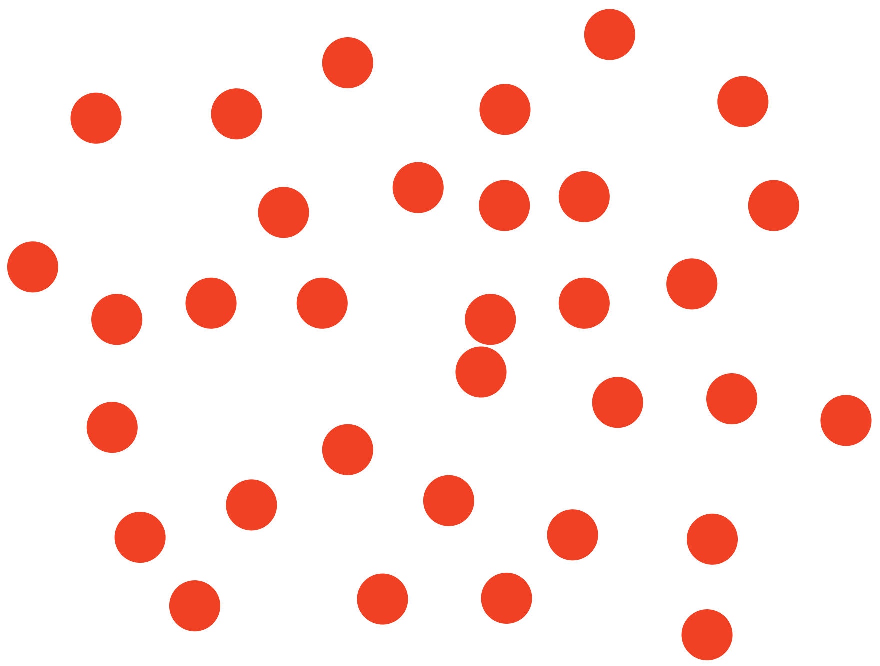
1. What is **order**?
2. What is **disorder**?
3. How can **disorder** lead to **order**?

Can't we just say it is what order *isn't*?

- If order is **correlation at long distances** disorder a **lack thereof?**

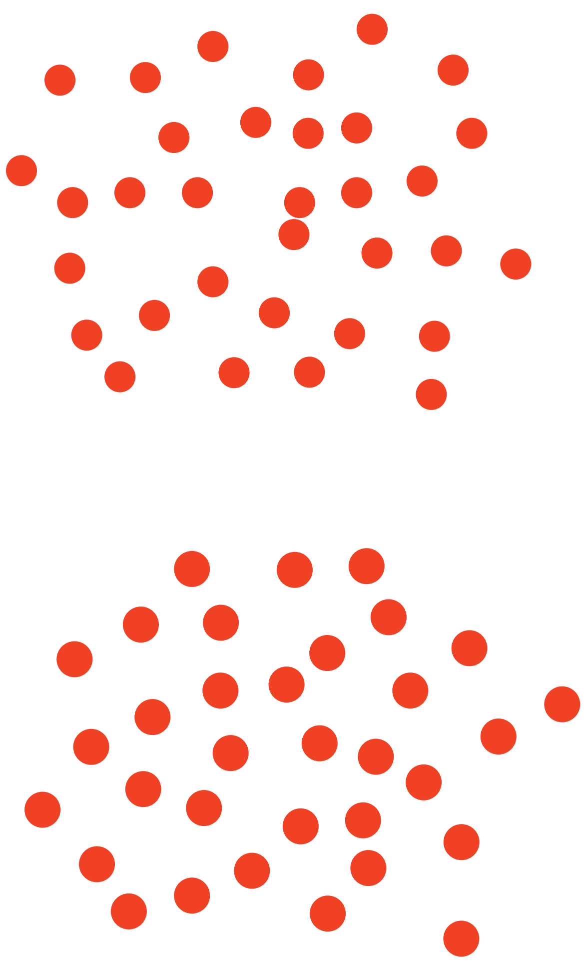


Order

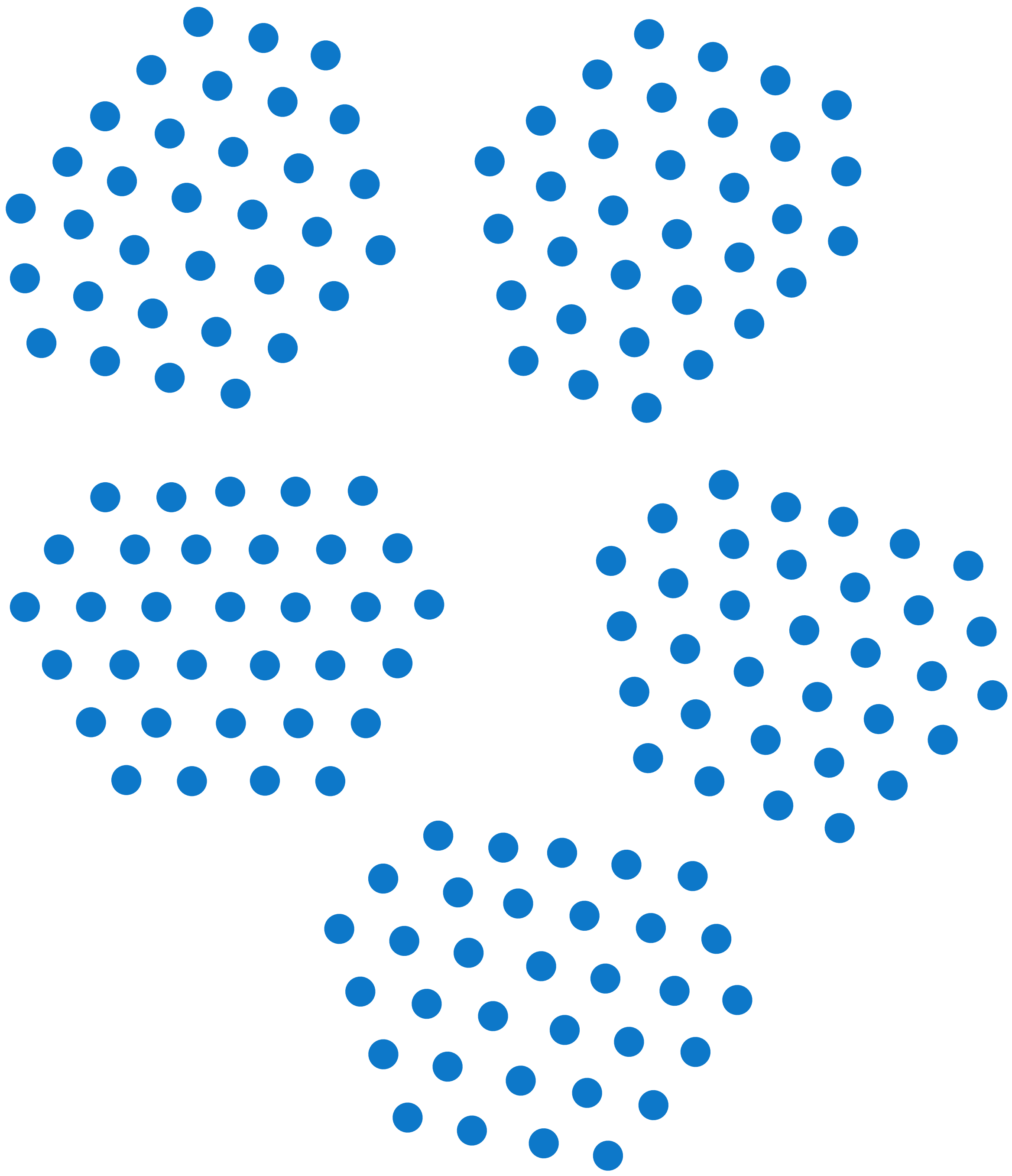


Disorder?

Lots of disordered states "look" the same



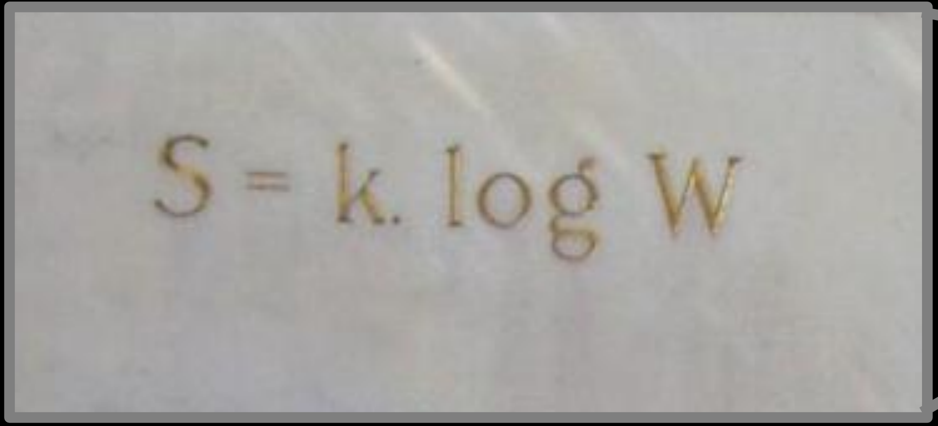
- **Qualitatively** these different disordered states are distinguishable *by eye*
- Lots of atoms have been moved …
- … but whatever **macroscopic** properties we're seeing don't look different!

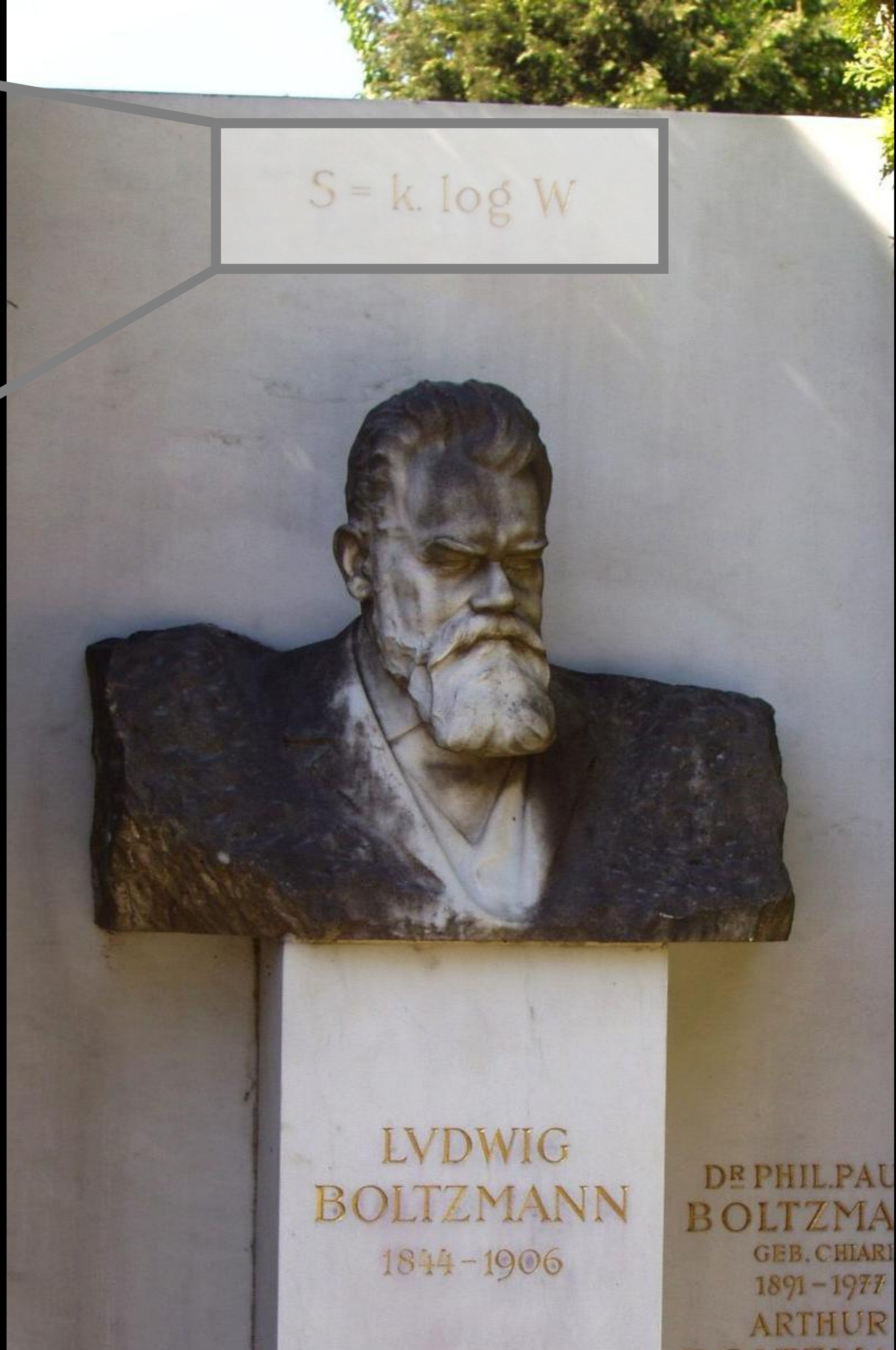


Ordered states *aren't* like this

- All we can do is a few simple changes:
  - **Translation:** Shift the atoms all together
  - **Rotation:** Rotate the atoms all together

*How do we make this **precise**?*





The general struggle for existence of animate beings is not a struggle for raw materials, these for organisms are air water & soil, all abundantly available, nor for energy which exists in plenty in the sun and any hot body in the form of heat, but rather a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth.

- Ludwig Boltzmann

Entropy

Why a logarithm? W gets really, really big

<u>Definition:</u> The **entropy** of a system is:

Entropy

$$S = k_B \log W$$

Number of states ***consistent*** *with our* ***macroscopic description***

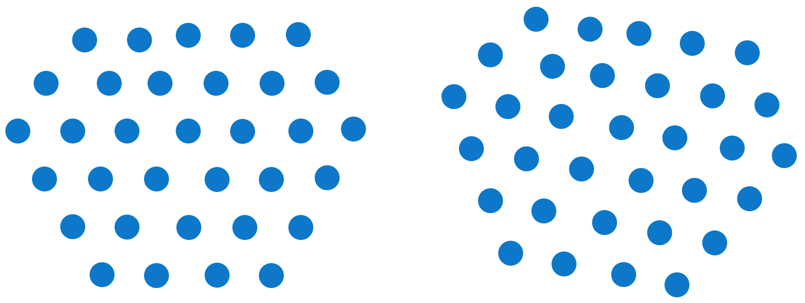
Boltzmann's constant (just sets units)

- What do we mean by **macroscopic description?**
  Almost anything involving the state of all the atoms at once

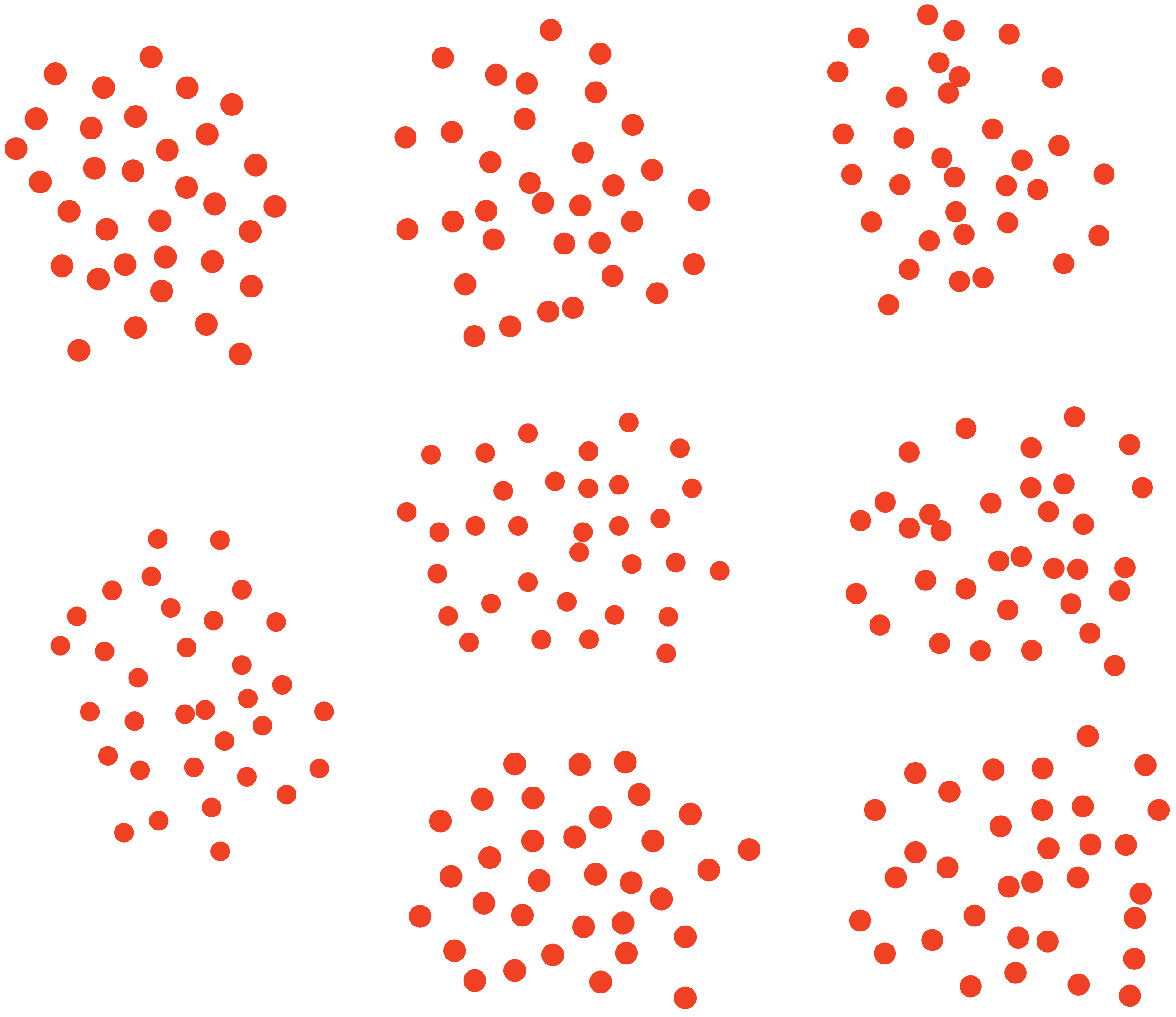
- **Examples:** Total Energy, Number of Particles, Volume, Pressure, Magnetization, …

For the gas?

- Simple macroscopic variable: **the total energy**
- Lower when atoms near *preferred* distance

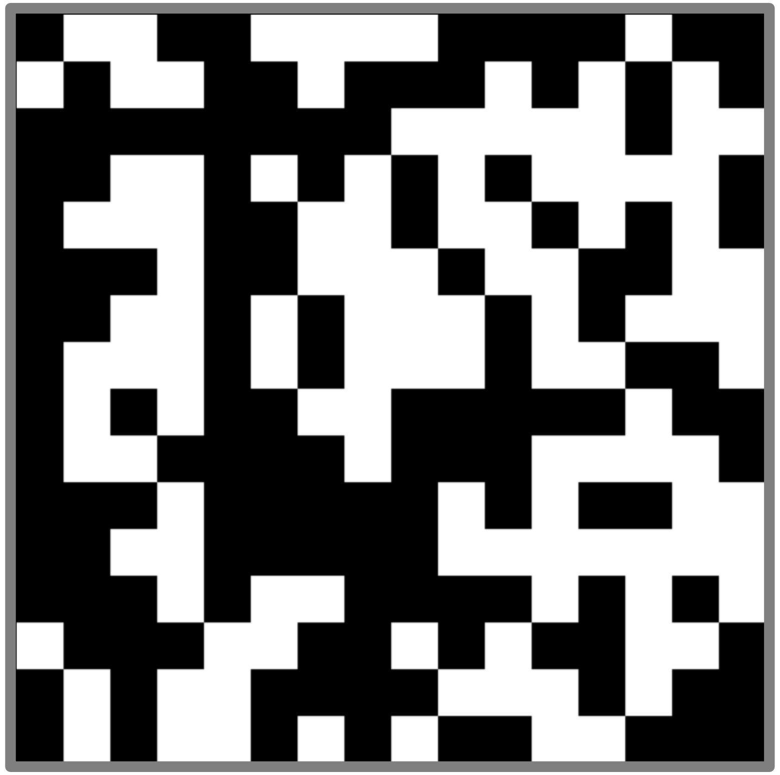


*Atoms **minimizing energy***



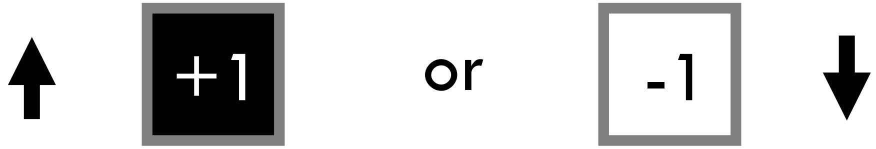
*Atoms too far & too close, energy **higher***

Simple Example: Ising Model



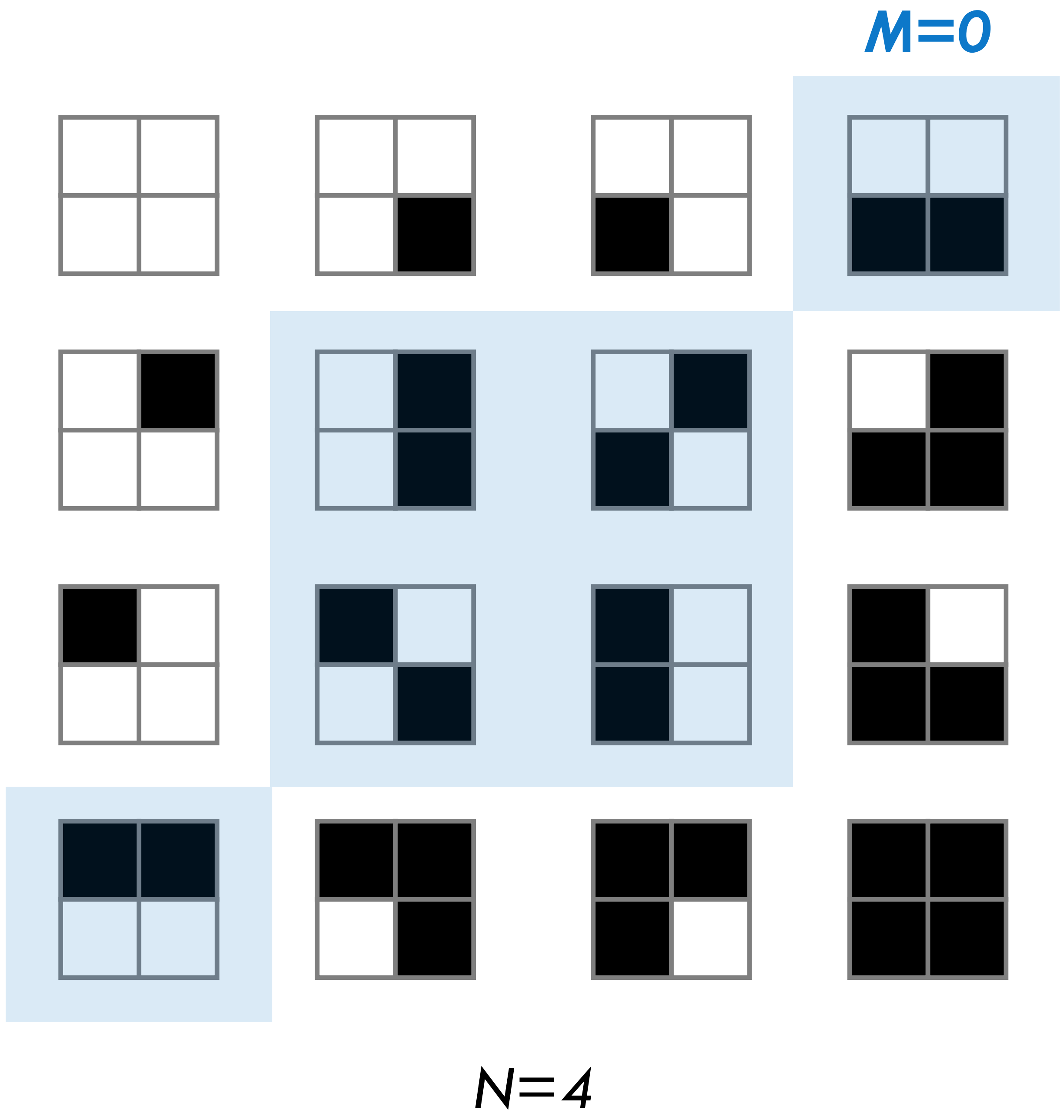
***M* = 0**

- Array of variables, each taking one of two values



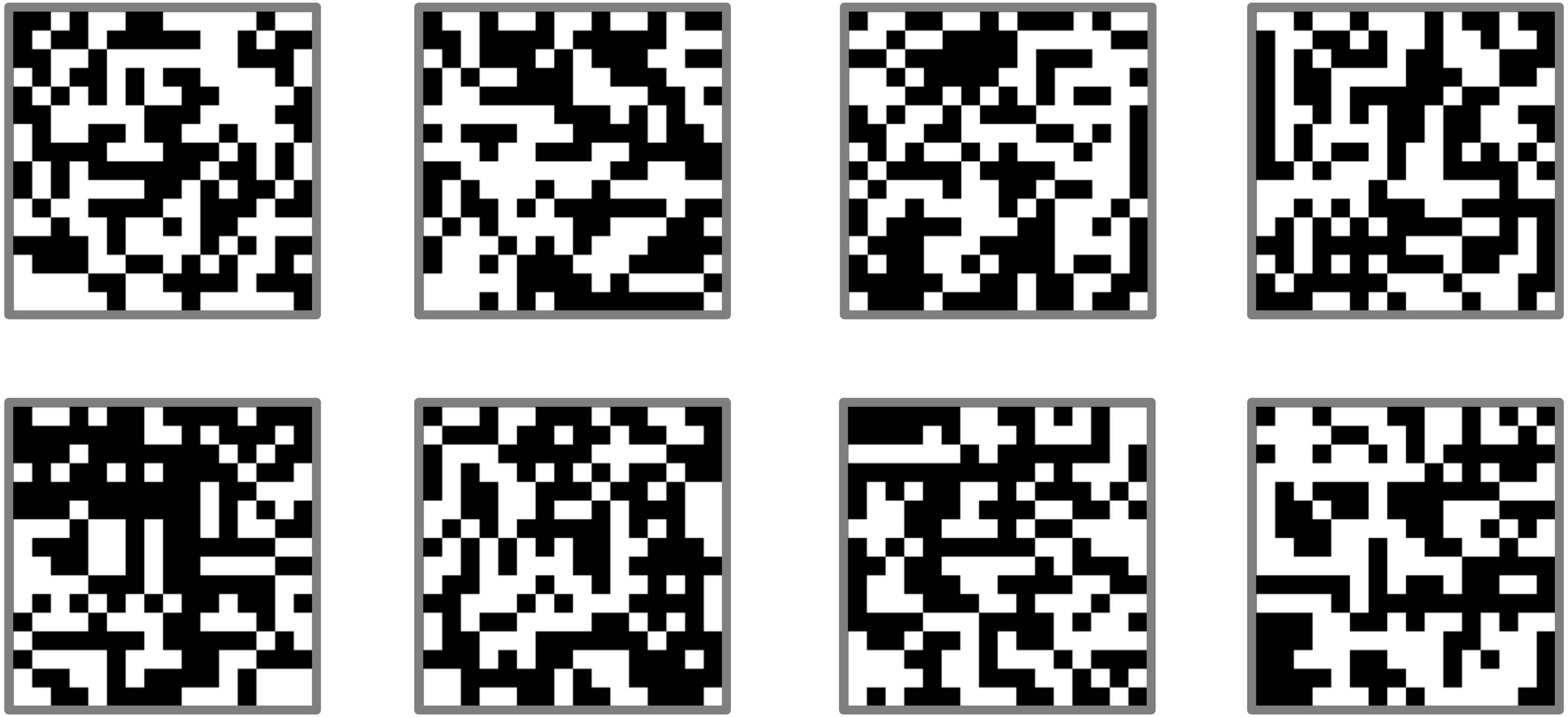
- This could be **spin,** atom type, …
- **Macroscopic state?**

M = (Sum over all variables)



- Look at small case: **just four variables**
- Say we are only talking about states where **M=0**
- **Fewer** states with M=+2,-2 or M=+4,-4
- Discrepancy *grows* with *N*

Lots and lots of states with $M = 0$ …



High entropy, look "disordered" in usual sense

How many states?

N=4096

- When number of variables is large, **exponentially many** with **M=0,** roughly ~ 2^N

$$S \sim N \log 2$$

- Exponentials grow **fast**

  2^{16} ~ 65,536

  2^{32} ~ 4,294,967,296

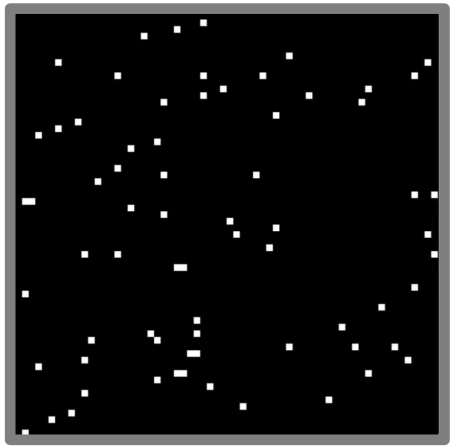
  2^{64} ~ 18,446,744,073,709,551,616

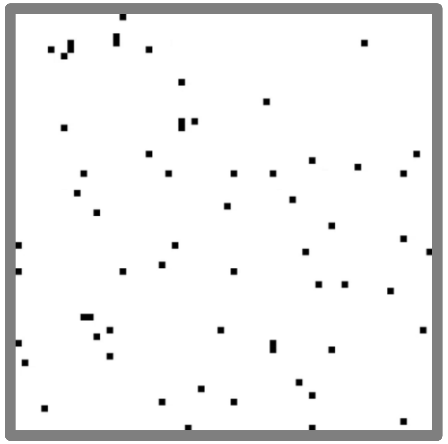
Ordered States?

- **Two** possilbilities: **All +1** or **All -1**
- Entropy?

$$S \sim \log(2)$$

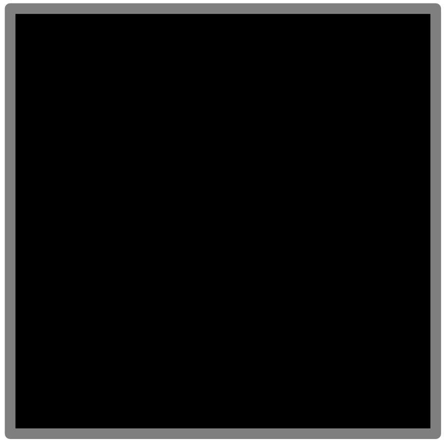
Near maximum M?



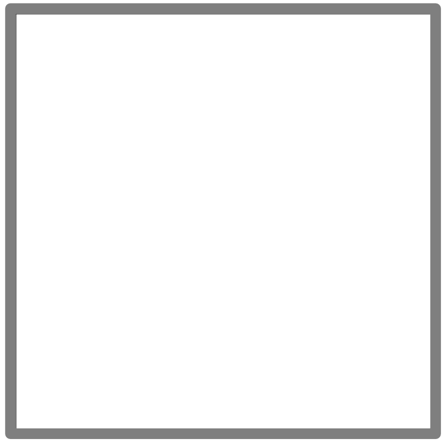


- Variety of states much lower even **near** all +1 or all -1
- Entropy *shrinks* with larger *M*

All +1



All -1



Why do we care about this?

Fundamental principle of statistical physics:

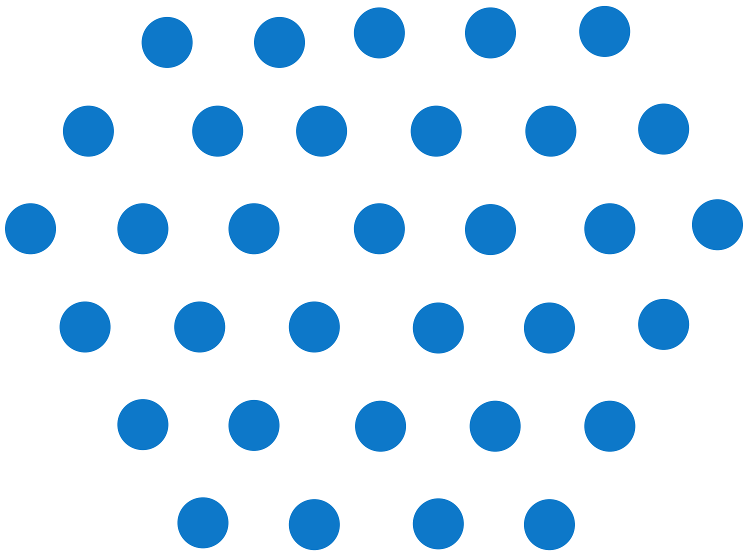
All else being equal, a system is most likely to be found in (accessible) states that **maximize its entropy**

Consistent with our macroscopic description

Principle of "Ignorance": Assume all (accessible) states are equally likely. You'll end up in high entropy states just because **there are more of them.**

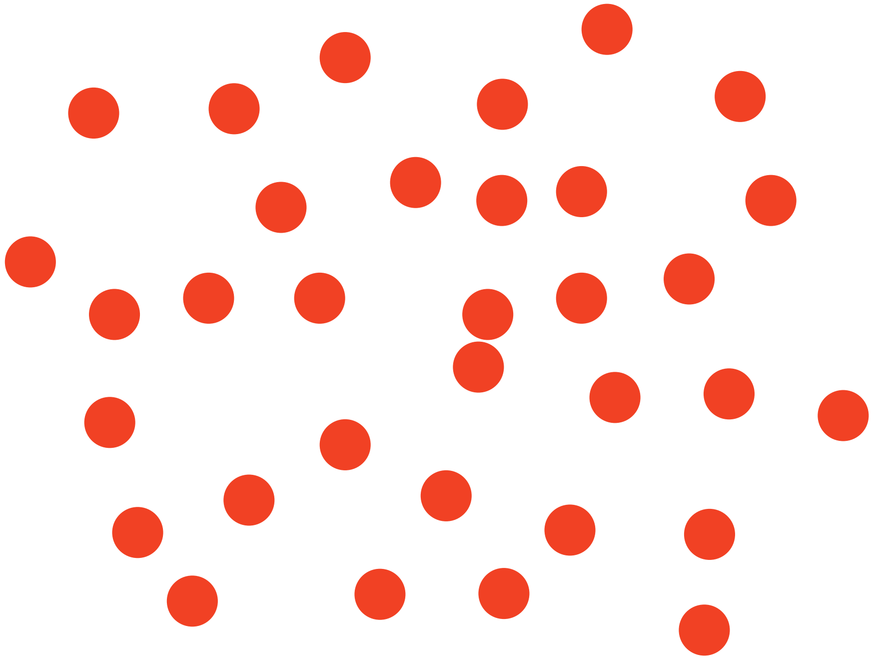
Competition between entropy and energy

Low-entropy
Low energy



*Favoured at **low** temperature*

High entropy
High energy



*Favoured at **high** temperature*

Three questions:

1. What is **order**?

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Three questions:

1. What is **order**?

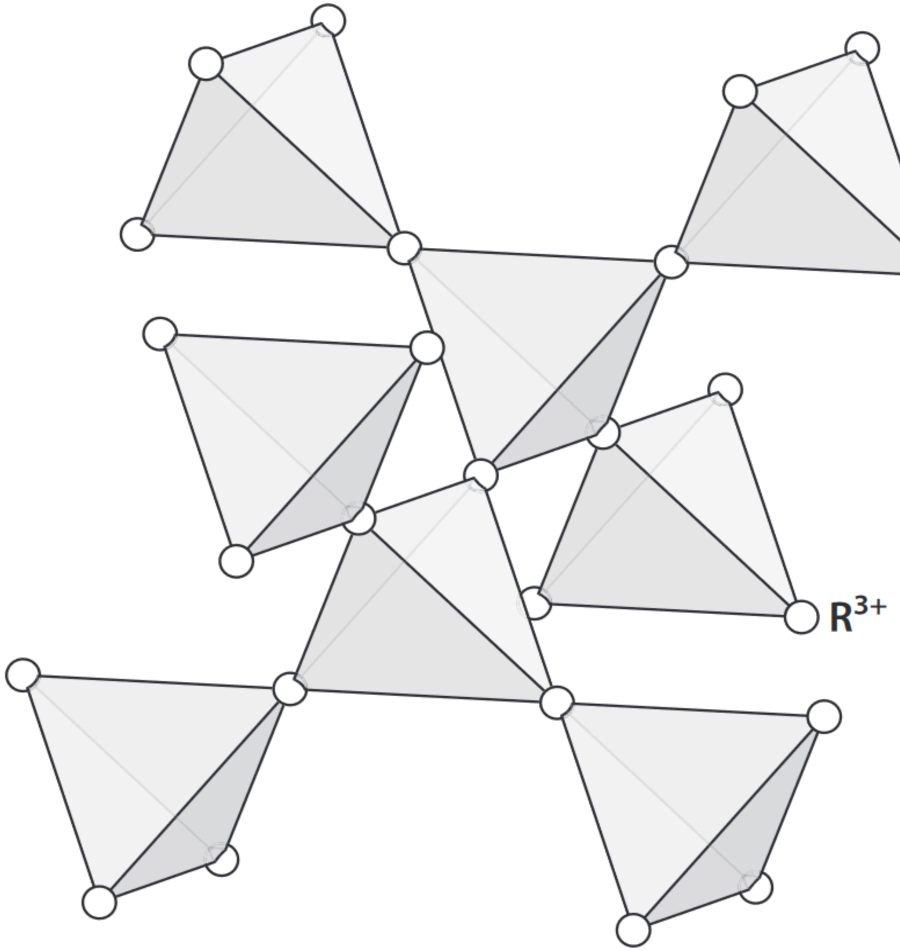
2. What is **disorder**?

3. How can ~~**disorder**~~ ***entropy*** lead to **order**?

Answer:

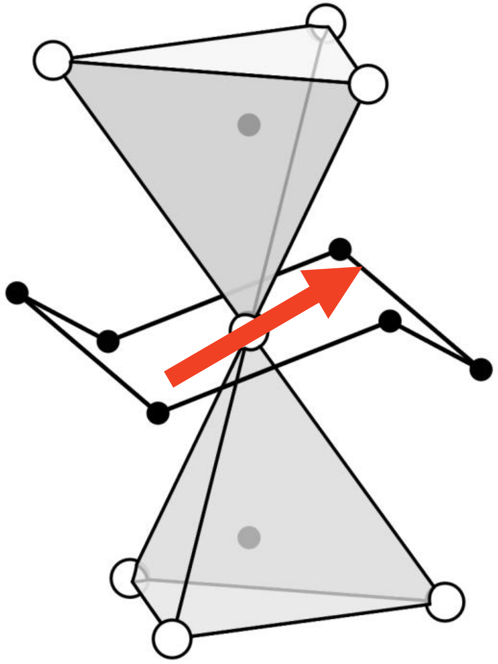
If the energies are all **the same**, it is left to the **entropy** to decide which state is preferred

Erbium Titanate



Chemical formula: ***$Er_2Ti_2O_7$***

- Magnetic ion is a trivalent **Erbium** (rare-earth)
- Forms *three-dimensional* **pyrochlore lattice**
  - *Network of corner-sharing tetrahedra*



Each atom has a ***spin****, pointing in some direction*

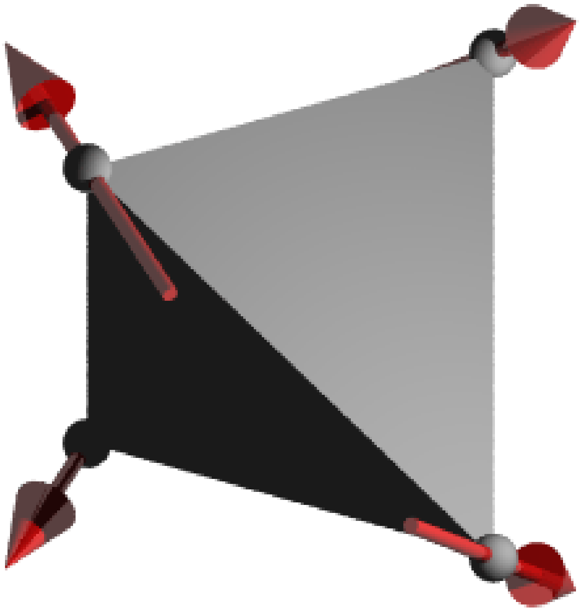
For a review, see: Rev. Mod. Phys. ***82****, 53 (2010)*

Minimum energy states?

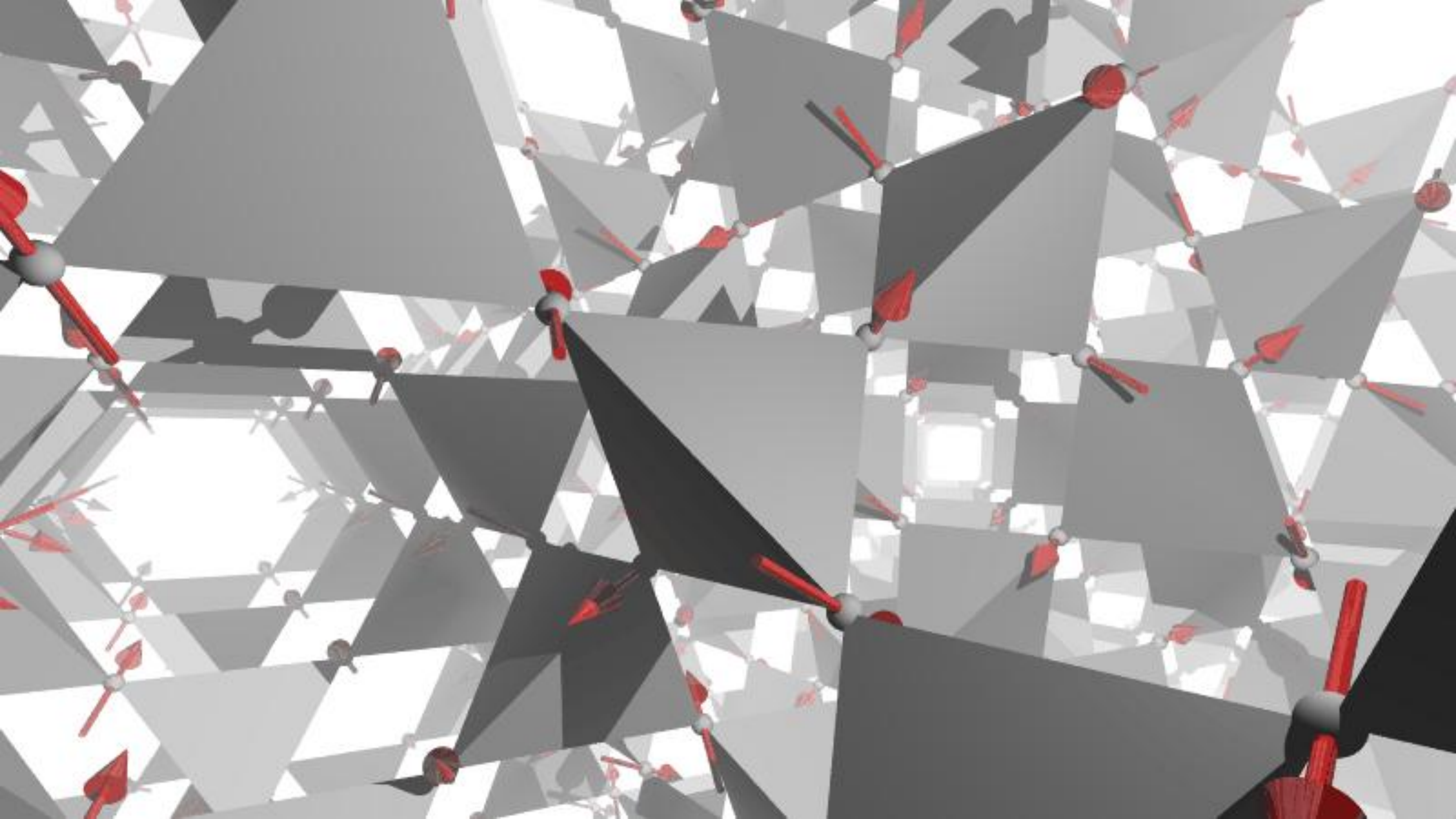
- Energy of different arrangements of spins is **complicated**

- Minimum has each tetrahedron with *same* spin configuration

- Spins can be **rotated together in their planes** at no (classical) cost

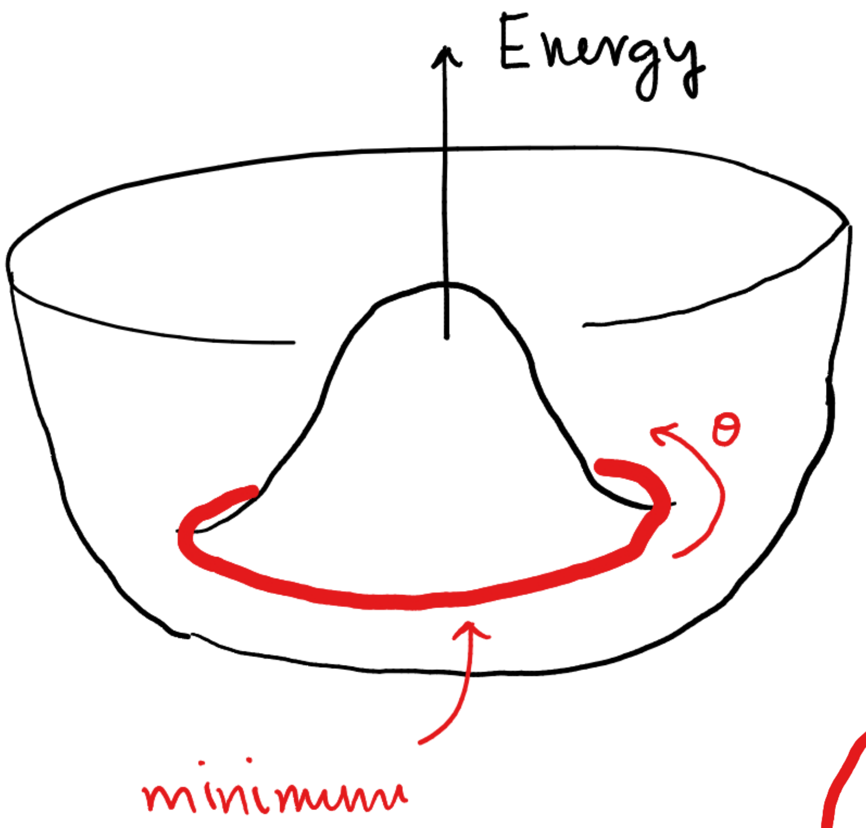


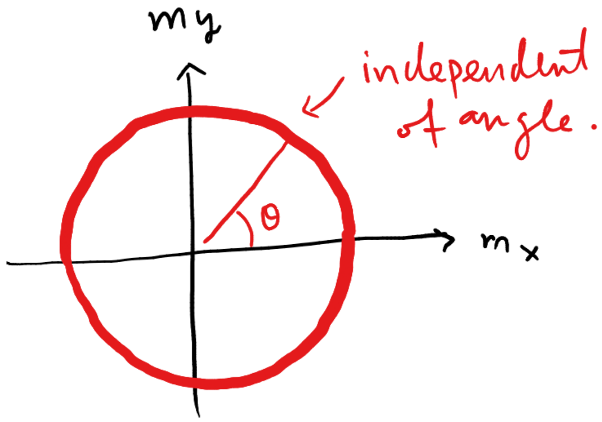
State with minimum energy isn't unique



When energy is not enough …

- We have a system where there are **many states with the same energy …**



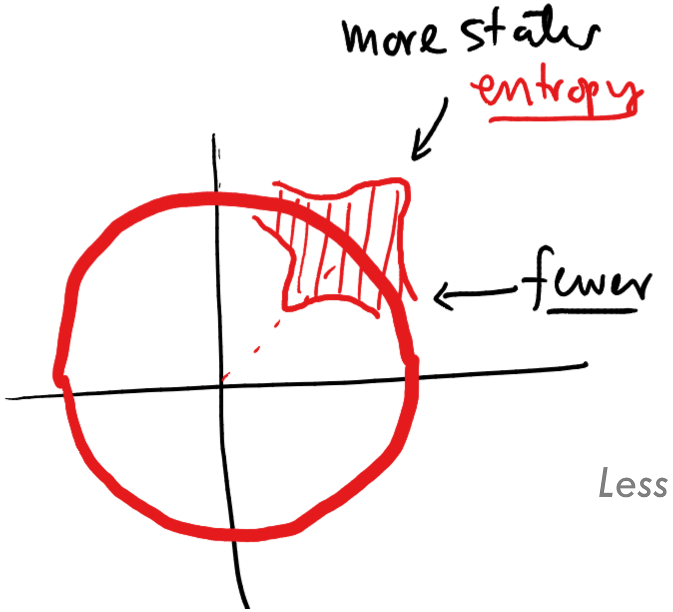


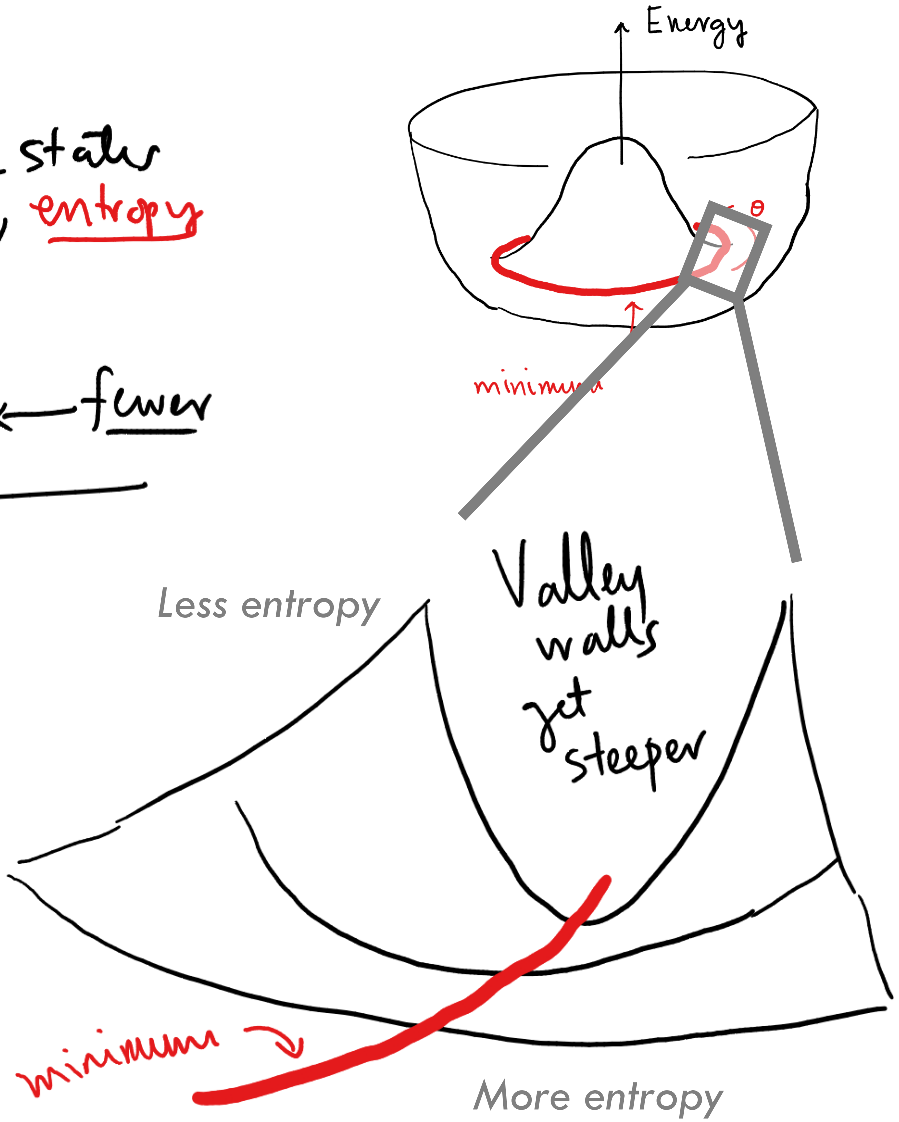
Which state does it pick?

Answer: None!

What about the entropy?

- Even though the energy is the same, the **entropy might does not have to be**
- Look at how many states there are **just off the minimum**
- Regions with **higher entropies** are chosen!





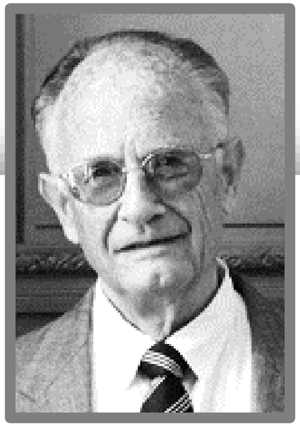
Order *by* Disorder

So what happened?

- Without entropy: **No order**
- With entropy: **Order**

- Not limited to only *thermal* disorder

***Any* kind of fluctuations can serve same purpose!**



Jacques Villain (1934-2022)

J. Physique **41** (1980) 1263-1272

Classification
Physics Abstracts
75.10H

Order as an effect of disorder

J. Villain (*), R. Bidaux, J.-P. Carton and R. Conte

DPh-G/PSRM, CEN de Saclay, B.P. Nº 2, 91190 Gif-s/Yvette, France

(*Reçu le 9 avril 1980, révisé le 3 juillet, accepté le 11 juillet 1980*)

Résumé. — On considère un modèle d'Ising frustré généralisé sur un réseau bidim
magnétique à température nulle mais ferromagnétique pourvu que $0 < T < T_c$.
la dilution sur ce système, et l'on montre que l'ordre à longue distance est rétabli dan
conditions de concentration, température et interactions qui sont discutées en co
usuelle.

Abstract. — A generalized frustrated Ising model on a two-dimensional lattice is c
magnetic at zero temperature but ferromagnetic provided $0 < T < T_c$. The effec
also investigated, and long range order is shown to be restored in the dilute model un
concentration, temperature and interactions which are discussed in comparison w

Quantum Fluctuations?

Heisenberg's Uncertainty Principle

Fluctuation in momentum

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

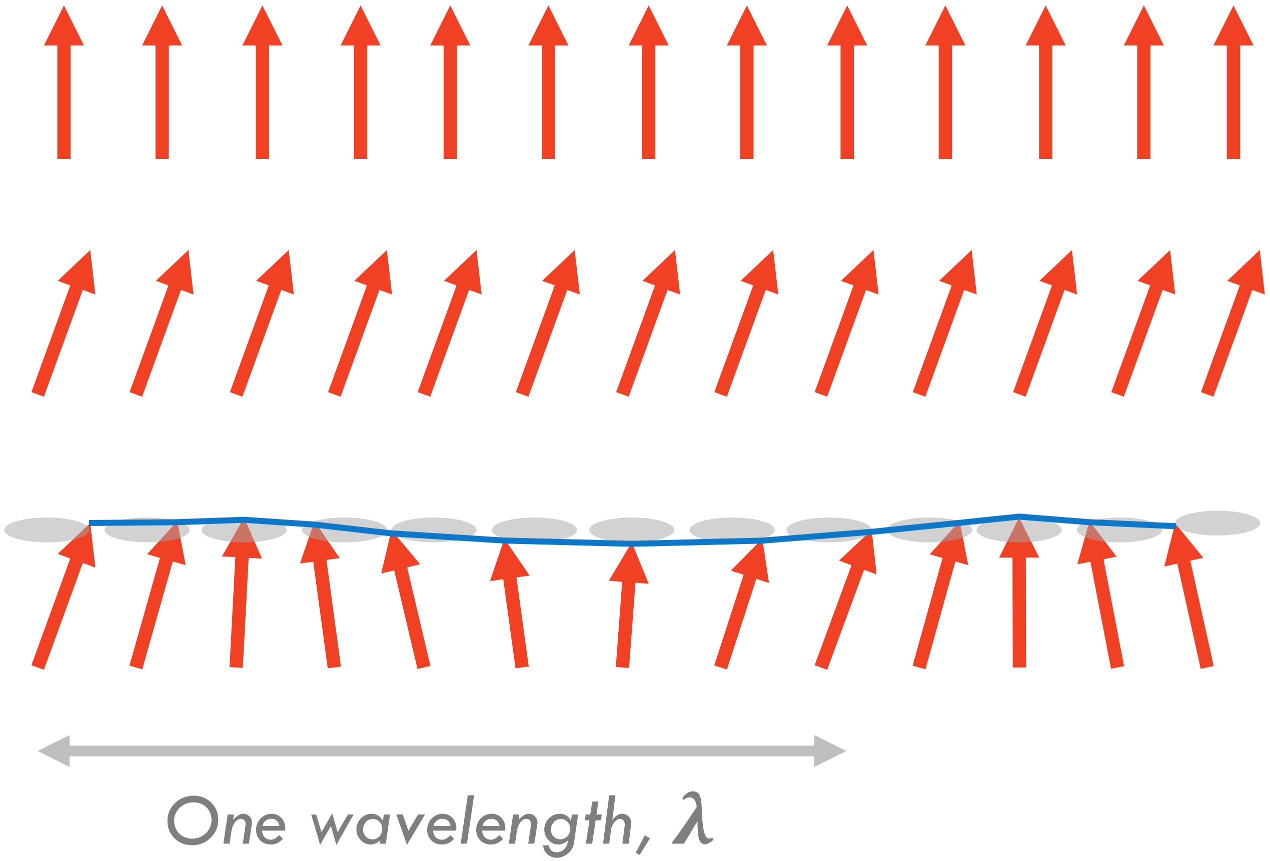
Planck's Constant (reduced)

Fluctuation in position

*Cannot have **no fluctuations**; one of x or p must be fluctuating*

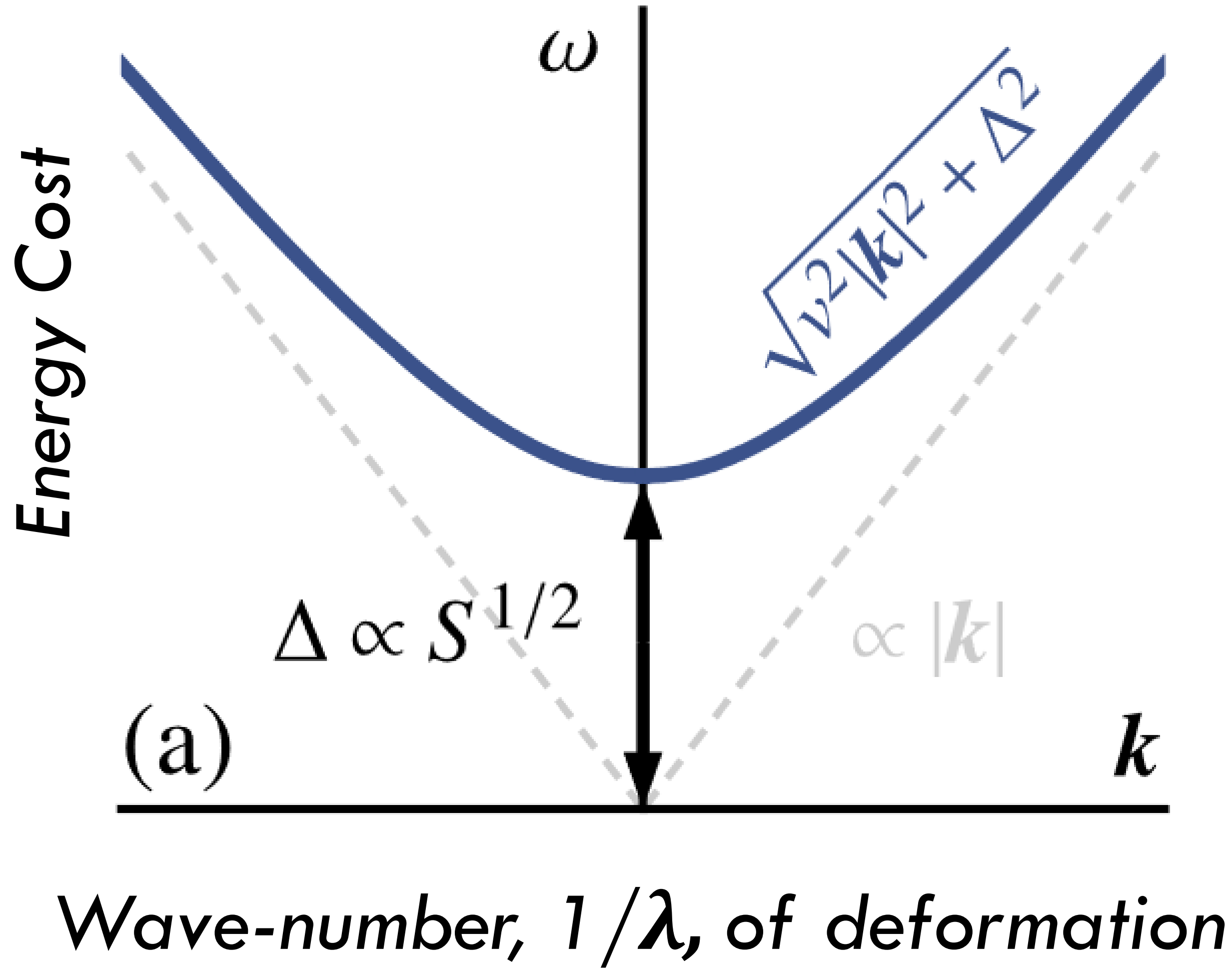
- Order by *thermal* disorder needs finite temperature
- Even at **zero temperature** a system can fluctuate due to **quantum mechanics**
- Preference? ***More fluctuations!***

How do we detect it?



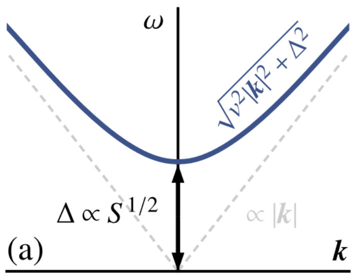
- *Without fluctuations* we have states at the **same energy**
- No cost to change all at once
- **Small** cost for change over long distances – **"Goldstone mode"**

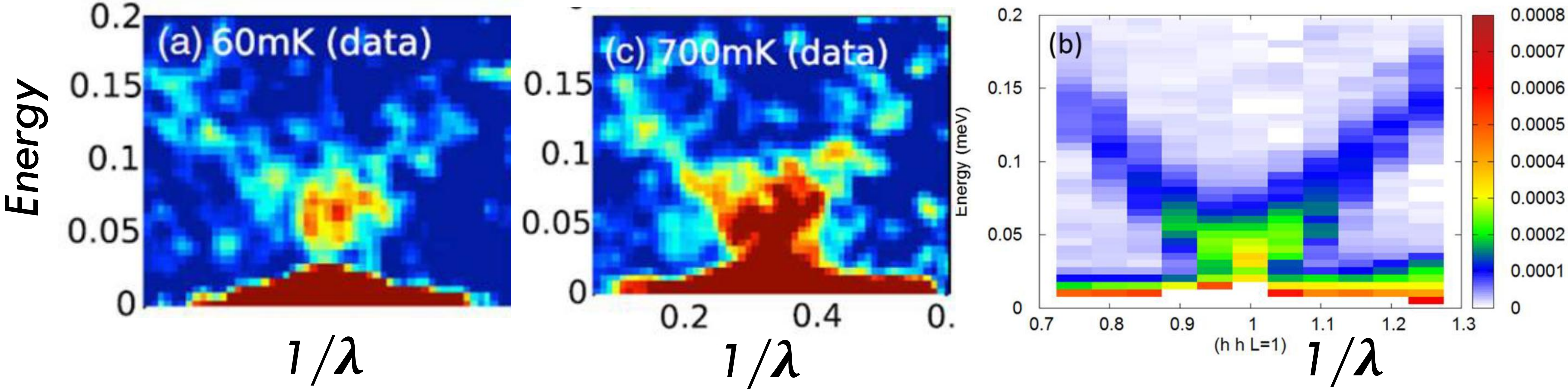
Pseudo-Goldstone Modes



- Well defined relationship between **wavelength or wavenumber** and **energy cost**
- Called a **"dispersion relation"**
- *Experimentally observable*

Measurement of Gap





- There is a **gap**!
  - *Measured independently by two experimental groups*
- *Is it what we expect from quantum fluctuations?*

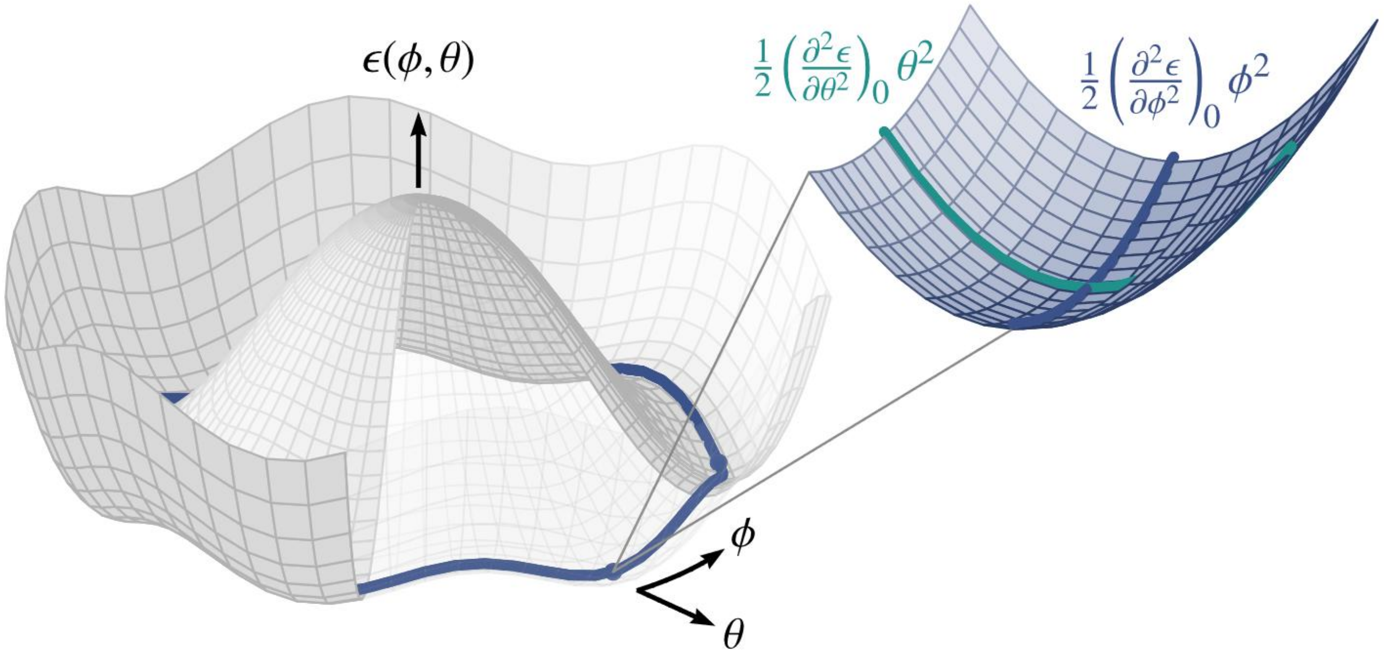
Gap is roughly ~0.04 - 0.05 meV

Ross et al, Phys. Rev. Lett. (2014); Petit et al, Phys. Rev. B (2014)

How to compute the gap?

- Can relate it **directly to curvatures of "fluctuation free energy"**

  (Proof somewhat involved)



$$\Delta = \frac{1}{S}\sqrt{\left(\frac{\partial^2\epsilon}{\partial\theta^2}\right)_0\left(\frac{\partial^2\epsilon}{\partial\phi^2}\right)_0 - \left(\frac{\partial^2\epsilon}{\partial\theta\partial\phi}\right)_0^2},$$

Pseudo-Goldstone Gap

Derivatives of "fluctuation free energy"

*This formula works for thermal ObD **and** quantum ObD*

***J. G. Rau** et al, Phys. Rev. Lett. (2018); Rau et al, unpublished (2022)*

$Er_2Ti_2O_7$ [61,67,68]	Savary *et al.* [61]	I	31.1 μeV	43 – 53 μeV [82,83]

Theoretical Value

Experimental Value

TABLE I. Calculations showing the equality of the pseudo-Goldstone gap, Δ, computed from nonlinear spin-wave theory [Eqs. (5) and (6)] and then independently from the curvatures of the classical and quantum zero-point energies [Eq. (1)]. For each model, the lattice, the exchange regime, the type of pseudo-Goldstone mode, and several choice of parameters are listed. When available, additional theoretical or experimental estimates of the pseudo-Goldstone gap are shown.

Model or material	Parameters	Type	Δ	$[(\partial^2\epsilon/\partial\theta^2)]_0$	$[(\partial^2\epsilon/\partial\phi^2)]_0$	$S^{-1}\sqrt{[(\partial^2\epsilon/\partial\theta^2)]_0[(\partial^2\epsilon/\partial\phi^2)]_0}$	$S=\frac{1}{2}$/Exp.
Heisenberg-compass (Square, Ferromagnet)	$\lvert K\rvert/\lvert J\rvert \ll 1$	I	$0.52S^{\frac{1}{2}}\lvert K\rvert^{\frac{3}{2}}/\lvert J\rvert^{\frac{1}{2}}$	$2\lvert K\rvert S^2$	$0.137K^2S/\lvert J\rvert$	$0.52S^{\frac{1}{2}}\lvert K\rvert^{\frac{3}{2}}/\lvert J\rvert^{\frac{1}{2}}$	
	$K/\lvert J\rvert = -0.5$	I	$0.17\lvert J\rvert S^{\frac{1}{2}}$	$\lvert J\rvert S^2$	$0.0286\lvert J\rvert S$	$0.17\lvert J\rvert S^{\frac{1}{2}}$	
Heisenberg-compass [16] (Cubic, Ferromagnet)	$\lvert K\rvert/\lvert J\rvert \ll 1$	II	$0.093K^2/\lvert J\rvert$	$0.093K^2S/\lvert J\rvert$	$0.093K^2S/\lvert J\rvert$	$0.093K^2/\lvert J\rvert$	
	$K/\lvert J\rvert = +0.5$	II	$0.030\lvert J\rvert$	$0.030\lvert J\rvert S$	$0.030\lvert J\rvert S$	$0.030\lvert J\rvert$	
	$K/\lvert J\rvert = -0.5$	II	$0.024\lvert J\rvert$	$0.024\lvert J\rvert S$	$0.024\lvert J\rvert S$	$0.024\lvert J\rvert$	
Heisenberg-Kitaev [60] (Honeycomb, Ferromagnet)	$\lvert K\rvert \ll \lvert J\rvert$	II	$0.0897K^2/\lvert J\rvert$	$0.0897K^2S/\lvert J\rvert$	$0.0897K^2S/\lvert J\rvert$	$0.0897K^2/\lvert J\rvert$	
	$K/\lvert J\rvert = -2.0$	II	$0.208\lvert J\rvert$	$0.208\lvert J\rvert S$	$0.208\lvert J\rvert S$	$0.208\lvert J\rvert$	
	$K/\lvert J\rvert = -0.65$	II	$0.03\lvert J\rvert$	$0.0300\lvert J\rvert S$	$0.0300\lvert J\rvert S$	$0.0300\lvert J\rvert$	$\sim 0.05\lvert J\rvert$ [80]
Heisenberg-Kitaev [60] (Honeycomb, Néel)	$\lvert K\rvert \ll J$	I + I	$0.83\lvert K\rvert S^{\frac{1}{2}}$	$2(3J+K)S^2$	$0.115K^2S/J$	$0.83\lvert K\rvert S^{\frac{1}{2}}$	
	$K/J = +2.0$	I + I	$1.66JS^{\frac{1}{2}}$	$10JS^2$	$0.274JS$	$1.66JS^{\frac{1}{2}}$	
	$K/J = -0.5$	I + I	$0.434JS^{\frac{1}{2}}$	$5JS^2$	$0.038JS$	$0.434JS^{\frac{1}{2}}$	
Heisenberg-Γ [62] (Honeycomb, Ferromagnet)	$\Gamma \ll \lvert J\rvert$	I	$0.29\Gamma^2/\lvert J\rvert\, S^{\frac{1}{2}}$	$3\Gamma S^2$	$0.028\Gamma^3S/\lvert J\rvert^2$	$0.29\Gamma^2/\lvert J\rvert S^{\frac{1}{2}}$	
	$\Gamma/\lvert J\rvert = +0.5$	I	$0.081\lvert J\rvert S^{\frac{1}{2}}$	$1.5\lvert J\rvert S^2$	$0.00437\lvert J\rvert S$	$0.081\lvert J\rvert S^{\frac{1}{2}}$	
	$\Gamma/\lvert J\rvert = +1.0$	I	$0.355\lvert J\rvert S^{\frac{1}{2}}$	$3\lvert J\rvert S^2$	$0.042\lvert J\rvert S$	$0.355\lvert J\rvert S^{\frac{1}{2}}$	
$J_1 - J_2$ [7,11,13] (Square, stripe)	$J_1/J_2 \ll 1$	I + I	$1.44J_1S^{\frac{1}{2}}$	$4(2J_2 - J_1)S^2$	$0.2604J_1^2S/J_2$	$1.44J_1S^{\frac{1}{2}}$	
	$J_1/J_2 = 0.5$	I + I	$0.63J_2S^{\frac{1}{2}}$	$6J_2S^2$	$0.0668J_2S$	$0.63J_2S^{\frac{1}{2}}$	$0.61J_2S^{\frac{1}{2}}$ [81]
	$J_1/J_2 = 1$	I + I	$1.08J_2S^{\frac{1}{2}}$	$4J_2S^2$	$0.294J_2S$	$1.08J_2S^{\frac{1}{2}}$	$0.96J_2S^{\frac{1}{2}}$ [81]
$J_1 - J_2$ [13,14] (Triangular, stripe)	$J_2/J_1 = 0.25$	II + II	$0.53J_1$	$0.53J_1S$	$0.53J_1S$	$0.53J_1$	
	$J_2/J_1 = 0.5$	II + II	$0.45J_1$	$0.45J_1S$	$0.45J_1S$	$0.45J_1$	
	$J_2/J_1 = 0.75$	II + II	$0.58J_1$	$0.58J_1S$	$0.58J_1S$	$0.58J_1$	
$Er_2Ti_2O_7$ [61,67,68]	Savary *et al.* [61]	I	31.1 μeV	157.5 μeV	1.536 μeV	31.1 μeV	43 – 53 μeV [82,83]
$Ca_3Fe_2Ge_3O_{12}$ [8,65]	Bruecker *et al.* [65]	I + I	262 μeV	4 meV	107.5 μeV	262 μeV	136 μeV [65]

- Theoretical value is of **right order of magnitude**
- **Quantitative?** Off by 30%-50%
- **How to improve?** Better model/energy, better experiment …

Summary & Conclusions

- **Order and disorder are fundamental in physics**
  - Long-range order characterizes many phases of matter
  - Entropy counts the number of states compatible with macroscopic properties
  - At finite temperature, entropy and energy compete
- **Lots to explore!**
  - Better understanding of the variety of forms of order by disorder in **real materials**
  - **Frustration:** States with **low-energy, but high entropy.** What happens when we include fluctuations?

Thank you for your attention

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