The Partition Function for a Lattice Gas

Link: https://www.youtube.com/watch?v=-LGHCcr6LOM

AMA4004: Statistical mechanics

Make microscopic description in terms of position & momentum of all the individual atoms & molecules in our system with the macroscopic extensive Thermodynamic variable

Model Systems I: Lattice Gases

The canonical ensemble

(NVT) Canonical ensemble

Probability of being in a microstate

$$P_j = \frac{e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}}{e^{\Psi}} \qquad \beta = \frac{1}{k_B T}$$

Partition Function

$$Z = e^{\Psi} = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

Calculating macroscopic quantities

Helmholtz free energy $F = -k_B T \ln Z_c$

$$\boxed{\langle E \rangle = -\frac{\partial \psi}{\partial \beta}}$$

An analytical way to calculate the ensemble average

Heat capacity can be calculated from average fluctuations

$$\boxed{C_v = \frac{1}{k_B T^2} \langle (H - \langle E \rangle)^2 \rangle}$$

Must be positive

The importance of the partition function:

0) The probability of being each of the micro-states is given by the partition function.

1) The thermodynamic potential and various ensemble averages can be calculated from this quantity directly. In addition, we can also derive the equation of state for the system by taking appropriate partial derivatives.

2) Statistical mechanics related the heat capacity to a second derivative of the partition function and this second derivative is related to the fluctuations in the energy. Thus we can see that the probabilistic formalism of statistical mechanics is fully consistent with 2nd law of thermodynamics

What we now need to do

We need to learn how to use this with model systems. In other words we need to calculate the partition function for various model Hamiltonians

$$Z = e^{\Psi} = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

Here we will study how to apply the statistical mechanics to model Hamiltonians. This will allow us to make a connection between what we have observed for macroscopic systems and the inter- and intra-molecular forces that act on the constituent particles from which these macroscopic systems are composed.

What model Hamiltonians do we look at

	particles on a lattice	independent particles
non-interacting particles		
Interacting particles		

Hamiltonian for Independent spins on a lattice in a magnetic field

M: Magnetic dipole moment of a single spin

Magnetic field strength H (same as 'h' in the right)

$$E = -\sum_{i=1}^{n} s_i \mu H$$

These are the 2 parameters.

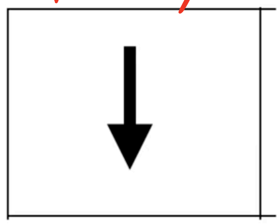
The Hamiltonian used here is frequently used to model spins interacting with an applied magnetic field.

Although in the beginning, we assumed the system is a canonical ensemble, but we are not really studying here a system with a constant volume. In fact, only the number of particles and the temperature are constant as it makes little sense to talk about volume of this particular system of magnetic spins. What we are really doing is operating in a NhT ensemble, where the magnetic field strength h is fixed and the magnetic field strength plays the role of the volume. In this sense, it is also often referred as canonical ensemble.

Hamiltonian for Independent spins on a lattice in a magnetic field

The only term that depends on the particular microstate of the system

$$E = -\sum_{i=1}^{n} s_i \mu H$$



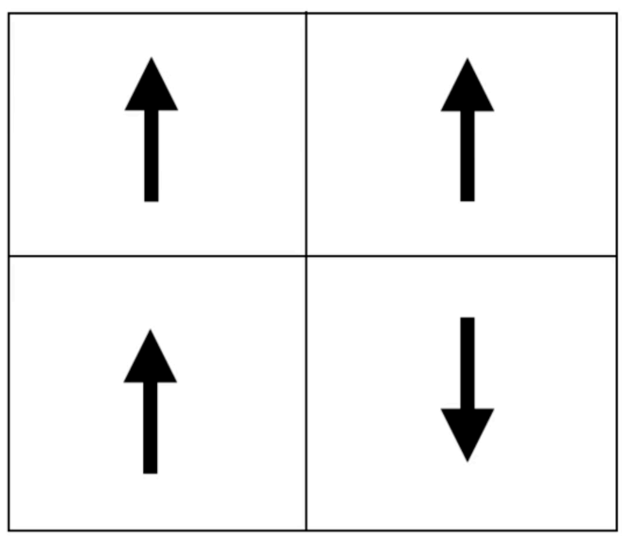
Each spin
has two states
spin-down (-1) and
spin-up (+1)

Each of the *Si* term tells us whether a particular spin is aligned against the magnetic field or with the magnetic field.

Hamiltonian for Independent spins on a lattice in a magnetic field

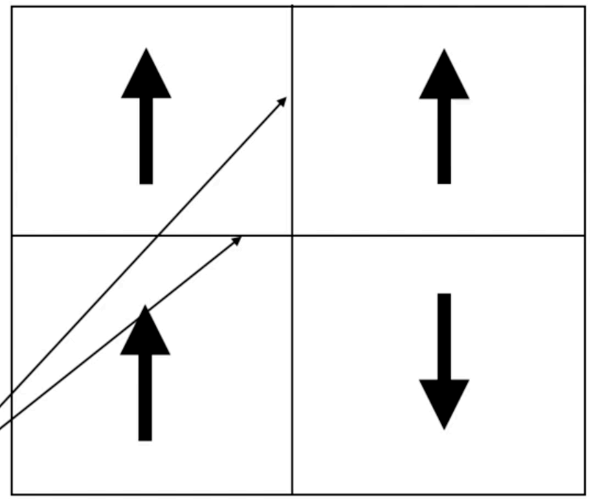
$$E = -\sum_{i=1}^{n} s_i \mu H$$

We have multiple
spins. Hence
the sum



Hamiltonian for Independent spins on a lattice in a magnetic field

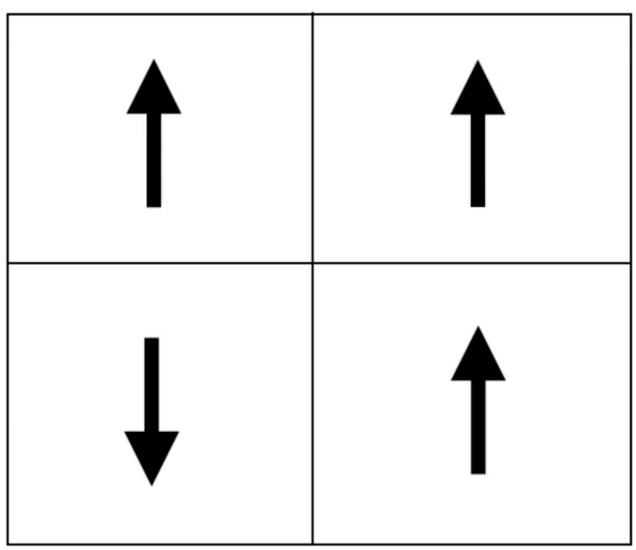
$$E = -\sum_{i=1}^{n} s_i \mu H$$



spins **do not** interact. Only one spin value in each term in sum

Hamiltonian for Independent spins on a lattice in a magnetic field

$$E = -\sum_{i=1}^{n} s_i \mu H$$



The microstate we are in changes when any spin is flipped

Enumerating all microstates

$$Z = e^{\Psi} = \sum_{j} e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

up down

1 spin: u or d 2 microstates $\sum_{s_1=0}^{1}$

2 spins: uu, ud, du or dd

3 spins:

Different because the down spin is on a different lattice site

Enumerating all microstates

枚举

$$Z = e^{\Psi} = \sum_{j} e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

1 spin: u or d 2 microstates $\sum_{s_1=0}^{1}$

2 spins: uu, ud, du or dd 4 microstates $\sum_{s_1=0}^{1}\sum_{s_2=0}^{1}$

3 spins: uuu, uud, udd, udu, ddu, ddu, dud, ddd 8 microstates $\sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\sum_{s_3=0}^{1}$

n spins: 2^n microstates $\sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_n=0}^{1}$

Bringing it all together

$$\sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_n=0}^{1}$$

$$E = -\sum_{i=1}^{n} s_i \mu H$$

magnetic field

Hamiltonian

$$Z = e^{\Psi} = \sum_j e^{-\beta H(\mathbf{x}_j, \mathbf{p}_j)}$$

s_i could be only 0 or 1.

$$z(x) = \begin{cases} -1 & \text{if} \quad x = 0 \\ +1 & \text{if} \quad x = 1 \\ 0 & \text{otherwise} \end{cases}$$

$$Z = \sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_n=0}^{1} \exp\left(\beta \sum_{i=1}^{n} z(s_i)\mu H\right)$$

Bringing it all together II

$$Z = \sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_n=0}^{1} \exp\left(\beta \sum_{i=1}^{n} z(s_i)\mu H\right)$$

$$Z = \sum_{s_1=0}^{1}\sum_{s_2=0}^{1}\cdots\sum_{s_n=0}^{1} \prod_{i=1}^{n} \exp\left(\beta\, z(s_i)\mu H\right)$$

$$Z = \sum_{s_1=0}^{1} e^{\beta\mu H z(s_1)} \sum_{s_2=0}^{1} e^{\beta\mu H z(s_2)} \cdots \sum_{s_n=0}^{1} e^{\beta\mu H z(s_n)}$$

See next slides.

→ Note that each of the summations are identical!

Bringing it all together II

$$Z = \sum_{s_1=0}^{1} \sum_{s_2=0}^{1} \cdots \sum_{s_n=0}^{1} \exp\left(\beta \sum_{i=1}^{n} z(s_i)\mu H \right)$$

$$Z = \sum_{s_1=0}^{1} \sum_{s_2=0}^{1} \cdots \sum_{s_n=0}^{1} \prod_{i=1}^{n} \exp\left(\beta \; z(s_i)\mu H \right)$$

$$Z = \left[\sum_{s_1=0}^{1} e^{\beta\mu H z(s_1)}\right]^n = \left[e^{+\beta\mu H} + e^{-\beta\mu H}\right]^n$$

$$\Downarrow$$

$$Z = 2^N \cosh^N(\beta\mu H)$$

The average energy

$$Z = 2^N \cosh^N(\beta\mu H)$$

$$\boxed{\langle E \rangle = -\frac{\partial \psi}{\partial \beta}}$$

$$Z = e^{\psi} \quad \Longrightarrow \quad \psi = \ln Z$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta}\left\{\cancelto{0}{N \ln 2} + N \ln\left[\cosh\left(\beta\mu H\right)\right]\right\}$$

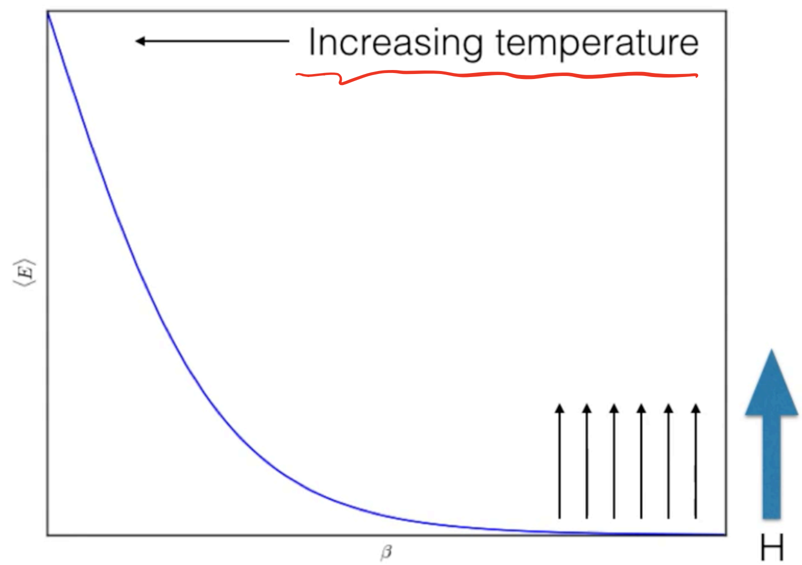
It's a constant, so its derivative is 0.

$$\langle E \rangle = -\frac{N\mu H \sinh(\beta\mu H)}{\cosh(\beta\mu H)} = -N\mu H \tanh(\beta\mu H)$$

For this system, the equation of spin state will be an expression that allows one to calculate analytically the average magnetization of the system from the temperature and the applied magnetic field.

The average energy

$$E = -\sum_{i=1}^{n} s_i \mu H \quad \langle E \rangle = -N\mu H \tanh(\beta\mu H)$$



$\beta = \frac{1}{k_B T}$

The average energy

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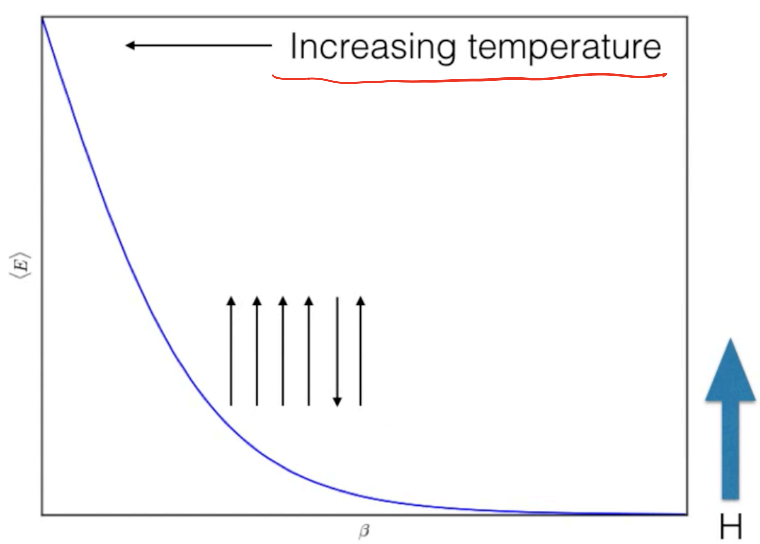
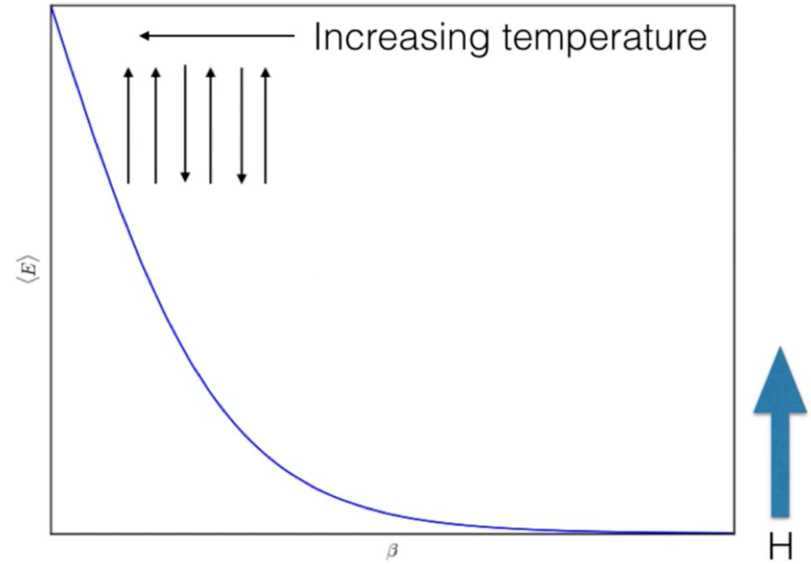
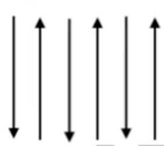


The average energy

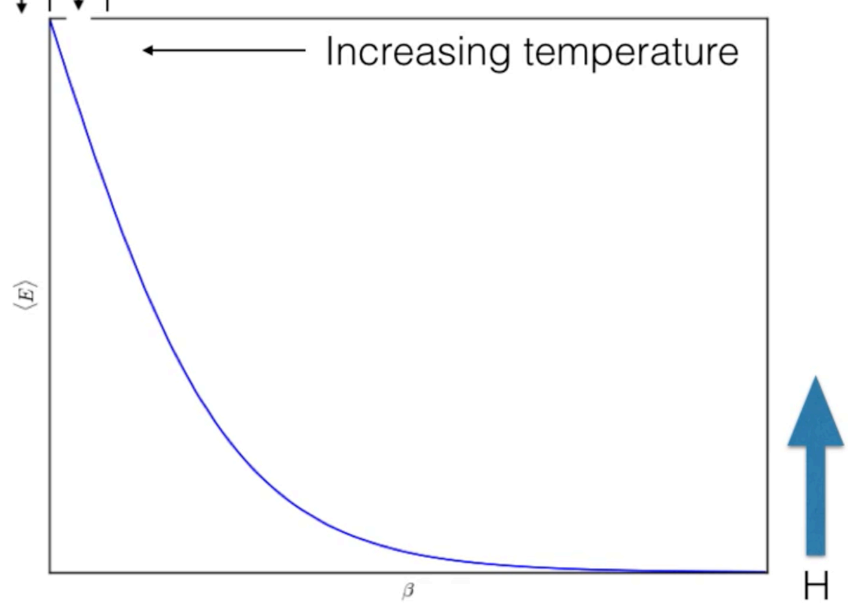
$$E = -\sum_{i=1}^{n} s_i \mu H \qquad \langle E \rangle = -N\mu H \tanh(\beta \mu H)$$



The average energy



$$E = -\sum_{i=1}^{n} s_i \mu H \qquad \langle E \rangle = -N\mu H \tanh(\beta \mu H)$$



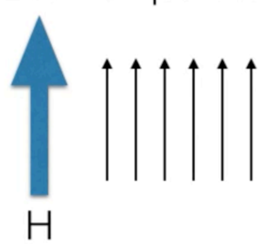
In conclusion

We studied a system composed of non-interacting spins sitting on a lattice and interacting with a magnetic field

$$Z = 2^N \cosh^N(\beta\mu H)$$

$$\langle E \rangle = -N\mu H \tanh(\beta\mu H)$$

Low temperature



High temperature