Chapter 1

Role of the models in statistical mechanics

1.1 Role of the models

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Which is the role of models in statistical mechanics? There are two possible approaches:

1. The model must describe the real system in a very detailed way. The maximum number of details and parameters to be tuned are included. The *pro* is the closer to the real specific system (faithfull description). The *drawback* is that the model is so complicated that no analytical solution is possible. Moreover, even numerically, these models can be studied for very short times and small sizes. An example is the simulation of the folding dynamics that can be performed for few nanoseconds. On the other hand the introduction of many details are often not crucial if one is interested in large scale properties.

2. Try to introduce the most simple model that satisfies few essential properties of the real system such as its symmetries, dimensionality, range of interactions etc. Since most of the microscopic details are integrated, these models cannote describe the full physics of a specific system but they can reproduce its main features. Moreover these models can be studied numerically and, to some extent also analitically (exact solution).

Let us start by introducing what is, perhaps, the most paradigmatic model in the statistical mechanics of p hase transition, the *Ising model*.

1.2 Ising model (1925)

Suggested by Lenz to Ising for his Phd thesis, it is supposed to describe a magnetic system that undergoes a transition between a pramagnetic and a ferromagnetic phase. In $d = 1$ the model was solved exactly by Ising. Unfortunately, he found that for $T > 0$ the model does not display a phase transition. The wrong conclusion was that this model is not able to describe a phase transition. In fact, it turns out that, for $d > 1$, the model does display a paramagnetic-ferromagnetic phase transition. Let us first discuss some general feature of the model for any dimension d.

1.2.1 D-dimensional Ising model

For hypercubic lattice with given $N(\Omega)$ sites $\{i\}_{i=1,\dots,N(\Omega)}$ and linear size $L(\Omega)$, we have $N(\Omega) = L^D$. The microscopic degrees of freedom are the spins S_i defined at each i-esim lattice site. Each spin can assume the values $S_i = \pm 1$, that means that at each site the possible values are the spin up or down. The minimal model that can try to capture the interaction between the spin is the following.

For a lattice with $N(\Omega)$ spins, there are $2^{N(\Omega)}$ possible configurations.

Remark. Since we do not consider the spin as a vector, this is a model for a strongly anysotropic ferromagnet (along a given direction).

Suppose to have also an external magnetic field H_i (it values depends on the site i). One can consider interactions between spins whose strength are described by functions $J_{ij}, k_{ijk}, \dots$. For instance, there is a coupling that derives from electrons coupling $J_{ij} = f(|\vec{\mathbf{r_i}} - \vec{\mathbf{r_j}}|)$

The physical origin is the overlap between the electronic orbitals of the neighbouring atoms forming the Bravais lattice. Remember that a term as $\sum_i S_i$ is not correlated, while we need an interaction.

A general Hamiltonian of the model can be written as

$$\mathcal{H}_\Omega(\{S_i\}) = \sum_{ij} J_{ij} S_i S_j - \sum_i H_i S_i - \sum_{ijk} S_i S_j S_k + \dots \tag{1.1}$$

Standard Ising model one keeps only the two-body interactions:

$$\mathcal{H}_\Omega(\{S_i\}) = -\frac{1}{2} \sum_{i \neq j}^{N} J_{ij} S_i S_j - \sum_{i=1}^{N} H_i S_i \tag{1.2}$$

where the first second is a one body interaction, while in the first term we consider the two body interaction that is a quadratic term. We have put the minus because we want to minimize the energy, but it dipends on the sign of J.

For this model the sum over all configurations on trace is given by

$$\mathrm{Tr} \equiv \sum_{S_1=\pm} \sum_{S_2=\pm} \cdots \sum_{S_N=\pm} \equiv \sum_{\{S\}} \tag{1.3}$$

Our problem is to find the partition function with N sites, which depends on T and in principle depends in the configuration given (it is fixed both for H and J!). Hence the canonical partition function is given by

$$Z_\Omega(T, \{H_i\}, \{J_{ij}\}) = \mathrm{Tr}\, e^{-\beta \mathcal{H}_\Omega(\{S\})} \tag{1.4}$$

and the corresponding free-energy

$$F_\Omega(T, \{H_i\}, \{J_{ij}\}) = -k_B T \ln Z_\Omega \tag{1.5}$$

The bulk limiting free energy is

$$f_b(T, \{H_i\}, \{J_{ij}\}) = \lim_{N \to \infty} \ln \frac{1}{N} F_\Omega \tag{1.6}$$

How do we know that the above limit does exist? It must be proven. The surface is not important in the bulk limit. Note that we are assuming that the interaction between the spin is a short range force, it is not as the size of the system.

For this model it is possible to show that the limit exists if

$$\sum_{j \neq i} |J_{ij}| < \infty \tag{1.7}$$

Remark. In general what determines the existence of the limit of these spin models are the dimension D and the range of the spins interactions.

For example it is possible to show that, if

$$J_{ij} = A|\vec{\mathbf{r_i}} - \vec{\mathbf{r_j}}|^{-\sigma} \tag{1.8}$$

(so it is a long range interaction) the limit exists when

$$\sigma > D \tag{1.9}$$

Remark. If the interaction is *dipolar* since it decades as $1/r^3$, for the case $d = 3$ the limit does not exists. However it is still possible to prove the existence of the limit for this case if one assumes that not all dipoles are fully aligned.

Assuming that the thermodynamic limit exists we now look at some additional rigorous results on the limiting free energy and its derivatives.

1.2.2 Mathematical properties of the Ising model with neirest neighbours interactions

For simplicity let us consider the case in which the external magnetic field is homogeneous i.e. $H_i \equiv H$ and the spin-spin interaction is only between spins that are nearest-neighbours on the lattice:

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are neirest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{1.10}$$

The model is nowe very simple:

$$-\mathcal{H}_\Omega(\{S\}) = J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + H \sum_i^{N(\Omega)} S_i \tag{1.11}$$

where the notation $\langle ij \rangle$ means a double sum over i and j, with the constraint that i and j are nearest-neighboyrs. Since H is uniform, the average magnetization per spin is

$$\langle m \rangle = \frac{1}{N(\Omega)} \sum_{i=1}^{N(\Omega)} \langle S_i \rangle \tag{1.12}$$

where $\langle \dots \rangle$ means average over the chosen ensemble. Since

$$\sum_{i=1}^{N} \langle S_i \rangle = \frac{1}{Z} \operatorname{Tr} \left[(\sum_i S_i) e^{-\beta \mathcal{H}_\Omega(\{S_i\})} \right] = \frac{1}{Z} \operatorname{Tr} \left[\sum_i S_i \exp\left(\beta J \sum_{\langle ij \rangle} S_i S_j + \beta H \sum_i S_i \right) \right] \tag{1.13}$$

it is easy to show that:

$$\langle m \rangle = -\frac{1}{N} \frac{\partial F_\Omega}{\partial H} \tag{1.14}$$

where

$$F_\Omega(T, J, H) = -k_B T \ln Z_N(T, J, H) \tag{1.15}$$

1.3 Ising Model

We have to figure out that if we look at the magnetization per site:
with

$$\sum_i \langle S_i \rangle = \frac{1}{Z} \operatorname{Tr}\left[(\sum_i S_i) e^{-\beta H} \right] \tag{1.16}$$

We have again a connection between the free energy and the magnetization (?). Now, suppose that $f_b < 0$, and f_b is continuous function of T,J,H.

$$s = -\frac{\partial f_b}{\partial T} \geq 0 \tag{1.17}$$

with $\frac{\partial f_b}{\partial T}$ monotone non increasing function of T, that means $\frac{\partial^2 f_b}{\partial T^2} \leq 0$ and therefore

$$\Rightarrow c = -T\left(\frac{\partial^2 f_b}{\partial T^2}\right) \geq 0 \tag{1.18}$$

Theorem 1.3.1. *$f_b(T, H, J)$ is a concave function of* H.

Proof. To proof this we use the *Holden inequality.* If $\{g_k\}, \{f_k\} \geq 0 \quad \forall k$ and $\alpha_1, \alpha_2 \in \mathbb{R}^+$ with $\alpha_1 + \alpha_2 = 1$.

$$\sum_k (g_k)^{\alpha_1} (f_k)^{\alpha_2} \leq \left(\sum_k g_k\right)^{\alpha_1} \left(\sum_k f_k\right)^{\alpha_2} \tag{1.19}$$

□

The partiction function is:

$$Z_N(H) = \operatorname{Tr}\left[\exp\left(\beta H \sum_i S_i\right) \underbrace{\exp\left(\beta J \sum_{\langle ij \rangle} S_i S_j\right)}_{\psi(S)} \right] \tag{1.20}$$

Since $\psi(S) = \psi(S)^{\alpha_1} \psi(S)^{\alpha_2}$

$$Z_N(H_1\alpha_1 + H_2\alpha_2) = \operatorname{Tr}\left(\exp\left\{ \beta\alpha_1 H_1 \sum_i S_i + \beta\alpha_2 H_2 \sum_i S_i \right\} \psi(S)^{\alpha_1} \psi(S)^{\alpha_2} \right) \tag{1.21}$$

$$\Rightarrow= \operatorname{Tr}\left[(e^{\beta H_1 \sum_i S_i} \psi(S))^{\alpha_1} (e^{\beta H_2 \sum_i S_i} \psi(S))^{\alpha_2} \right] \tag{1.22}$$

$$\leq \left(\operatorname{Tr}\left(e^{\beta H_1 \sum_i S_i} \psi(S)\right)^{\alpha_1}\right) \left(\operatorname{Tr}\left(e^{\beta H_2 \sum_i S_i} \psi(S)\right)^{\alpha_2}\right) = Z(H_1)^{\alpha_1} Z(H_2)^{\alpha_2} \tag{1.23}$$

So:

$$\lim_{N\to\infty} -\frac{1}{N} k_B T \ln Z_N(H_1\alpha_1 + H_2\alpha_2) \geq -\lim_{N\to\infty} \frac{\alpha_1}{N} \ln Z_N(H_1\alpha_1) - \lim_{N\to\infty} \frac{\alpha_2}{N} \ln Z_N(H_2\alpha_2) \tag{1.24}$$

$$f_b(H_1\alpha_1 + H_2\alpha_2) \geq \alpha_1 f_b(H_1\alpha_1) + \alpha_2 f_b(H_2\alpha_2) \tag{1.25}$$

The symmetry of the system in sense of the Hamiltonian is: you can invert the value of the S and the Hamiltonian does not change. It is valid when $H = 0$ (? or T is at the critical point booh). Otherwise is not true. Let us see this Z symmetry. Another interesting relation is the following:

$$\sum_{\{S_i\}} \Phi(\{S_i\}) = \sum_{\{S_i\}} \Phi(\{-S_i\}) \tag{1.26}$$

this is true for all function of the spin.

$$-\mathcal{H} = J \sum_{\langle ij \rangle} S_i S_j + H \sum S_i \tag{1.27}$$

$$\mathcal{H}(H, J, \{S_i\}) = \mathcal{H}(-H, J, \{-S_i\}) \tag{1.28}$$

This is a spontaneous broken symmetry.

$$Z_N(-H, J, T) = \sum_{\{S_i\}} \exp[-\beta\mathcal{H}(-H, J, \{S_i\})] = \sum_{\{S_i\}} \exp[-\beta\mathcal{H}(-H, J, \{-S_i\})] \tag{1.29}$$

using equation (1.26)

$$= \sum_{\{S_i\}} \exp[-\beta\mathcal{H}(-H, J, \{S_i\})] = Z_N(H, J, T) \tag{1.30}$$

It implies also that:

$$F_N(T, J, H) = F_N(T, J, -H) \Rightarrow f_b(T, J, H) = f_b(T, J, -H) \tag{1.31}$$

We have:

$$Nm(H) = -\frac{\partial F_N(H)}{\partial H} \underset{(1.31)}{=} -\frac{\partial F_N(-H)}{\partial (H)} = \frac{\partial F_N(-H)}{\partial (-H)} = -Nm(-H) \tag{1.32}$$

$$m(H) = -m(-H) \quad \forall H \Rightarrow m(0) = -m(0) \Rightarrow m = 0, H = 0 \quad \forall N \text{finite} \tag{1.33}$$

Even if you haven't seen any transition, it is an interesting model because we can use this model to solve other problems that seems different. Consider for example the *Lattice gas model*, where a gas is put in a lattice. Another is the *Fluid lattice model*.

1.3.1 Lattice gas model

What is a lattice gas model? Consider a system divided into cell (Fig 1) with only one particle in each cell, where the distance from neighbour cell is the constant lattice a. The n_i is the i-esim cell and it is

$$n_i = \begin{cases} 0 & \text{if empty} \\ 1 & \text{if occupied} \end{cases} \tag{1.34}$$

and $N = \sum_{i=1}^{N_c} n_i$. Let us consider the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N_c} U_1(i) n_i + \frac{1}{2} \sum_{ij} U_2(i, j) n_i n_j + \dots \tag{1.35}$$

where U_1 is an external field for instance, while U_2 is a many body interaction.

$$\mathcal{H} - \mu N = \sum_{i=1}^{N_c} (\cancel{U_1(i)} - \mu) n_i + \frac{1}{2} \sum_{ij} U_2(i, j) n_i n_j + \dots \tag{1.36}$$

we put $U_1 = 0$ for convenience. We can write

$$n_i = \frac{1}{2}(1 + S_i) \tag{1.37}$$

What we get finally is:

$$\mathcal{H} - \mu N = E_0 - H \sum_{i=1}^{N} S_i - J \sum_{\langle ij \rangle} S_i S_j \tag{1.38}$$

$$E_0 = -\frac{1}{2}\mu N_c + \frac{z}{8} U_2 N_c \tag{1.39a}$$

$$H = -\frac{1}{2}\mu + \frac{z}{4} U_2 \tag{1.39b}$$

$$-J = \frac{U_2}{4} \tag{1.39c}$$

where z is the coordination number of neighbours.

$$\mathcal{Z}_{LG} = \mathrm{Tr}_{\{n\}}(e^{-\beta(\mathcal{H}-\mu N)}) = e^{-\beta E_0} Z_{N_c}^{\mathrm{Ising}}(H, J) \tag{1.40}$$

We have seen that the Ising model is something more general than the magnetization transition.

1.4 Ising d=1

The Bravais lattice is just a one dimensional lattice (Figure 2) and the partition function is (we solve it in the case $H = 0$):

$$Z_N(T) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp\left[\overbrace{\beta J}^{K} \sum_{i=1}^{N-1} S_i S_{i+1} \right] \tag{1.41}$$

the two body interaction is the sum in all the neighbours that in that case are *i-1* and *i+1*, but you have only to consider the one after, because the one behind is yet taken by the behind site. Solve now this partition function. Consider *free boundary* condition, therefore the N does not have a *N+1*, almost for the moment. We have

$$K \equiv \beta J, \quad h \equiv \beta H \tag{1.42}$$

What if we just add another spin at the end S_{N+1} ? Which is the partition function with that spin ?

$$Z_{N+1}(T) = \sum_{S_{N+1}=\pm 1} \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N)} e^{K S_N S_{N+1}} \tag{1.43}$$

This sum is just involve this term:

$$\sum_{S_{N+1}=\pm 1} e^{K S_N S_{N+1}} = e^{K S_N} + e^{-K S_N} = 2\cosh(K S_N) = 2\cosh(K) \tag{1.44}$$

$$Z_{N+1}(T) = (2\cosh(K)) Z_N(T) \tag{1.45}$$

$$Z_N(T) = (2\cosh(K)) Z_{N-1}(T) \tag{1.46}$$

In general, we get:

$$\Rightarrow Z_N(T) = Z_1(2\cos(K))^{N-1} \quad \text{with} \quad Z_1 = \sum_{S_1=\pm 1} 1 = 2 \tag{1.47}$$

therefore

$$Z_N(T) = 2(2\cosh(K))^{N-1} \tag{1.48}$$

$$F_N(T) = -k_B T \ln Z_N(T) = -k_B T \ln 2 - k_B T(N-1)\ln 2\cosh(K) \tag{1.49}$$

$$f_b \equiv \lim_{N\to\infty} \frac{1}{N} F_N = -k_B T \ln 2\cosh\left(\frac{J}{k_B T}\right) \tag{1.50}$$

The function goes as Figure 3.

Now introduce another way to introduce the same story: compute the magnetization analitic again. Magnetization is the average over spin. Assume $S_i = \pm 1$:

$$\exp[kS_iS_{i+1}] = \cosh(K) + S_iS_{i+1}\sinh(K) = \cosh(K)[1 + S_iS_{i+1}\tanh(K)] \tag{1.51}$$

It means that

$$Z_N(T) = \sum_{S_1=\pm 1}\sum_{S_2=\pm 1}\cdots\sum_{S_N=\pm 1} \exp\left[K\sum_{i=1}^{N-1} S_iS_{i+1}\right] \Rightarrow \sum_{S_1=\pm 1}\cdots\sum_{S_N=\pm 1}\prod_{i=1}^{N-1}[\cosh(K)(1+S_iS_{i+1}\tanh(K))] \tag{1.52}$$

$$= (\cosh K)^{N-1}\sum_{\{S\}}\prod_{i=1}^{N-1}(1 + S_iS_{i+1}\tanh K) \tag{1.53}$$

In principle there will be a generic term written as this

$$\sum_{\substack{S_{i_e}=\pm 1\\ e=1,\dots,M}} (\tanh K)^M S_{i_1}S_{i_{1+1}}S_{i_2}S_{i_{2+1}}\dots S_{i_M}S_{i_{M+1}} = 0 \tag{1.54}$$

The sum is zero and there is something we can do, except $M = 0$. Therefore:

$$(1.53) = 2^N(\cosh K)^{N-1} \tag{1.55}$$

If I want to compute the average $\langle S_i\rangle$ we have a term S_i inside the equation shown prevously, this is the only difference.

$$(\tanh K)^M S_{i_1}S_{i_{1+1}}S_{i_2}S_{i_{2+1}}\dots S_{i_M}S_{i_{M+1}} S_j \tag{1.56}$$

In that way it depends on S_j which sum is also zero, therefore we have prove that even if $M = 0$ there is no magnetization and

$$\langle S_j\rangle = 0 \tag{1.57}$$