Chapter 1

Role of the models in statistical mechanics

1.1 Role of the models

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 $\{i\}_{i=1,...,N(\Omega)}$ 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 $J_{ij}, k_{ijk}, \ldots$. For instance, there is a coupling that derives from electrons coupling $J_{ij} = f(|\vec{r_i} - \vec{r_j}|)$

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

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

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

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

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

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

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

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

(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 $\langle \ldots \rangle$ means average over the chosen ensemble. Since

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

it is easy to show that:

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

where

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

Let us now consider the properties of the limiting free-energy

$$f_b = \lim_{N \to \infty} \frac{1}{N} (-k_B T \ln Z_N) \tag{1.16}$$

It is possible to prove the following properties

1. $f_b < 0$.

2. $f_B(T, J, H)$ is a continuous function of T, J and H.

3. The right and left derivatives of $f_b(T, J, H)$ exist and are equal almost everywhere.

4. The molar entropy $s = -\frac{\partial f_b}{\partial T} \geq 0$ almost everywhere.

5. $\frac{\partial f_b}{\partial T}$ is a monotone non increasing function of T. That is $\frac{\partial^2 f_b}{\partial T^2} \leq 0$. In particular this implies that:

$$c_H = T \left(\frac{\partial S}{\partial T} \right)_M = -T \left(\frac{\partial^2 f_b}{\partial T^2} \geq 0 \right) \tag{1.17}$$

6. $\frac{\partial f_b}{\partial H}$ is a monotonic non increasing function of H. That is

$$\frac{\partial^2 f_b}{\partial H^2} \leq 0 \tag{1.18}$$

This implies that

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T = -\left(\frac{\partial^2 f_b}{\partial H^2} \right)_T \geq 0 \tag{1.19}$$

Remark. The above properties have been postulated in thermodynamics but here it has been rigorously proved for the Ising model using statistical mechanics.

Proof of property (4). Almost everywhere we have to prove that:

$$s \equiv -\frac{\partial f_b}{\partial T} \geq 0 \tag{1.20}$$

Let us consider a finite system

$$\begin{aligned}
-\frac{\partial F_\Omega}{\partial T} &= k_B \ln \left(\text{Tr} \, e^{-\beta \mathcal{H}_\Omega} \right) + k_B T \frac{1}{k_B T^2} \frac{\text{Tr}\left(\mathcal{H}_\Omega e^{-\beta \mathbb{H}} \right)}{\text{Tr}(e^{-\beta \mathcal{H}})} \\
&= k_B \left[\ln Z + \frac{\text{Tr}\left(\beta \mathcal{H}_\Omega e^{-\beta \mathcal{H}_O} \right)}{Z_\Omega} \right] = -k_B T \, \text{Tr}(\rho_\Omega \ln \rho_\Omega)
\end{aligned} \tag{1.21}$$

where we used the definition of the probability distribution

$$\rho_\Omega = \frac{e^{-\beta \mathcal{H}_\Omega}}{ZA} (????) \tag{1.22}$$

Since $\rho_\Omega \leq 1$ it implies $\ln \rho_\Omega \leq 0$ and so $-\text{Tr}(\rho_\Omega) \ln \rho_\Omega$ is positive. Let us divide by $N(\Omega)$ and take the thermodynamic limit:

$$\lim_{N \to \infty} -\frac{1}{N} \frac{\partial F_\Omega}{\partial T} = -k_B T \lim_{N \to \infty} \frac{1}{N} \underbrace{\text{Tr}(\rho_\Omega \ln \rho_\Omega)}_{S_\Omega} = Ts \geq 0 \quad \Rightarrow \quad s \geq 0 \tag{1.23}$$

$\square$

All the other properties listed before (except (a)) are consiquences of the *convexity* property of f_b

Theorem 1.2.1. *$f_b(T, J, H)$ is an upper convex (i.e. concave) function of* H.

Proof. The proof is based on the Hölder inequality for two seuqnces $\{g_k\}$, $\{h_k\}$.

Definition 1 (Hölder inequality). Given $\{g_k\}, \{h_k\}$ with $g_k, h_k \geq 0, \forall k$ and two non negative real numbers α_1, α_2 such that $\alpha_1 + \alpha_2 = 1$, the following inequality holds

$$\sum_k (g_k)^{\alpha_1} (h_k)^{\alpha_2} \leq \left(\sum_k g_k\right)^{\alpha_1} \left(\sum_k h_k\right)^{\alpha_2} \tag{1.24}$$

Consider now the partition function

$$Z_\Omega(H) = \text{Tr}\left[\exp\left(\beta H \sum_i S_i\right) \underbrace{\exp\left(\beta J \sum_{\langle ij \rangle} S_i S_j\right)}_{G(S)}\right] = \text{Tr}\left[\exp\left(\beta H \sum_i S_i\right) G(s)\right] \tag{1.25}$$

it implies that

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \text{Tr}\left(\exp\left\{\beta \alpha_1 H_1 \sum_i S_i + \beta \alpha_2 H_2 \sum_i S_i\right\} G(S)\right) \tag{1.26}$$

On the other hand, since $\alpha_1 + \alpha_2 = 1$:

$$G(S) = G(S)^{\alpha_1} G(S)^{\alpha_2} \tag{1.27}$$

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \text{Tr}\left[(e^{\beta H_1 \sum_i S_i} G(S))^{\alpha_1} (e^{\beta H_2 \sum_i S_i} G(S))^{\alpha_2}\right] \tag{1.28}$$

If we now apply the Hölder inequality we get

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) \leq \left(\text{Tr}\left(e^{\beta H_1 \sum_i S_i} G(S)\right)^{\alpha_1}\right)\left(\text{Tr}\left(e^{\beta H_2 \sum_i S_i} G(S)\right)^{\alpha_2}\right) \\ = Z_\Omega(H_1)^{\alpha_1} Z_\Omega(H_2)^{\alpha_2} \tag{1.29}$$

If we now take the logs and multiply by $-k_B T$ both sides we have

$$\lim_{N \to \infty} -\frac{1}{N} k_B T \ln Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) \geq -\lim_{N \to \infty} \frac{\alpha_1}{N} k_B T \ln Z_\Omega(H_1) - \lim_{N \to \infty} \frac{\alpha_2}{N} k_B T \ln Z_\Omega(H_2) \tag{1.30}$$

It implies

$$f_b(H_1 \alpha_1 + H_2 \alpha_2) \geq \alpha_1 f_b(H_1) + \alpha_2 f_b(H_2) \tag{1.31}$$

That is a concave function of H. $\square$

1.2.3 Ising model and $\mathbb{Z}^2$ symmetry.

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:

Lemma 1.2.2. $\forall$ *function* Φ *of the configuration* $\{S_i\}$ *the following relation holds*

$$\sum_{\{S_i = \pm 1\}} \Phi(\{S_i\}) = \sum_{\{S_i = \pm 1\}} \Phi(\{-S_i\}) \tag{1.32}$$

this is true for all function of the spin.

We now consider the Hamiltonian of the Ising model:

$$-\mathcal{H}_\Omega = J \sum_{\langle ij \rangle} S_i S_j + H \sum S_i \qquad (1.33)$$

Clearly

$$\mathcal{H}(H, J, \{S_i\}) = \mathcal{H}_\Omega(-H, J, \{-S_i\}) \qquad (1.34)$$

This is a spontaneous broken symmetry. Hence

$$Z_\Omega(-H, J, T) = \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{S_i\})] \underset{(??)}{=} \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{-S_i\})]$$

$$\underset{(??)}{=} \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(H, J, \{S_i\})] = Z_\Omega(H, J, T)$$

$$(1.35)$$

Taking $-k_B T \log$ and the $\lim_{N \to \infty} \frac{1}{N}$ we got

$$F_\Omega(T, J, H) = F_\Omega(T, J, -H) \qquad (1.36)$$

If we now take the thermodynamic limit we have

$$\Rightarrow f_b(T, J, H) = f_b(T, J, -H) \qquad (1.37)$$

It means that the free energy density is an even function of H!

Remark. From the finite-size relation (**??**) one can show that a finite-size Isin model does not displat a transition to a ferromagnetic phase (for all dimension D). Indeed

$$N(\Omega)M(H) = -\frac{\partial F(H)}{\partial H} \underset{(??)}{=} -\frac{\partial F(-H)}{\partial (H)} = \frac{\partial F_N(-H)}{\partial(-H)} = -N(\Omega)M(-H) \qquad (1.38)$$

Therefore:

$$M(H) = -M(-H) \quad \forall H \qquad (1.39)$$

If $H = 0$, we have $M(0) = -M(0)$, that is valid if and only if $M(0) = 0$!

The magnetization of a finite system is, at $H = 0$, always zero. This is simply consequence of the symmetry argument shown above. It is only in the thermodynamic limit where the symmetry is spontaneously broken.

1.2.4 Lattice gas model

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. In fact, the importance of the Ising model relies also on the fact that it can be mapped into other discrete systems. One of these is the *lattice gas model*, where a gas is put in a lattice. What is a lattice gas model? Let us consider a d-dimensional lattice with coordination number z and lattice spacing a, divided into cell as in Figure **??** . Let us suppose that each cell is either empty or occupied by a single particle (this is more true if $a \sim \text{Å}$). The n_i is the occupation of the i-esim cell and it is

$$n_i = \begin{cases} 0 & \text{if empty} \\ 1 & \text{if occupied} \end{cases} \qquad (1.40)$$

$$N_\Omega = \sum_{i=1}^{N_c} n_i \qquad (1.41)$$
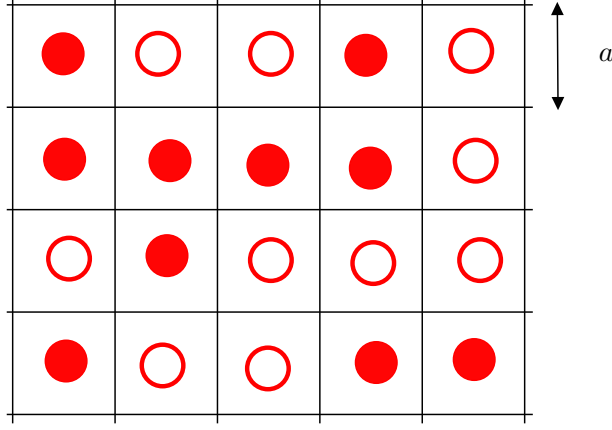
Figure 1.1: Description.

where N_c is the number of the lattice cells. In particular, $N_c > N$. The hamiltonian of the model is

$$\mathcal{H}_\Omega = \sum_{i=1}^{N_c} U_1(i) n_i + \frac{1}{2} \sum_{ij} U_2(i,j) n_i n_j + O(n_i n_j n_k) \tag{1.42}$$

where U_1 is an external field for instance, while U_2 is a many body interaction. Since we want to work in the gran-canonical ensemble

$$\mathcal{H}_\Omega - \mu N = \sum_{i=1}^{N_c} (U_1(i) - \mu) n_i + \frac{1}{2} \sum_{ij} U_2(i,j) n_i n_j + \ldots \tag{1.43}$$

we put $U_1 = 0$ for convenience. A formal relation with the Ising model can be obtained by choosing

$$n_i = \frac{1}{2}(1 + S_i) \quad \text{with } S_i = \pm 1 \tag{1.44}$$

The one body term:

$$\sum_i (U_1(i) - \mu) \frac{1}{2}(1 + S_i) = \frac{1}{2} \sum_i (U_1(i) - \mu) + \frac{1}{2} \sum_i S_i (U_1(i) - \mu) \tag{1.45}$$

while the two bies term:

$$\frac{1}{2} \sum_{ij} U_2(i,j) \left[\frac{1}{4}(1 + S_i)(1 + S_j) \right] = \frac{1}{8} 2 \sum_{ij}^{N_c} U_2(i,j) S_i + \frac{1}{8} \sum_{ij}^{N_c} U_2(i,j) S_i S_j + \frac{1}{8} \sum_{ij}^{N_c} U_2(i,j) \tag{1.46}$$

Let us consider only short-range interactions, i.e.

$$U_2(i,j) = \begin{cases} U_2 & i,j \text{ neirest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{1.47}$$

It implies

$$\frac{1}{8} U_2 Z N_c + \frac{1}{4} z U_2 \sum_i^{N_c} S_i + \frac{U_2}{4} \sum_{\langle ij \rangle} S_i S_j \tag{1.48}$$

Remember that we put $U_1 = 0$ for simplicity:

$$\mathcal{H}_\Omega - \mu N = E_0 - H \sum_{i=1}^{N} S_i - J \sum_{\langle ij \rangle} S_i S_j \tag{1.49}$$

where

$$E_0 = -\frac{1}{2}\mu N_c + \frac{z}{8}U_2 N_c \tag{1.50a}$$

$$H = -\frac{1}{2}\mu + \frac{z}{4}U_2 \tag{1.50b}$$

$$-J = \frac{U_2}{4} \tag{1.50c}$$

where remember that z is the coordination number of neighbours. It implies

$$\mathcal{Z}_{LG} = \text{Tr}_{\{n\}}(e^{-\beta(\mathcal{H}_\Omega - \mu N)}) = e^{-\beta E_0} Z_{\text{Ising}}(H, J, N_c) \tag{1.51}$$

We have seen that the Ising model is something more general than the magnetization transition. In the next section we show how to pass from the partition $\mathcal{Z}$ of a fluid in the continuum to the $\mathcal{Z}_{LG}$ of the lattice gas model.

1.3   Fluid system in a region Ω

We can consider the system with periodic boundary condition or within a box or confined by an external one-body potential. The hamiltonian for N particles in D-dimension is

$$\mathcal{H}_\Omega = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + U_1(\vec{\mathbf{r}_i})\right] + \frac{1}{2}\sum_{i\neq j}U_2(\vec{\mathbf{r}_i},\vec{\mathbf{r}_j}) + \frac{1}{3!}\sum_{i\neq j\neq k}U_3(\vec{\mathbf{r}_i},\vec{\mathbf{r}_j},\vec{\mathbf{r}_k}) \tag{1.52}$$

In the gran-canonical ensemble

$$\mathcal{Z}_\Omega = \text{Tr}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) = \sum_{N=0}^{\infty}\frac{1}{N!}\int\prod_{i=1}^{N}\frac{\mathrm{d}^D\vec{\mathbf{p}_i}\,\mathrm{d}^D\vec{\mathbf{r}_i}}{h^{dN}}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) \tag{1.53}$$

and the gran-canonical potential

$$\omega_\Omega(T,\mu,U_1,U_2,\dots) = -k_B T\ln\mathcal{Z}_\Omega \tag{1.54}$$

Remark. $\omega_\Omega(\dots)$ even if it contains an infinite sum is not singular if Ω is finite!

Indeed if U_2 is an hard-core repulsion, each particle has a finite volume and, within a finite Ω, only N_{max} particles can fit in

$$\Rightarrow \sum_{N=0}^{\infty} \sim \sum_{N=0}^{N_{max}} \tag{1.55}$$

In the thermodynamic limit

$$\omega_b(T,\mu,U_1,U_2,\dots) = \lim_{V(\Omega)\to\infty}\frac{o_\Omega}{V(\Omega)} \tag{1.56}$$

with the contraint

$$\rho = \lim_{V\to\infty}\frac{\langle N\rangle}{V(\Omega)} = const \tag{1.57}$$

remember also that

$$\mathrm{d}\omega_b(T,\mu) = -\sigma\,\mathrm{d}T - p\,\mathrm{d}\mu = -P \tag{1.58}$$

Now:

$$\mathcal{Z}_N = \sum_{N=0}^{\infty}\frac{1}{N!}\left[\prod_{i=1}^{N}\left\{\int_{-\infty}^{+\infty}\mathrm{d}^D\vec{\mathbf{p}}\,\frac{1}{h^{DN}}e^{-\beta\vec{\mathbf{p}_i}^2/2m}\right\}Q_N(T)\right] \tag{1.59}$$

On the other hand since $\int \mathrm{d}x\, e^{-\alpha x^2} = \sqrt{2\pi/\alpha}$

$$\int_{-\infty}^{+\infty} \mathrm{d}^D \vec{\mathbf{p}}\, \frac{1}{h^{DN}} e^{-\beta \vec{\mathbf{p}_i}^2/2m} = \frac{1}{\Lambda(T)^d} \tag{1.60}$$

where

$$\Lambda(T) = \frac{1}{\sqrt{2\pi m k_B T}} \tag{1.61}$$

Therefore:

$$\mathcal{Z}_\Omega = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda(T)^d} \right)^N Q_N \tag{1.62}$$

where

$$Q_N(T) = \int \prod_{i=1}^{N} \mathrm{d}\vec{\mathbf{r}_i}\, e^{-\beta(U(\vec{\mathbf{r}}))} \tag{1.63}$$

1.3.1 From the continuous to the lattice gas model

Let us divied Ω in discrete cells of size a. If a is approximate a repulsive range between particles we have that the probability that there is more than a particles sits in a cell is $\ll 1$. The potentials of the continuoum model depend on $\{\vec{\mathbf{r}_i}\}$. Consider $n_\alpha = n_\alpha(\vec{\mathbf{r}_i})$ the occupation numbers. We have

$$\sum_\alpha n_\alpha = N = \int \mathrm{d}^D \vec{\mathbf{r}} \sum_{i=1}^{N} \delta(\vec{\mathbf{r}_i} - \vec{\mathbf{r}}) = \int \mathrm{d}\vec{\mathbf{r}}\, \rho(\vec{\mathbf{r}}) \tag{1.64}$$

where

$$\rho(\vec{\mathbf{r}}) = \sum_{i=1}^{N} \delta(\vec{\mathbf{r}_i} - \vec{\mathbf{r}}) \tag{1.65}$$

$$\sum_i U_1(\vec{\mathbf{r}_i}) = \sum_i \int_\Omega \mathrm{d}^D \vec{\mathbf{r}}\, U_1(\vec{\mathbf{r}}) \delta(\vec{\mathbf{r}_i} - \vec{\mathbf{r}}) = \int_\Omega \mathrm{d}\vec{\mathbf{r}}\, U_1(\vec{\mathbf{r}}) \rho(\vec{\mathbf{r}}) \tag{1.66}$$

We have $U(\{\vec{\mathbf{r}_i}\}) \to U(\{n_\alpha\})$:

$$Q_N \propto \int \prod_{i=1}^{N} \mathrm{d}^D \vec{\mathbf{r}_i} \to \sum_{\{n_\alpha\}} \tag{1.67}$$

Indeed, for each configuration specified bt the set $\{n_\alpha\}$ there are $N!$ possible configurations of $\{\vec{\mathbf{r}_i}\}$. This is because the particles can exchange position between occupied cells. Hence $Q_N \propto \int \prod_{i=1}^{N} \mathrm{d}^D \vec{\mathbf{r}_i} \simeq N!(a^D)^{N_c} \sum'_{\{n_\alpha=0,1\}} \cdots$

Remark. The symbol $\sum'$ means that the sum has the contraint that the toal number of particles is fixed to N.

$$Q_N \propto N!(a^D)^N \sum_{\{n_\alpha\}}^{'} e^{-\beta U(\{n_\alpha\})} \tag{1.68}$$

$$\mathcal{Z}_N = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda^D(T)} \right)^N Q_N = \sum_{N=0}^{\infty} \left[\left(e^{\beta\mu} \frac{a}{\Lambda(T)} \right)^D \right]^N \sum_{\{n_\alpha\}}^{'} e^{-\beta U(\{n_\alpha\})} \tag{1.69}$$

where $\sum' = \sum_{\{n_\alpha\}}$ with the contraint $\sum_\alpha n_\alpha = N$.

Remark. In general it is difficult to perform sum with contraints. Fortunately, we are considering the gran-canonical ensemble. Indeed we can write

$$\sum_{N=0}^{\infty}{\sum_{\{n_\alpha\}}}' f(n_\alpha) = {\sum_{\substack{\{n_\alpha\} \\ \sum_\alpha n_\alpha=0}}}' f(n_\alpha) + {\sum_{\substack{\{n_\alpha\} \\ \sum_\alpha n_\alpha=1}}}' f(n_\alpha) \cdots + {\sum_{\substack{\{n_\alpha\} \\ \sum_\alpha n_\alpha=\infty}}}' f(n_\alpha) = \sum_{\{n_\alpha\}} f(n_\alpha) \tag{1.70}$$

with no restriction.

Remark. In the final sum all the 2^N possible microscopic states are inclued (considering $U_1 = 0$):

$$z_\Omega^{GC} \propto \sum_{\{n_\alpha\}} \exp\left[-\beta\left(-\mu - \frac{D}{\beta}\log\frac{a}{\Lambda} \right) \sum_{\alpha=0}^{N_c} n_\alpha + \beta U_2 \sum_{\langle\alpha\beta\rangle} n_\alpha n_\beta + \dots \right] \tag{1.71}$$

$$\mathcal{Z}_\Omega = \mathrm{Tr}\, e^{-\beta(\mathcal{H}_\Omega - \widetilde{\mu}N)} = Z_{LG}(\widetilde{\mu}) \tag{1.72}$$

where

$$\widetilde{\mu} = \mu_{LG} = \mu_{phys} + Dk_B T\log\frac{a}{\Lambda} \tag{1.73}$$

Chapter 2

Some exactly solvable models of phase transitions

The bibliography of the entire chapter is taken by [**?**], [**?**], [**?**].

2.1 One dimensional Ising model

The Ising model in $d = 1$ can be solved exactly. There are two techniques: the *recursive methods* and the *transfer matrix method*.

2.1.1 Recursive methods

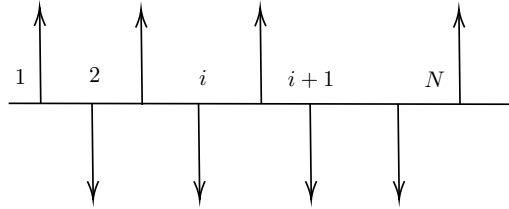**Case with $H = 0$ and free boundary conditions**

Figure 2.1: One dimensional Bravais Lattice.

The Bravais lattice is just a one dimensional lattice as in Figure **??**. The partition function of such a system is:

$$Z_N(T) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp\left[\overbrace{\beta J}^{K} \sum_{i=1}^{N-1} S_i S_{i+1} \right] \tag{2.1}$$

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

$$K \equiv \beta J, \quad h \equiv \beta H \tag{2.2}$$

Making explicit the sum in the exponential:

$$Z_N(K) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N)} \tag{2.3}$$

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

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

(2.4)

On the other hand, this sum is just involve this term:

$$\sum_{S_{N+1}=\pm 1} e^{KS_N S_{N+1}} = e^{KS_N} + e^{-KS_N} = 2\cosh(KS_N) = 2\cosh(K) \qquad (2.5)$$

where the last equivalence derive from the fact that cosh is an even function and it does not depend on ± 1. Therefore:

$$Z_{N+1}(K) = (2\cosh(K))Z_N(K) \quad \text{and} \quad Z_N(T) = (2\cosh(K))Z_{N-1}(T) \qquad (2.6)$$

By performing a backward iteration

$$Z_N(K) = Z_1(2\cos(K))^{N-1} \qquad (2.7)$$

Since $Z_1 = \sum_{S_1=\pm 1} 1 = 2$ we have

$$Z_N(T) = 2(2\cos(K))^{N-1} \qquad (2.8)$$

The free energy is:

$$F_N(T) = -k_B T \ln Z_N(K) = -k_B T \ln 2 - k_B T(N-1)\ln(2\cosh(K)) \qquad (2.9)$$

we not take the thermodynamic limit

$$f_b(T) \equiv \lim_{N\to\infty} \frac{1}{N} F_N(K) = -k_B T \ln\left(2\cosh\left(\frac{J}{k_B T}\right)\right) \qquad (2.10)$$

As one can see $f_b(T)$ is an analytic function of T; we have no phase transition at $T \neq 0$.
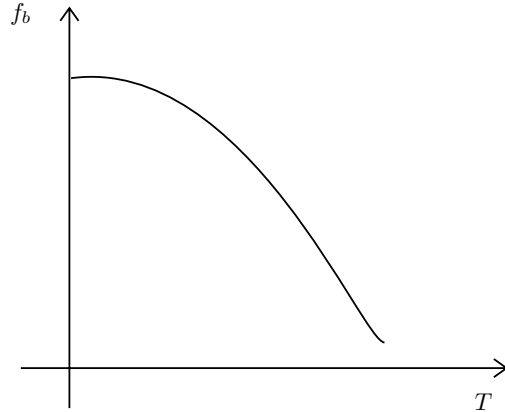

Figure 2.2: Free energy function in thermodynamic limit.

We can compute the magnetization (the average over the spin)$\langle S_j \rangle$ for a generic site j. This can be done in many ways. Assume again that$S_i = \pm 1$. Here we choose one that consider another way to compute Z for $d = 1$ Ising. This method can be useful for other calculations. It is based on the following identity:

$$\exp[KS_i S_{i+1}] = \cosh(K) + S_i S_{i+1}\sinh(K) = \cosh(K)[1 + S_i S_{i+1}\tanh(K)] \quad (2.11)$$

It means that

$$Z_N(K) = \sum_{\{S\}} \exp\left[K \sum_{i=1}^{N-1} S_i S_{i+1}\right] = \sum_{\{S\}} \prod_{i=1}^{N-1} [\cosh(K)(1 + S_i S_{i+1} \tanh(K))] \quad (2.12)$$

by rearranging

$$Z_N(K) = (\cosh K)^{N-1} \sum_{\{S\}} \prod_{i=1}^{N-1} (1 + S_i S_{i+1} \tanh K) \quad (2.13)$$

If we now expand the products we get terms of the following form:

$$\sum_{\substack{S_{i_e}=\pm 1 \\ e=1,\dots,M}} (\tanh K)^M S_{i_1} S_{i_{1+1}} S_{i_2} S_{i_{2+1}} \dots S_{i_M} S_{i_{M+1}} = 0 \quad (2.14)$$

where $i_1 \dots i_m$ is a set of M sites of the lattice.

Remark. The terms above, when summed over $\{S\}$ are zero, except the term $M = 0$ that is equal to 1 and, when summed over $\{S\}$, gives 2^N.

Therefore:

$$Z_N(K) = 2^N (\cosh K)^{N-1} \quad (2.15)$$

that coincides with the result obtained before. If we now compute the average $\langle S_j \rangle$ the procedure is similar but now there will be terms as (**??**) but with the addiction of an S_j:

$$(\tanh K)^M S_{i_1} S_{i_{1+1}} S_{i_2} S_{i_{2+1}} \dots S_{i_M} S_{i_{M+1}} \boxed{S_j} \quad (2.16)$$

that, when one sums over $\{S\}$ are all zero, included the term with $H = 0$ that now is equal to S_j and $\sum_{S_j = \pm 1} = 0$. Hence, we have the result

$$\langle S_j \rangle = 0 \quad \forall j \quad (2.17)$$

The magnetization is always zero $\forall j \neq \infty$!

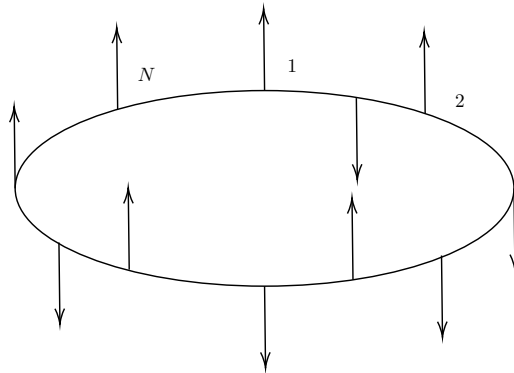## Case with $H \neq 0$ and periodic boundary conditions

Figure 2.3: Onde dimensional lattice ring.

Consider the spins sitting on a 1D lattice ring as in Figure **??**. The periodic boundary conditions are:

$$S_{N+1} = S_1 \quad (2.18)$$

We have:

$$-\beta\mathbb{H}_\Omega(\{S\}) = K\sum_{i=1}^{N} S_i S_{i+1} + h\sum_{i=1}^{N} S_i \tag{2.19}$$

where

$$K \equiv \beta J, \quad h \equiv \beta H \tag{2.20}$$

The 1d Ising model with this setup can be solved in several ways. Here we will use the method of the transfer matrix. This is a quite general technique that we will discuss within the Ising model.