

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 (coarse-graining approach) 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 cannot 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 analytically (exact solution).

It is the latter approach that we shall take here. Let us start by introducing what is, perhaps, the most paradigmatic model in the statistical mechanics of phase transition, the *Ising model*.

1.2 The Ising model

Suggested by Lenz to Ising for his PHD thesis (1925), it is supposed to describe a magnetic system that undergoes a transition between a paramagnetic 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 was 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 .

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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. 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 anisotropic ferromagnet (along a given direction).

The minimal model that can try to capture the interaction between the spin is the following. 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 for describing the model.

A general Hamiltonian of the model can be written as:

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

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

$$\mathcal{H}_\Omega(\{S_i\}) = -\frac{1}{2} \sum_{i,j}^N J_{ij} S_i S_j - \sum_{i=1}^N H_i S_i \quad (1.1)$$

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

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

$$\text{Tr} \equiv \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \dots \sum_{S_N=\pm 1} \equiv \sum_{\{S\}}$$

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

$$Z_\Omega(T, \{H_i\}, \{J_{ij}\}) = \text{Tr} e^{-\beta \mathcal{H}_\Omega(\{S\})} \quad (1.2)$$

and the corresponding *free-energy*,

$$F_\Omega(T, \{H_i\}, \{J_{ij}\}) = -k_B T \ln Z_\Omega \quad (1.3)$$

The *bulk limiting free energy* is:

$$f_b(T, \{H_i\}, \{J_{ij}\}) = \lim_{N \rightarrow \infty} \frac{1}{N} F_\Omega \quad (1.4)$$

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

$$\sum_{j \neq i} |J_{ij}| < \infty \quad (1.5)$$

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

$$J_{ij} = A |\vec{r}_i - \vec{r}_j|^{-\sigma} \quad (1.6)$$

so it is a long range interaction, the limit exists when

$$\sigma > d$$

Remark. If the interaction is *dipolar*, since it decays as $1/r^3$, for the case $d = 3$ the limit does not exist. 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 nearest 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 (n.n.) on the lattice:

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are n.n.} \\ 0 & \text{otherwise} \end{cases} \quad (1.7)$$

Now, the model is very simple:

$$-\mathcal{H}_\Omega(\{S\}) = J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + H \sum_i^{N(\Omega)} S_i \quad (1.8)$$

where the notation $\langle ij \rangle$ means a double sum over i and j , with the constraint that i and j are nearest-neighbours.

Since H is uniform, the average magnetization per spin is

$$\langle m \rangle = \frac{1}{N(\Omega)} \sum_{i=1}^{N(\Omega)} \langle S_i \rangle \quad (1.9)$$

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

Remark. For $J = 0$, (1.8) is the Hamiltonian of a paramagnet. The only influence ordering the spins is the field H . They do not interact, there are no cooperative effects and hence no phase transition.

Since

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

it is easy to show that:

$$\langle m \rangle = -\frac{1}{N} \frac{\partial F_\Omega}{\partial H} \quad (1.10)$$

where

$$F_\Omega(T, J, H) = -k_B T \ln Z_N(T, J, H) \quad (1.11)$$

Now, let us consider the properties of the limiting free-energy

$$f_b = \lim_{N \rightarrow \infty} \frac{1}{N} F_\Omega = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T \ln Z_N) \quad (1.12)$$

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 *monotonic non increasing* function of T . That is $\frac{\partial^2 f_b}{\partial T^2} \leq 0$. This implies that:

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

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

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

This implies that

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

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

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

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

Let us consider a finite system

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

where

$$\rho_\Omega = \frac{e^{-\beta \mathcal{H}_\Omega}}{Z_\Omega}$$

is the probability distribution.

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

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

■

All the other properties listed before (except (1)) are consequences of the *convexity* property of f_b .

Theorem 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 sequences $\{g_k\}, \{h_k\}$:

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

$$\sum_k (g_k)^{\alpha_1} (h_k)^{\alpha_2} \leq \left(\sum_k g_k \right)^{\alpha_1} \left(\sum_k h_k \right)^{\alpha_2} \quad (1.13)$$

Now, consider the partition function:

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

It implies that

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

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

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

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

If we now apply the Hölder inequality we get

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

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

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

It implies

$$f_b(H_1 \alpha_1 + H_2 \alpha_2) \geq \alpha_1 f_b(H_1) + \alpha_2 f_b(H_2)$$

That is a concave function of H ¹.

■

¹A real-valued function f on an interval is said to be concave if, for any x and y in the interval and for any $\alpha \in [0, 1]$, $f((1 - \alpha)x + \alpha y) \geq (1 - \alpha)f(x) + \alpha f(y)$.

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

The symmetry of the system in sense of the Hamiltonian is: we can invert the value of the S and the Hamiltonian does not change. It is valid when $H = 0$, otherwise it is not true. Let us see the \mathbb{Z}^2 symmetry and the following interesting relation:

Lemma 1

\forall function Φ of the configuration $\{S_i\}$, the following relation holds:

$$\sum_{\{S_i=\pm 1\}} \Phi(\{S_i\}) = \sum_{\{S_i=\pm 1\}} \Phi(\{-S_i\}) \quad (1.14)$$

this is true for all function of the spin.

Now, we consider the Hamiltonian of the Ising model:

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

Clearly,

$$\mathcal{H}(H, J, \{S_i\}) = \mathcal{H}_\Omega(-H, J, \{-S_i\}) \quad (1.15)$$

This is a spontaneous broken symmetry.

Hence,

$$\begin{aligned} Z_\Omega(-H, J, T) &= \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{S_i\})] \stackrel{(1.14)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{-S_i\})] \\ &\stackrel{(1.15)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(H, J, \{S_i\})] = Z_\Omega(H, J, T) \end{aligned} \quad (1.16)$$

Taking $-k_B T \ln$, we got:

$$F_\Omega(T, J, H) = F_\Omega(T, J, -H) \quad (1.17)$$

If we take the thermodynamic limit $\lim_{N \rightarrow \infty} \frac{1}{N}$, we have

$$\Rightarrow f_b(T, J, H) = f_b(T, J, -H) \quad (1.18)$$

and it means that the *free energy density is an even function of H* !

Remark. From the finite-size relation (1.17), one can show that a *finite-size* Ising model does not display a transition to a ferromagnetic phase (for all dimension d). Indeed,

$$N(\Omega)M(H) = -\frac{\partial F(H)}{\partial H} \stackrel{(1.17)}{=} -\frac{\partial F(-H)}{\partial(H)} = \frac{\partial F(-H)}{\partial(-H)} = -N(\Omega)M(-H) \quad (1.19)$$

Therefore:

$$M(H) = -M(-H), \quad \forall H \quad (1.20)$$

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. We have not a phase transition.

Hence, it is only in the thermodynamic limit, where the symmetry is spontaneously broken, that the model displays a transition.

For resuming, although the Hamiltonian is invariant with respect to the transformation $H \rightarrow -H, \{S_i\} \rightarrow \{-S_i\}$, the thermodynamic state is not. This situation is called *spontaneous symmetry breaking*.

1.3 Lattice gas model

Even if we had not seen any transition, the Ising model is interesting because we can use this model to solve other problems that seems different but are not. In fact, the importance of the Ising model relies also on the fact that it can be mapped into other discrete systems. Despite its simplicity, the Ising model is widely applicable because it describes any interacting two-state system. One of these applications is the *lattice gas model*, where a gas is put in a lattice.

What is a lattice gas model in more details? The archetypal lattice gas is a model where each lattice site can either be occupied by an atom or vacant. Let us consider a d -dimensional lattice with coordination number z and lattice spacing a , divided into cells, as in Figure 1.1. Let us suppose that each cell is either empty or occupied by a single particle (this is more true if $a \sim \text{\AA}$).

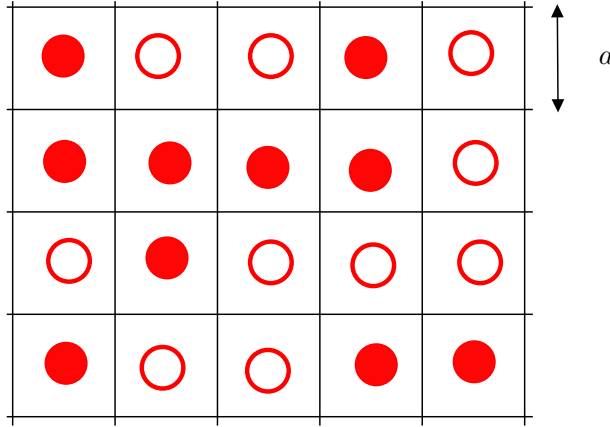


Figure 1.1: d -dimensional lattice with lattice spacing a .

The n_i is the occupation of the i -esim cell and it is:

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

We have:

$$N_\Omega = \sum_{i=1}^{N_c} n_i \quad (1.21)$$

where N_c is the number of the lattice cells. In particular, $N_c > N_\Omega$.

The Hamiltonian of the model is

$$\mathcal{H}_\Omega = \sum_{i=1}^{N_c} U_1(i)n_i + \frac{1}{2} \sum_{ij}^{N_c} U_2(i,j)n_i n_j + O(n_i n_j n_k) \quad (1.22)$$

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

Since we want to work in the gran-canonical ensemble,

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

and we will put $U_1 = 0$ for convenience.

A formal relation with the Ising model can be obtained by choosing

$$n_i = \frac{1}{2}(1 + S_i), \quad \text{with } S_i = \pm 1 \quad (1.23)$$

The one body term becomes:

$$\sum_i (U_1(i) - \mu) \frac{1}{2} (1 + S_i) = \frac{1}{2} \sum_i (U_1(i) - \mu) + \frac{1}{2} \sum_i S_i (U_1(i) - \mu) \quad (1.24)$$

while the two bodies term is equal to:

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

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

$$U_2(i, j) = \begin{cases} U_2 & i, j \text{ are n.n.} \\ 0 & \text{otherwise} \end{cases}$$

It implies

$$\frac{1}{2} \sum_{ij} U_2(i, j) \left[\frac{1}{4} (1 + S_i)(1 + S_j) \right] = \frac{1}{4} z U_2 \sum_i S_i + \frac{U_2}{4} \sum_{\langle ij \rangle} S_i S_j + \frac{1}{8} U_2 z N_c \quad (1.25)$$

Remark. Note that the \sum_{ij} becomes $z \sum_i$, where z is the coordination number of neighbours.

Remember that, for simplicity, we put $U_1 = 0$. We can rewrite:

$$\mathcal{H}_\Omega - \mu N_\Omega = E_0 - H \sum_{i=1}^{N_c} S_i - J \sum_{\langle ij \rangle} S_i S_j \quad (1.26)$$

where

$$E_0 = -\frac{1}{2} \mu N_c + \frac{z}{8} U_2 N_c \quad (1.27a)$$

$$-H = -\frac{1}{2} \mu + \frac{z}{4} U_2 \quad (1.27b)$$

$$-J = \frac{U_2}{4} \quad (1.27c)$$

and remember that z is the coordination number of neighbours. J is a nearest neighbour interaction which favours neighbouring sites being occupied.

The last equation implies that, in the gran canonical ensemble, we have:

$$Z_{LG} = \text{Tr}_{\{n\}} (e^{-\beta(\mathcal{H}_\Omega - \mu N_\Omega)}) = e^{-\beta E_0} Z_{\text{Ising}}(H, J, N_c) \quad (1.28)$$

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 Z of a fluid, in the continuum, to the Z_{LG} of the lattice gas model.

1.4 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

$$\mathcal{H}_\Omega = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U_1(\vec{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_i, \vec{r}_j) + \frac{1}{3!} \sum_{i \neq j \neq k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) \quad (1.29)$$

In the gran-canonical ensemble, we have:

$$Z_\Omega = \text{Tr} \left(e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{d^d \vec{\mathbf{p}}_i d^d \vec{\mathbf{r}}_i}{h^{dN}} \left(e^{-\beta(\mathcal{H}_\Omega - \mu N)} \right) \quad (1.30)$$

and the gran-canonical potential is

$$\omega_\Omega(T, \mu, U_1, U_2, \dots) = -k_B T \ln Z_\Omega \quad (1.31)$$

Remark. Even if $\omega_\Omega(\dots)$ contains an infinite sum, it 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

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

In the thermodynamic limit, it corresponds to

$$\omega_b(T, \mu, U_1, U_2, \dots) = \lim_{V(\Omega) \rightarrow \infty} \frac{\omega_\Omega}{V(\Omega)}$$

with the constraint

$$\rho = \lim_{V, N \rightarrow \infty} \frac{\langle N \rangle}{V(\Omega)} = \text{const}$$

Remember also that

$$d\omega_b(T, \mu) = -\sigma dT - \rho d\mu = -P \quad (1.32)$$

Now:

$$Z_N = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\prod_{i=1}^N \left\{ \int_{-\infty}^{+\infty} d^d \vec{\mathbf{p}} \frac{1}{h^{dN}} e^{-\beta \vec{\mathbf{p}}_i^2 / 2m} \right\} Q_N(T) e^{\beta \mu N} \right] \quad (1.33)$$

where

$$Q_N(T) = \int \prod_{i=1}^N d^d \vec{\mathbf{r}}_i e^{-\beta(U(\vec{\mathbf{r}}))} \quad (1.34)$$

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

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

where

$$\Lambda(T) = \frac{h}{2\sqrt{\pi m k_B T}} \quad (1.35)$$

Hence,

$$Z_\Omega = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta \mu}}{\Lambda^d(T)} \right)^N Q_N \quad (1.36)$$

1.4.1 From the continuous to the lattice gas model

Let us divide 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 one particle sits in a cell is $\ll 1$. The potentials of the continuous model depend on $\{\vec{\mathbf{r}}_i\}$.

Consider the occupation numbers $n_\alpha = n_\alpha(\vec{\mathbf{r}}_i)$. We have:

$$\sum_{\alpha} n_{\alpha} = N = \int_{\Omega} d^d \vec{\mathbf{r}} \sum_{i=1}^N \delta(\vec{\mathbf{r}}_i - \vec{\mathbf{r}}) = \int_{\Omega} d^d \vec{\mathbf{r}} \rho(\vec{\mathbf{r}}) \quad (1.37)$$

where

$$\rho(\vec{r}) = \sum_{i=1}^N \delta(\vec{r}_i - \vec{r}) \quad (1.38)$$

Moreover,

$$\sum_i U_1(\vec{r}_i) = \sum_i \int_{\Omega} d^d \vec{r} U_1(\vec{r}) \delta(\vec{r}_i - \vec{r}) = \int_{\Omega} d^d \vec{r} U_1(\vec{r}) \rho(\vec{r}) \quad (1.39)$$

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

$$Q_N \propto \int \prod_{i=1}^N d^d \vec{r}_i \rightarrow \sum_{\{n_{\alpha}\}}$$

Indeed, for each configuration specified by the set $\{n_{\alpha}\}$ there are $N!$ possible configurations of $\{\vec{r}_i\}$. This is because the particles can exchange position between occupied cells. Hence, more precisely,

$$Q_N \propto \int \prod_{i=1}^N d^d \vec{r}_i \simeq N!(a^d)^N \sum'_{\{n_{\alpha}=0,1\}} \dots$$

Remark. The symbol \sum' means that the sum has the constraint that the total number of particles is fixed to N , that is $\sum_{\alpha} n_{\alpha} = N$.

Therefore,

$$Q_N \propto N!(a^d)^N \sum'_{\{n_{\alpha}\}} e^{-\beta U(\{n_{\alpha}\})} \quad (1.40)$$

and we can rewrite the equation (1.36) as

$$Z_{\Omega} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda^d(T)} \right)^N Q_N = \sum_{N=0}^{\infty} \left[e^{\beta\mu} \left(\frac{a}{\Lambda(T)} \right)^d \right]^N \sum'_{\{n_{\alpha}\}} e^{-\beta U(\{n_{\alpha}\})} \quad (1.41)$$

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

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

$$\sum_{N=0}^{\infty} \sum'_{\{n_{\alpha}\}} f(n_{\alpha}) = \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=0}} f(n_{\alpha}) + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=1}} f(n_{\alpha}) \dots + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=\infty}} f(n_{\alpha}) = \sum_{\{n_{\alpha}\}} f(n_{\alpha})$$

with no restriction.

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

Eventually, we have²

$$Z_{\Omega}^{GC} \propto \sum_{\{n_{\alpha}\}} \exp \left[-\beta \left(-\mu - \frac{d}{\beta} \log \frac{a}{\Lambda} \right) \sum_{\alpha=0}^{N_c} n_{\alpha} + \beta U_2 \sum_{\langle \alpha \beta \rangle} n_{\alpha} n_{\beta} + \dots \right] \quad (1.42)$$

$$\Rightarrow Z_{\Omega} = \text{Tr} e^{-\beta(\mathcal{H}_{\Omega} - \tilde{\mu}N)} = Z_{LG}(\tilde{\mu}) \quad (1.43)$$

where

$$\tilde{\mu} = \mu_{LG} = \mu_{phys} + dk_B T \log \frac{a}{\Lambda} \quad (1.44)$$

² $b^a = e^{a \ln b} \Rightarrow e^{\beta\mu} \left(\frac{a}{\Lambda} \right)^d = e^{\beta\mu} \exp(d \ln(\frac{a}{\Lambda}))$

Chapter 2

Some exactly solvable models of phase transitions

2.1 1-dim Ising model

In this section, we arrive at the exact solution of the one dimensional Ising model. There are two techniques for solving the model:

1. the *recursive method*;
2. the *transfer matrix method*.

2.1.1 Recursive method

Case with $H = 0$ and free boundary conditions

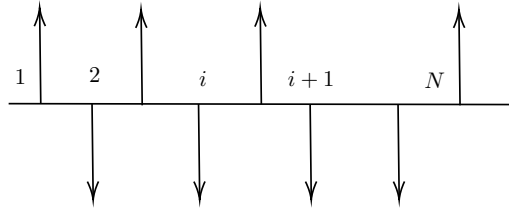


Figure 2.1: One dimensional Bravais Lattice.

Let us consider a Bravais lattice in the one dimensional case, that is just a one dimensional lattice, as in Figure 2.1.

The canonical partition function of such a system is:

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

The two body interaction is the sum in all the neighbours that in that case are $(i-1)$ and $(i+1)$, but we have only to consider the one after, because the one behind is yet taken by the behind site.

We want to solve this partition function. If we consider *free boundary* condition, the N does not have a $N+1$, almost for the moment. Let us define

$$K \equiv \beta J, \quad h \equiv \beta H \quad (2.2)$$

Making explicit the sum in the exponential:

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

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

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

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

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

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

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

By performing a backward iteration,

$$Z_N(K) = Z_1 (2 \cosh(K))^{N-1}$$

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

$$Z_N(K) = 2 (2 \cosh(K))^{N-1} \quad (2.3)$$

The free energy is

$$F_N(K) = -k_B T \ln Z_N(K) = -k_B T \ln 2 - k_B T (N-1) \ln (2 \cosh(K)) \quad (2.4)$$

and taking the thermodynamic limit it becomes

$$f_b(T) \equiv \lim_{N \rightarrow \infty} \frac{1}{N} F_N(K) = -k_B T \ln \left(2 \cosh \left(\frac{J}{k_B T} \right) \right) \quad (2.5)$$

As one can see (Figure 2.2) $f_b(T)$ is an analytic function of T , so we have no phase transition at $T \neq 0$.

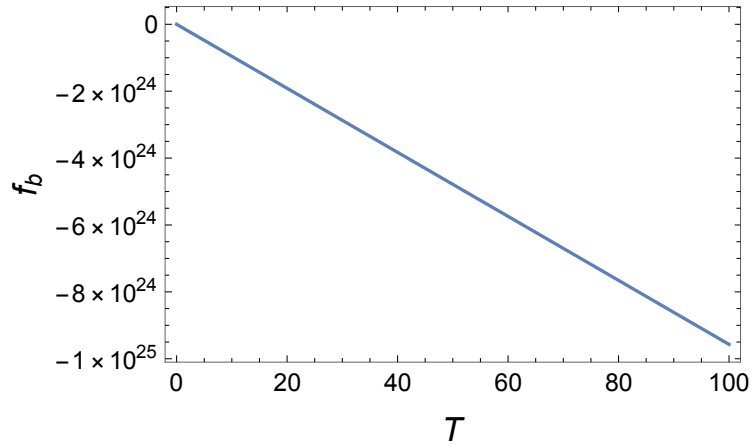


Figure 2.2: Free energy function in thermodynamic limit for the one dimensional Ising model, for $k_B = 1.38 \times 10^{23}$, $J = 1$.

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

$$\exp[K S_i S_{i+1}] \underset{(proof)}{=} \cosh(K) + S_i S_{i+1} \sinh(K) = \cosh(K) [1 + S_i S_{i+1} \tanh(K)] \quad (2.6)$$

Proof of identity (2.6). Remind that

$$\cosh x = \frac{e^x + e^{-x}}{2}, \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

Hence,

$$e^x = \cosh x + \sinh x$$

In our case,

$$e^{KS_i S_{i+1}} = \cosh(KS_i S_{i+1}) + \sinh(KS_i S_{i+1}) = \cosh K + S_i S_{i+1} \sinh K$$

where the last step was obtained considering that \cosh is an even function, while \sinh is an odd one. ■

Using identity (2.6), we obtain

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

by rearranging,

$$Z_N(K) = (\cosh K)^{N-1} \sum_{\{S\}} \prod_{i=1}^{N-1} (1 + S_i S_{i+1} \tanh K) \quad (2.7)$$

If we now expand the products, we get 2^{N-1} terms of the following form:

$$\sum_{\substack{S_{i_e} = \pm 1 \\ e=1, \dots, M}} (\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_M+1} = 0 \quad (2.8)$$

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 with $M = 0$ that is equal to 1 and, when summed over $\{S\}$, gives 2^N .

Therefore:

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

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 (2.8) with the addition of an S_j :

$$(\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_M+1} S_j \quad (2.9)$$

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

$$\langle S_j \rangle = 0 \quad \forall j \quad (2.10)$$

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

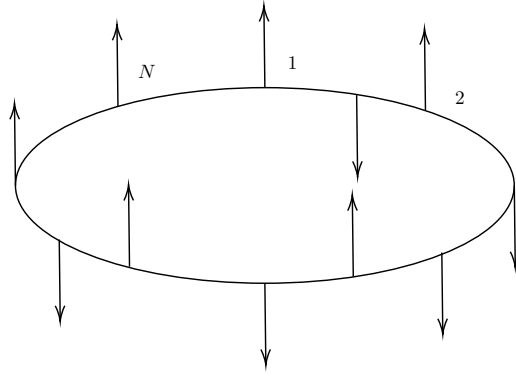


Figure 2.3: One dimensional lattice ring: Ising model with periodic boundary conditions.

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

Consider the spins sitting on a 1D lattice ring as in Figure 2.3. The periodic boundary conditions are:

$$S_{N+1} = S_1$$

We have:

$$-\beta\mathcal{H}_\Omega(\{S\}) = K \sum_{i=1}^N S_i S_{i+1} + h \sum_{i=1}^N S_i \quad (2.11)$$

where

$$K \equiv \beta J, \quad h \equiv \beta H$$

The 1 – *dim* 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.