LECTURE NOTES
OF
STATISTICAL MECHANICS

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Contents

Introduction

In this course,classical statistical mechanics of system at equilibrium is treated. The outline of the course is:

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- Thermodinamic limit and phase transitions in statistical mechanics.

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The exam is divided into two parts: first, common oral exam (same exercise and question for everyone, it is a written part), second part, oral.

Chapter 1

Recall of Thermodynamics

1.1 A short recap of thermodynamics definitions

The systems we are considering are

1. In equilibrium with an external bath at fixed temperature T.

2. Made by a (large) number N of degrees of dreedom. For instance, we remind that $1 \, \text{mol} \approx N_A \sim 10^{23}$ elementary units.

Thermodynamic is a macroscopic theory of matter at equilibrium. It starts either from experimental observations or from *assiomatic assumptions* and establishes rigorous relations between macroscopic variables (**observables**) to describe systems at equilibrium. One of the first important concept is the one of **extensive variables**. For instance, the extensive variables that caracterize the system at equilibrium are the internal energy U, volume V, number of particles N and magnetization $\vec{\mathbf{M}}$ that "scale with the system". In general, the extensive variable are additive.

In thermodynamic, it is important the concept of walls and thermodynamic constrains that are necessary for a complete definition of a thermodynamic system. With their presence or absence it is possible to control and redistribute the thermodynamic variables for changing the system. The typical walls are:

- **Adiabatic walls**: no heat flux. If it is removed we obtain a *diathermic walls*.

- **Rigid walls**: no mechanical work. If it is removed we obtain a *flexible or mobile walls*.

- **Impermeable walls**: no flux of particles (the number of particles remain constraints). If it is removed we obtain a *permeable walls*.

1.2 Equilibrium states

Consider a system in an equilibrium state, if the system changes our aim is to study the next equilibrium state of the system. Therefore we move from a system in equilibrium to another. The fundamental problem of thermodynamcs is how to characterize the new system.

Now, we define the concept of **equilibrium states**. Consider macroscopic states that are fully described by *extensive* variables such as the internal energy U, the volume V, the number of particles N, the magnetization $\vec{\mathbf{M}}$, etc .... If these variables are time indipendent, the system is in a *steady state*. If moreover there are no macroscopic currents, the system is at *equilibrium*. Therefore, we describe a system by characterizing all the extensive variables at equilibrium.

Suppose that the system changes slow in time, it goes from an equilibrium state to another one and the transformation is so slow that in each Δt the system is at equilibrium. Therefore, consider a sequence of equilibrium states, the **quasi-static transormation** are described by the 1st *Law of Thermodynamic*:

$$\mathrm{d}U = \delta Q - \delta W \tag{1.1}$$

The variation of the internal energy of the systems depends by two factors, δw that is the work done by the system during a *quasi-static process* (infinitively slow), and δQ that is the heat absorbed by the system during the process. Remember that we write $\mathrm{d}U$ because it is a differential quantity, while the other quantities with the δ are only small quanties. Therefore, $\mathrm{d}U$ is a function of state, the other are not.

Remark. The convention is $\delta Q > 0$ if the heat is absorbed by the system, and $\delta W > 0$ if the work is done by the system.

For example, for a simple fluid with a given pressure if we change the volume, the work done by the systems is $\delta W = P \, \mathrm{d}V$. For a magnetized system, we have $\delta W = -\vec{\mathbf{H}} \cdot \mathrm{d}\vec{\mathbf{M}}$.

In conclusion, starting from an equilibrium state and removing some constraints (i.e. wall properties), we want to find the new equilibrium state compatible with the new constrains.

Suppose a system with adiabatic rigid impermeable constraints. The system on the left is characterized by V_1, N_1, U_1, the one on the right by V_2, N_2, U_2. There are many ways for solving this problem. We use the most general way, that is by using the *maxium entropy principle*. If exists a function S of the extensive variables of the system that is defined for all equilibrium states, we call it **entropy** and the fundamental relation is

$$S = S(U, V, N) \tag{1.2}$$

The new values taken by the extensive parameters when a constraint has been removed are the ones that *maximize* S. It means $\mathrm{d}S = 0$ and $\mathrm{d}^2 S < 0$, given the remaining constraint.

The properties of S are:

1. S is an additive function with respect to the subsystems in which the system is partitioned:

$$S = \sum_\alpha S^{(\alpha)} \tag{1.3}$$

2. S is differentiable and *monotonically increasing* with respect to the internal energy U. It means that $\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$.

3. For each subsystem (α) we have:

$$S^{(\alpha)} = S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)}) \tag{1.4}$$

This fundamental relation holds for each subsystem.

4. S is an *homogeneous function* of 1st order with respect to the extensive parameters, namely:

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N), \quad \forall \lambda > 0 \tag{1.5}$$

It means that S is an extensive quantity.

Remark. Since S is monotonically increasing in U, the following inequality holds:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$$

Therefore, we have $\left(\frac{\partial S}{\partial U}\right)_{V,N} \neq 0$ and it can be inverted locally.

Afterwards, $S = S(U, V, N)$ inverted in U gives the second fundamental relation

$$U = U(S, V, N) \tag{1.6}$$

It means that, we can look or S or U and, when this quantities are known, all the informations about the system can be obtained.

By taking the differential of the fundamental relation

$$U = U(S, V, N_1, \ldots, N_r) \tag{1.7}$$

one gets

$$\mathrm{d}U = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N_j}}_{\substack{T \\ \text{absolute} \\ \text{temperature}}} \mathrm{d}S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N_j}}_{\substack{-P \\ \text{pressure}}} \mathrm{d}V + \sum_{j=1}^{r} \underbrace{\left(\frac{\partial U}{\partial N_j}\right)_{S,V}}_{\substack{\mu_j \\ \text{elettrochemical} \\ \text{potential}}} \mathrm{d}N_j \tag{1.8}$$

1.3 Equations of states

Now, we define another set of variables that are called **intensive variables**. The term *intensive* means that it is indipendent of the size of the system, namely that the value of the variable relative to a subsystem is equal to that of the whole system. The intensive variables are themselves functions of S,V,N, and examples of intensive variables are the pressure, P, and the temperature of the system, T.

The **state equations** are defined as:

$$T = T(S, V, N_1, \ldots, N_r) \tag{1.9a}$$
$$P = P(S, V, N_1, \ldots, N_r) \tag{1.9b}$$
$$\mu_j = \mu_j(S, V, N_1, \ldots, N_r) \tag{1.9c}$$

Remark. If all the state equations are known, the fundamental relation is determined a part from a constant. It means that the coefficients of the differential (1.8) are known.

Example 1. Suppose an *ideal* gas, for which is valid the relation

$$PV = NK_bT \tag{1.10}$$

The *Van-Der Walls equation* of the state is

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - Nb) = Nk_bT \tag{1.11}$$

Another equation of state for magnetic systems is the *Curie Law*:

$$M = \frac{CH}{T} \tag{1.12}$$

We compute $\left(\frac{\partial U}{\partial M}\right)_{S,N} = H$.

The state equations are homogenous functions of *zero* degree:

$$T(\lambda S, \lambda V, \lambda N) \overset{0}{=} T(S, V, N) \tag{1.13}$$

At equilibrium the temperature of a subsystem is equal to the one of the whole system. Similarly

$$P(\lambda S, \lambda V, \lambda N) = P(S, V, N) \tag{1.14}$$

Now, we keep S parameter separates from the other that are substituted by *generalized displacements*, as $(V, N_1, \ldots, N_r) \rightarrow X_j$. The fundamental relation is

$$U = U(S, X_1, \ldots, X_{r+1}) \tag{1.15}$$

We define:

$$\left(\frac{\partial U}{\partial S}\right) \equiv T \tag{1.16a}$$

$$\left(\frac{\partial U}{\partial X_j}\right) \equiv P_j \tag{1.16b}$$

The differential is written as the following:

$$dU = T\,dS + \sum_{j=1}^{r+1} P_j\,dX_j \tag{1.17}$$

where $P_1 = -P$ is the *pressure* and $X_1 = V$ is the volume.

From the equilibrium condition, $dU = 0$, one can get a relation between intensive variables in differential form as the **Gibbo-Duhem relation**:

$$S\,dT + \sum_{j=1}^{r+1} X_j\,dP_j = 0 \tag{1.18}$$

For a one-component simple fluid system, the equation (1.18) simplifies into

$$S\,dT - V\,dP + N\,d\mu = 0 \tag{1.19}$$

and dividing by the number of moles N

$$d\mu = -s\,dT + v\,dP \tag{1.20}$$

that is the Gibbs-Duhem relation in *molar form.*
For a magnetic system we have $dU = T\,dS + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} + \mu\,dN$.

Remark. Note that $\mu = \mu(T, P)$ is a relation between intensive variables.

To summarize, the fundamental relations are $S = S(U, V, N_1, \ldots, N_r)$ or $S = S(U, \vec{\mathbf{M}}, N_1, \ldots, N_r)$ for magnetic systems. In the energy representation we have $U = U(S, V, N_1, \ldots, N_r)$ or $U = U(S, \vec{\mathbf{M}}, N_1, \ldots, N_r)$.

1.4   Legendre transform and thermodynamic potentials

In many situations it is convenient to change some extensive variables with their conjiugate intensive ones that became indipendent and free to vary. We have new thermodynamic potentials. It works as following; suppose we have a function as

$$Y = Y(X_0, X_1, \ldots, X_k, \ldots, X_{r+1}) \tag{1.21}$$

such that Y is *strictly convex* in say, X_k ($\frac{\partial^2 Y}{\partial X_k^2} > 0$) and smooth. The idea is to find a transformation such that $Y = Y(X_0, X_1, \ldots, P_k, \ldots, X_{r+1})$, where

$$X_k \to P_k \equiv \frac{\partial Y}{\partial X_k} \tag{1.22}$$

i.e. P_k substitutes X_k as a new indipendent variable. In mathematic this is called *Legendre transform*.

   Thermodynamic potentials are extremely useful tools, whose name derives from an analogy with mechanical potential energy: as we will later see, in certain circumstances the work obtainable from a macroscopic system is related to the change of an appropriately defined function, the thermodynamic potential. They are useful because they allow one to define quantities which are experimentally more easy to control and to rewrite the fundamental thermodynamic relations in terms of them.

   Mathematically all the thermodynamic potentials are the result of a Legendre transformation of the internal energy, namely they are a rewriting of the internal energy so that a variable has been substituted with another.

Example 2. Suppose we want to replace the entropy S with its conjiugate derivative

$$T = \frac{\partial U}{\partial S}$$

One starts form the fundamental relation

$$U = U(S, V, N_1, \ldots)$$

and transforms U such that S is replaced by T as new indipendent variable. Let us consider the transformation

$$A \equiv U - S\frac{\partial U}{\partial S} = U - TS$$

By differentiating A we get

$$\mathrm{d}A = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T$$

On the other hand

$$\mathrm{d}U = T\,\mathrm{d}S + \sum_j P_j\,\mathrm{d}X_j$$

It implies that

$$\mathrm{d}A = -S\,\mathrm{d}T + \sum_j P_j\,\mathrm{d}X_j$$

For such a system we have $A = A(T, V, N_1, \ldots, N_r)$. It is a function of T instead of S, as wanted. Similarly for a magnetic system $A = A(T, \vec{\mathbf{M}}, N_1, \ldots, N_r)$.

Helmholtz free energy

   The **Helmholtz free energy** is defined as:

$$A \equiv U - TS \tag{1.23}$$

In terms of heat and mechanical work, since $\mathrm{d}U = \delta Q - \delta W$:

$$\mathrm{d}A = \mathrm{d}U - \mathrm{d}(TS) = \delta Q - T\,\mathrm{d}S - S\,\mathrm{d}T - \delta W \tag{1.24}$$

Hence,

$$\delta W = (\delta Q - T\,\mathrm{d}S) - S\,\mathrm{d}T - \mathrm{d}A \tag{1.25}$$

On the other hand, for a *reversible transformation* we have $\delta Q = T \, dS$, which implies

$$\delta W = -S \, dT - dA \tag{1.26}$$

If the reversible transformation is also *isothermal*, $dT = 0$ and we obtain $dA = dW$. It is reminiscent of a potential energy.

Remark. For an isothermal but *not reversible* (spontaneous) process we know the 2nd *Law of Thermodynamics*

$$\delta Q \leq T \, dS \tag{1.27}$$

which implies

$$(\delta W)_{irr} = \delta Q - T \, dS - dA \leq -dA \,.$$

Hence, if $\delta W = 0$ and $dT = 0$, we have $dA \leq 0$. Therefore, in a spontaneous (irreversible) process, the thermodynamc system, as a function of T, V, N etc, evolves towards a *minimum* of the Helmoltz free energy $A = A(T, V, N_1, \ldots, N_r)$.

In the case of a system with (P, V, T) we have:

$$dA = -S \, dT - P \, dV + \sum_j \mu_j \, dN_j \tag{1.28}$$

where

$$-S = \left(\frac{\partial A}{\partial T}\right)_{V, N_j} \tag{1.29a}$$

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T, N_j} \tag{1.29b}$$

$$\mu_j = \left(\frac{\partial A}{\partial N_j}\right)_{T, V} \tag{1.29c}$$

For a magnetic system $(\vec{\mathbf{H}}, \vec{\mathbf{M}}, T)$:

$$dA = -S \, dT + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} + \sum_j \mu_j \, dN_j \tag{1.30}$$

with

$$H_\alpha = \left(\frac{\partial A}{\partial M_\alpha}\right)_{T, \{N_j\}} \tag{1.31}$$

Heltalpy

The **Hentalpy** is the partial Legendre transform of U that replaces the volume V with the pressure P as indipendent variable.

Consider $U = U(S, V, N_1, \ldots, N_r)$ and $-P = \frac{\partial U}{\partial V}$, we define the hentalpy as

$$H = U + PV \tag{1.32}$$

Remark. Note that the plus sign in the definition of the hentalpy is just because the minus of the P.

We have:

$$\begin{aligned}
dH &= dU + P \, dV + V \, dP \\[2mm]
&= T \, dS - P \, dV + \sum_j \mu_j \, dN_j + P \, dV + V \, dP \\[2mm]
&= T \, dS + V \, dP + \sum_j \mu_j \, dN_j
\end{aligned} \tag{1.33}$$

Finally, we obtain the relation $H = H(S, P, N_1, \ldots, N_r)$.

Gibbs potential

The **Gibss potential** is obtained by performing the Legendre transform of U to replace S and V with T and P.

Consider again $U = U(S, V, N_1, \ldots, N_r)$ and $T = \frac{\partial U}{\partial S}, -P = \frac{\partial U}{\partial V}$, then we have:

$$G = U - TS + PV = A + PV \tag{1.34}$$

For a simple fluid system

$$
\begin{aligned}
\mathrm{d}G &= \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T + P\,\mathrm{d}V + V\,\mathrm{d}P \\
&= T\,\mathrm{d}S - P\,\mathrm{d}V + \sum_j \mu_j\,\mathrm{d}N_j - T\,\mathrm{d}S - S\,\mathrm{d}T + P\,\mathrm{d}V + V\,\mathrm{d}P \\
&= -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_j \mu_j\,\mathrm{d}N_j
\end{aligned}
\tag{1.35}
$$

Hence, $G = G(T, P, N_1, \ldots, N_r)$.

For a magnetic system, the Gibbs potential is defined as

$$G = A - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \tag{1.36}$$

and

$$
\begin{aligned}
\mathrm{d}G &= \mathrm{d}A - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} = \mathrm{d}(U - TS) - \mathrm{d}(-\vec{\mathbf{M}} \cdot \vec{\mathbf{H}}) \\
&= \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot \mathrm{d}\vec{\mathbf{H}} \\
&= T\,\mathrm{d}S + \vec{\mathbf{H}} \cdot \mathrm{d}\vec{\mathbf{M}} - T\,\mathrm{d}S - S\,\mathrm{d}T - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot \mathrm{d}\vec{\mathbf{H}} \\
&= -S\,\mathrm{d}T - \vec{\mathbf{M}} \cdot \mathrm{d}\vec{\mathbf{H}}
\end{aligned}
\tag{1.37}
$$

and finally $G = G(T, \vec{\mathbf{H}})$ and also

$$S = -\left(\frac{\partial G}{\partial T}\right)_{\vec{\mathbf{H}}} \tag{1.38a}$$

$$\vec{\mathbf{M}} = -\left(\frac{\partial G}{\partial \vec{\mathbf{H}}}\right)_T \tag{1.38b}$$

Grancanonical potential

The two intensive variables to became indipendent are T and μ. The corresponding Legendre transform is

$$\Omega = U - TS - \sum_{i=1}^{r} \mu_i N_i = A - \sum_{i=1}^{r} \mu_i N_i \tag{1.39}$$

Differentiating this relation we obtain:

$$
\begin{aligned}
\mathrm{d}\Omega &= \mathrm{d}U - S\,\mathrm{d}T - T\,\mathrm{d}S - \sum_{ij} \mathrm{d}\mu_j\,N_j - \sum_{i=1}^{r} \mu_i\,\mathrm{d}N_i \\
&= (\delta Q - T\,\mathrm{d}S) - \delta W - S\,\mathrm{d}T - \sum_{j=1}^{r} \mathrm{d}\mu_j\,N_j - \sum_{j=1}^{r} \mu_j\,\mathrm{d}N_j
\end{aligned}
\tag{1.40}
$$

Hence, $\Omega = \Omega(T, P, \{\mu_j\})$.

1.5   Maxwell relations

Internal energy U and entropy S are homogeneus function of the first order. A consequence of this fact is the relation called **Euler equation**:

$$U = TS - PV + \sum_j \mu_j N_j \tag{1.41}$$

Instead, the **Maxwell relations** are relations between the mixed derivatives of the thermodynamic potentials. They can be obtained from the expressions of dU, dH, dA, dG and $d\Omega$ and from the Schwarz theorem on mixed partial derivatives.

Due to Schwarz theorem, if a thermodynamic potential depends on $t+1$ variables there will be $\frac{t(t+1)}{2}$ indipendent mixed derivatives.

Example 3 (Internal energy $U = U(S, V, N)$).

$$dU = T\,dS - P\,dV + \mu\,dN \tag{1.42}$$

where

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad -P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

It implies that

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_{S,N} \underset{\substack{\text{from} \\ \text{Schwarz inequality}}}{=} \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

therefore, we have the *1° Maxwell relation* :

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

All the *3 Maxweel relations* obtained by the differential (1.42) with $t = 2$, for which we have $t+1 = 3$ and $\frac{t(t+1)}{2} = 3$ ($[S, V, N]$), are

$$(S, V): \qquad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \tag{1.43a}$$

$$(S, N): \qquad \left(\frac{\partial T}{\partial N}\right)_{V,S} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \tag{1.43b}$$

$$(V, N): \qquad -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \tag{1.43c}$$

Example 4 (Helmholz $A = A(T, V, N)$).

$$dA = -S\,dT - P\,dV + \mu\,dN \tag{1.44}$$

In this case the *3 Maxweel relations* ($[T, V, N]$) are

$$(T, V): \qquad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \tag{1.45a}$$

$$(T, N): \qquad -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \tag{1.45b}$$

$$(V, N): \qquad -\left(\frac{\partial P}{\partial N}\right)_{V,T} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \tag{1.45c}$$

Example 5 (Gibbs $G = G(T, P, N)$)**.**

$$\mathrm{d}G = -S\,\mathrm{d}T - V\,\mathrm{d}P + \mu\,\mathrm{d}N \tag{1.46}$$

In this case the *3 Maxweel relations* ($[T, P, N]$) are

$$(T, P): \qquad -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{1.47a}$$

$$(T, N): \qquad -\left(\frac{\partial S}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,N} \tag{1.47b}$$

$$(P, N): \qquad \left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \tag{1.47c}$$

1.6   Response functions

Response functions are quantities that express how a system reacts when some external parameters are changed.

In fact, aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variatious of thermodynamic variables. Any osservation is just the pertubation of a system and looking for the response. A list of the commonly used response functions is the following:

- *Thermal expansion coefficient at constant pressure.*

$$\alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{1.48}$$

- *Adiabatic compressibility.*

$$k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} \underset{V=\left(\frac{\partial H}{\partial P}\right)_{S,N}}{=} -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} \tag{1.49}$$

- *Isothermal compressibility.*

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \underset{V=\left(\frac{\partial G}{\partial P}\right)_{T,N}}{=} -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} \tag{1.50}$$

Remark. Remember that k_T it is the second derivative of the Gibbs potential write respect to pressure.

- *Molar heat capacity at constant pressure.*

$$c_P = \left(\frac{\delta Q}{\mathrm{d}T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \underset{-S=\left(\frac{\partial G}{\partial T}\right)_{P,N}}{=} -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} \tag{1.51}$$

- *Specific heat at constant volume.* Consider a quasi static transformation.

$$c_V = \left(\frac{\delta Q}{\mathrm{d}T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial(-\partial A/\partial T)_{V,N}}{\partial T}\right)_{V,N} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} \tag{1.52}$$

- *Magnetic suscettibility (d=1)* for a magnetic system $(\vec{\mathbf{M}}, \vec{\mathbf{H}}, T)$.

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_{T \underset{M = -\frac{\partial G}{\partial H}\big|_T}{=}} -\left(\frac{\partial^2 G}{\partial H^2}\right)_T \tag{1.53}$$

More generals, $\vec{\mathbf{M}}, \vec{\mathbf{H}}$ we have

$$\chi_{\alpha\beta} = \left(\frac{\partial M_\alpha}{\partial H_\beta}\right)_T, \quad M_\alpha = -\left.\frac{\partial G}{\partial H_\alpha}\right|_T \Rightarrow \chi_{\alpha\beta} = \left.\frac{\partial^2 G}{\partial H_\beta \partial H_\alpha}\right|_T \tag{1.54}$$

Note that the response functions, when used with the Maxwell relations, allow to express observables usually inaccessible to experiments with measurable quantitites.

Let us illustrate a lemma useful for calculation:

Lemma 1.6.1. *Let x, y, z be quantities that satisfy the relation $f(x, y, z) = 0$. If w is a function of two any variables chosen between x, y, z, then:*

1. $\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w = \left(\frac{\partial x}{\partial z}\right)_w$

2. $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

3. $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ *(concatenation relation or triple product rule).*

Example 6. The Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

obtained from

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$$

and the response function α_P permit to write

$$\underbrace{\left(\frac{\partial S}{\partial P}\right)_{T,N}}_{\substack{\text{inaccessible} \\ \text{to experiments}}} = \underbrace{-V\alpha_P}_{\text{measurable}} \tag{1.55}$$

Example 7. Let us start with the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$$

obtained from

$$\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}N$$

From some property of multi-variable differential calculus one has the *triple product rule*:

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} \left(\frac{\partial V}{\partial P}\right)_{T,N} \left(\frac{\partial T}{\partial V}\right)_{P,N} = -1 \tag{1.56}$$

Hence

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_{T,N}\left(\frac{\partial T}{\partial V}\right)_{P,N}} = -\frac{\left(\frac{\partial V}{\partial T}\right)_{P,N}}{\left(\frac{\partial V}{\partial P}\right)_{T,N}} \tag{1.57}$$

$$= \frac{-V\alpha_P}{-Vk_T} = \frac{\alpha_P}{k_T}$$

1.6.1   Response functions and thermodynamic stability

Now, we analyze the concept of *thermal stability*. If one injects heat in a system either at constant volume or at constant pressure, its temperature will inevitably increase

$$\begin{cases} c_V \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_V \geq 0 \\ c_P \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_P \geq 0 \end{cases} \tag{1.58}$$

Remark. The thermal capacities are *non-negative functions*!

It is useful also the concept of *mechanical stability*. If one compress a system by keeping T constant, we would expect that it shrinks

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \geq 0 \tag{1.59}$$

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_M \geq 0 \tag{1.60}$$

Remark. In diamangetic systems χ_M can also be negative.

Exercise 1. By using Maxwell relations show that

$$c_P - c_V = \frac{TV\alpha_P^2}{k_T} = \frac{1}{Vk_T}T\left(\frac{\partial V}{\partial T}\right)_P^2 \tag{1.61a}$$

$$c_H - c_M = \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)_H^2 \tag{1.61b}$$

Solution. Let us start considering a system with a fixed number of particles (namely $\mathrm{d}N = 0$) and such that S is explicitly expressed in terms of T and V. Then:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

Dividing by $\mathrm{d}T$ both sides keeping the pressure constant, and then multiplying by T:

$$T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

it implies

$$c_P - c_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Now, using the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and using the triple product rule we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

we get:

$$c_P - c_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2 = -T\alpha_P^2 V^2\left(\frac{\partial P}{\partial V}\right)_T = \frac{TV}{k_T}\alpha_P^2$$

It can be shown similarly for magnetic systems.

A consequence is that since the right hand terms are non negative it follows that

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \tag{1.62}$$

For reasuming, we have seen the thermodynamic of a phase, where the equilibrium state can be described by the maximum of the entropy. If we have a given phase, we can look for the Gibbs function. If we have more phases, we want to change between these phases.

Chapter 2

Equilibrium phases and thermodynamics of phase transitions

2.1 Equilibrium phases as minima of Gibbs free energy

Equilibrium states are given by *maxima* of the entropy and *minima* of internal energy, or by *minima* of thermodynamics potentials such as A and G. Let us consider for example the Gibbs potential per particle of a fluid system

$$\frac{G}{N} \equiv g = g(T, P) \tag{2.1}$$

that depends on two intensive variables T and P and is not anymore a function of N because we have divided for N. Let us define α the phase of a one-component system (say α = gas or liquid). Therfore, the thermodynamic properties are described by surfaces of function $g_\alpha(T, P)$ and for all equilibrium phase we have a surface on the space (T,P,g). For each value of T and P the thermodynamically stable phase is the one for which $g_\alpha(T, P)$ is minimum.

2.2 First order phase transition and phase coexistence

Consider the surface g_α and g_β, we are looking for the lower one (Figure 2.1) and there is a moment in which they coexist. The coexistence line is the projection on the *(T,P)* plane of the intersection between different surfaces, so the **coexistence condition** is:

$$g_\alpha(T, P) = g_\beta(T, P) \tag{2.2}$$
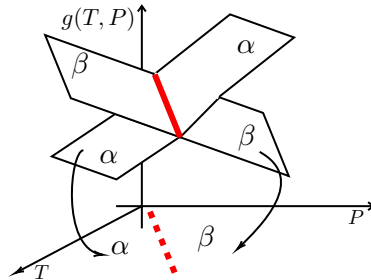
Figure 2.1: Description.

To fix the ideas, let us choose a given value of pressure $P = P^*$ and study the behaviour of $g(T, P^*)$ as a function of T when we go from solid to gas (Figure 2.2a).

At the triple point $g_{\text{solid}}(T_a, P^*) = g_{\text{liq}}(T_a)$ and $g_{\text{liq}}(T_b) = g_{\text{gas}}(T_b, P^*)$ (see Figure 2.2b). Note also that:

- At the coexistence points a and b of the two phases, one has $g_\alpha(T) = g_\beta(T)$.

- $g(T)$ is a continuous function of T.

- Note that, $S = -\left(\frac{\partial G}{\partial T}\right)_V$ and $c_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right) > 0$. This implies that $g(T)$ is concave in T at fixed P.

(a) Description
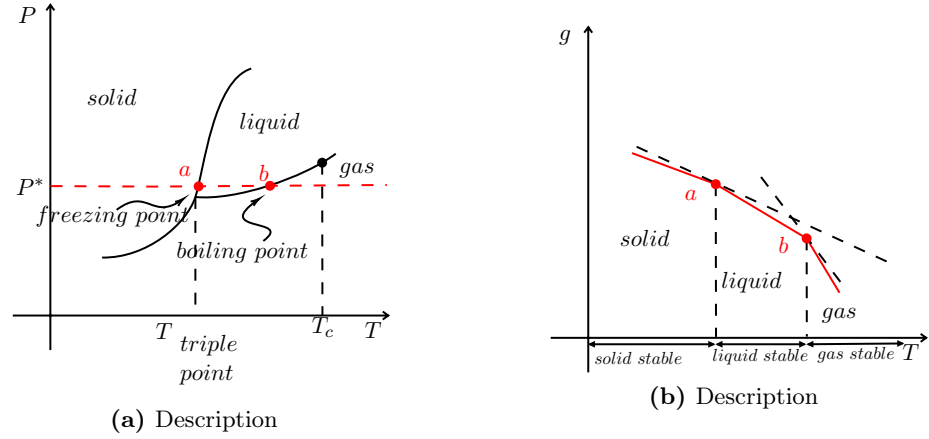
(b) Description

Figure 2.2:   Description

How about its derivatives? Since P is fixed we can vary T and look for $s = -\left(\frac{\partial g}{\partial T}\right)_P$. As we cross different phases (Figure 2.3) we have discontinuities, where $\Delta s T$ is called the *latent heat*.
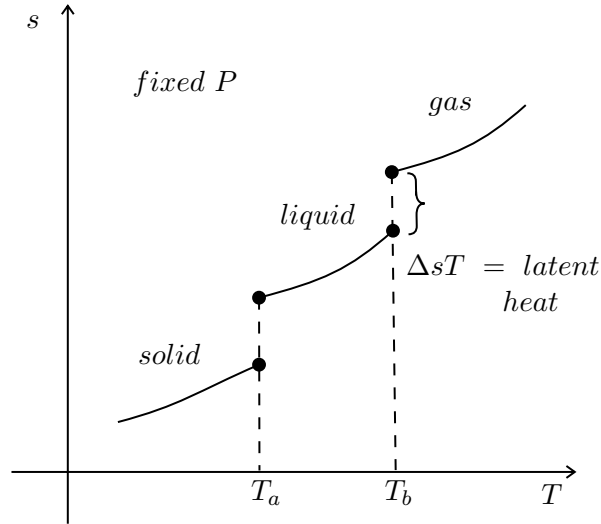
Figure 2.3:   Description.

We can also fix the temperature T and look at the variation of P (Figure 2.4) and we have (Figure 2.5) $v = \left(\frac{\partial g}{\partial P}\right)_T > 0$:

$$\left(\frac{\partial^2 g}{\partial P^2}\right) = \left(\frac{\partial U}{\partial P}\right)_T = -v k_T < 0 \qquad (2.3)$$
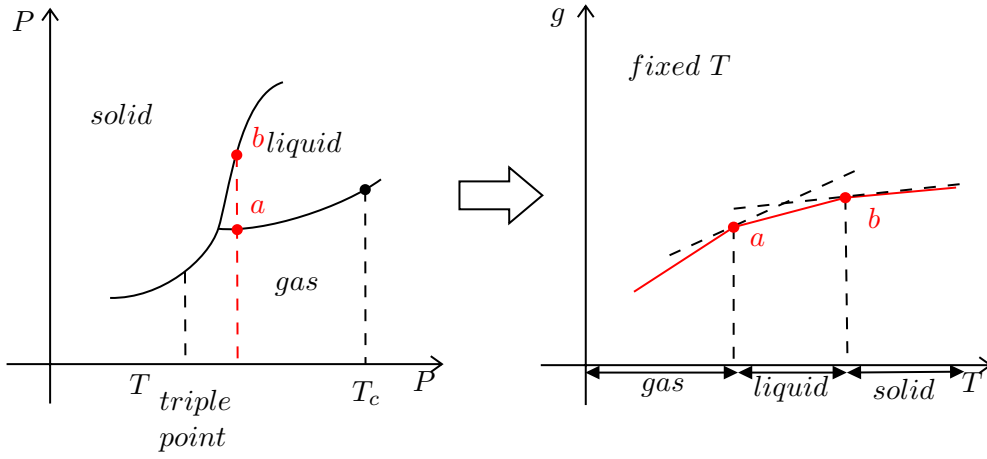
Figure 2.4: Description.
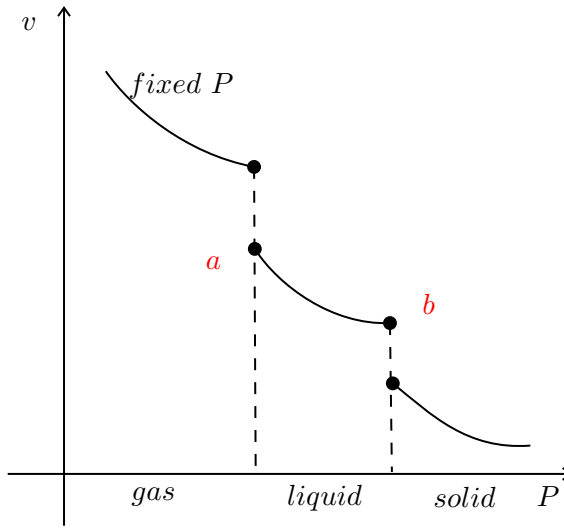
Figure 2.5: Description.

2.3   Second order phase transition

There are other cases in which we do not have these effects, as in Figure 2.6. This is different from the previous situation in which we had a jump:

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \tag{2.4a}$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v \tag{2.4b}$$

This implies:

$$\left(\frac{\partial^2 g}{\partial T \partial P}\right) = \left(\frac{\partial v}{\partial T}\right)_P = v_{\alpha p} \tag{2.5}$$

An example is *superconductivity*.

If we look for example at the specific heat in Figure 2.6d, it represent the transition from superconduction.

The critical point is special beacause there is not a jump, so we can go continuously from gas to liquid. The response function when we plot this point shows that the specific heat diverges. The transitions are classified in the first order transition and continuous transition. The superfluid transition is a transition where the second

(a) Description

(b) Description

(c) Description
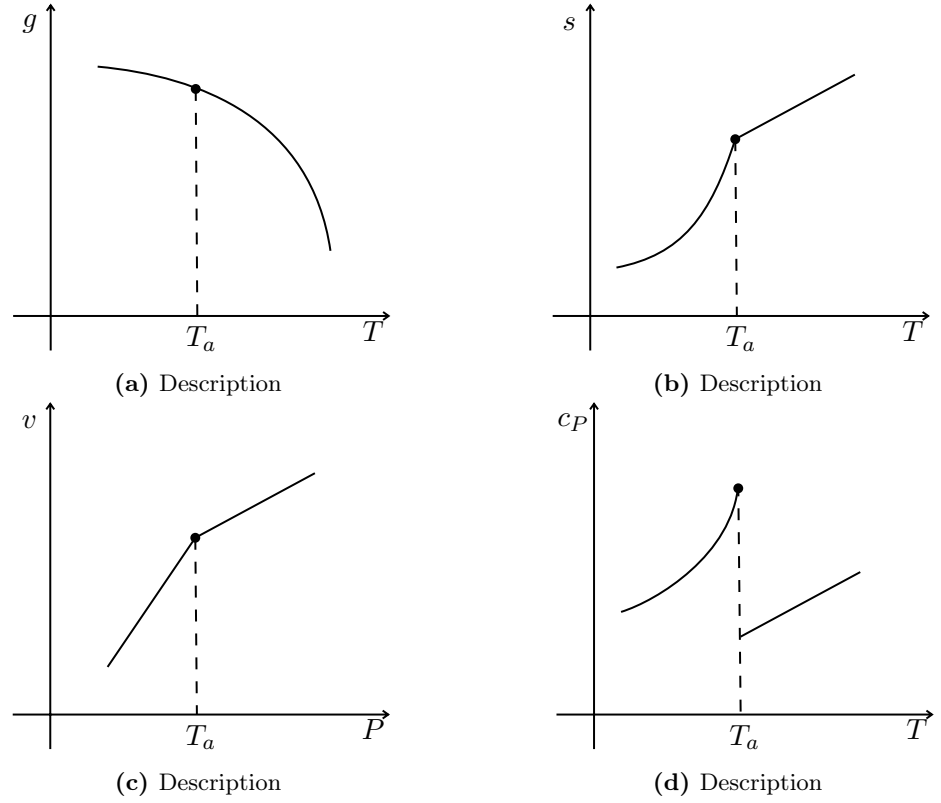
(d) Description

Figure 2.6: Description

derivative of the thermodynamic potential diverges. There are many phase transitions that can be classified in different ways. We note that at the coexistence line we increase V, but the pression remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles becames bigger and bigger and at the V_G , becames a liquid.

2.4   Helmholtz free-energy

Consider $A = A(T, V, N)$, here P is replaced by V which is discontinuous at the first order transition. Moreover $P > 0$ implies $\partial A/\partial V < 0$ and

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V}\left(\frac{\partial^2 A}{\partial V^2}\right)_T > 0 \qquad (2.6)$$

A is an overall convex function of V. The behaviour of A when there is a first order phase transition is as in Figure 2.7a. The linear sector becomes an horizontal one in the $P = -(\partial A/\partial V)_T = P(V)$ curve (Figure 2.7b).

2.5   Critical points

At the critical point (P_c, T_c) the system can pass from the liquid to the gas phase (and viceversa) in a continuous way

$$\Delta s = \Delta v = 0 \qquad (2.7)$$

Usually critical points are end point of first order transition phases. Why there is no critical point between solid and liquid? The crossover between phases having the same symmetry define the Landau point. There is a break of symmetry, for instance

(a) Description **(b)** Description
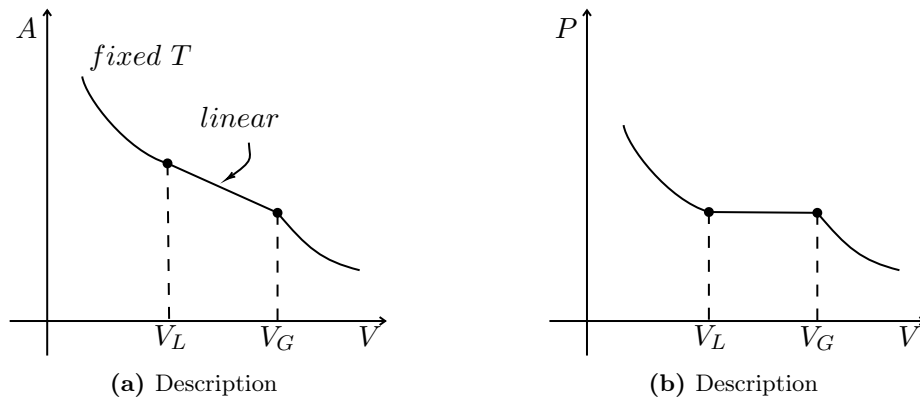
Figure 2.7: Description

we can think about the structure of the bravais lattice. Instead, from gas to liquid symmetries are not broken.
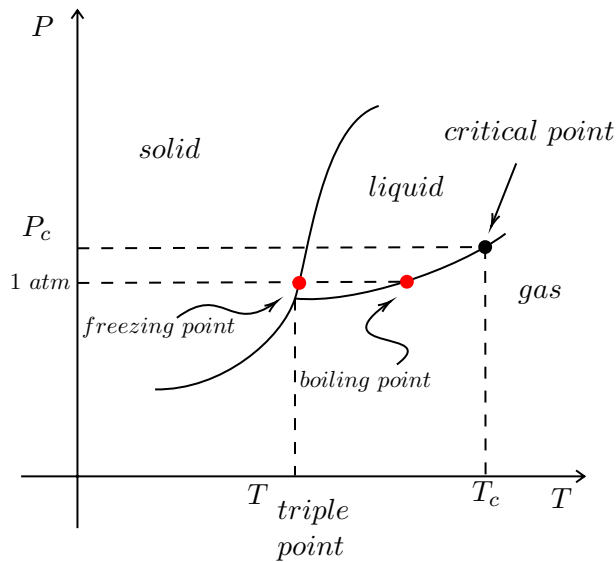
Figure 2.8: Description.

2.6 Ferromagnetic system

We can have a magnetization different from 0 even when the is no magnetic field. Supposing $P \leftrightarrow H, V \leftrightarrow M$, we have $(P,T) \leftrightarrow (H,T)$. We have two equilibrium states that are connected continuosly, this is a first order transition. For instance consider Figure 2.10. At the critical point the magnetization would pass through zero.

2.7 Lever Rule

Consider the Figure 2.11, at all points between A and B the system is a mixsture of gas and liquid. Points D has global density $P_D = P_A + P_B$ and therefore $v_D = \frac{1}{P_D}, v_A = \frac{1}{P_A}, v_B = \frac{1}{P_B}$ which implies:

$$v_D = \frac{N_A}{N}v_A + \frac{N_B}{N}v_B = x_A v_A + x_B v_B \qquad (2.8)$$
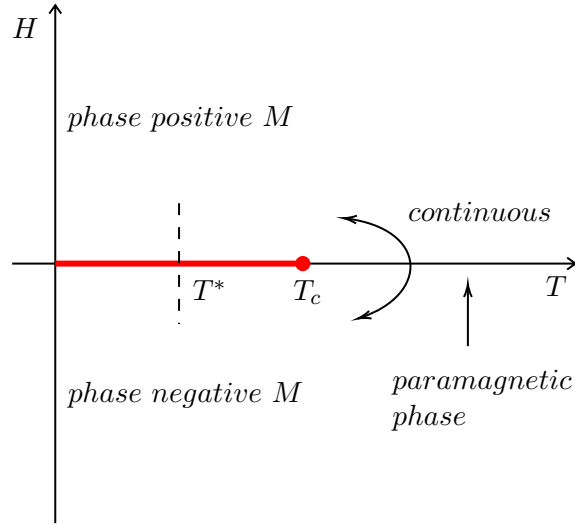
Figure 2.9: Description.
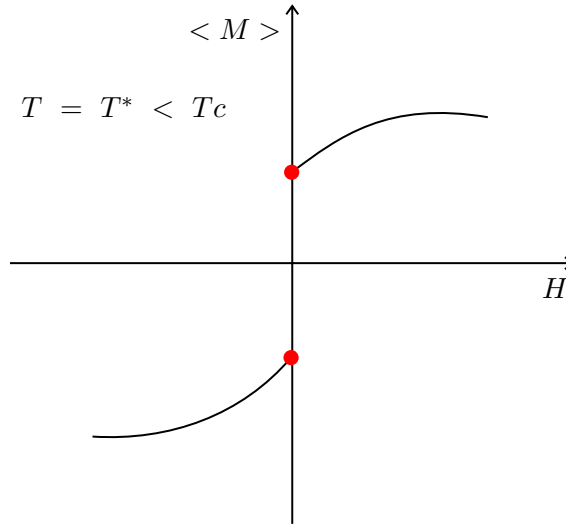
Figure 2.10: Description.

Since $x_A + x_B = 1$ we have $(x_A + x_B)v_D = x_A v_A + x_B v_B$ and finally the **Lever Rule**:

$$\frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A} \tag{2.9}$$

2.8   Thermodynamic of phase coexistence (one component system)

Consider a (P, V, T) system as a mixture of two species $(1, 2)$ at temperature T_1, T_2, pressure P_1, P_2 and chemical potentials μ_1, μ_2. The equilibrium condition is given by the maximum of the total entropy $S = S_1 + S_2$ and gives the conditions

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 \tag{2.10}$$

this is the *coexistence condition* of the two phases. In terms of the Gibbs potential $G = U - TS + PV$, where U is given by the Euler equation $U = TS - PV + \mu_1 N_1 + \mu_2 N_2$,
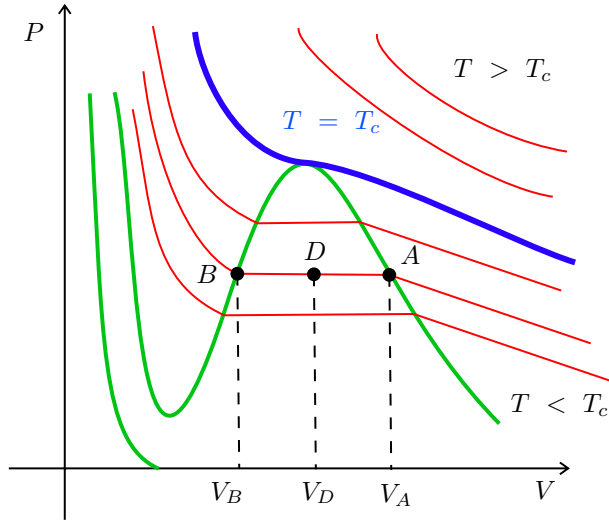
Figure 2.11: Description.

the Gibbs per mole is

$$g_1(T, P) \equiv \frac{G_1}{N_1} = \mu_1 \tag{2.11a}$$

$$g_2(T, P) \equiv \frac{G_2}{N_2} = \mu_2 \tag{2.11b}$$

Therefore, on the coexistence line it should hold the relation

$$g_1(T, P) = g_2(T, P) \tag{2.12}$$

2.9 Clausius-Clapeyron equation

Suppose to know the position an the coexistence line (for example the melt temperature T_m at the atmospheric pressure P_0, as in Figure 2.12). Is it possible to find other points on the curve? For example T_m at lower or higher pressure ?

The answer is yes for small deviations of T and P from a. Rhe idea is to compute the slope of the tangent of the coexistence curve, i.e. $(\mathrm{d}P / \mathrm{d}T)$. This is given by the Clausius-Clapeyron equation. Both at a and b the two phases 1 and 2 coexist. This means that at the coexistence line

$$\begin{cases} g_1^{(a)} = g_2^{(a)} \\ g_1^{(b)} = g_2^{(b)} \end{cases} \tag{2.13}$$

Hence, if a and b are very close:

$$\begin{cases} \mathrm{d}g_1 = g_1^{(b)} - g_1^{(a)} \\ \mathrm{d}g_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \tag{2.14}$$

Therefore, the *starting point* for *Clausius-Clapeyron* is

$$\Rightarrow \mathrm{d}g_1 = \mathrm{d}g_2 \tag{2.15}$$
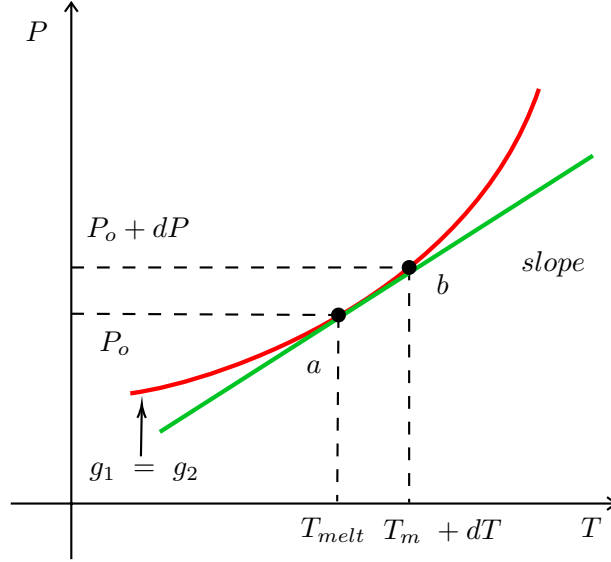
Figure 2.12: Description.

From the molar version of the Gibbs-Duhem relation we have

$$\begin{cases} \mathrm{d}g_1 = -s_1\,\mathrm{d}T + v_1\,\mathrm{d}P = \mathrm{d}\mu_1 \\ \mathrm{d}g_2 = -s_2\,\mathrm{d}T + v_2\,\mathrm{d}P = \mathrm{d}\mu_2 \end{cases} \tag{2.16}$$

taking the difference, one obtains

$$-(s_2 - s_1)\,\mathrm{d}T + (v_2 - v_1)\,\mathrm{d}P = 0 \tag{2.17}$$

The splope is called **Clausius-Clapeyron equation**:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \tag{2.18}$$

Remark. Since $(\mathrm{d}P/\mathrm{d}T)_{coex}$ is finite, the equation explains why a first order transition is characterised by discontinuous changes in entropy and volume (or density). ΔS gives the heat L_{12} that is exchanged with the environment:

$$L_{12} = \Delta S T \tag{2.19}$$

2.9.1   Application of C-C equation to the liquid-gas coexistence line

Now, we go from gas to liquid (we call it respectively region 2 and 1), we have:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1} \tag{2.20}$$

Since for liquid-gas :

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} > 0 \Rightarrow \frac{s_2 - s_1}{v_2 - v_1} > 0 \tag{2.21}$$

and since $v_2 > v_1$, we have $s_2 > s_1$. The gas has more entropy as it should be. When going from a low-temperature phase to a high-temperature phase entropy always increases $\Delta S > 0$, because $c_P \equiv T(\partial S/\partial T)_P > 0$.

The sign of ΔV is more uncertain though. To see this point let us consider the C-C equation at the solid-liquid (now solid is region 1 and liquid region 2) coexistence curve. At the melt temperature:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{coex} = \frac{\delta Q_{melt}}{T_{melt}\Delta v_{melt}} \qquad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0 \tag{2.22}$$

In general, $\Delta v_m = v_{liq} - v_{solid} > 0$ which implies $(\mathrm{d}P \, / \, \mathrm{d}T)_{coex} > 0$. There are cases, however, where $\Delta v_m = v_{liq} - v_{solid} < 0$ because $\rho_{liq} > \rho_{solid}$ (for instance the H_20, or also Silicon and Germanium). The paradigmatic example is the freezing of water where $v_{ice} > v_{liq}$ since ice is less dense than liquid water at the coxistence ($0 < T < 4$). This implies that $\mathrm{d}P \, / \, \mathrm{d}T < 0$.

Example 8 (Melting point on Everest)**.**
    Consider $T = 237K$ and $P = P_0$. If $\delta Q_m = 6.01kJ/mol$ and $\Delta v = -1.7cm^3/mol$ we have:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\delta Q_m}{T \Delta v} = \frac{6.01 10^3 J/mol}{273 \cdot (-1.7cm^3/mol)} = -1.29 \cdot 10^4 J/m^3 = -1.29 bar/K \quad (2.23)$$

$$\Delta T = \frac{\Delta P}{(-1.29 Pa/K)} = \frac{(P_0 - P_{\text{Everest}})}{(-1.29 Pa/K)} = \frac{(1 - 0.36)atm}{(-1.29 Pa/K)} = -0.5C \quad (2.24)$$

$$\Rightarrow T_m(\text{Everest}) = T_m(P_0) + 0.5C \quad (2.25)$$

Example 9 (Boiling point on Everest)**.**
    Consider $P_{\text{Everest}} = 0.36atm$, $\rho(T = 100°\text{C}) = 0.598kg/m^3$ and $L_{ge} = 2.257 \cdot 10^3 J/g$. The density of the vapour is about 1000 less than water, it implies that: $\Delta V = V_g - V_e \approx V_g = \frac{1}{\rho g}$. We have:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_{ge}}{T \Delta V} = \frac{L_{ge} \rho_g}{T} = \frac{2.25 \cdot 10^3 J/g \cdot 0.593 kg/m^3}{373K} = \frac{3.6}{K} \frac{10^3 J}{g} \frac{kg}{m^3} = 3.6 \cdot 10^3 Pa/K$$
$$(2.26)$$
$$\Rightarrow \Delta T \approx \Delta P/(3.6 10^3 Pa/K) = 18°\text{C} \rightarrow T_0 - T_{\text{Everest}} = 18°\text{C} C \Rightarrow T_{\text{Everest}} \approx 80°\text{C}$$
$$(2.27)$$

2.10   Order parameter of a phase transition

The *order parameters* are macroscopic observable that are equal to zero above the critical temperature, and different from zero below:

$$O_p \begin{cases} \neq 0 & T < T_c \\ = 0 & T \rightarrow T_c^- \end{cases} \quad (2.28)$$

When a phase transition implies a breaking of a phase symmetry, the order parameter is related to this symmetry.Therefore, the order parameter reflects the symmetry of the system. Recall that, at T_c the system has a symmetry broken.
    For instance, consider the densities of liquid and gas and the related order parameter of the gas-liquid transition $\Delta \rho = \rho_l - \rho_g$, that is $\neq 0$ for $T \neq T_c$ but $\rightarrow 0$ when $T \rightarrow T_c$ (see Figure 2.13).
    In Figure 2.14 is shown the behaviour for a ferromagnetic system. Clearly $M \neq 0$ if $H \neq 0$. Recall that M is the order parameter of the paramagnetic-ferromagnetic phase transition:

$$H = 0 \Rightarrow \begin{cases} M \neq 0 & T < T_c \\ M \rightarrow 0 & T \rightarrow T_c^- \end{cases} \quad (2.29)$$

Consider *ferromagnetic system*, we have $\vec{\mathbf{M}} \rightarrow \vec{\mathbf{H}}$ (magnetic field), while for *ferro electric* we have $\vec{\mathbf{P}} \rightarrow \vec{\mathbf{E}}$ (electric field). For *liquid crystals* $Q_{\alpha\beta} \rightarrow \vec{\mathbf{E}}, \vec{\mathbf{H}}$, for *fluid* $V \rightarrow P$ (pressure) or $rho \rightarrow \mu$.

Remark. Note that $\rho = \frac{N}{V} = \frac{1}{v}$ hence either N or V varies.
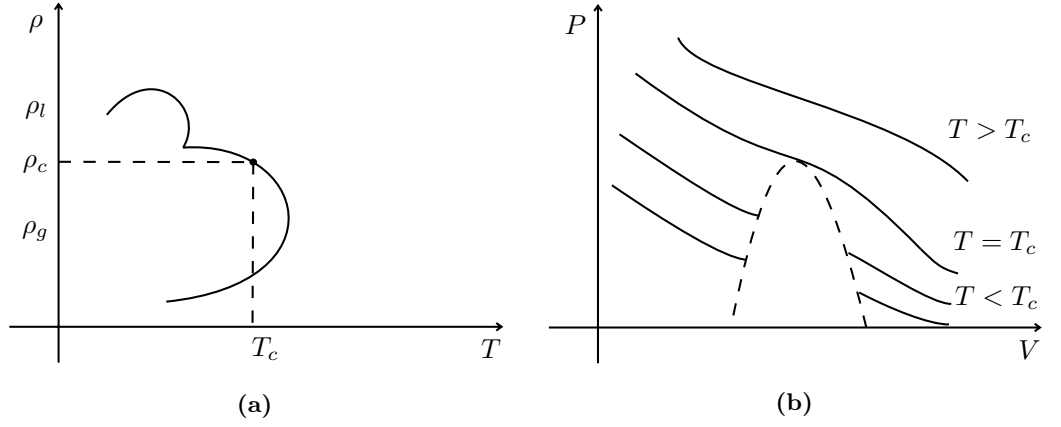
Figure 2.13: Description
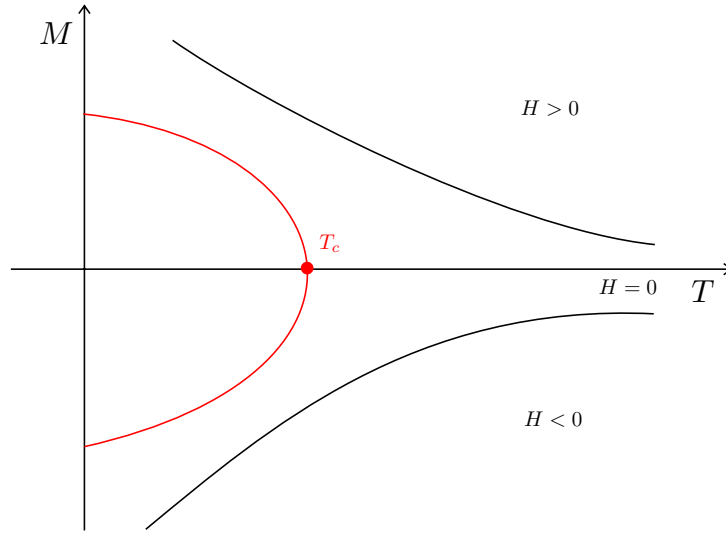
Figure 2.14: Description.

2.11   Divergence of the responde functions at the critical point

While at the critical point the order parameter goes to zero continuously as $T \to T_c^-$, the responde function may develop divergences.

Example 10. In a fluid system since at $T = T_c$ the curve $P = P(V)$ develops an horizontal flex (Figure 2.13b), we have $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \to \infty$. Similarly, in a magnetic since the curve is like Figure , we have $\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \underset{T \to T_c}{\to} \infty$

2.12   Thermodynamic classification of the phase transitions

Thermodynamically one can distinguish two kinds of phase transitions:

1. Ones who develop latent heat.

2. Ones who do not develop latent heat. The entropy changes continuously at the transition.

2.12.1   Eherenfest classification

The *Eherenfest classification* is based on the behaviour of the derivatives of the thermodynamic potentials.

A phase transition is of order *n* if all the *n-1* derivatives are continuous and the nth derivative displays a finite discontinuity.

Example 11. For instance, the first order transition $S = -(\partial G/\partial T)_P$ has finite discontinuity.

Remark. There are first order transitions where S is continuous (no latent heat) but ρ is discontinuous ($v = (\partial G/\partial P)_T$).

Example 12. Second order transition. The specific heat displays a finite jump, see Figure 2.15c in the conductor-superconductor transition.

Second order transition but with divergence. Consider the fluid-superfluid transition (or λ transition) of the He_4 (Figure 2.15d).

(a)

(b) Liquid gas $k_T = -\frac{1}{V}\frac{\partial V}{\partial P}$

(c) 2° order phase transition

(d) Superfluid in λ-transition
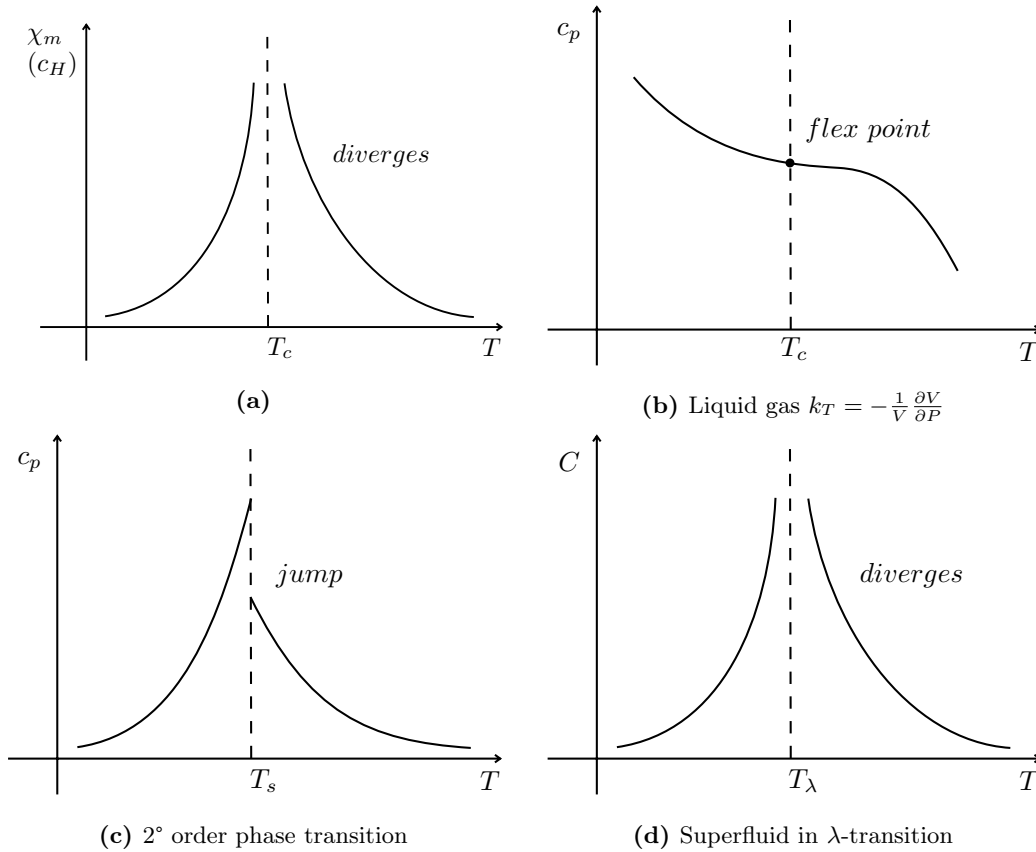
Figure 2.15:   Description

2.12.2   Modern classification

A phase transition is of the first order if exists a finite discontinuity in either one or more partial derivatives of the thermodynamic potentials. If instead the first derivatives are all continuous but the second are either discontinuous or infinite one talks of continuous transitions. A critical point is a continuous transition.

2.13   Critical exponents

At the critical point response functions may diverge. How are these divergence? In general, when you are close to T_c, there are singolarities. Now, we can ask, how the curve diverges? What is the behaviour close to the critical point? Power law, so which are the values of these critical exponents? The notion of *critical exponent* describes the behaviour of the order parameter and the responde functions in proximity of the critical point. In order to answer to these questions, let us define:

Definition 1 (**Critical Exponent** (or *Scale Exponent*))**.** Define the adimensional parameter measuring the distance from the critical point $t \equiv \frac{T-T_c}{T_c}$, the *Critical Exponent* λ associated to the function $F(t)$ is defined as:

$$\lambda_\pm = \lim_{t \to 0^\pm} \frac{\ln |F(t)|}{\ln |t|} \tag{2.30}$$

We note that it behaves like a power low and that one can also write the **power law**:

$$F(t) \overset{t \to 0^\pm}{\sim} |t|^{\lambda_\pm} \tag{2.31}$$

More generally, for $t \ll 1$:

$$F(t) = A|t|^{\lambda_\pm}(1 + bt^{\lambda_1} + \dots) \quad \lambda_1 > 0 \tag{2.32}$$

where all other terms are less important.

Definition 2 (Thermodynamic critical exponents)**.**

- **Exponent** β : tells how the order parameter goes to zero. Consider Figure 2.16a, we have $M \overset{t \to 0^-}{\sim} (-t)^\beta$. No sense in going from above where it stays 0.

- **Exponent** $\gamma_\pm$ (suscettibility): related to the response function. Consider Figure 2.16b, we have $\chi_T \overset{t \to 0^\pm}{\sim} |t|^{-\gamma_\pm}$. In principle, the value of γ can depend on the sign of t i.e. $\gamma^+ \neq \gamma^-$, but they are the same in reality and we have $\gamma^+ = \gamma^- = \gamma$.

- **Exponent** $\alpha_\pm$: how specific heat diverges (second order derivative in respect of T). For instance see Figure 2.16c, we have $c_H \sim |t|^{-\alpha_\pm}$.

- **Exponent** δ: in this case one consider the isotherm $T = T_c$ and look for the behaviour of M at the critical point at small H (or viceversa). The result is $M \sim H^{1/\delta}$. In Figure 2.16d, $H \sim |M|^\delta \text{sign}(M)$.

2.13.1   Law of the corresponding states

The system displays correlation at very long distance, these goes to the size of the system when $T \to T_c$. We are talking about long range correlation. The *correlation function* is $\xi \sim t^{-\nu}$. For instance, consider a polymer as in Figure 2.17a.

The critical exponents are more interesting than T_c since their values do not depend on microscopic details but only on few parameters such as the space dimension d and the symmetry of the system. One of the first experimental evidence of this universality was given by the work of Guggenheim on the coexistence curves of g different fluids: A, Kn, χ_e, Ne, N_2, CO_2 and O_2. By plotting T/T_c versus ρ/ρ_c

(a) Exponent β

(b) Exponent $\gamma_\pm$

(c) Exponent $\alpha_\pm$

(d) Exponent γ
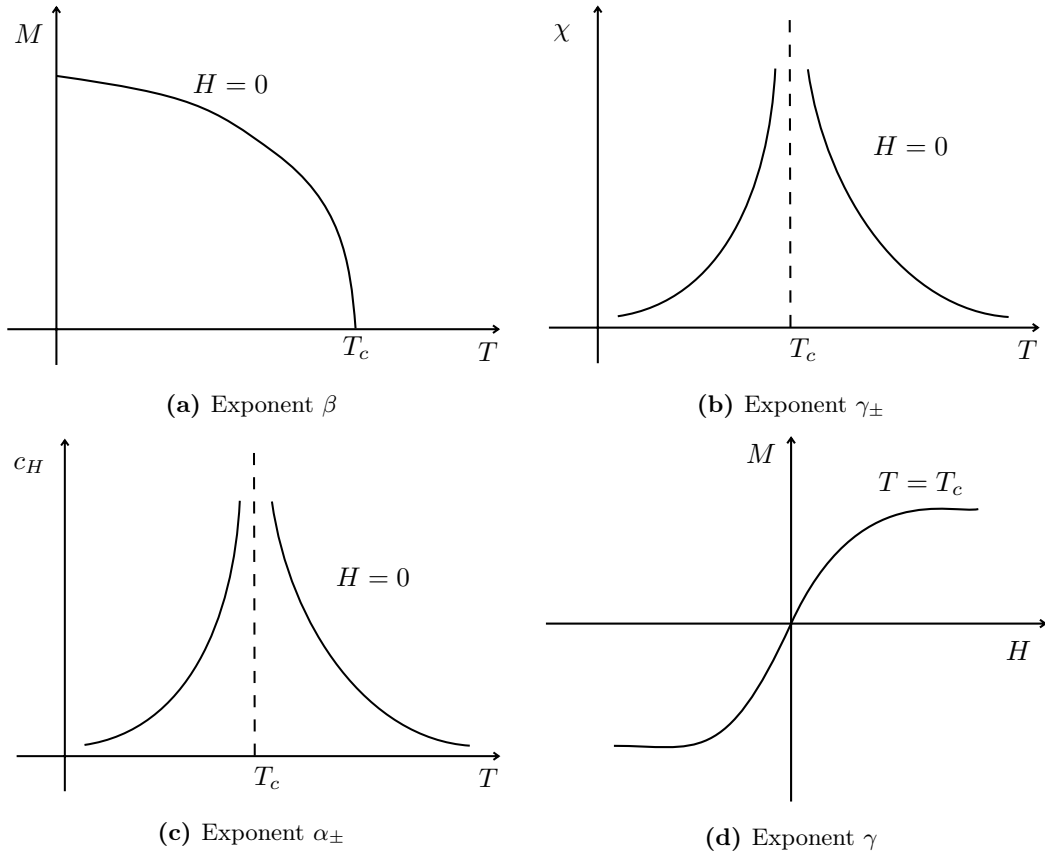
Figure 2.16: Description

(Figure 2.17b) he found that all the data collapse on the same curve, i.e. different sets of data fit the same function. Moreover for $t \to 0$:

$$(\rho_l - \rho_c) \sim (-t)^\beta \tag{2.33}$$

and $\beta \sim 1/3 \approx 0.335$. If you do the same for a string ferromagnetic is $1/3$ too.

Remark. The law of corresponding states gives a universal liquid-gas coexistence curve.

The law is quite remarkable considering the spread in the values of critical parameters of the substances considered.

2.13.2 Thermodynamic inequalities between critical exponents

Rushbrocke inequality

Remember the relation between response functions:

$$\begin{cases} k_T(c_p - c_v) = Tv\alpha^2 = Tv\frac{1}{v^2}\left(\frac{\partial v}{\partial T}\right)_P^2 = T\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P^2 \\ \chi_T(c_H - c_M) = T\left(\frac{\partial M}{\partial T}\right)_H^2 \end{cases} \tag{2.34}$$

from the thermodynamic stability we have $c_M \geq 0, \chi_T \geq 0$. Hence from the previous relation we have

$$c_H \geq \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)^2 \tag{2.35}$$

On the other hand, for $T \to T_c^-$ and $H = 0$ we have

$$\begin{cases} c_H \sim (-t)^{-\alpha} \\ \chi_T \sim (-t)^{-\gamma} \end{cases} \tag{2.36}$$

Therefore $M \sim (-t)^{\beta}$, which implies $\left(\frac{\partial M}{\partial T}\right)_{H=0} \sim (-t)^{\beta-1}$. Since the inequality is valid for all temperature T it follows

$$B(T_c - T)^{-\alpha} \geq B'T\frac{[(T_c - T)^{\beta-1}]^2}{(T_c - T)^{-\gamma}} \tag{2.37}$$

with $B, B' > 0$. Take the limit $T \to T_c^-$ we have:

$$\lim_{T \to T_c^-} (T_c - T)^{2-\alpha-2\beta-\gamma} \geq \frac{B'T}{B} > 0 \tag{2.38}$$

Since the left hand side must be strictly greater than zero we have the **RushBrook inequality**:

$$\alpha + 2\beta + \gamma \geq 2 \tag{2.39}$$

Is obtained from the convexity property (in T and V) of the Helmolds free energy and from $A \sim t^{2-\alpha}$:

$$\Rightarrow \alpha + \beta(1 + \delta) \geq 2 \tag{2.40}$$

N

(a) Description

(b) Description
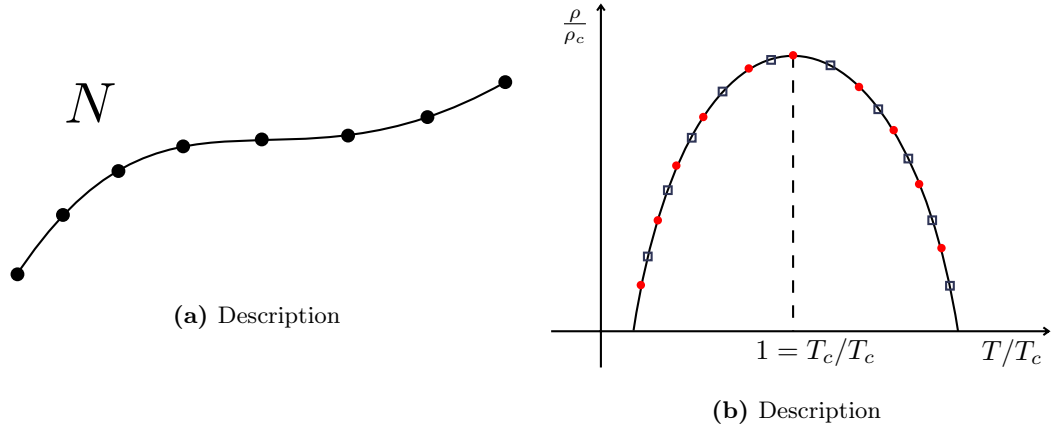
Figure 2.17

Chapter 3

Recall of statistical mechanics and theory of ensambles

3.1 Statistical ensambles

Statistical mechanics roughly speaking was born as a sort of theory from microscopic and try to compute the macroscopic lenght using thermodynamics. The problem is going from the countinuous problems to the macroscopic problems. In origin was statistical mechanics of equilibrium system. Each microstate with a given energy fixed, will have the same probability, this is the equal probability statement.

In general, if we consider a system with N, V (number of particles and volume) fixed and also the total energy E fixed, we call $\Omega(E, V, N)$ the number of microstate with total energy E , volume V and number of particles N.

If the system is *isolated* and in *equilibrium* the rule of **equal probability** of the microstates holds:

> If the system is isolated and in equilibirum with energy E it visits each microstate consistent with energy E with equal probability.

Another way to say is: the system spends the same amount of time in each of the $\Omega(E, V, N)$ microstates.

Therefore, we call a single configuration of a given microstate $\mathcal{C}$. A configuration is just when you have the spatial part, because momentum can be obtained by integrating. Suppose you want to compute the probability of a given configuration $\mathcal{C}$, $P_{\mathcal{C}}$, because there is equal probability:

$$P_{\mathcal{C}} = \frac{1}{\Omega(E, V, N)} \tag{3.1}$$
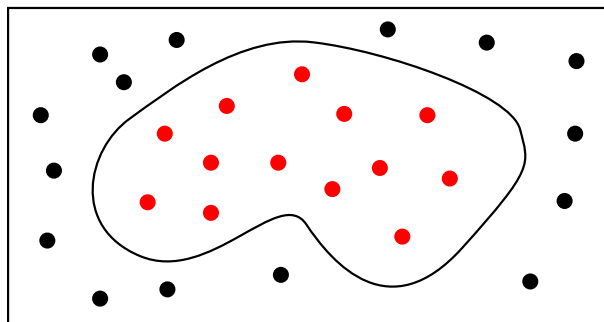
Figure 3.1: Description.

Let us now consider two subsystem 1 and 2 that can exchange energy,volume and/or particles. The number of microstates of the combined system of total energy $E_T = E_1 + E_2$, total volume $V_T = V_1 + V_2$ and $N_T = N_1 + N_2$ is given by:

$$\Omega(E_T, V_T, N_T) = \sum_{E_1, V_1, N_1} \Omega_1(E_1, V_1, N_1)\Omega_2(E_T - E_1, V_T - V_1, N_T - N_1) \quad (3.2)$$

One can shot that in the thermodynamic limit at equal $\Omega(E_T, V_T, N_T)$ is strongly peaked around a given point (E_1^*, V_1^*, N_1^*) and the fluctuations around this value are rare and small. Writing $\Omega(E_T, V_T, N_T)$ as

$$\Omega(E_T, V_T, N_T) \propto e^{\frac{S(E_T, V_T, N_T)}{k_B}} = \sum_{E_1, V_1, N_1} \exp\left[\frac{1}{k_B}(S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2))\right]$$
$$(3.3)$$

The values (E_1^*, V_1^*, N_1^*) are obtained by the max entropy condition that can be written as

$$\frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2} \Rightarrow T_1 = T_2 \quad\quad\quad (3.4a)$$

$$\frac{d\ln\Omega_1}{dV_1} = \frac{d\ln\Omega_2}{dV_2} \Rightarrow P_1 = P_2 \quad\quad\quad (3.4b)$$

$$\frac{d\ln\Omega_1}{dN_1} = \frac{d\ln\Omega_2}{dN_2} \Rightarrow \mu_1 = \mu_2 \quad\quad\quad (3.4c)$$

We next consider these properties to the case in which 1 is the system we want to study and 2 is a much larger system than 1 (a bath). This setup will bring us to the *canonical ensemble*.

3.2   The canonical ensemble

Let us consider an isolate system made by two subsystems, one S and one much larger, B, that we call *thermal bath* (Figure 3.1). The total number of particles is given by $N_T = N_B + N_S$ with $N_B \gg N_S \gg 1$ (they are both large but B is much larger than S), where N_B are the particles in the thermal bath and N_S the particle of the system. Let E_T be the energy of the composite system. The two subsystems can exchange energy but the whole system has constant energy E_T. Therefore, let the energy to be free to fluctuate in time at fixed temperature T_B (isotherma ensambles). Note that V_S, N_S, V_B, N_B are fixed (no exchange of volume and particles). For reasuming, other quantitites fixed are the temperature of the bath T_B , the number of the total particles of the system N_T, and also the total volume V_T . We have also $V_T = V_B + V$, with $V_B \gg V$.

If one assumes that the system and the bath are *weakly coupled* (neglet interaction energy):

$$E_T = E_S + E_B = const \quad\quad E_B \gg E_S \quad\quad\quad (3.5)$$

Let $\mathcal{C}$ by the microstate of the system, and $\mathcal{G}$ the microstate of the heat bath. A given microstate of the isolated composite system B-S is given from a pair $(\mathcal{C}, \mathcal{G})$ of microstate $\mathcal{C} \in S$ and $\mathcal{G} \in B$. The number of microstates of the isolated system with total energy E_T and system energy E_S is given by:

$$\Omega_T(E_T, E_S) = \Omega(E_S)\Omega_B(E_T - E_S) \quad\quad\quad (3.6)$$

Remark. In this analysis V and N are fixed. Since E_T is fixed

$$\Omega_T(E_T) = \sum_{E_S} \Omega(E_S)\Omega_B(E_T - E_S) \quad\quad\quad (3.7)$$

From the principle of equal probability for microstates at equilibrium, the probability of a composed microstate $(\mathcal{C} \circ \mathcal{G})$ is given by:

$$P_{\mathcal{C} \circ \mathcal{G}} = \begin{cases} \frac{1}{\Omega_T(E_T)} & E_{\mathcal{C}} + E_{\mathcal{G}} = E_T \\ 0 & \text{otherwise} \end{cases} \tag{3.8}$$

Since we are not interested to the microstates of the heat bath

$$P_{\mathcal{C}} = \sum_{\substack{\text{all } \mathcal{G} \\ \text{such that} \\ g(E_T - E_{\mathcal{C}} - E_{\mathcal{G}})}} P_{\mathcal{C} \circ \mathcal{G}} = \sum_{\mathcal{G}} \frac{1}{\Omega_T(E_T)} = \frac{1}{\Omega_T} \sum_{\mathcal{G}} 1 \tag{3.9}$$

The number of microstates $\mathcal{G}$ with energy $E_{\mathcal{G}} = E_T - E_{\mathcal{C}}$ is given by:

$$\Omega_B(E_{\mathcal{G}}) = \Omega_B(E_T - E_{\mathcal{C}}) \tag{3.10}$$

This implies that the probability of a given configuration is related to the number of microstate of the bath:

$$\Rightarrow P_{\mathcal{C}} = \frac{\Omega_B(E_T - E_{\mathcal{C}})}{\Omega_T(E_T)} \propto \Omega_B(E_T - E_{\mathcal{C}}) \tag{3.11}$$

It is more convenient to deal with the logarithmic of $P_{\mathcal{C}}$ that is smoother

$$\Rightarrow \ln \Omega_B(E_T - E_{\mathcal{C}}) \tag{3.12}$$

This is the entropy of B and is a function of N_B. Since $E_{\mathcal{C}} \ll E_B \simeq E_T$ we can expand $S_B(E_T - E_{\mathcal{C}})$ around E_T by the small amount

$$\Delta \equiv x - x_0 = -E_{\mathcal{C}} \tag{3.13}$$

$$f(E_B) = f(E_T) + \left. \frac{df}{dE_B} \right|_{E_B = E_T} (E_B - E_T) + \ldots \tag{3.14}$$

Therefore:

$$k_B \ln \Omega_B(E_B) = S_B(E_B) = S_B(E_T) - E_{\mathcal{C}} \left(\frac{\partial S_B}{\partial E_B} \right)_{E_B = E_T} + \frac{E_{\mathcal{C}}^2}{2} \left(\frac{\partial^2 S_B}{\partial E_B^2} \right)_{E_B = E_T} + \ldots \tag{3.15}$$

To make explicit the N_B dependence let us consider the molar version

$$S_B \to N_B s_B \qquad E_B \to N_B e_B \tag{3.16}$$

$$s_B N_B = N_B s_B(E_T) - E_{\mathcal{C}} \left(\frac{\partial s_B}{\partial e_B} \right)_{e_B = e_T} + \frac{E_{\mathcal{C}}^2}{2N_B} \left(\frac{\partial^2 s_B}{\partial e_B^2} \right) \tag{3.17}$$

Let us consider the limit in ehich the system size is fixed while the one of the heat bath is going to ∞:

$$\lim_{N_B \to \infty} \frac{E_T}{N_B} = \frac{E + N_B e_B}{N_B} \to e_B \tag{3.18a}$$

$$\lim_{N_B \to \infty} k_B \ln \Omega_B(E_T - E_{\mathcal{C}}) \to N_B s_B - E_{\mathcal{C}} \frac{ds_B}{de_B} \tag{3.18b}$$

On the other hand

$$\frac{ds_B}{de_B} \equiv \frac{1}{T_B} = \frac{1}{T} \tag{3.19}$$

which implies

$$P_{\mathcal{C}} \propto \Omega_B(E_T - E_{\mathcal{C}}) = \exp\left(\frac{N_B s_B}{k_B} - \frac{E_{\mathcal{C}}}{k_B T} \right) \tag{3.20}$$

Since the first therm does not depend on $\mathcal{C}$, it can be absorbed in the constant and what we get by expanding considering the huge number of particles

$$P_{\mathcal{C}} \propto \exp(-E_{\mathcal{C}}/k_B T) \tag{3.21}$$

Observation 1. Since the energy of the system fluctuates, its microstates are not anywhere equiprobable but are visited with probability given by (3.21).

Remark. Since the bath is very large T is the only property of the bath that affects the system. The **Boltzmann factor** is defined as:

$$\beta \equiv \frac{1}{k_B T} \tag{3.22}$$

The normalization consists in dividing by the normalization factor that is the sum of all microstates

$$P_{\mathcal{C}} = \frac{e^{-\beta E_{\mathcal{C}}}}{\sum_{\mathcal{C}} e^{-\beta E_{\mathcal{C}}}} \tag{3.23}$$

Finally, the **canconical partition function** is defined as

$$Q(T, V, N) \equiv \sum_{\substack{\text{all } \mathcal{C} \\ \text{with } V, N \\ \text{fixed}}} \exp(-\beta E_{\mathcal{C}}) \tag{3.24}$$

Given $Q(T, V, N)$ one gets the *Helhmoltz free energy*

$$A(T, V, N) = -k_B T \ln Q(T, V, N) \tag{3.25}$$

that is the free energy describing the isothermal (or canonical) ensemble at fixed T, volume V and number of particles N.

Remark.

$$Q(T, V, N) = \sum_{\substack{\mathcal{C} \\ V, N \text{fixed}}} e^{(-\beta E(\mathcal{C}))} = \sum_E e^{-\beta E} \Omega(E, V, N) \tag{3.26}$$

What we have done is a *foliation* in energy of the space, that is a sum over the energy (keeping $\{V, N\}$ fixed):

$$Q(T, V, N) = \sum_E e^{-\beta E} \Omega(E, V, N) = \sum_E e^{-\beta E} e^{S/k_B} = \sum_E e^{-\beta(E - TS)} \tag{3.27}$$

3.2.1   Energy fluctuations in the canonical ensemble

Despite energy in the canonical ensemble fluctuates while in the microcanonical one is constant this does not contradict the equivalence principle of the ensemble (in the thermodynamic limit). The reason is that the relative size of the energy fluctuation decreases in the large system limit. Remember that thermodynamic assume that the number of number of freedom is related to the number of Avogadro. To see it let us compute the average square fluctuations of E.

$$\langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \tag{3.28}$$

On the other hand

$$\langle E \rangle = \sum_{\mathcal{C}} P_{\mathcal{C}} E_{\mathcal{C}} = \sum_{\mathcal{C}} E_{\mathcal{C}} \frac{e^{-\beta E_{\mathcal{C}}}}{\sum_{\mathcal{C}} e^{-\beta E_{\mathcal{C}}}}$$
$$= -\left(\frac{\partial Q(T, V, N)}{\partial \beta} / Q \right) = -(\partial \ln Q / \partial \beta)_{N, V} \tag{3.29}$$

$$\langle E^2 \rangle = \sum_{\mathcal{C}} P_{\mathcal{C}} E_{\mathcal{C}}^2 = (\partial^2 Q / \partial \beta^2) / Q \tag{3.30}$$

$$\langle(\delta E)^2\rangle = \langle(E - \langle E\rangle)^2\rangle = Q^{-1}\left(\frac{\partial^2 Q}{\partial\beta^2}\right)_{N,V} - Q^{-2}\left(\frac{\partial Q}{\partial\beta}\right)_{N,V}^2$$

$$= \left(\frac{\partial^2 \ln Q}{\partial\beta^2}\right)_{N,V} = -\left(\frac{\partial \langle E\rangle}{\partial\beta}\right)_{N,V} \tag{3.31}$$

Since

$$c_v = \left(\frac{\partial E}{\partial T}\right)_{N,V} \tag{3.32}$$

we have

$$\langle(\delta E)^2\rangle = k_B T^2 c_v \tag{3.33}$$

Both c_V and $\langle E\rangle$ are extensive

$$\frac{\sqrt{\langle(\delta E)^2\rangle}}{\langle E\rangle} = \frac{\sqrt{k_B T^2 c_v}}{\langle E\rangle} \sim O\left(\frac{1}{\sqrt{N}}\right) \Rightarrow 0 \tag{3.34}$$

because $N \sim 10^{23}$.

3.3   Isothermal and isobaric ensemble

Now the system is coupled both to a thermal and a volumic bath at temperature T_B and pressure P_B. The idea is now: consider the same system with the bath. Now the system can exchange energy but also volume (we continue to keep the temperature of the bath fixed). At this point the ensamble is *isothermal* and *isobaric*. All the assumputions done before are valid, in particular assuming as before *weak coupling* between the degrees of freedom of the bath and those of the system

$$E_T = E + E_B \tag{3.35a}$$
$$V_T = V + V_B \tag{3.35b}$$

we look for the partition function that describes this isothermal and isobaric ensemble. Similarly to the previous case one can write

$$P_{\mathcal{C}} \propto \Omega_B(E_B, V_B) \propto \Omega_B(E_T - E_{\mathcal{C}}, V_T - V_{\mathcal{C}}) \propto \exp[S_B(E_T - E_{\mathcal{C}}, V_T - V_{\mathcal{C}})/k_B] \tag{3.36}$$

Remark. Now $\mathcal{C}$ is specified both by its volume V and energy E. As before one can expand $\log\Omega_B$ both in E_B and in V_B (around E_T and V_T) and take the limit $N_B \to \infty$.

$$P_{\mathcal{C}} \propto \exp\left[\frac{S_B(E_T, V_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B}\frac{\partial S_B}{\partial E_B}\bigg|_{E_T,V_T} - \frac{V_{\mathcal{C}}}{k_B}\frac{\partial S_B}{\partial V_B}\bigg|_{V_T,E_T} + (term \simeq \frac{1}{N_B})\right] \tag{3.37}$$

Recalling that

$$\frac{\mathrm{d}S}{\mathrm{d}V}\bigg|_E = \frac{P}{T} \qquad \begin{cases} P_B \to P \\ T_B \to T \end{cases} \tag{3.38}$$

$$\Rightarrow P_{\mathcal{C}} \propto \exp\left[-\frac{E_{\mathcal{C}}}{k_B T} - \frac{P V_{\mathcal{C}}}{k_B T}\right] \tag{3.39}$$

If we normalize, at this point the only quantity fixed is N:

$$P_{\mathcal{C}} = \frac{e^{-\beta(E_{\mathcal{C}} + P V_{\mathcal{C}})}}{\Delta(T, P, N)} \quad \text{where} \quad \Delta(T, P, N) = \sum_{\mathcal{C}} e^{-\beta(E(\mathcal{C}) + P V(\mathcal{C}))} \tag{3.40}$$

Note that $\Delta(T, P, N)$ is called the *Gibbs partition function*:

$$
\Delta(T, P, N) = \sum_V e^{-\beta PV} \Big(\sum_{\substack{\mathfrak{e} \\ V, N \text{fixed}}} e^{-\beta E_{\mathfrak{e}}} \Big) \underset{\substack{Laplace \\ transform}}{=} \sum_V e^{-\beta PV} Q(T, V, N)
$$

$$
= \underbrace{\sum_V \sum_E}_{\substack{\text{fluctuating} \\ \text{variables}}} e^{-\beta(E+PV)} \Omega(E, V, N) \tag{3.41}
$$

By summing over all the microstates compatible with E and V:

$$
P(E, V) = \frac{\Omega(E, V, N)}{\Delta(T, P, N)} e^{-\beta(E+PV)} \tag{3.42}
$$

Remark.

$$
\Delta(T, P, N) = \underbrace{\sum_E \sum_V e^{-\beta E - \beta PV}}_{\text{Laplace transform}} \Omega(E, V, N) = \sum_{E,V} e^{-\beta E - \beta PV + S(E,V,N)/k_B} \tag{3.43}
$$

3.3.1   Saddle point approximation

The sum can be approximated by the maximum of the integrand (this is fair for highly peaked functions):

$$
\sum_{E,V} \exp[-\beta E - \beta PV + S(E, V, N)/k_B] \approx e^{-\beta E^* - \beta PV^* + S(E^*, V^*, N)/k_B} \tag{3.44}
$$

where

$$
\left(\frac{\mathrm{d}S(E^*, V^*, N)}{\mathrm{d}E} \right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\mathrm{d}S(E^*, V^*, N)}{\mathrm{d}V} \right)_{E,N} = \frac{P}{T} \tag{3.45}
$$

this implies

$$
-k_B T \ln \Delta(T, P, N) \simeq E^* + PV^* - TS \tag{3.46}
$$

We define the *Gibbs free energy*:

$$
G(T, P, N) = -k_B T \ln \Delta(T, P, N) \tag{3.47}
$$

For classical systems (fluids)

$$
\Delta(T, P, N) = \int_0^\infty \mathrm{d}V \, e^{-\beta PV} [\frac{1}{h^{3N} N!} \int \mathrm{d}\vec{p_1} \dots \mathrm{d}\vec{p_N} \, e^{-\beta \mathcal{H}(p^N, r^N)}] \tag{3.48}
$$

which implies

$$
\Delta(T, P, N) = \int_0^\infty \mathrm{d}V \, e^{-\beta PV} Q(T, V, N) \tag{3.49}
$$

that is the Laplace transform of the canonical partition function Q.

$$
\beta P \equiv \frac{P}{T} = \frac{\partial S}{\partial V} \tag{3.50}
$$

3.4 Magnetic system

Ensamble in which both E and M can fluctuate $\Omega(E, M)$ (both with T_B and H_B).

$$P_{\mathcal{C}} \propto e^{S_B(E_T, M_T)/k_B - \frac{E_{\mathcal{C}}}{k_B}\frac{\mathrm{d}S_B}{\mathrm{d}E_B} - \frac{M_{\mathcal{C}}}{k_B}\frac{\mathrm{d}S_B}{\mathrm{d}M_B}} \tag{3.51}$$

Since $\frac{\mathrm{d}S_B}{\mathrm{d}M_B} = -\frac{H_B}{T_B}$ and $\frac{\mathrm{d}S_B}{\mathrm{d}E_B} = \frac{1}{T_B}$:

$$\Rightarrow P_{\mathcal{C}} \propto \exp[-\beta(E_{\mathcal{C}} - HM_{\mathcal{C}})] \qquad T_B \to T, H_B \to H \tag{3.52}$$

Normalization function:

$$\Delta(T, H, N) = \sum_{\mathcal{C}} e^{-\beta(E_{\mathcal{C}} - HM_{\mathcal{C}})} = \sum_{E, M} e^{-\beta E + \beta MH}\Omega(E, M) \tag{3.53}$$

that is the *Gibbs partition function* for magnetic systems.

3.5 Gran canonical ensemble

In this case N varies instead than V.

$$
\begin{aligned}
P_{\mathcal{C}} &= \exp\left[\frac{S_B(E_T - E_{\mathcal{C}}, N_T - N_{\mathcal{C}})}{k_B}\right] \\
&\sim \exp\left[\frac{S_B(E_T, N_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B}\frac{\mathrm{d}S_B}{\mathrm{d}E_B} - \frac{N_{\mathcal{C}}}{k_B}\frac{\mathrm{d}S_B}{\mathrm{d}N_B} + (\text{terms of order} \le \frac{1}{V_B})\right] \\
&= \frac{\exp[-\beta E_{\mathcal{C}} + \beta\mu N_{\mathcal{C}}]}{\Theta(T, V, \mu)}
\end{aligned}
\tag{3.54}
$$

where the *grancanonical partition function* is:

$$\Theta(T, V, \mu) = \sum_N \sum_{\substack{\mathcal{C} \\ V, N\text{fixed}}} e^{-\beta(E_{\mathcal{C}} - \mu N)} = \sum_{N=0}^{\infty} z^N \left(\sum_{\substack{\mathcal{C} \\ V, N\text{fixed}}} e^{-\beta E_{\mathcal{C}}}\right) \tag{3.55}$$

with the *fugacity*: $z \equiv e^{\beta\mu}$.

In principle, if one is able to compute the partition function is able to compute the thermodynamic quantitites.

Chapter 4

Statistical mechanics and phase transitions

4.1 Statistical mechanics of phase transitions

From the microscopic degrees of freedom one compute the partition function in the appropriate ensemble, then the corresponding thermodynamic potential and from it all the thermodynamic properties of the system as *equilibrium phases* and, if present *phase transitions*. Actually, until the '30 there were strong concerns about the possibility that statistical mechanics could describe phase transitions.

(a) Description
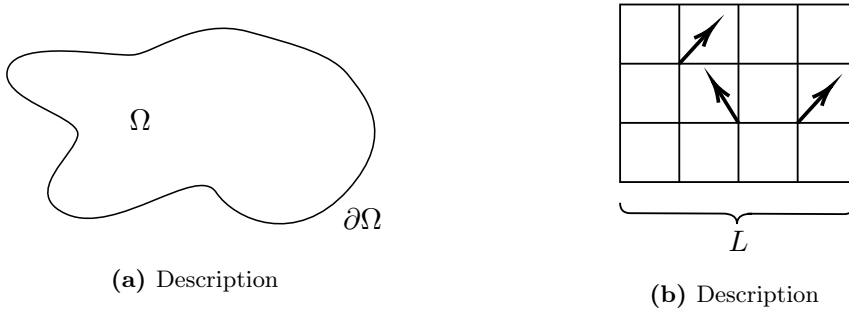
(b) Description

Figure 4.1: Description

Let us consider a system withing a region Ω of volume $V(\Omega)$ and boundary $\partial\Omega$ of area $S(\Omega)$. Denoting by L a characteristic lenght of the system

$$V(\Omega) \propto L^d, \quad S(\partial\Omega) \propto L^{d-1} \tag{4.1}$$

where d is the spatial dimension.

Remark. Space Ω can be either *discrete* or *continuous*.

Suppose the system is *finite*. Formally we can write

$$\mathcal{H}_\Omega = -\sum_n k_n \Theta_n \tag{4.2}$$

where

- k_n: are the coupling constants. In general, but not always, they are *intensive thermodynamic variables*.

- Θ_n: is a linear of higher order combination of the dynamical microscopic degrees of freedom (local operators in quantum statistical mechanics).

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- $k_n \Theta_n$: must obey the symmetry of the system. It is important that in principle the term satisfies the symmetry of the system. This is a master rule!

To fix the idea let us consider two classical examples: the magnetic system and the fluid system.

4.1.1   Magnetic system

The degrees of freedom are the *spins* lying on a Bravais lattice $\vec{\mathbf{S_i}}$ with $1 \leq i \leq N(\Omega)$, where the $N(\Omega)$ are the number of lattice sites (Figure 4.1b). A configuration is the orientation of the spin in each site $\mathcal{C} = \{\vec{\mathbf{S_1}}, \dots, \vec{\mathbf{S_N}}\}$. We have:

$$\Theta_1 = \sum_i \vec{\mathbf{S_i}} \tag{4.3a}$$

$$\Theta_2 = \sum_{ij} \vec{\mathbf{S_i}} \cdot \vec{\mathbf{S_j}} \tag{4.3b}$$

We consider the trace operation that is the sum over all possible values that each degree of freedom can assume:

$$\mathrm{Tr} \equiv \sum_{\{\mathcal{C}\}} \equiv \sum_{\vec{\mathbf{S_1}}} \sum_{\vec{\mathbf{S_2}}} \cdots \sum_{\vec{\mathbf{S_N}}} \tag{4.4}$$

where $\sum$ can also indicate an integration if values are continuous. The canonic partition function is

$$Q_\Omega(T, \{k_n\}) = \mathrm{Tr}\left(e^{-\beta \mathcal{H}_\Omega}\right) \quad \text{with} \quad \beta \equiv \frac{1}{k_B T} \tag{4.5}$$

4.1.2   Fluid system (gran canonical)

Consider N particles in a volume V, with number density $\rho = N/V$. The $2dN$ degrees of freedom are

$$\{\mathcal{C}\} = \{(\vec{\mathbf{x_i}}, \vec{\mathbf{p_i}})_{i=1,\dots,N}\} \tag{4.6}$$

and

$$\Theta_1 = \sum_i \left[\frac{\vec{\mathbf{p_i}}^2}{2m_i} + U_1(\vec{\mathbf{x_i}}) \right] \tag{4.7a}$$

$$\Theta_2 = \frac{1}{2} \sum_{i>j} U(|\vec{\mathbf{x_i}} - \vec{\mathbf{x_j}}|) \tag{4.7b}$$

The trace operation is

$$\mathrm{Tr} \equiv \sum_{\{\mathcal{C}\}} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{(d\vec{\mathbf{p_i}})(d\vec{\mathbf{x_i}})}{h^{dN}} \tag{4.8}$$

$$\mathcal{F}_\Omega = \mathrm{Tr}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) \tag{4.9}$$

For a generic partition function $Q_\Omega(T, \{k_n\})$ we can define the finite system *free energy* as

$$F_\Omega[T, \{k_n\}] = -k_B T \ln Q_\Omega(T, \{k_n\}) \tag{4.10}$$

The relation with thermodynamic is trough the *theromdynamic limit*. Since the free energy is an extensive function

$$F_\Omega \propto V(\Omega \sim L^d \tag{4.11}$$

In general, one can write

$$F_\Omega[T, \{k_n\}] = V(\Omega) f_b[T, \{k_n\}] + S(\Omega) f_s[T, \{k_n\}] + O(L^{d-2}) \qquad (4.12)$$

where $f_b[T, \{k_n\}]$ is the bulk free energy density.

Definition 3. We define

$$f_b[T, \{k_n\}] \equiv \lim_{V(\Omega) \to \infty} \frac{F_\Omega[T, \{k_n\}]}{V(\Omega)} \qquad (4.13)$$

If the limit exists (to prove for each system) and does not depend on Ω.

For a system defined on a lattice we have

$$L(\Omega) \propto N(\Omega)^{1/d}, \quad V(\Omega) \propto N(\Omega) \qquad (4.14)$$

$$f_b[T, \{k_n\}] = \lim_{N(\Omega) \to \infty} \frac{1}{N(\Omega)} F_N[T, \{k_n\}] \qquad (4.15)$$

To get information on surface property of the system

$$f_s[T, \{k_n\}] \equiv \lim_{S(\Omega) \to \infty} \frac{F_\Omega[T, \{k_n\}] - V(\Omega) f_b}{S(\Omega)} \qquad (4.16)$$

4.2 Thermodynamic limit with additional constraints

For a fluid we cannot simply take the limit $V(\Omega) \to \infty$ by keeping N fixed, otherwise we will always get a infiinite system with *zero density*. One has to take also the limit $N(\Omega) \to \infty$ such that:

$$\frac{N(\Omega)}{V(\Omega)} \equiv \rho = const \qquad (4.17)$$

In general is not so easy to prove the existence of the limit and it depends on the range of the particle-particle interactions.

4.2.1 Statistical mechanics and phase transitions

Since all the thermodynamic information of a system can be obtained by the partition function, in principle also the ones concerning the existence and nature of the phase transition must be contained in Z (or Q). On the other hand we know from thermodynamic that phase transitions are characterized by singularities in the derivation of F. Also Z must display these singularities. On the other hand Z is a sum of exponentials

$$Z_\Omega = \mathrm{Tr}\left(e^{-\beta \mathcal{H}_\Omega}\right) \qquad (4.18)$$

These are analytic functions everywhere (it converges), therefore Z_Ω is analytic for Ω finite! The question is: where the singularities came from? It is only in the thermodynamic limit that singularities in F and hence points describing phase transitions can arise!

For summarizing, there is no way in you can produce singularities out of this. The singularities will develop in the thermodynamic limits. For reach singulariities we have to reach so precision in thermodynamic that we are not able to go extactly into the critical point. How can we relate singularities in the behaviour of the system geometrically?

4.3   Critical point and correlations of fluctuations

From thermodynamics we know that, at the critical point, some response functions may diverge. We now show that this is a consequence pf the onset of microscopic fluctuactions that are spatially correlated over long distances. To see this let us compute the response of a ferromagnetic in presence of an external magnetic field H. The Gibbs partition function of a generic magnetic system is

$$Z_{\text{Gibbs}}[T, \{k_n\}] = \text{Tr}\left(e^{-\beta(\mathcal{H}(\mathcal{C}) - HM(\mathcal{C}))}\right) = \sum_{M,E} e^{-\beta E + \beta HM} \Omega(E, M) \tag{4.19}$$

Remark. The term $-HM$ is the work done by the system against the external field H to mantain a given magnetization M.

$$\langle M \rangle = \left.\frac{\partial \ln Z_G}{\partial(\beta H)}\right|_T = \frac{1}{Z_G} \text{Tr}\left[M(\mathcal{C})e^{-\beta(\mathcal{H}(\mathcal{C}) - HM(\mathcal{C}))}\right] \tag{4.20}$$

$$\chi_T = \frac{\partial \langle M \rangle}{\partial H} = \left\{\frac{\beta}{Z_G} \text{Tr}\left[M^2(\mathcal{C})e^{-\beta\mathcal{H} + \beta HM}\right] - \frac{\beta}{Z_G^2}\left[\text{Tr}\left[M(\mathcal{C})e^{-\beta\mathcal{H} + \beta HM}\right]\right]^2\right\} \tag{4.21}$$

$$\chi_T = \frac{1}{k_B T}\left(\langle M^2 \rangle - \langle M \rangle^2\right) \tag{4.22}$$

The thermodynamic response function χ_T in statistical mechanics is related to the variance of the magnetization. We can relate the above expressione with the correlation of the microscopic by performing a coarse-graining of the system where the magnetization $M(\mathcal{C})$ can be computed an integral

$$M(\mathcal{C}) = \int d^3\vec{\mathbf{r}}\, m(\vec{\mathbf{r}}) \tag{4.23}$$

Hence

$$k_B T \chi_T = \int d\vec{\mathbf{r}}\, d\vec{\mathbf{r'}} \left[\left\langle m(\vec{\mathbf{r}})m(\vec{\mathbf{r'}})\right\rangle - \langle m(\vec{\mathbf{r}})\rangle \left\langle m(\vec{\mathbf{r'}})\right\rangle\right] \tag{4.24}$$

Let us assume the *translational symmetry*:

$$\begin{cases} \langle m(\vec{\mathbf{r}})\rangle = m & \text{homogeneous} \\ \left\langle m(\vec{\mathbf{r}})m(\vec{\mathbf{r'}})\right\rangle \equiv G(\vec{\mathbf{r}} - \vec{\mathbf{r'}}) & \text{two-point correlation function} \end{cases} \tag{4.25}$$

Let us consider instead the *connected correlation function* i.e. the correlation function of the fluctuations $\delta m = m - \langle m \rangle$:

$$\left\langle m(\vec{\mathbf{r}})m(\vec{\mathbf{r'}})\right\rangle_C \equiv \left\langle (m(\vec{\mathbf{r}}) - \langle m(\vec{\mathbf{r}})\rangle)\left(m(\vec{\mathbf{r'}}) - \left\langle m(\vec{\mathbf{r'}})\right\rangle\right)\right\rangle = G(\vec{\mathbf{r}} - \vec{\mathbf{r'}}) - m^2 \tag{4.26}$$

Given the translational inviariance on can centre the system such that its centre of mass coincides with the origin

$$\vec{\mathbf{r}}_{CM} \Rightarrow \vec{\mathbf{r}}_0 \equiv \vec{\mathbf{0}} \tag{4.27}$$

$$\Rightarrow \int d\vec{\mathbf{r}} \int d\vec{\mathbf{r'}}\, [G(\vec{\mathbf{r}} - \vec{\mathbf{r}}_0) - m^2] \tag{4.28}$$

The integration over $\vec{\mathbf{r'}}$ gives the volume $V(\Omega)$ of the system

$$\underbrace{k_B T \chi_T}_{\substack{\text{response} \\ \text{function}}} = V(\Omega) \int d\vec{\mathbf{r}} \quad \underbrace{\langle m(\vec{\mathbf{r}})m(\vec{\mathbf{r}}_0)\rangle_C}_{\substack{\text{correlation function} \\ \text{of the fluctuations} \\ \text{of the local magnetization}}} \tag{4.29}$$

The Equation (4.29) is called the **fluctuation-dissipation relation**.

How $G_c(\vec{r})$ behaves? In general one has

$$G_c(\vec{r}) \sim e^{-|\vec{r}|/\xi} \tag{4.30}$$

Meaning that for $|\vec{r}| > \xi$ the fluctuations are uncorrelated. We define the ξ as the *correlation length*. It is related to the correlation function. In general is finite but if you approach T_c diverges. In fact, at the critical point this correlation will expand in the whole space and reaches the size of all the system, it goes to infinity. When ξ will diverge, there is not anymore the exponential and the integrall cannote be keeped finite.

Let g be the value of G_c for $|\vec{r}| < \xi$:

$$k_B T \chi_T \leq V g \xi^3 \tag{4.31}$$

where there is an inequality because we are understimating the integral (see Figure 4.2):

$$\frac{k_B T \chi_T}{V} < g \xi^3 \tag{4.32}$$

Hence if χ_T diverges at the critical point it implies $\xi \to \infty$. In particular one can see
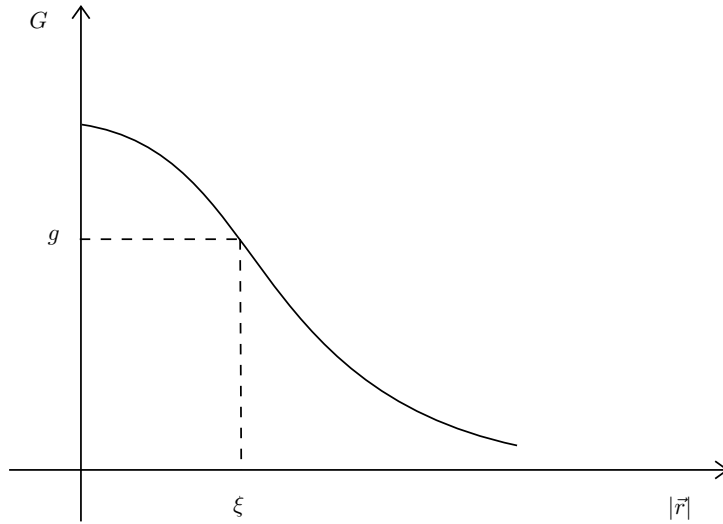
Figure 4.2: Description.

that for $H = 0$ and $T \to T_C^{\pm}$:

$$\xi_{\pm}(T, H = 0) \sim |t|^{-\nu_{\pm}} \tag{4.33}$$

where $\nu_+ = \nu_- = \nu$ is the correlation length critical exponent.

Remark. It does not derive from thermodynamic considerations.

Scaling (4.33) is often used as the most general definition of a critical point. One can also show that at $T = T_c$ (i.e. $t = 0$)

$$G_c(r) \sim \frac{1}{r^{d-2+\mu}} \tag{4.34}$$

where μ is the correlation critical exponent. The formula is a power law decays instead than exponential.

4.4   Finite size effects and phase transitions

Actually the thermodynamic limit is a mathematical trick and in real systems it is never reached. Is it then physically relevant?

If we had instrumetns with *infinite* precision each change of the physical properties of a system would occur within a finite range, therefore we would observe a smooth crossover instead than a singularity. In this respect the notion of correlatio length ξ is extremely important. To illustrate this point let us consider the gas-liquid system in proximity of its critical point ($T \sim T_c$). If we approach T_c from the gas phase there will be fluctuations of ρ with respect to ρ_G, $\Delta\rho = \rho - \rho_G$, due to the presence od denser droplets (liquid) in the continuum gas phase. These droplets will have different diameters, bu the average size would be ξ, where it is the typical size of the liquid droplets. Clearly $\xi = \xi[T]$ and, in proximity of the critical point $\xi \overset{t\to 0}{\sim} |t|^{-\nu}$.

On the other hand, in a finite system, ξ cannot diverge since is bounded above, $\xi \leq L$, where L is the linear system size.

As $T \to T_c$, where ξ should be larger than the system size, the behaviour of the system should deviate from the one expected by the theory that is obtained in the limit $L \to \infty$. How far the real system would be from the critical point $t = 0$ where singularities develop? Let us try to give an estimate of this deviation.

Let us consider a system of size $L = 1\,\text{cm}$ and $t \equiv (T - T_c)/T_c$ and $\xi \sim \xi_0 t^{-\nu}$. Let us assume $\xi_0 = 10\,\text{Å}$, the lattice distance:

$$t \sim \left(\frac{\xi}{\xi_0}\right)^{-1/\nu} \sim \left(\frac{L}{10\,\text{Å}}\right)^{-1/\nu} \sim (10^{10})^{-1/\nu} \tag{4.35}$$

we will see that $\nu < 1$ and close to $1/2$:

$$t \sim (10^{10})^{-2} = 10^{-20} \tag{4.36}$$

Therefore we have $t \approx 10^{-20}$ as distance from T_c.

This estimate suggests that the experimental instrument that measures temperature must have a precision of 10^{-20} to see deviations from the results obtained in the thermodynamic limit.

4.5   Numerical simulations and phase transitions

In this case the size L of the simulated system is few multiples of ξ_0 and the finite-size effects of the simulated data can strongly affect the location and the scaling laws of the phase transition under numerical investigation.

Finite size scaling analysis of the numerical data is needed.

We can find the critical point by doing Montecarlo simulation. Supposing a Montecarlo simulation of a Ising model, for which there is no an analitic solution and compute the energy. Try to estrapolate for example the position of the peak as N increases. If we start to see this behaviour it shown that something is happening. Nevertheless, there are two approaches: studying the system by looking for all the details. An example could be a protein, that interact with other proteins; we can look at all the electrons (or atoms). Even if we think at the simple protein that exist there are a lot of degree of freedom. For doing a simulation, if we are interested in long time behaviour and in large scale behaviur, details are not important. What it is important are symmetries, ranges of interaction. Therefore, we can forget about all the details. We can introduce the effective potentials as wander-walls or Lenard Jones potential and studying collective effects. This is the second approach.
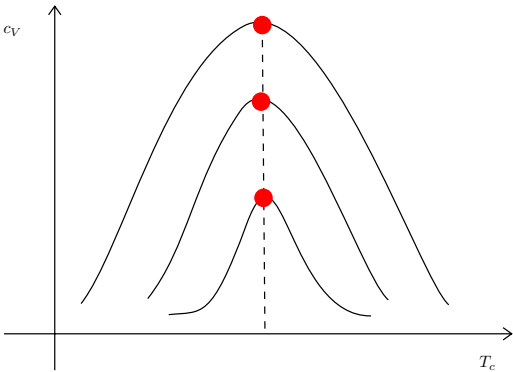
Figure 4.3: Description.

Chapter 5

Role of the models in statistical mechanics

5.1 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*.

5.2 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.

5.2.1 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

$$\mathcal{H}_\Omega(\{S_i\}) = \sum_{ij} J_{ij} S_i S_j - \sum_i H_i S_i - \sum_{ijk} S_i S_j S_k + \ldots \tag{5.1}$$

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

$$\mathcal{H}_\Omega(\{S_i\}) = -\frac{1}{2} \sum_{i \neq j}^N J_{ij} S_i S_j - \sum_{i=1}^N H_i S_i \tag{5.2}$$

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

$$\text{Tr} \equiv \sum_{S_1 = \pm} \sum_{S_2 = \pm} \cdots \sum_{S_N = \pm} \equiv \sum_{\{S\}} \tag{5.3}$$

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

$$Z_\Omega(T, \{H_i\}, \{J_{ij}\}) = \text{Tr}\, e^{-\beta \mathcal{H}_\Omega(\{S\})} \tag{5.4}$$

and the corresponding free-energy

$$F_\Omega(T, \{H_i\}, \{J_{ij}\}) = -k_B T \ln Z_\Omega \tag{5.5}$$

The bulk limiting free energy is

$$f_b(T, \{H_i\}, \{J_{ij}\}) = \lim_{N \to \infty} \ln \frac{1}{N} F_\Omega \tag{5.6}$$

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

$$\sum_{j \neq i} |J_{ij}| < \infty \tag{5.7}$$

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

$$J_{ij} = A|\vec{\mathbf{r_i}} - \vec{\mathbf{r_j}}|^{-\sigma} \tag{5.8}$$

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

$$\sigma > D \tag{5.9}$$

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.

5.2.2   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:

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are neirest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{5.10}$$

The model is nowe very simple:

$$-\mathcal{H}_\Omega(\{S\}) = J \sum_{\langle ij \rangle}^{N(\Omega)} S_i S_j + H \sum_i^{N(\Omega)} S_i \tag{5.11}$$

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

$$\langle m \rangle = \frac{1}{N(\Omega)} \sum_{i=1}^{N(\Omega)} \langle S_i \rangle \tag{5.12}$$

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

$$\sum_{i=1}^N \langle S_i \rangle = \frac{1}{Z} \text{Tr} \left[\left(\sum_i S_i \right) e^{-\beta \mathcal{H}_\Omega(\{S_i\})} \right] = \frac{1}{Z} \text{Tr} \left[\sum_i S_i \exp \left(\beta J \sum_{\langle ij \rangle} S_i S_j + \beta H \sum_i S_i \right) \right] \tag{5.13}$$

it is easy to show that:

$$\langle m \rangle = -\frac{1}{N} \frac{\partial F_\Omega}{\partial H} \tag{5.14}$$

where

$$F_\Omega(T, J, H) = -k_B T \ln Z_N(T, J, H) \tag{5.15}$$

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

$$f_b = \lim_{N \to \infty} \frac{1}{N} (-k_B T \ln Z_N) \tag{5.16}$$

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:

$$c_H = T \left(\frac{\partial S}{\partial T} \right)_M = -T \left(\frac{\partial^2 f_b}{\partial T^2} \geq 0 \right) \tag{5.17}$$

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

$$\frac{\partial^2 f_b}{\partial H^2} \leq 0 \tag{5.18}$$

This implies that

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T = -\left(\frac{\partial^2 f_b}{\partial H^2} \right)_T \geq 0 \tag{5.19}$$

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:

$$s \equiv -\frac{\partial f_b}{\partial T} \geq 0 \tag{5.20}$$

Let us consider a finite system

$$
\begin{aligned}
-\frac{\partial F_\Omega}{\partial T} &= k_B \ln \left(\mathrm{Tr}\, e^{-\beta \mathcal{H}_\Omega} \right) + k_B T \frac{1}{k_B T^2} \frac{\mathrm{Tr}\left(\mathcal{H}_\Omega e^{-\beta \mathbb{H}} \right)}{\mathrm{Tr}(e^{-\beta \mathcal{H}})} \\
&= k_B \left[\ln Z + \frac{\mathrm{Tr}\left(\beta \mathcal{H}_\Omega e^{-\beta \mathcal{H}_O} \right)}{Z_\Omega} \right] = -k_B T \, \mathrm{Tr}(\rho_\Omega \ln \rho_\Omega)
\end{aligned} \tag{5.21}
$$

where we used the definition of the probability distribution

$$\rho_\Omega = \frac{e^{-\beta \mathcal{H}_\Omega}}{ZA} (????) \tag{5.22}$$

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

$$\lim_{N \to \infty} -\frac{1}{N} \frac{\partial F_\Omega}{\partial T} = -k_B T \lim_{N \to \infty} \frac{1}{N} \underbrace{\mathrm{Tr}(\rho_\Omega \ln \rho_\Omega)}_{S_\Omega} = Ts \geq 0 \quad \Rightarrow \quad s \geq 0 \tag{5.23}$$

$\square$

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

Theorem 5.2.1. $f_b(T, J, H)$ *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 4 (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

$$\sum_k (g_k)^{\alpha_1}(h_k)^{\alpha_2} \leq \left(\sum_k g_k\right)^{\alpha_1}\left(\sum_k h_k\right)^{\alpha_2} \tag{5.24}$$

Consider now the partition function

$$Z_\Omega(H) = \mathrm{Tr}\left[\exp\left(\beta H \sum_i S_i\right) \underbrace{\exp\left(\beta J \sum_{\langle ij \rangle} S_i S_j\right)}_{G(S)}\right] = \mathrm{Tr}\left[\exp\left(\beta H \sum_i S_i\right) G(s)\right] \tag{5.25}$$

it implies that

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \mathrm{Tr}\left(\exp\left\{\beta \alpha_1 H_1 \sum_i S_i + \beta \alpha_2 H_2 \sum_i S_i\right\} G(S)\right) \tag{5.26}$$

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

$$G(S) = G(S)^{\alpha_1} G(S)^{\alpha_2} \tag{5.27}$$

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) = \mathrm{Tr}\left[(e^{\beta H_1 \sum_i S_i} G(S))^{\alpha_1}(e^{\beta H_2 \sum_i S_i} G(S))^{\alpha_2}\right] \tag{5.28}$$

If we now apply the Hölder inequality we get

$$Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) \leq \left(\mathrm{Tr}\left(e^{\beta H_1 \sum_i S_i} G(S)\right)^{\alpha_1}\right)\left(\mathrm{Tr}\left(e^{\beta H_2 \sum_i S_i} G(S)\right)^{\alpha_2}\right)$$
$$= Z_\Omega(H_1)^{\alpha_1} Z_\Omega(H_2)^{\alpha_2} \tag{5.29}$$

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

$$\lim_{N \to \infty} -\frac{1}{N} k_B T \ln Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) \geq -\lim_{N \to \infty} \frac{\alpha_1}{N} k_B T \ln Z_\Omega(H_1) - \lim_{N \to \infty} \frac{\alpha_2}{N} k_B T \ln Z_\Omega(H_2) \tag{5.30}$$

It implies

$$f_b(H_1 \alpha_1 + H_2 \alpha_2) \geq \alpha_1 f_b(H_1) + \alpha_2 f_b(H_2) \tag{5.31}$$

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

5.2.3 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 5.2.2. $\forall$ *function* Φ *of the configuration* $\{S_i\}$ *the following relation holds*

$$\sum_{\{S_i = \pm 1\}} \Phi(\{S_i\}) = \sum_{\{S_i = \pm 1\}} \Phi(\{-S_i\}) \tag{5.32}$$

this is true for all function of the spin.

We now consider the Hamiltonian of the Ising model:

$$-\mathcal{H}_\Omega = J \sum_{\langle ij \rangle} S_i S_j + H \sum S_i \tag{5.33}$$

Clearly

$$\mathcal{H}(H, J, \{S_i\}) = \mathcal{H}_\Omega(-H, J, \{-S_i\}) \tag{5.34}$$

This is a spontaneous broken symmetry. Hence

$$Z_\Omega(-H, J, T) = \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{S_i\})] \underset{(5.32)}{=} \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{-S_i\})]$$

$$\underset{(5.34)}{=} \sum_{\{S_i = \pm 1\}} \exp[-\beta \mathcal{H}_\Omega(H, J, \{S_i\})] = Z_\Omega(H, J, T)$$

$$\tag{5.35}$$

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

$$F_\Omega(T, J, H) = F_\Omega(T, J, -H) \tag{5.36}$$

If we now take the thermodynamic limit we have

$$\Rightarrow f_b(T, J, H) = f_b(T, J, -H) \tag{5.37}$$

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

Remark. From the finite-size relation (5.36) one can show that a finite-size Isin model does not displat a transition to a ferromagnetic phase (for all dimension D). Indeed

$$N(\Omega)M(H) = -\frac{\partial F(H)}{\partial H} \underset{(5.36)}{=} -\frac{\partial F(-H)}{\partial (H)} = \frac{\partial F_N(-H)}{\partial(-H)} = -N(\Omega)M(-H) \tag{5.38}$$

Therefore:

$$M(H) = -M(-H) \quad \forall H \tag{5.39}$$

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.

5.2.4   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 5.1 . 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

$$n_i = \begin{cases} 0 & \text{if empty} \\ 1 & \text{if occupied} \end{cases} \tag{5.40}$$

$$N_\Omega = \sum_{i=1}^{N_c} n_i \tag{5.41}$$
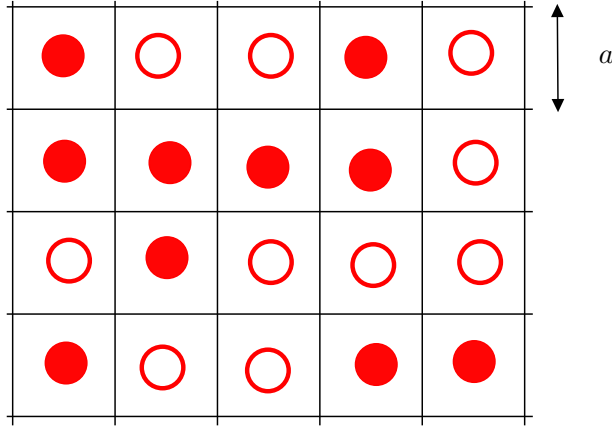
Figure 5.1: Description.

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

$$\mathcal{H}_\Omega = \sum_{i=1}^{N_c} U_1(i)n_i + \frac{1}{2}\sum_{ij} U_2(i,j)n_i n_j + O(n_i n_j n_k) \tag{5.42}$$

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

$$\mathcal{H}_\Omega - \mu N = \sum_{i=1}^{N_c} (U_1(i) - \mu)n_i + \frac{1}{2}\sum_{ij} U_2(i,j)n_i n_j + \ldots \tag{5.43}$$

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

$$n_i = \frac{1}{2}(1 + S_i) \quad \text{with } S_i = \pm 1 \tag{5.44}$$

The one body term:

$$\sum_i (U_1(i) - \mu)\frac{1}{2}(1 + S_i) = \frac{1}{2}\sum_i (U_1(i) - \mu) + \frac{1}{2}\sum_i S_i(U_1(i) - \mu) \tag{5.45}$$

while the two bies term:

$$\frac{1}{2}\sum_{ij} U_2(i,j)\left[\frac{1}{4}(1 + S_i)(1 + S_j)\right] = \frac{1}{8}2\sum_{ij}^{N_c} U_2(i,j)S_i + \frac{1}{8}\sum_{ij}^{N_c} U_2(i,j)S_i S_j + \frac{1}{8}\sum_{ij}^{N_c} U_2(i,j) \tag{5.46}$$

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

$$U_2(i,j) = \begin{cases} U_2 & i,j \text{ neirest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{5.47}$$

It implies

$$\frac{1}{8}U_2 Z N_c + \frac{1}{4}z U_2 \sum_i^{N_c} S_i + \frac{U_2}{4}\sum_{\langle ij \rangle} S_i S_j \tag{5.48}$$

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

$$\mathcal{H}_\Omega - \mu N = E_0 - H\sum_{i=1}^{N} S_i - J\sum_{\langle ij \rangle} S_i S_j \tag{5.49}$$

where

$$E_0 = -\frac{1}{2}\mu N_c + \frac{z}{8}U_2 N_c \tag{5.50a}$$

$$H = -\frac{1}{2}\mu + \frac{z}{4}U_2 \tag{5.50b}$$

$$-J = \frac{U_2}{4} \tag{5.50c}$$

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

$$\mathcal{Z}_{LG} = \text{Tr}_{\{n\}}(e^{-\beta(\mathcal{H}_\Omega - \mu N)}) = e^{-\beta E_0} Z_{\text{Ising}}(H, J, N_c) \tag{5.51}$$

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.

5.3   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

$$\mathcal{H}_\Omega = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U_1(\vec{\mathbf{r_i}})\right] + \frac{1}{2}\sum_{i \neq j} U_2(\vec{\mathbf{r_i}}, \vec{\mathbf{r_j}}) + \frac{1}{3!}\sum_{i \neq j \neq k} U_3(\vec{\mathbf{r_i}}, \vec{\mathbf{r_j}}, \vec{\mathbf{r_k}}) \tag{5.52}$$

In the gran-canonical ensemble

$$\mathcal{Z}_\Omega = \text{Tr}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) = \sum_{N=0}^\infty \frac{1}{N!}\int \prod_{i=1}^N \frac{\mathrm{d}^D\vec{\mathbf{p_i}}\,\mathrm{d}^D\vec{\mathbf{r_i}}}{h^{dN}}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) \tag{5.53}$$

and the gran-canonical potential

$$\omega_\Omega(T, \mu, U_1, U_2, \dots) = -k_B T \ln \mathcal{Z}_\Omega \tag{5.54}$$

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

$$\Rightarrow \sum_{N=0}^\infty \sim \sum_{N=0}^{N_{max}} \tag{5.55}$$

In the thermodynamic limit

$$\omega_b(T, \mu, U_1, U_2, \dots) = \lim_{V(\Omega) \to \infty} \frac{o_\Omega}{V(\Omega)} \tag{5.56}$$

with the contraint

$$\rho = \lim_{V \to \infty} \frac{\langle N \rangle}{V(\Omega)} = const \tag{5.57}$$

remember also that

$$\mathrm{d}\omega_b(T, \mu) = -\sigma\,\mathrm{d}T - p\,\mathrm{d}\mu = -P \tag{5.58}$$

Now:

$$\mathcal{Z}_N = \sum_{N=0}^\infty \frac{1}{N!}\left[\prod_{i=1}^N\left\{\int_{-\infty}^{+\infty}\mathrm{d}^D\vec{\mathbf{p}}\,\frac{1}{h^{DN}}e^{-\beta\vec{\mathbf{p_i}}^2/2m}\right\}Q_N(T)\right] \tag{5.59}$$

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

$$\int_{-\infty}^{+\infty} \mathrm{d}^D \vec{\mathbf{p}} \, \frac{1}{h^{DN}} e^{-\beta \vec{\mathbf{p_i}}^2/2m} = \frac{1}{\Lambda(T)^d} \tag{5.60}$$

where

$$\Lambda(T) = \frac{1}{\sqrt{2\pi m k_B T}} \tag{5.61}$$

Therefore:

$$\mathcal{Z}_\Omega = \sum_{N=0}^\infty \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda(T)^d} \right)^N Q_N \tag{5.62}$$

where

$$Q_N(T) = \int \prod_{i=1}^N \mathrm{d}\vec{\mathbf{r_i}} \, e^{-\beta(U(\vec{\mathbf{r}}))} \tag{5.63}$$

5.3.1 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

$$\sum_\alpha n_\alpha = N = \int \mathrm{d}^D \vec{\mathbf{r}} \sum_{i=1}^N \delta(\vec{\mathbf{r_i}} - \vec{\mathbf{r}}) = \int \mathrm{d}\vec{\mathbf{r}} \, \rho(\vec{\mathbf{r}}) \tag{5.64}$$

where

$$\rho(\vec{\mathbf{r}}) = \sum_{i=1}^N \delta(\vec{\mathbf{r_i}} - \vec{\mathbf{r}}) \tag{5.65}$$

$$\sum_i U_1(\vec{\mathbf{r_i}}) = \sum_i \int_\Omega \mathrm{d}^D \vec{\mathbf{r}} \, U_1(\vec{\mathbf{r}}) \delta(\vec{\mathbf{r_i}} - \vec{\mathbf{r}}) = \int_\Omega \mathrm{d}\vec{\mathbf{r}} \, U_1(\vec{\mathbf{r}}) \rho(\vec{\mathbf{r}}) \tag{5.66}$$

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

$$Q_N \propto \int \prod_{i=1}^N \mathrm{d}^D \vec{\mathbf{r_i}} \to \sum_{\{n_\alpha\}} \tag{5.67}$$

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.

$$Q_N \propto N!(a^D)^N \sum_{\{n_\alpha\}}' e^{-\beta U(\{n_\alpha\})} \tag{5.68}$$

$$\mathcal{Z}_N = \sum_{N=0}^\infty \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\Lambda^D(T)} \right)^N Q_N = \sum_{N=0}^\infty \left[\left(e^{\beta\mu} \frac{a}{\Lambda(T)} \right)^D \right]^N \sum_{\{n_\alpha\}}' e^{-\beta U(\{n_\alpha\})} \tag{5.69}$$

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

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

(5.70)

with no restriction.

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

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

(5.71)

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

(5.72)

where

$$
\widetilde{\mu} = \mu_{LG} = \mu_{phys} + D k_B T \log \frac{a}{\Lambda}
$$

(5.73)

Chapter 6
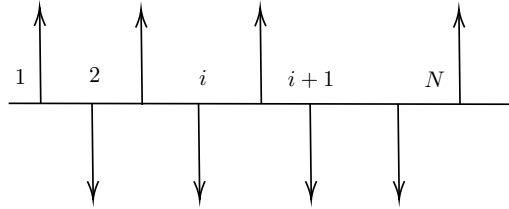
Some exactly solvable models of phase transitions

The bibliography of the entire chapter is taken by [1], [2], [3].

6.1 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*.

6.1.1 Recursive methods

Case with $H = 0$ and free boundary conditions

Figure 6.1: One dimensional Bravais Lattice.

The Bravais lattice is just a one dimensional lattice as in Figure 6.1. The partition function of such a system is:

$$Z_N(T) = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} \cdots \sum_{S_N = \pm 1} \exp\left[\overbrace{\beta J}^{K} \sum_{i=1}^{N-1} S_i S_{i+1}\right] \tag{6.1}$$

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

$$K \equiv \beta J, \quad h \equiv \beta H \tag{6.2}$$

Making explicit the sum in the exponential:

$$Z_N(K) = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} \cdots \sum_{S_N = \pm 1} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N)} \tag{6.3}$$

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

$$Z_{N+1}(K) = \sum_{S_{N+1}=\pm1} \sum_{S_1=\pm1} \sum_{S_2=\pm1} \cdots \sum_{S_N=\pm1} e^{K(S_1S_2+S_2S_3+\cdots+S_{N-1}S_N)} e^{KS_NS_{N+1}}$$

(6.4)

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

$$\sum_{S_{N+1}=\pm1} e^{KS_NS_{N+1}} = e^{KS_N} + e^{-KS_N} = 2\cosh(KS_N) = 2\cosh(K)$$

(6.5)

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

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

(6.6)

By performing a backward iteration

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

(6.7)

Since $Z_1 = \sum_{S_1=\pm1} 1 = 2$ we have

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

(6.8)

The free energy is:

$$F_N(T) = -k_BT \ln Z_N(K) = -k_BT \ln 2 - k_BT(N-1)\ln(2\cosh(K))$$

(6.9)

we not take the thermodynamic limit

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

(6.10)

As one can see $f_b(T)$ is an analytic function of T; we have no phase transition at $T \neq 0$.
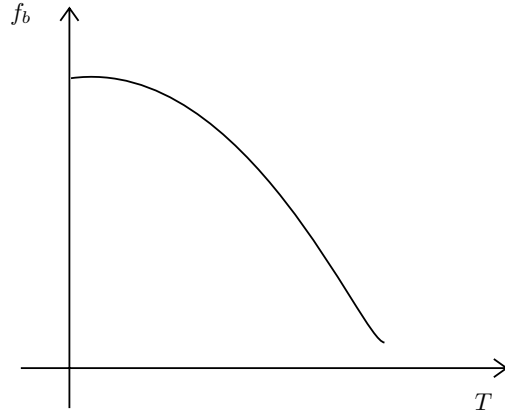
Figure 6.2: Free energy function in thermodynamic limit.

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$S_i = \pm1$. 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:

$$\exp[KS_iS_{i+1}] = \cosh(K) + S_iS_{i+1}\sinh(K) = \cosh(K)[1 + S_iS_{i+1}\tanh(K)] \quad (6.11)$$

It means that

$$Z_N(K) = \sum_{\{S\}} \exp\left[K \sum_{i=1}^{N-1} S_i S_{i+1} \right] = \sum_{\{S\}} \prod_{i=1}^{N-1} [\cosh(K)(1 + S_i S_{i+1} \tanh(K))] \quad (6.12)$$

by rearranging

$$Z_N(K) = (\cosh K)^{N-1} \sum_{\{S\}} \prod_{i=1}^{N-1} (1 + S_i S_{i+1} \tanh K) \quad (6.13)$$

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

$$\sum_{\substack{S_{i_e}=\pm 1 \\ e=1,\dots,M}} (\tanh K)^M S_{i_1} S_{i_{1+1}} S_{i_2} S_{i_{2+1}} \dots S_{i_M} S_{i_{M+1}} = 0 \quad (6.14)$$

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:
$$Z_N(K) = 2^N (\cosh K)^{N-1} \quad (6.15)$$

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 (6.14) but with the addiction of an S_j:

$$(\tanh K)^M S_{i_1} S_{i_{1+1}} S_{i_2} S_{i_{2+1}} \dots S_{i_M} S_{i_{M+1}} \; S_j \quad (6.16)$$

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

$$\langle S_j \rangle = 0 \quad \forall j \quad (6.17)$$

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

Case with $H \neq 0$ and periodic boundary conditions
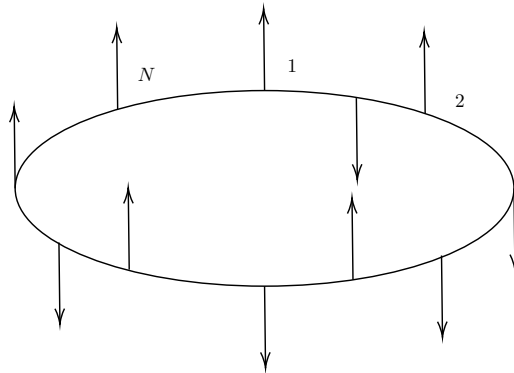
Figure 6.3: Onde dimensional lattice ring.

Consider the spins sitting on a 1D lattice ring as in Figure 6.3. The periodic boundary conditions are:

$$S_{N+1} = S_1 \quad (6.18)$$

We have:

$$- \beta \mathbb{H}_\Omega(\{S\}) = K \sum_{i=1}^{N} S_i S_{i+1} + h \sum_{i=1}^{N} S_i \tag{6.19}$$

where

$$K \equiv \beta J, \quad h \equiv \beta H \tag{6.20}$$

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.

6.1.2   Transfer Matrix method

Given the Hamiltonian above we can write the corresponding partition function in the following symmetric form:

$$Z_N(k, h) = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} \cdots \sum_{S_N = \pm 1} \left[e^{kS_1 S_2 + \frac{h}{2}(S_1 + S_2)} \right] \left[e^{kS_2 S_3 + \frac{h}{2}(S_2 + S_3)} \right] \cdots \left[e^{kS_N S_1 + \frac{h}{2}(S_N + S_1)} \right] \tag{6.21}$$

Suppose you have a sort of $\sum_j M_{ij} P_{jk}$, what we have done is doing something like that. In the previous form Z_N can be written as a product of matrices

$$\begin{aligned} Z_N(h, k) &= \sum_{S_1 = \pm 1} \cdots \sum_{S_N = \pm 1} \prod_{i=1}^{N} \exp \left[kS_i S_{i+1} + \frac{h}{2}(S_i + S_{i+1}) \right] \\ &= \sum_{S_1 = \pm 1} \cdots \sum_{S_N = \pm 1} \langle S_1 | \mathbb{T} | S_2 \rangle \langle S_2 | \mathbb{T} | S_3 \rangle \ldots \langle S_N | \mathbb{T} | S_1 \rangle \end{aligned} \tag{6.22}$$

where $\mathbb{T}$ is a 2×2 matrix defined as

$$\langle S | \mathbb{T} | S' \rangle = \exp \left[kSS' + \frac{h}{2}(S + S') \right] \tag{6.23}$$

Note that the labels of the matrix corresponds to the values of S_i. Hence its dimension depdens on the number of possible values a spin S_i can assume. It can also depends on how many spins are involved in the interacting terms that are present in the hamiltonian ($k_{LL} \sum S_i S_{i+1} S_{i+2} S_{i+3}$). For Ising $S_i = \pm 1$ and neirest neighbour interaction implies that we have 2 values and that $\mathbb{T}$ is a 2×2 matrix whose components are

$$\langle +1 | \mathbb{T} | +1 \rangle = \exp[k + h] \tag{6.24a}$$
$$\langle +1 | \mathbb{T} | -1 \rangle = \langle -1 | \mathbb{T} | +1 \rangle = \exp[k - h] \tag{6.24b}$$
$$\langle -1 | \mathbb{T} | -1 \rangle = \exp[-k] \tag{6.24c}$$

The explicit representation is

$$\mathbb{T} = \begin{pmatrix} e^{k+h} & e^{-k} \\ e^{-k} & e^{k-h} \end{pmatrix} \tag{6.25}$$

Let us now introduce some useful notations and relations using the bra-ket formalism: subequations

$$\left| S_i^{(+)} \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_i \quad \left| S_i^{(-)} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_i \tag{6.26}$$

$$\left\langle S_i^{(+)} \right| = (1^*, 0)_i \quad \left\langle S_i^{(-)} \right| = (0, 1^*)_i \tag{6.27}$$

The identity relation is:

$$\sum_{S_i=\pm 1} |S_i\rangle \langle S_i| = \left|S_i^{(+)}\right\rangle\!\left\langle S_i^{(+)}\right| + \left|S_i^{(-)}\right\rangle\!\left\langle S_i^{(-)}\right| = \mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad (6.28)$$

By using the last property we can write

$$\begin{aligned}
Z_N(K,h) &= \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \langle S_1|\, \mathbb{T}\, |S_2\rangle \langle S_2|\, \mathbb{T}\, |S_3\rangle \ldots |S_i\rangle \langle S_i|\, \mathbb{T}\, |S_{i+1}\rangle \ldots \\
&= \sum_{S_1=\pm 1} \langle S_1|\, \mathbb{T}^N\, |S_1\rangle = \mathrm{Tr}\!\left[\mathbb{T}^N\right]
\end{aligned} \qquad (6.29)$$

this is exactly the trace of the matrix. Being $\mathbb{T}$ symmetric, we can diagonalize it by an unitary transformation

$$\mathbb{T}_D = \mathbb{P}^{-1}\mathbb{T}\mathbb{P} \qquad (6.30)$$

with $\mathbb{P}\mathbb{P}^{-1} = \mathbb{1}$.

$$\begin{aligned}
\mathrm{Tr}\!\left[\mathbb{T}^N\right] &= \mathrm{Tr}\Big[\underbrace{\mathbb{T}\mathbb{T}\mathbb{T}\ldots\mathbb{T}}_{N}\Big] = \mathrm{Tr}\!\left[\mathbb{P}\mathbb{P}^{-1}\mathbb{T}\mathbb{P}\mathbb{P}^{-1}\mathbb{T}\mathbb{P}\ldots\mathbb{P}^{-1}\mathbb{T}\mathbb{P}\mathbb{P}^{-1}\right] \\
&= \mathrm{Tr}\!\left[\mathbb{P}\mathbb{T}_D^N\mathbb{P}^{-1}\right] \underset{\substack{\text{ciclyc property} \\ \text{of the trace}}}{=} \mathrm{Tr}\!\left[\mathbb{T}_D^N\mathbb{P}^{-1}\mathbb{P}\right] \\
&= \mathrm{Tr}\!\left[\mathbb{T}_D^N\right]
\end{aligned} \qquad (6.31)$$

where

$$\mathbb{T}_D = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \qquad \mathbb{T}_D^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \qquad (6.32)$$

with $\lambda_\pm$ are the eigenvalues with $\lambda_+ > \lambda_-$.

Remark. $\mathbb{P}$ is the similitude matrix whose colums are given by the eigenvectors of $\lambda_\pm$.

We finally have:

$$Z_N(K,h) = \mathrm{Tr}\!\left[\mathbb{T}_{\mathbb{D}}^{\mathbb{N}}\right] = \lambda_+^N + \lambda_-^N \qquad (6.33)$$

Remark. As mentioned previously the dimension of the transfer matrix $\mathbb{T}$ and hence the number of eigenvalues $\{\lambda\}$ depend both on the possible values of S_i and on the number of sites involved in terms of the Hamiltonian (range of interaction).

Example 13. For example consider the Ising ($S_i = \pm 1$) with neirest neighbour and next neirest neighbour interactions. The hamiltonian is:

$$\mathcal{H} = k_1 \sum_i S_i S_{i+1} + k_2 \sum_i S_i S_{i+1} S_{i+2} S_{i+3} \qquad (6.34)$$

Because of the second term now there are $2^4 = 16$ possible configurations that can be described by using a 4×4 transfer matrix that we can write formally as

$$\langle S_i S_{i+1}|\, \mathbb{T}\, |S_{i+2}S_{i+3}\rangle \qquad (6.35)$$

Let us now consider the transfer matrix formalism in a more general setting.

General transfer matrix method

Let $\mathbb{T}$ be a square matrix $(n+2) \times (n+2)$ that, for example, it is built if the spin variables mary assume $(n+2)$ possible values. The k-esim value can be defined by the bra-ket notation where the two vectors are given by a sequence of "0" and a single "1" at the k-esim position.

Example 14. For example, suppose $S_i = +1, 0, -1$, therefore it can assume three different values. This is a *deluted* ising model.

If $k = 3$ and there are $(n+2)$ possible values:

$$\left\langle S_i^{(3)} \right| = (0, 0, 1^*, 0, \ldots, 0) \qquad \left| S_i^{(3)} \right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \tag{6.36}$$

Similarly to the 2×2 (Ising) case it is easy to show that

$$\sum_{S_i} |S_i\rangle \langle S_i| = \mathbb{1}, \quad \mathbb{1} \in (n+2) \times (n+2) \tag{6.37}$$

where now the sum is over $(n+2)$ values.

Let us now consider the *diagonal matrix* $\mathbb{S}_i$ where the elements along the diagonal are all the $(n+2)$ possible values of the i-esim spin (or of some of their combination if longer interaction terms are considered)

$$\mathbb{S}_i \equiv \sum_{S_i} |S_i\rangle S_i \langle S_i| \tag{6.38}$$

Example 15. Ising model $n + 2 = 2$

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} S^{(1)} (1^*, 0) + \begin{pmatrix} 0 \\ 1 \end{pmatrix} S^{(2)} (0, 1^*) = \begin{pmatrix} S^{(1)} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & S^{(2)} \end{pmatrix} = \begin{pmatrix} S^{(1)} & 0 \\ 0 & S^{(2)} \end{pmatrix} \tag{6.39}$$

Ising: $S^{(1)} = +1, S^{(2)} = -1$.

Note that in this case the matrix $\mathbb{S}_i$ is equal to the Pauli matrix σ_z.

Remark. By constrution $\langle S_i|$ and $|S_i\rangle$ are the eigenvectors related to the eigenvalues $S_i = S^{(1)}, S^{(2)}, \ldots, S^{(n+2)}$.

Similarly let $\langle t_i|$ and $|t_i\rangle$ be the eigenvectors related to the $(n+2)$ eigenvalues of the transfer matrix $\mathbb{T}$: $\{\lambda_+, \lambda_-, \lambda_1, \ldots, \lambda_n\}$, with $\lambda_+ > \lambda_- \geq \lambda_1 \geq \cdots \geq \lambda_n$. Clearly

$$\mathbb{T} = \mathbb{P} \mathbb{T}_D \mathbb{P}^{-1} = \sum_i |t_i\rangle \lambda_i \langle t_i| \tag{6.40}$$

Indeed

$$\mathbb{T} |t_j\rangle = \sum_i |t_i\rangle \lambda_i \langle t_i | t_j\rangle = \sum_i |t_i\rangle \lambda_i \delta_{ij} = \lambda_j |t_j\rangle \tag{6.41}$$

Given the set of lambda described above, the N particle partition function is given by

$$Z_N(\{k\}, h) = \lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \tag{6.42}$$

Now, we are interested in the limit of the bulk free energy:

$$F_N() = -k_B T \log Z_N() \tag{6.43}$$

In general, looking at the thermodynamic limit, by factorizing λ_+

$$f_b(\{k\}, h) = \lim_{N \to \infty} \frac{1}{N} F_N = \lim_{N \to \infty} \frac{1}{N} (-k_B T) \log \left[\lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \right] \tag{6.44}$$

by rearringing

$$f_b = \lim_{N \to \infty} \frac{-k_B T}{N} \log \left[\lambda_+^N \left(1 + \frac{\lambda_-^N}{\lambda_+^N} + \sum_{i=1}^{n} \left(\frac{\lambda_i}{\lambda_+} \right)^N \right) \right] \tag{6.45}$$

Since $\lambda_+ > \lambda_- > \lambda_1 > \dots \lambda_n$

$$\left(\frac{\lambda_-}{\lambda_+} \right)^N \xrightarrow{N \to \infty} 0, \quad \left(\frac{\lambda_i}{\lambda_+} \right)^N \xrightarrow{N \to \infty} 0 \quad \forall i \tag{6.46}$$

we obtain

$$\boxed{f_b = -k_B T \log \lambda_+} \tag{6.47}$$

The limiting free-energy depends only on the largest eigenvalue of the transfer matrix $\mathbb{T}$! This is important since sometime it is much simpler to computer only the largest eigenvalue than the whole spectrum of $\mathbb{T}$. This is also an important theorem about λ_+.

Theorem 6.1.1 (Perron-Frobenius). *Let $\mathbb{A}$ be a $n \times n$ matrix. If $\mathbb{A}$ is finite ($n < \infty$) and $\mathbb{A}_{ij} > 0, \forall i, j$, ($\mathbb{A}_{ij} = \mathbb{A}_{ij}(\vec{x})$), therefore its largest eigenvalue λ_+ has the following properties:*

1. $\lambda_+ \in \mathbb{R}^+$

2. $\lambda_+ \neq$ *from* $\{\lambda_i\}_{i=1,\dots,n-1}$. *It means there is no degeneracy.*

3. λ_+ *is a analytic function of the parameters of $\mathbb{A}$.*

Remark. Since in our case $\mathbb{A} \leftrightarrow \mathbb{T}$, λ_+ is related to f_b from the theorem. This means that f_b is an analytic function!

If the conditions of the Perron-Frobenius theorem are satisfied by $\mathbb{T}$, the model described by $\mathbb{T}$ cannot display a phase transition!

Remark. This is trye for $T > 0$ since for $T = 0$ some T_{ij} can be either 0 or ∞ violating the hypothesis of the theorem.

If $\mathbb{T}$ has infinite dimension (see $D > 1$) the hypothesis of the theorem are not valid any more and f_b can be non-analytic.

Two point correlation function

Let us consider the correlation between two spins at distance R to another. The fluctuation respect to the average is:

$$\Gamma_R \equiv \langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle \tag{6.48}$$

Since

$$\Gamma_R \underset{R \to \infty}{\sim} \exp[-R/\xi] \tag{6.49}$$

we can define the correlation length ξ as

$$\xi^{-1} \equiv \lim_{R \to \infty} \left[-\frac{1}{R} \log |\langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle| \right] \tag{6.50}$$

We have to compute the terms $\langle S_1 S_R \rangle_N$ and $\langle S_1 \rangle_N \langle S_R \rangle_N$. From the definition

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{\{S\}} S_1 S_R \exp[-\beta \mathcal{H}] \tag{6.51}$$

Let us now write this expression by using the transfer matrix formalism.

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{\{S\}} S_1 \langle S_1| \, \mathbb{T} \, |S_2 \rangle \ldots \langle S_{R-1}| \, \mathbb{T} \, |S_R \rangle \, S_R \, \langle S_R| \, \mathbb{T} \, |S_{R+1} \rangle \ldots \langle S_N| \, \mathbb{T} \, |S_1 \rangle$$

(6.52)

Summing over the free spins

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{S_1, S_R} S_1 \langle S_1| \, \mathbb{T}^{R-1} \, |S_R \rangle \, S_R \, \langle S_R| \, \mathbb{T}^{N-R+1} \, |S_1 \rangle \qquad (6.53)$$

On the other hand since

$$\mathbb{T} = \sum_{i=1}^{n+2} |t_i \rangle \, \lambda_i \, \langle t_i| \qquad (6.54)$$

we have

$$\mathbb{T}^{R-1} = \sum_{i=1}^{n+2} |t_i \rangle \, \lambda_i^{R-1} \, \langle t_i| \qquad (6.55\text{a})$$

$$\mathbb{T}^{N-R+1} = \sum_{i=1}^{n+2} |t_i \rangle \, \lambda_i^{N-R+1} \, \langle t_i| \qquad (6.55\text{b})$$

Hence

$$\langle S_1| \, \mathbb{T}^{R-1} \, |S_R \rangle = \sum_{i=1}^{n+2} \langle S_1|t_i \rangle \, \lambda_i^{R-1} \, \langle t_i|S_R \rangle \qquad (6.56)$$

and plugging this expression in (6.53) one gets

$$\sum_{\{S\}} S_1 S_R e^{-\beta \mathcal{H}} = \sum_{S_1 S_R} S_1 \sum_{i=1}^{n+2} \langle S_1|t_i \rangle \, \lambda_i^{R-1} \, \langle t_i|S_R \rangle \, S_R \sum_{j=1}^{n+2} \langle S_R|t_j \rangle \, \lambda_j^{N-R+1} \, \langle t_j|S_1 \rangle$$

(6.57)

Since the term $\langle t_j|S_1 \rangle$ is a scalar it can be moved at the beginning of the product. Remembering the notations

$$\mathbb{S}_1 = \sum_{S_1} |S_1 \rangle \, S_1 \, \langle S_1| \qquad (6.58\text{a})$$

$$\mathbb{S}_R = \sum_{S_R} |S_R \rangle \, S_R \, \langle S_R| \qquad (6.58\text{b})$$

one gets

$$\sum_{\{S\}} S_1 S_R e^{-\beta \mathcal{H}} = \sum_{ij} \langle t_j| \, \mathbb{S}_1 \, |t_i \rangle \, \lambda_i^{R-1} \, \langle t_i| \, \mathbb{S}_R \, |t_j \rangle \, \lambda_j^{N-R+1} \qquad (6.59)$$

Since $\sum_k \lambda_k^N = Z_N$ for $k = +, -, 1, \ldots, n$:

$$\langle S_1 S_R \rangle_N = \frac{\sum_{ij} \langle t_j| \, \mathbb{S}_1 \, |t_i \rangle \, \lambda_i^{R-1} \, \langle t_i| \, \mathbb{S}_R \, |t_j \rangle \, \lambda_j^{N-R+1}}{\sum_{k=1}^n \lambda_k^N} \qquad (6.60)$$

If we now multiply and divide by λ_+^N, we get

$$\langle S_1 S_R \rangle_N = \frac{\sum_{ij} \langle t_j| \, \mathbb{S}_1 \, |t_i \rangle \, (\lambda_i/\lambda_+)^{R-1} \, \langle t_i| \, \mathbb{S}_R \, |T_j \rangle \, (\lambda_j/\lambda_T)^{N-R+1}}{\sum_{k=1}^n (\lambda_k/\lambda_+)^N} \qquad (6.61)$$

Remark. In the thermodynamic limit $N \to \infty$, only the terms with $j = +$ and $k = +$ survive in the sum. Remind that R is fixed.

$$\langle S_1 S_R \rangle = \lim_{N \to \infty} \langle S_1 S_R \rangle_N = \sum_{i=\pm,1\dots n} \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \qquad (6.62)$$

rembember that $\lambda_+ > \lambda_T \geq \lambda_1 \dots \lambda_n$:

$$\langle S_1 S_R \rangle = \langle t_+ | \mathbb{S}_1 | t_+ \rangle \langle t_+ | \mathbb{S}_R | t_+ \rangle + \sum_{i \neq +}^{n} \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \qquad (6.63)$$

Since one can show that

$$\lim_{N \to \infty} \langle S_R \rangle_N = \langle t_+ | \mathbb{S}_R | t_+ \rangle \qquad (6.64)$$

we obtain

$$\langle S_1 S_R \rangle = \langle S_1 \rangle \langle S_R \rangle + \sum_{i \neq +} \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \qquad (6.65)$$

Hence

$$\Gamma_R = \langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle = \sum_{i \neq +}^{n} \left(\frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_i \rangle \langle t_i | \mathbb{S}_R | t_+ \rangle \qquad (6.66)$$

Remark. Γ_R depends only on the eigenvalues and eigenvectors of the transfer matrix $\mathbb{T}$ and by the values of the spins S_1 and S_R.

In the limit $R \gg 1$ dominates the ratio (λ_-/λ_+):

$$
\begin{aligned}
\xi^{-1} &= \lim_{N \to \infty} \left\{ -\frac{1}{R-1} \log |\langle S_1 S_R \rangle \langle S_1 \rangle \langle S_R \rangle| \right\} \\
&= \lim_{N \to \infty} \left\{ -\frac{1}{R-1} \log \left[\left(\frac{\lambda_-}{\lambda_+} \right)^{R-1} \langle t_+ | \mathbb{S}_1 | t_- \rangle \langle t_- | \mathbb{S}_R | t_+ \rangle \right] \right\} \\
&= -\log \left[\left(\frac{\lambda_-}{\lambda_+} \right) \right] - \lim_{R \to \infty} \frac{1}{R-1} \log \langle t_+ | \mathbb{S}_1 | t_- \rangle \langle t_+ | \mathbb{S}_R | t_+ \rangle \\
&= -\log \left(\frac{\lambda_-}{\lambda_+} \right)
\end{aligned}
\qquad (6.67)
$$

The important results is

$$\xi^{-1} = -\log \left(\frac{\lambda_-}{\lambda_+} \right) \qquad (6.68)$$

The correlation length does depend only on the ratio between the two largest eigenvalues of the transfer matrix $\mathbb{T}$.

Explicit computation for the $D = 1$ Ising model

The transfer matrix is given by

$$\mathbb{T} = \begin{pmatrix} \exp(K+h) & \exp(-K) \\ \exp(-K) & \exp(K-h) \end{pmatrix} \qquad (6.69)$$

Calculate the eigenvalues:

$$|\mathbb{T} - \lambda\mathbb{1}| = (e^{K+h} - \lambda)(e^{K-h} - \lambda) - e^{-2K} = 0 \qquad (6.70)$$

The solutions are

$$\lambda_\pm = e^K \cosh(h) \pm \sqrt{e^{2K} \sinh^2(h) + e^{-2K}} \tag{6.71}$$

The free energy is

$$
\begin{aligned}
f_b &\equiv \lim_{N \to \infty} \frac{-k_B T}{N} \log Z_N(K, h) \\
&= -k_B T \lim_{N \to \infty} \frac{1}{N} \log \left[\lambda_+^N \left(1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right) \right] \\
&= -k_B T \log \lambda_+
\end{aligned}
\tag{6.72}
$$

and inserting the explicit expression of λ_+ for the Ising model we get

$$
\begin{aligned}
f_b &= -k_B T \log e^K \cosh h + \sqrt{e^{2K} \sinh^2(h) + e^{-2K}} \\
&= -K k_B T - k_B T \log \left(\cosh(h) + \sqrt{\sinh^2(h) + e^{-4K}} \right)
\end{aligned}
\tag{6.73}
$$

rembember $K \equiv \beta J, h \equiv \beta H$.

Exercise 2. Check that if $h = 0$ we get back the expression found previously with the iterative method (what is the important of boundary conditions?).

Let us now consider the limits $T \to 0$ and $T \to \infty$ by keeping H fixed and J fixed.

- Case: $T \to 0 \Rightarrow K \to \infty, h \to \infty$.

$$e^{-4K} \xrightarrow{K \to \infty} 0 \tag{6.74a}$$

$$\sqrt{\sinh^2 h} \overset{h \to \infty}{\sim} \sinh(h) \tag{6.74b}$$

This implies that

$$\cosh(h) + \sinh h \sim \frac{2e^h}{2} \simeq e^h \tag{6.75}$$

and

$$f \overset{h \to \infty}{\underset{K \to \infty}{\sim}} -K k_B T - k_B T \log e^h \sim -J - H \quad const \tag{6.76}$$

Therefore, as $T \to 0^+$, f goes to a constant that depends on J and H.

- Case: $T \to \infty \Rightarrow K \to 0, h \to 0$. In this case we suppose also that H and J that are fixed, are also finite.

$$e^{-4K} \simeq 1 \tag{6.77a}$$

$$\sqrt{\sinh^2 h + e^{-4K}} \sim \sqrt{1} \tag{6.77b}$$

Since $\cosh h \overset{h \to 0}{\sim} 1$:

$$f_B \sim -K k_B T - k_B T \log (1 + 1) \sim -J - k_B T \ln 2 \tag{6.78}$$

Therefore, as $T \to \infty$, the free energy goes linearly to zero, as in figure 6.4.
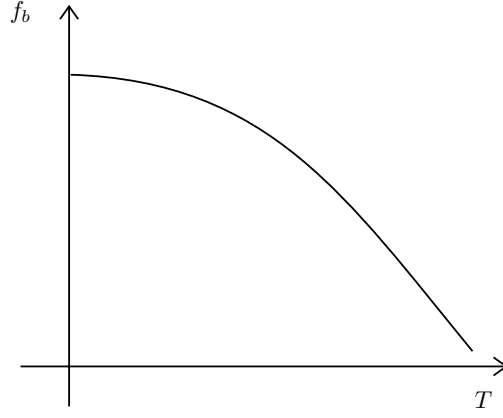
Figure 6.4: Description.

Magnetization

$$m = -\frac{\partial f_b}{\partial H} = -\frac{1}{k_B T} \frac{\partial f_b}{\partial h} = \frac{\partial}{\partial h} \left[\log \left(\cosh(h) + \sqrt{\sinh^2(h) + e^{-4K}} \right) \right] \tag{6.79}$$

The result is

$$m = \frac{\sinh h + \frac{\sinh h \cosh h}{\sqrt{\sinh^2 h + e^{-4k}}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4k}}} \tag{6.80}$$

- Case: $T > 0$ fixed, $H \to 0 \leftrightarrow h \to 0$.

$$\sinh h \sim h \sim 0, \tag{6.81a}$$
$$\cosh h \sim 1 \tag{6.81b}$$

When $h \to 0, m \to 0 \quad \forall T > 0$. It means that there is no spontaneous magnetization!

Magnetic suscettibility

$$\chi_T \equiv \frac{\partial m}{\partial H} = \frac{1}{k_B T} \frac{\partial m}{\partial h} \tag{6.82}$$

If we consider the case $h \ll 1$ it is convenient first expand the (6.80) for $h \to 0$ and take the derivative to get χ_T. Since $\sinh(h) \sim h + h^3$ and $\cosh(h) \sim 1 + h^2$, we have

$$m \overset{h \ll 1}{\sim} \frac{h(1 + e^{2K})}{1 + e^{-2K}} \tag{6.83}$$

If we now derive with respect to h

$$\chi_T = \frac{1}{k_B T} \frac{\partial m}{\partial h} \overset{h \ll 1}{\approx} \frac{1}{k_B T} \frac{(1 + e^{2K})}{(1 + e^{-2K})} \tag{6.84}$$

- Case: $T \to \infty \Leftrightarrow k \to 0$.

$$e^{2K} \simeq e^{-2K} \simeq 1 \tag{6.85}$$

The **Curie's Law** for paramagnetic systems is:

$$\chi_T \sim \frac{1}{k_B T} \tag{6.86}$$

- Case: $T \to 0 \Leftrightarrow k \to \infty$.

$$e^{-2K} \simeq 0 \tag{6.87}$$

The **Curie's Law** for paramagnetic systems is:

$$\chi_T \sim \frac{1}{k_B T} e^{2K} \sim \frac{1}{k_B T} e^{2J/k_B T} \tag{6.88}$$

Correlation length

$$\xi^{-1} = -\log\left(\frac{\lambda_-}{\lambda_+}\right) = -\log\left[\frac{\cosh h - \sqrt{\sinh^2 h + e^{-4K}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4K}}}\right] \tag{6.89}$$

For for $h = 0$, we have $\cosh h \to 1, \sinh h \to 0$:

$$\xi^{-1} = -\log\left[\frac{1 - e^{-2K}}{1 + e^{-2K}}\right] = -\log\left[\frac{1}{\coth K}\right] \tag{6.90}$$

Therefore:

$$\xi = \frac{1}{\log(\coth K)} \tag{6.91}$$

- Case: $T \to 0 \Leftrightarrow K \to \infty$.

$$\coth K = \frac{e^K + e^{-K}}{e^K - e^{-K}} \overset{K \to \infty}{\simeq} 1 + 2e^{-2K} + \dots \overset{K \to \infty}{\longrightarrow} 1 \tag{6.92}$$

It implies

$$\xi \overset{K \gg 1}{\sim} \frac{1}{\ln(1 + 2e^{-2K})} \sim \frac{e^{2K}}{2} \tag{6.93}$$

Hence

$$\xi \overset{T \to 0}{\sim} \frac{1}{2} e^{J/k_B T} \tag{6.94}$$

It diverges exponentially as $T \to 0$.

- Case: $T \to \infty \Leftrightarrow K \to 0$.

$$\coth K = \frac{e^K + e^{-K}}{e^K - e^{-K}} \overset{K \to 0}{\simeq} \frac{1 + K + \frac{K^2}{2} + 1 - K + \frac{K^2}{2}}{1 + K + \frac{K^2}{2} - 1 + K - \frac{K^2}{2}} \sim \frac{2 + 2\frac{K^2}{2}}{2K} \sim \frac{1 + K^2}{K} \tag{6.95}$$

$$\xi^{-1} = \log(\coth K) \overset{K \to 0}{\sim} \ln\frac{1}{K} + \ln(1 + K^2) \sim +\infty \tag{6.96}$$

Therefore:

$$\xi \overset{K \to 0}{\longrightarrow} 0 \tag{6.97}$$

More precisely

$$\xi \overset{K \to 0}{\sim} \frac{1}{\ln(1/K) + \ln(1 + K^2)} \overset{K \to 0}{\sim} -\frac{1}{\ln K} \tag{6.98}$$

6.2   Classical Heisenberg model: $D = 1$

Suppose to study something different from the Ising model, we do not anymore assume spin that can assume values as -1 or +1, but spin that can assume a continuous value. This is the classical Heisenberg model.

In this case the spins are unit length vectors $\vec{\mathbf{S}}_i$, i.e. $\vec{\mathbf{S}}_i \in \mathbb{R}^3$, $\left|\vec{\mathbf{S}}_i\right|^2 = 1$ (continuous values on the unit sphere):

$$\vec{\mathbf{S}}_i = (S_i^x, S_i^y, S_i^z) \tag{6.99}$$

($1D$ lattice) with periodic boundary condition: $\vec{\mathbf{S}}_{N+1} = \vec{\mathbf{S}}_1$.

Assuming $H = 0$:

$$- \beta \mathcal{H}(\{\vec{\mathbf{S}}\}) = K \sum_{i=1}^{N} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1} \quad (\longrightarrow \sum_i \vec{\mathbf{h}} \cdot \vec{\mathbf{S}}_i) \tag{6.100}$$

The model satisfies $O(3)$ symmetry. In the transfer matrix formalism:

$$Z_N(K) = \sum_{\{\vec{\mathbf{S}}\}} e^{-\beta \mathcal{H}} = \text{Tr}\left(\mathbb{T}^N\right) \tag{6.101}$$

where $\left\langle \vec{\mathbf{S}}_i \left| \mathbb{T} \right| \vec{\mathbf{S}}_{i+1} \right\rangle = e^{K\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1}}$. Similarly to the Ising case:

$$\mathbb{T} = \sum_i |t_i\rangle \lambda_i \langle t_i| \tag{6.102}$$

and

$$\mathbb{T}_D = \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \tag{6.103}$$

Problem: compute the eigenvalues λ_i of $\mathbb{T}$. Formally we should find

$$\exp\left[K\vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2\right] = \left\langle \vec{\mathbf{S}}_1 \left| \mathbb{T} \right| \vec{\mathbf{S}}_2 \right\rangle = \sum_{i \in \text{eigenvalues}} \lambda_i \left\langle \vec{\mathbf{S}}_1 \middle| t_i \right\rangle \left\langle t_i \middle| \vec{\mathbf{S}}_2 \right\rangle = \sum_i \lambda_i f_i(\vec{\mathbf{S}}_1) f^*(\vec{\mathbf{S}}_2) \tag{6.104}$$

We start by noticing that the term $e^{K\vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2}$ is similar to the plane wave $e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}}$, that in scattering problems is usually expanded in spherical coordinates. Plane wave can be expanded as a sum of spherical harmonics

$$e^{i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (i)^l j_l(qr) Y_{lm}^*(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{r}}) \tag{6.105}$$

where

$$j_l(qr) = -\frac{(i)^l}{2} \int_0^{\pi} \sin(\theta) e^{iqr\cos(\theta)} P_l(\cos(\theta)) \, d\theta \tag{6.106}$$

are the *spherical Bessel functions* and $P_l(\cos(\theta))$ the *Legendre polynomial* of order l.

From a formal comparison we have

$$\vec{\mathbf{S}}_1 \leftrightarrow \hat{\mathbf{S}}_1 \qquad \begin{cases} i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}} = iqr \\ K\vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2 = K\left|\vec{\mathbf{S}}_1\right|\left|\vec{\mathbf{S}}_2\right| = K \end{cases} \tag{6.107}$$

multiplying by i we can write

$$qr = -iK\left|\vec{\mathbf{S}}_1\right|\left|\vec{\mathbf{S}}_2\right| = -iK \tag{6.108}$$

In our case we have $\hat{\mathbf{q}} = \vec{\mathbf{S}}_1, \hat{\mathbf{r}} = \vec{\mathbf{S}}_2$. Hence

$$e^{K\vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (i)^l j_l(-iK) Y_{lm}^*(\vec{\mathbf{S}}_1) Y_{lm}(\vec{\mathbf{S}}_2) = \sum_i \lambda_i f_i(\vec{\mathbf{S}}_1) f^*(\vec{\mathbf{S}}_2) \tag{6.109}$$

where

$$\lambda_i = \lambda_{lm}(K) = 4\pi(i)^l j_l(-iK) \tag{6.110}$$

note that λ_i does not depend on m!

If $l = 0$, the largest eigenvalue is:

$$\lambda_+ = \lambda_0(K) = 4\pi j_0(-iK) = 4\pi \frac{\sin K}{K} \tag{6.111}$$

and

$$\lambda_- = \lambda_1(K) = 4\pi i j_1(-iK) = 4\pi \left[\frac{\cosh K}{K} - \frac{\sinh K}{K^2} \right] \tag{6.112}$$

Exercise 3. Given the largest eigenvalue λ_+:

$$\lambda_+ = 4\pi \frac{\sin(K)}{K} \tag{6.113}$$

find the bulk free energy density of the model and discuss its behaviour in the limits of low ($T \to 0$) and high ($T \to \infty$) temperatures.

How can we violate the hypothesis of the Perron-Frobenius theorem hoping to find a phase transition also in a $D = 1$ model? One of the hypothesis is the one in which $A_{ij} > 0 \quad \forall i,j$. Hence, one possibility is to build a model in which its transfer matrix has same A_{ij} that are equal to zero also for $T \neq 0$.

6.3   Zipper model

It is a model introduced by Kittel to describe oligomers undergoing *denaturation transition*. Simplest model of DNA thermal denaturation transition (no bubbles). Better model for the denaturation of short oligomers.

The hypothesis are: the binding energy between two bases located at the end of the molecule is smaller than the one for pairs away from the ends. The unbinding starts and develops from the ends as a *zipper*.
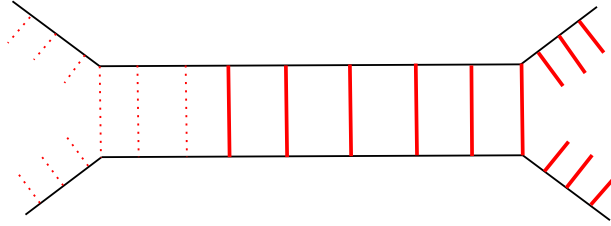
Figure 6.5: Sequential unzipping from the ends.

In this denaturation transition we do not allow bubbles. Let us consider first the zingle-ended zipper, i.e. a molecular zipper of N parallel links that can be opened only from one end as in Figure 6.6.

If the first k bonds are open (unbounded pairs) the energy to open the $k+1$ is ε_0. Note that if at least one of the previous k bond is closed the energy needed to open the $k + 1$ band is infinite! One a bond is open it can orient itself in G different ways. In other words there is an entropy

$$S_0 = k_B \log G \tag{6.114}$$

associated to each open band. If k bands ($i = 1, \ldots, k$) are open the associated weight is given by

$$G^k e^{-k\varepsilon_0/k_B T} \tag{6.115}$$
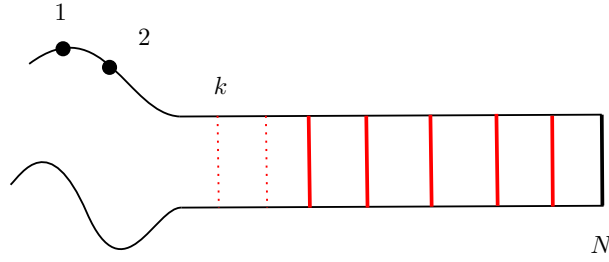
Figure 6.6

By summing over the possible values of k, the partition function is

$$Z_N(T, G, \varepsilon_0) = \sum_{k=0}^{N-1} G^k e^{-k\varepsilon_0/k_B T} = \sum_{k=0}^{N-1} e^{k(S_0 T - \varepsilon_0)/k_B T} \qquad (6.116)$$

Let us call

$$\chi \equiv G e^{-\varepsilon_0/k_B T} \qquad (6.117)$$

and simplify the previous expression

$$Z_N = \sum_{k=0}^{N-1} \chi^k = \frac{1 - \chi^N}{1 - \chi} \qquad (6.118)$$

We see immidiately there is a single pole singularity. The free energy is

$$F_N = -k_B T \ln Z_N = -k_B T \ln \left[\frac{1 - \chi^N}{1 - \chi} \right] \qquad (6.119)$$

We can now compute some observables of interest.

Calculate average number of open links

The equal of our magnetization in this case is

$$\langle k \rangle_N \equiv \frac{\sum_{k=0}^{N-1} k \chi^k}{\sum_{k=0}^{N-1} \chi^k} = \chi \frac{\mathrm{d}}{\mathrm{d}\chi} \ln Z_N = \frac{N \chi^N}{\chi^N - 1} - \frac{\chi}{\chi - 1} \qquad (6.120)$$

There is a pole in $\chi = 1$ and the last quantity can be drawn as in Figure 6.7.
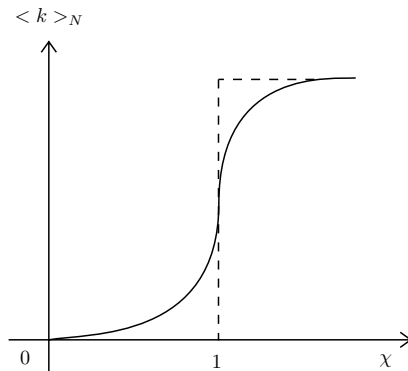
Figure 6.7: Description.

In order to analyze what happens near 1, we expand $\chi \equiv 1 + \varepsilon$:

$$
\begin{aligned}
\log Z_N(\chi) &= \log\left[\frac{1-(1+\varepsilon)^N}{1-(1+\varepsilon)}\right] \\
&= \log\left[\frac{1-(1+\varepsilon N + \frac{N(N-1)}{2!}\varepsilon^2 + \frac{N(N-1)(N-2)}{3!}\varepsilon^3 + O(\varepsilon^4))}{\varepsilon}\right] \\
&= \log\left[N + \frac{N(N-1)}{2}\varepsilon + \frac{N(N-1)(N-2)}{6}\varepsilon^2 + \dots\right] \\
&= \log N + \log\left[1 + \frac{N-1}{2}\varepsilon + \frac{N(N-1)}{6}\varepsilon^2\right] \\
&= \log N + \log\left[1 + \frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right] \\
&= \log N + \left(\frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right) + \frac{1}{2}\left(\frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{6} + \dots\right)^2 + \dots \\
&= \log N + \frac{N\varepsilon}{2} + \frac{N^2\varepsilon^2}{24} + \dots
\end{aligned}
\tag{6.121}
$$

By doing the same for $\langle k\rangle_N = \frac{N\chi^N}{\chi^N-1} - \frac{\chi}{\chi-1}$, one gets

$$
\langle k\rangle_N = \frac{N}{2}\left(1 + \frac{N\varepsilon}{6} - \frac{N^3\varepsilon^3}{360} + \dots\right)
\tag{6.122}
$$

this is true for $N \gg 1, \varepsilon \ll 1$. A the transition point $\chi_C = 1$, where $\varepsilon = 0$:

$$
\langle k\rangle_N \simeq \frac{N}{2}
\tag{6.123}
$$

We can define the variation (slope per site) as a response function (the derivative with respect to the parameter):

$$
\frac{1}{N}\frac{d\langle k\rangle}{d\varepsilon} \simeq \frac{N}{12} - \frac{N^3\varepsilon^3}{240} + \dots
\tag{6.124}
$$

It is max at $\varepsilon = 0$ and diverges as $N \to \infty$ (linearly). The response function diverges linearly to N. This is a good signal that we have a transition. The temperature T_c corresponding to the pole $\chi = 1$ is given

$$
Ge^{-\varepsilon_0/k_B T_C} = 1
\tag{6.125}
$$

Hence

$$
T_C = \frac{\varepsilon_0}{k_B \log G}
\tag{6.126}
$$

Note that as $G \to 1$, $T_c \to 0$. For $G = 1$ there is no solution and hence the model does not display a phase transition for any finite T! This is telling you that if $G = 1$ what is important it is the energy, you have no entropy as disorder. At that point everything can happen.

Remark. Despite the model is $1D$, for $G > 1$ there is a phase transition. This is due to two contributions:

1. Existence of forbidden configuration (infinite energy). Necessary condition for a phase transition in $d = 1$ with finite range interactions.

2. Degeneracy of the excited state (G).

6.3.1 Transfer matrix method for the Kittel model

The idea is: we want to map this model to an Ising model. The spin like model consists on associating to each bond a spin such that $S_i = 0$ if the i-esim bond is *closed* , while $S_i = 1, \ldots, G$ if the i-esim bond is *open* with G possible orientations.

- Case: $S_i \neq 0$ open. We have two subcases:

  - S_{i-1} open: $S_{i-1} \neq 0 \Rightarrow E(S_i \neq 0 | S_{i-1} \neq 0) = \varepsilon_0$.
  - S_{i-1} closed: $S_{i-1} = 0 \Rightarrow E(S_i \neq 0 | S_{i-1} = 0) = \varepsilon_0 + V_0$

- Case: $S_i = 0$ closed. We have $E(S_i = 0) = 0$ irrespective of S_{i-1}.

Therefore

$$E(S_i, S_{i-1}) = (\varepsilon_0 + V_0 \delta_{S_{i-1},0})(1 - \delta_{S_i,0}) \tag{6.127}$$

The boundary condition is $S_N = 0$ (always closed). The full Hamiltonian of the model can be written as (it could be also a function of delta, but it is not a problem):

$$\mathcal{H}_N = \varepsilon_0(1 - \delta_{S_1,0}) + \sum_{i=2}^{N-1} (\varepsilon_0 + V_0 \delta_{S_{i-1},0})(1 - \delta_{S_i,0}) \tag{6.128}$$

THe Kittel's version is obtained by assuming $V_0 = \infty$.

The partition function is

$$Z_N = \sum_{\{S\}} \exp(-\beta \mathcal{H}_N) \tag{6.129}$$

In order to implement the transfer matrix formalism we rewrite Z_N as follows (DUB-BIIOOOOOO per la prossima equazione)

$$Z_N = \sum_{\{S\}} e^{-\beta \varepsilon_0 (1 - \delta_{S_1,0})} \prod_{i=1}^{N-2} e^{-\beta \varepsilon_0 (1 - \delta_{S_{i+1},0})(\ldots)} \left(1 + (e^{-\beta V_0} - 1)\delta_{S_i,0}(1 - \delta_{S_{i+1},0})\right) \tag{6.130}$$

Consider the Kittel model, $V_0 = \infty$ which implies $\exp(-\beta V_0) = 0$. We can define the transfer matrix as

$$\mathbb{T} = \{\langle S | \mathbb{T} | S' \rangle \equiv t_{S,S'}\} \tag{6.131}$$

where

$$t_{S,S'} = e^{-\beta \varepsilon_0 (1 - \delta_{S',0})}[1 - \delta_{S,0}(1 - \delta_{S',0})] \tag{6.132}$$

or in matrix form

$$\mathbb{T} = \begin{bmatrix} 1 & 0 & \ldots \ldots 0 \\ 1 & a & \ldots \ldots a \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ 1 & a & \ldots \ldots a \end{bmatrix} \tag{6.133}$$

where $a \equiv e^{-\beta \varepsilon_0}$.

The first think to notice that the constraint that the bond S_{i+1} cannot be open if bond S_i is closed ($S_i = 0$) yields the null entries in the first row of $\mathbb{T}$. This violates the hypothesis of the Perron-Frobenius theorem!

The matrix $\mathbb{T}$ has three differen eigenvalues

$$\lambda_1 = Ga, \quad \lambda_2 = 1, \quad \lambda_1 = 0 \tag{6.134}$$

The partition function can be written as

$$Z_N = (1, a, \ldots, a) \, \mathbb{T}^{N-2} \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} \tag{6.135}$$

$$\lambda_1 \to \vec{\mathbf{v}}_1 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 1 \end{pmatrix}, \qquad \lambda_2 \to \vec{\mathbf{v}}_2 = \begin{pmatrix} 1 - Ga \\ 1 \\ \vdots \\ 1 \end{pmatrix} \tag{6.136}$$

We can then write

$$\begin{pmatrix} 1 \\ a \\ \vdots \\ a \end{pmatrix} = \frac{a(1 - Ga) - 1}{1 - Ga} \vec{\mathbf{v}}_1 + \frac{1}{1 - Ga} \vec{\mathbf{v}}_2 \tag{6.137a}$$

$$\begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = \frac{-Ga}{1 - Ga} \vec{\mathbf{v}}_1 + \frac{1}{1 - Ga} \vec{\mathbf{v}}_2 \tag{6.137b}$$

Therefore

$$Z_N = \frac{1 - (Ga)^N}{1 - Ga} = \frac{1 - (Ge^{-\beta \varepsilon_0})^N}{1 - Ge^{-\beta \varepsilon_0}} \tag{6.138}$$

or

$$Z_N = \frac{1}{1 - Ge^{-\beta \varepsilon_0}} (-\lambda_1^N + \lambda_2^N) \tag{6.139}$$

Since in the thermodynamic limit only the contribution of the largest eigenvalue matters for f_b we have

$$f_b = -k_B T \ln \max(\lambda_1, \lambda_2) \tag{6.140}$$

Remark. Given that the λ_1 and λ_2 are positive, analytic function of T ($\lambda_1 = Ga, \lambda_2 = 1$). In order to have a phase transition (i.e. non analiticity of f_b) the two eigenvalues must cross for a given value of T. It is true if and only if:

$$Ga_c = 1 \Leftrightarrow Ge^{-\beta_c \varepsilon_0} = 1 \Leftrightarrow T_c = \frac{\varepsilon_0}{k_B \ln G} \tag{6.141}$$

It is agree with previous calculation.

6.4   Transfer matrix for $2D$ Ising

Dimensional reducation from d to d-1. You can to the same for the 3D Ising model. In order to go smoothly to the one dimensional to the two dimensional the idea is to solve the Ising model to surfaces.

Consider a square lattice with N rows and M colums, as in Figure 6.8, with periodic boundary conditions (wrapped around a torus). The spin in a site is identifed by $S_{\text{site}} = S_{m,n}$. The Hamiltonian is (if $H \neq 0$ we have also the term with the h):

$$-\beta \mathcal{H}_\Omega(\{S\}) = k \sum_{\langle ij \rangle} S_i S_j + h \sum_i S_i$$

$$= k \sum_{n=1}^{N} \sum_{m=1}^{M} (S_{m,n} S_{m+1,n} + S_{m,n} S_{m,n+1}) + h \sum_{n=1}^{N} \sum_{m=1}^{M} S_{m,n} \tag{6.142}$$
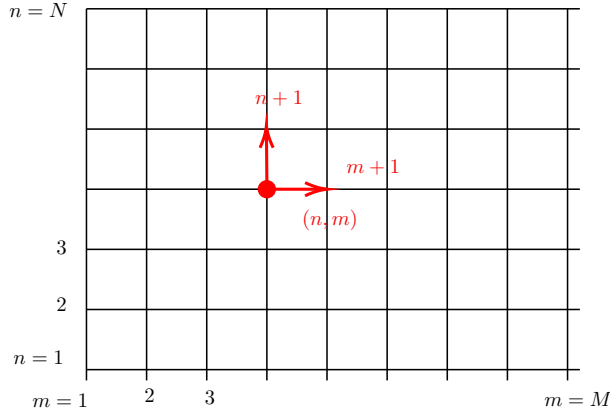
Figure 6.8: Description.

in fact

$$\sum_{\langle i,j \rangle} \rightarrow \sum_{i,j \in nn(i)} \quad \Rightarrow S_{m,n} \rightarrow S_{m+1,n} \tag{6.143}$$

The Hamiltonian can be rewritten as follows:

$$-\beta \mathcal{H}_\Omega(\{S\}) = \sum_{m=1}^{M} \left[E[\mu_m, \mu_{m+1}] + E[\mu_m] \right] \tag{6.144}$$

where the first term is the interaction between columns (two body interaction), the second term is the one body interaction of one column. Moreover, the μ is a m dimensional vector, in particular each μ_m represents the set of N spins along column m:

$$\mu_m = \{ S_{m,1}, S_{m,2}, \dots, S_{m,N} \} \tag{6.145}$$

We have:

$$E[\mu_m, h] = k \sum_{n=1}^{N} S_{m,n} S_{m,n+1} + h \sum_{n=1}^{N} S_{m,n} \tag{6.146a}$$

$$E[\mu_m, \mu_{m+1}, h] = k \sum_{n=1}^{N} S_{m,n} S_{m+1,n} \tag{6.146b}$$

where the first equation is the one body interaction, while the second equation represents the interaction between neirest neighbours columns.

We can write a transfer matrix between these new variables. The transfer matrix permit to transfer along the m. To make it simpler suppoe $h = 0$ (so the energy does not depend on h):

$$\langle \mu_m | \, \mathbb{T} \, | \mu_{m+1} \rangle = \exp[k(E[\mu_m, \mu_{m+1}] + E[\mu_m])] \tag{6.147}$$

Now we have to diagonalize. In the 2x2 tranfer matrix in the two dimensional we have 2 possible values. Now we have to do the same in principle, but we have to do for all of the (6.145). $\mathbb{T}$ is a matrix of dimension $2^N \times 2^N$. In the thermodynamic limit is an infinite matrix (violation of Perron-Frobenius). According to the formalism

$$Z_N(k,h) = \text{Tr}\left(\mathbb{T}^N \right) \tag{6.148}$$

To find the eigenvalues of $\mathbb{T}$ given by (6.147) is highly non trivial. The big problem it is that in the thermodynamic limit is that the dimension of the transfer matrix goes

to infinity, then it is diffucult to be diagonalized. This was first achived by Onsanger in 1944 for the case $H = 0$ and in the $N \to \infty$ limit. The result is given by

$$f_b(T) = -k_B T \log \left(2 \cosh(2\beta J)\right) - \frac{k_B T}{2\pi} \int_0^{2\pi} \log \left[\frac{1}{2}\left(1 + \sqrt{1 - g^2 \sin^2(\Phi)}\right)\right] d\Phi$$
(6.149)

that is the density bulk free energy, where

$$g = \frac{2}{\cosh(2\beta J) \coth(2\beta J)}$$
(6.150)

The equation for the critical T is

$$2 \tanh^2 \left(\frac{2J}{k_B T_c}\right) = 1 \quad \Rightarrow T_c \simeq 2,264 J/k_B \neq 0!$$
(6.151)

One can also show that

$$c \propto A\left[-\ln\left(1 - \frac{T}{T_c}\right) + B\right]$$
(6.152)

The specifi heat displays at the transition a logarithmic divergence (no power law!). Therefore the in $d = 2$ the Ising model as $\alpha_{\text{Ising 2D}} = 0$. You do Montecarlo simulation.

Chapter 7

The role of dimension, symmetry and range of interactions in phase transitions

Which is the role of dimensionality in phase transition? Consider D, the dimension of the system. For the Ising model we have seen that in $D = 1$ there is no phase transition while the Onsanger solution tell us that for $D = 2$ there is a paramagnetic-ferromagnetic transition for $T_c > 0$. Therefore, dimensionality seems a crucial parameter! Since in general analytic solutions are not available is there a simple argument to establish the existence of a phase transition? In the case of a para-ferro transition may we establish wheter a phase with long range order exists and is stable withn a range of $T > 0$?

We need an argument that can tell us which kind of system has a phase transition. The idea is to use the entropy energy argument. Indeed, our systems are ruled by a free energy and the previous states are found by making derivative. We have energy and entropy: low energy state can be stable respect thermal fluctuations, but the fluctuations will destroy the long range order. This idea can be generalized.

7.1 Energy-entropy argument

$$\mathrm{d}F = \underbrace{\mathrm{d}U}_{\text{energy}} - T\underbrace{\mathrm{d}S}_{\text{entropy}} \tag{7.1}$$

We expect that:

- $T \gg 1$: entropy should dominates.

- $T \ll 1$: energy should dominates.

Question: there is a temperature different to zero in which this is compatible?

7.1.1 Ising $D = 1$

Consider N the size of the system. Study the stability of the states with minimum energy to fluctuations for $T \neq 0$. We already know that in the case $T = 0$, two ground states exist, either all spins up or all spins down.

For instance, suppose that we have the ground state with all the spin up; the energy of the state is

$$E_G = -JN \tag{7.2}$$

Now consider $T \neq 0$, there could be a given number of elementary excitations of the kind spin up/down. What happens if we swap one or more spins? These are defects respect the ground state and they are also called *domain walls*. This is in one dimentional, but is valid also in many dimensional.

Which is the variation in energy ΔE respect the ground state? For each excitation there is an energy penalty $\Delta E = 2J$, indeed

$$E_G = -JN, \qquad E^* = -J(N-1) + J \qquad \Rightarrow \Delta E = 2J \qquad (7.3)$$

Here we have supposed that we have only one swap. If there is a finite concentration of domains, we have x such that there are $M = Nx$ domain walls. Therefore:

$$\Delta E_M = 2MJ \qquad (7.4)$$

Now compute the change in entropy. We can compute immediately the entropy of the ground state: this is zero because is the logarithm of the number of configurations, but in this case we have only one configuration, namely $S_G = \ln 1 = 0$. Therefore, the different of the entropies is just the entropy of the last state.

Now we estimate the entropy of the states with M domain walls. The number of possible ways to insert M domains in N positions, namely the number of configurations, is

$$\# = \binom{N}{M} = \binom{N}{xN} \qquad (7.5)$$

We have:

$$S_M = k_B \log \binom{N}{M} \qquad (7.6)$$

the difference is

$$\Delta S = S_M - S_G = S_M = -k_B \ln \binom{N}{xN} \qquad (7.7)$$

Consider:

$$\begin{aligned}
\Delta F = F_M - F_G &= \Delta E - T\Delta S \\
&= 2MJ - k_B T \ln \binom{N}{M} \\
&= 2xNJ - k_B T \ln \binom{N}{xN} \\
&= N\{2xJ + k_B T[x \ln x + (1-x) \ln (1-x)]\}
\end{aligned} \qquad (7.8)$$

were we have used the Stirling approximation: $\ln N! = N \ln N - N$.

Since equilibrium states are obtained by the minima of F we can minimize with respect to x. We are interested in the free energy in the bulk:

$$\Delta f_{b_N} = \frac{\Delta F_N}{N}, \qquad \frac{\partial \Delta f_b}{\partial x} = 0 \qquad (7.9)$$

this gives

$$\begin{aligned}
\frac{\partial}{\partial x}\{2xJ + k_B T[x \ln x + (1-x) \ln (1-x)]\} &= 2J + k_B T[\ln x + 1 - \ln (1-x) - 1] \\
&= 2J + k_B T[\ln x - \ln (1-x)] = 0
\end{aligned} \qquad (7.10)$$

therefore

$$\ln \frac{x}{1-x} = -\frac{2J}{k_B T} \qquad \Rightarrow \qquad \frac{x}{1-x} = e^{-2J/k_B T} \qquad (7.11)$$

and finally the results is

$$x = \frac{1}{1 + e^{2J/k_B T}} \tag{7.12}$$

It means that $\forall T \neq 0$ exist a finite concentration x. The ground state is unstable $\forall T > 0$. Indeed, if you have a finite density of x it means no long range order exist for $T > 0$. It tells you that at $T = 0$, $x = 0$.

Let us try to do the same for D dimensions.

7.1.2 D dimension

What is a *domain wall* in D dimension? The domain walls is an hypersurface of size L^{D-1}

$$\Delta E \propto 2JL^{D-1} \tag{7.13}$$

Computing the entropy it is a very difficult problem. In fact, the entropy of a fluctuating hypersurface is difficult to estimate. For a single domain wall we can say

$$S^* \geq k_B \ln L \tag{7.14}$$

the number of ways to place a straight wall within a system of linear size L. The ΔS is just S because the entropy of the ground state is again zero.

Remark. Understimate of S

$$\Delta F = 2JL^{D-1} - k_B T \ln L \tag{7.15}$$

it means that now energy can win if the temperature is different from zero. Therefore, for $D = 2$ or greater $(D > 1)$ that long range order can survive thermal fluctuations, the system could present an ordered phase!

Peierls argument

Idea: try to perturbe the system using an external magnetic field as perturbation (it is very small h). We are breaking explicity the symmetry, but then you take the limit $h \to 0$ and swich off the magnetic field. This is the typical way to see this stability.

An argument due to *Pierls* shows that this is indeed the case. We now that for finite systems, from the $\mathbb{Z}^2$ symmetry it follows

$$\langle m \rangle_N = 0 \tag{7.16}$$

If, as $N \to \infty$ we have $\langle m \rangle_\infty \neq 0$ with $T < T_c$. We have spontaneous symmetry breaking. This can be seen as a thermodynamical instability, namely the value of $\langle m \rangle_\infty$ in the ferromagnetic phase, is determined by small perturbations. Usually the value of $\langle m \rangle_\infty$ is determined by using an infinitesimal magnetic field:

$$\langle m \rangle_\infty = \lim_{h \to 0^+} \lim_{N \to \infty} \langle m \rangle_N^{(h)} \tag{7.17}$$

Remark. It is crucial to take first the thermodynamic limit and then the limit $h \to 0^+$!

That is to see the stability. Another way to do that is instead using a small h, using periodic boundary condition.

A different infinitesimal perturbation that trigger the instability is to chose appropriate boundary conditions. For example, if we want $\langle m \rangle_\infty > 0$ one can choose a boundary condition such that at the surface of the system all the spins are up ($S_i = +1$ with $i \in \partial\Omega$), as in Figure 7.1.
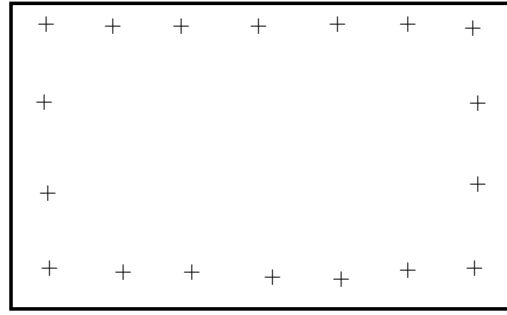
Figure 7.1

It is equivalent, because on the border we have a very high field, by it is at the border so it do not really count for the surface internal. This is a very smart way to do this perturbation. The idea is therefore to perturbe the surface. This particular configuration with all the spin up will give you a particular shape, you can do this also in higher dimensional. From this you can also exstimate the temperature.

In the paramagnetic phase this constraint at the boundary does not affect the disorder bulk phase. In the ferromagnetic phase, however, this boundary condition has the same effect of considering an infinitesim magnetic field.

This is the boundary condition chosen by Pierls to establish the existence of a $T_c \neq 0$ for the $< D$ Ising model.

Let us gives just a qualitative presentation of the (rigorous) result. If one is interested to the full proof refer for example to [4].

Let N_+, N_- the number of spin up and down respectively. Clearly, $N = N_+ + N_-$ and

$$\langle m \rangle_N = \frac{\langle N_+ \rangle - \langle N_- \rangle}{N} = 1 - 2 \frac{\langle N_- \rangle}{N} \qquad (7.18)$$

In order to show that $\langle m \rangle_\infty > 0$ (remember that we are considerin boundary conditions with spin ap at $\partial \Omega$) it is sufficient to show that $\forall N$

$$\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon \qquad (7.19)$$

where $\varepsilon > 0$ and indipendent on N. Indeed, if (7.19) holds

$$\langle m \rangle_N \geq 2\varepsilon \quad \forall N \qquad (7.20)$$

Pierles was indeed able to show that

$$\frac{\langle N_- \rangle}{N} \leq f_D(x) \qquad (7.21)$$

where f_D is a continuous function of x indipendent on N and so

$$x = q e^{-4J\beta} \qquad (7.22)$$

and such that $\lim_{x \to 0} f_D(x) = 0$.

In particular for T sufficiently small

$$\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon \qquad (7.23)$$

More precisely one has

$$\frac{\langle N_- \rangle}{N} \leq \frac{x^2}{36} \frac{2 - x}{(1 - x)^2} \qquad (7.24)$$

where $x = q e^{-4J\beta} < 1$.

Note that above bound gives also a lower bound on the critical temperature

$$\frac{\langle N_- \rangle}{N} \leq \frac{x^2}{36} \frac{2-x}{(1-x)^2} < \frac{1}{2} - \varepsilon \tag{7.25}$$

As long as $\frac{\langle N_- \rangle}{N} < \frac{1}{2} - \varepsilon$ the system is in the ferromagnetic phase. The critical value $x_c \equiv x(\beta_c)$ must be outside the interval $[0, x_{1/2}]$ where $x_{1/2}$ is the smallest positive solution of the equation

$$\frac{x^2}{36} \frac{2-x}{(1-x)^2} = \frac{1}{2} \tag{7.26}$$

From the solution $x_{1/2}$ and the condition $x_c > x_{1/2}$ one has

$$J\beta_c \leq J\beta_{1/2} \tag{7.27}$$

where $J\beta_{1/2} = \frac{1}{4} \log q/x_{1/2}$ which implies $T_c > T_{1/2}$.

Exercise 4. The equation

$$x^3 + 16x^2 - 36x + 18 = 0 \tag{7.28}$$

gives $x_{1/2}$. Found $T_{1/2}$.

7.2   Role of the symmetry

Interacting systems can be classified with respect to their *global symmetry group*.

Example 16 (Ising model).

$$\mathcal{H}_{\text{Ising}} = -\sum_{i<j} J_{ij}\sigma_i\sigma_j \tag{7.29}$$

where $\sigma_i \in \{-1, 1\}$. The symmetry gropu of this Hamiltonian is $\mathbb{Z}^2$, which has two elements $\{\mathbb{1}, \mu\}$. We have

$$\mathbb{1}: \text{ identity}, \quad \mu\sigma_i = -\sigma_i, \quad \mu^2 = \mathbb{1} \tag{7.30}$$

Example 17 (Potts model).

$$\mathcal{H}_{q-\text{Potts}} = -\sum_{i<j} J_{ij}\delta_{\sigma_i,\sigma_j} \tag{7.31}$$

where $\sigma_i \in [1, 2, 3, \ldots, q]$. $\mathcal{H}_{q-\text{Potts}}$ is invariant under the permutation group of the sequence $\{1, 2, 3, \ldots, q\}$. There are $q!$ elemtns, for example $\{2, 1, 3, \ldots, q\}$. The symmetry group is denoted by S_q.

Remark. The difference between a $\mathbb{Z}_q$ and S_q symmetry is that an Hamiltonian has symmetry $\mathbb{Z}_q$ if it is invariant with respect to *cyclic permutations*

$$\mu = \begin{pmatrix} 1 & 2 & \cdots & q-1 & q \\ 2 & 3 & \cdots & q & 1 \end{pmatrix} \tag{7.32}$$

and its powers μ^l with $l = 0, \ldots, q-1$. Both models satisfy a *discrete global symmetry*.

Now, we jump into the case in which we consider *continuous* symmetries.

7.3 XY model

This is a spin model that is invariant with respect to the continuous global symmetry $\theta_i \to \theta_i + \alpha$. Indeed the Hamiltonian of this model is

$$\mathcal{H}_{XY} = -\sum_{i<j} J_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j \tag{7.33}$$

where $\vec{\mathbf{S}}_i$ is a $2D$ spin vector

$$\vec{\mathbf{S}}_i = (S_{x_i}, S_{y_i}) \tag{7.34}$$

that can assume values on the unit circle ($\left|\vec{\mathbf{S}}_i\right| = 1$).

Suppose that you have spins that are sitting in hyper dimensional. Rotate along a circle this spins. They can assume all the value as in Figure 7.2.
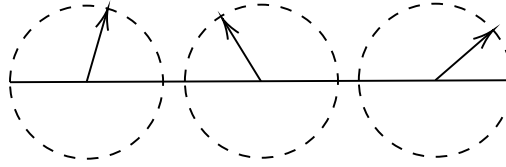

Figure 7.2

The simplest way to parametrize the Hamiltonian is by the angle. Denoting by θ_i the direction angle of spins $\vec{\mathbf{S}}_i$, the $\mathcal{H}_{XY}$ can be written as

$$\mathcal{H}_{XY} = -\sum_{i<j} J_{ij} \cos(\theta_i - \theta_j) \tag{7.35}$$

with $\theta_i \in [0, 2\pi]$.

Remark. The interaction term $\cos(\theta_i - \theta_j)$ can be written also as

$$\frac{1}{2}\left(Z_i^* Z_j + Z_i Z_j^*\right) \tag{7.36}$$

where $Z_j = \exp(i\theta_j)$.

The model is invariant under the global transformation

$$Z_i \to e^{i\alpha} Z_i \tag{7.37}$$

The phase $\exp(i\alpha)$ form a group under multiplication known as $U(1)$ that is equivalent to $O(2)$. Indeed the interaction term can be written also as

$$\hat{\mathbf{\Omega}}_i \cdot \hat{\mathbf{\Omega}}_j \tag{7.38}$$

where $\hat{\mathbf{\Omega}}_i = (\cos\theta_i, \sin\theta_i)$.

Remark. In n-dimensions $\hat{\mathbf{\Omega}}$ has n components $\hat{\mathbf{\Omega}} = \{\Omega^1, \Omega^2, \dots, \Omega^n\}$ and the corresponding Hamiltonian

$$\mathcal{H} = -\sum_{i>j} J_{ij} \hat{\mathbf{\Omega}}_i \cdot \hat{\mathbf{\Omega}}_j \tag{7.39}$$

It is symmetric with respect to the global symmetry group $O(n)$.

Which are the domain walls for continuous symmetries? Which are the implications for the stability of the ordered phase?
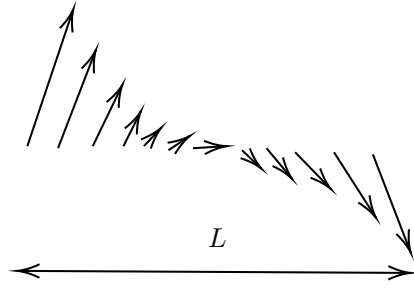
Figure 7.3

7.4   Continuous symmetries and phase transitions

The questions is: when it is not continuous which is the boundary? When the symmetry is continuous the domain walls interpolate smoothly between two ordered regions (see Figure 7.3).

The energy term that in Ising is proportional to $2JL^{D-1}$ how does it change here? Suppose that the variation of the direction between two neirest neighbours sites is very small, i.e. $(\theta_i - \theta_j) \ll 1$ for i, j neirest neighbours. Now we can diluite the energy, in other words weak the energy term.

Let us do a Taylor expainding of the interaction term

$$\cos(\theta_i - \theta_j) \simeq 1 - \frac{1}{2}(\theta_i - \theta_j)^2 \Rightarrow \sum_{\langle ij \rangle} \left(1 - \frac{1}{2}(\theta_i - \theta_j)^2 \right) \tag{7.40}$$

The Hamiltonian can be written as

$$\mathcal{H} \simeq -J \sum_{\langle ij \rangle} \left(1 - \frac{1}{2}(\theta_i - \theta_j)^2 \right) \tag{7.41}$$

The (7.40) corresponds to the discrete differential operator where $\theta_i - \theta_j = \partial_x \theta$, therefore

$$\mathcal{H} = E_0 + \underbrace{\frac{J}{2} \int \mathrm{d}\vec{r} \, (\boldsymbol{\nabla}\theta)^2}_{E \equiv \text{Stifness energy}} \tag{7.42}$$

where $E_0 = 2JN$ is the energy corresponding to the case in which all the spins are oriented along a given direction.

Definition 5 (Stifness energy)**.** The Stifness energy is defined as

$$E = \frac{J}{2} \int \mathrm{d}\vec{r} \, (\boldsymbol{\nabla}\theta)^2 \tag{7.43}$$

where $\theta(\vec{r})$ is the angle of a local rotation around an axis and J is the *spin rigidity*. For an ordered phase $\theta(\vec{r}) = \theta_0$.

Let us now imagine a domain wall where $\theta(\vec{r})$ rotates by 2π (or $2\pi m$) by using the entire length of the system (see again Figure 7.3):

$$\theta(\vec{r}) = \frac{2\pi n x}{L} \tag{7.44}$$

where n is the total number of 2π turn of θ in L. Note that there is no variation along the other $D - 1$ dimensions, therefore we just doing over one dimension.

Consider only the term called E

$$E = \frac{J}{2}L^{D-1} \int_0^L \mathrm{d}x \left(\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{2\pi n x}{L} \right) \right)^2 = \frac{J}{2}L^{D-1} \int_0^L \mathrm{d}x \left(\frac{2\pi n}{L} \right)^2 \approx 2\pi^2 n^2 JL^{D-2} \tag{7.45}$$

Remark. Unlike the Ising model where $E \sim L^{D-1}$, here $E \sim L^{D-2}$!

If $S \geq k_B \ln L$ for a single domain wall, S should dominate if $D \leq 2$, the ordered phase is always unstable and no phase transition is expected for $T \neq 0$!

Definition 6 (Lower critical dimension)**.** The Lower Critical dimension D_c is the dimension at which (and below which) the system does not display a ordered phase (there is no long range order). In other words if $D \leq D_c$, we have $T_c = 0$.

Theorem 7.4.1 (Mermin-Wagner)**.** *For continuous global symmetries the $D_c = 2$.*

From what we have dound before we can say that

- Discrete global symmetries: $D_c = 1$.

- Continuous global symmetries: $D_c = 2$.

Remark. The XY model in $D = 2$ is rather special. Although it dos not display an ordered phase, there exist at $T \neq 0$ a special phase transition known as the *Kosterlitz-thouless transition.* This transition dows not imply the spontaneous breaking of the $O(2)$ symmetry! There is no long range order for $T < T_{KT}$ (statistic of vortices, topological defects in $D = 2$).

7.5   Role of the interaction range

So far we have considered models where the interactions were short range. How things change if long range are considered instead? How does the symmetry broken depends on the range of interactions? One can show, for example, that if

$$J_{ij} = \frac{J}{|\vec{r}_i - \vec{r}_j|^\alpha} \tag{7.46}$$

with $1 \leq \alpha \leq 2$, phase with long range order is stable for $0 < T < T_c$ also for $D = 1$! So we have a long range order with $T_c \neq 0$, even for $D = 1$!

Remark. If $\alpha > 2 + \varepsilon$ we get back the physics found for short range interactions. If $\alpha < 1$ the thermodynamic limit does not exist.

A limiting case of long range interaction is the infinite range case where all the spins interact one to another with the same intensity indipendently on their distance. No metric is involed (instead of previously where the definition of J of before is a metric.). It can be solve exactly and later we will seen why.

7.6   Ising model with infinite range

The Hamiltonian is the following:

$$-\mathcal{H}_N(\{S\}) = \frac{J_0}{2} \sum_{i,j}^N S_i S_j + H \sum_i S_i \tag{7.47}$$

with $S_i \in [-1, +1]$. The problem is the double sum over i,j, indeed

$$\sum_{i,j} S_i S_j \propto O(N^2) \tag{7.48}$$

and the thermodynamic limit is ill-defined. To circumvent this problem *Kac* suggested to consider a strength

$$J_0 = \frac{J}{N} \tag{7.49}$$

this is called the *kac* approximation

$$- \mathcal{H}_N(\{S\}) = \frac{J}{2N} \sum_{i,j}^{N} S_i S_j + H \sum_i S_i \tag{7.50}$$

with this choice we recover $E \sim O(N)$. In this Hamiltonian since you have no metric you have no dimension.

The partition function is

$$Z_N(T, J, H) = \sum_{\{S\}} \exp\left[\frac{\beta J}{2N} \sum_{ij} S_i S_j + \beta H \sum_i S_i \right] \tag{7.51}$$

Since there are no restrictions on the double sum we can write

$$\sum_{ij} S_i S_j = \left(\sum_i S_i \right) \left(\sum_j S_j \right) = \left(\sum_i S_i \right)^2 \tag{7.52}$$

Rewriting the partition function:

$$Z_N(T, J, H) = \sum_{\{S\}} \exp\left[\frac{K}{2N} \left(\sum_i S_i \right)^2 + h \sum_i S_i \right] \tag{7.53}$$

In order to transform the quadratic term into al inear one we make use of the integral identity known as the *Hubbard-stratonovitch transformation* (we can do it in any dimension). The idea is to rewrite something as a square.

Let us define:

$$x \equiv \sum_i S_i \tag{7.54}$$

The following identity holds

$$e^{\frac{Kx^2}{2N}} = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} e^{-\frac{NK}{2} y^2 + Kxy} \, \mathrm{d}y, \quad \text{with} \quad \mathrm{Re}(K) > 0 \tag{7.55}$$

where y is a random field that follows a random distribution. To show the identity above it is sufficient to complete the square

Proof. (of (7.55))

$$-\frac{NK}{2} y^2 + Kxy = -\frac{NK}{2} \left(y - \frac{x}{N} \right)^2 + \frac{Kx^2}{2N} \tag{7.56}$$

Then we integrate:

$$e^{\frac{Kx^2}{2N}} \int_{-\infty}^{+\infty} e^{-\frac{NK}{2} \left(y - \frac{x}{N} \right)^2} \, \mathrm{d}y \stackrel{(a)}{=} e^{\frac{Kx^2}{2N}} \sqrt{\frac{2\pi}{NK}} \tag{7.57}$$

where in (a) we have considered $z \equiv \left(y - \frac{x}{N} \right)$, $\mathrm{d}z = \mathrm{d}y$:

$$\rightarrow \int_{-\infty}^{+\infty} e^{-\alpha z^2} \, \mathrm{d}z = \sqrt{\frac{\pi}{\alpha}} \tag{7.58}$$

with $\alpha \equiv \frac{NK}{2}$. $\square$

By using (7.55) we have

$$Z_N(K,h) = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy \, e^{-\frac{NK}{2}y^2} \underbrace{\left[\sum_{\{S\}} e^{(h+Ky)\sum_i S_i} \right]}_{Q_y} \qquad (7.59)$$

Sometimes y is called *auxiliary field*. If y is a fluctuating external field with Gaussian distribution

$$Q_y = \sum_{\{S\}} e^{(h+Ky)\sum_i S_i} = \prod_i^N \left(\sum_{S_i=\pm 1} \exp[(h+Ky)S_i] \right) \qquad (7.60)$$
$$= (2\cosh(h+Ky))^N$$

The partition function becomes

$$Z_N(K,h) = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy \, e^{-\frac{NK}{2}y^2} (2\cosh(h+Ky))^N = \sqrt{\frac{NK}{2\pi}} \int_{-\infty}^{+\infty} dy \, e^{N\alpha(K,h,y)} \qquad (7.61)$$

where

$$\alpha(K,h,y) = \ln\left[2\cosh(h+Ky)\right] - \frac{K}{2}y^2 \qquad (7.62)$$

Remark. In the limit $N \to \infty$ the integral can be computed exactly by the *saddle point method.* We can replace the medium of the integral with the maximum of the integrand, we say that all the information is coming only from a bit of information. Replace the all integral with the integrand computed where it is maximum. That is an approximation and we are loosing information, it depends on the form of the function. For example, for a delta function it works better. In general:

$$\int_{-\infty}^{+\infty} f(x)\, dy \to f(\bar{x}) \qquad (7.63)$$

where $\bar{x} = \max_x f(x)$.

Indeed as $N \to \infty$, since the integrand is $\exp(N\alpha(K,h,y))$, the integral is dominated by the global maximum in y of the function $\alpha(K,h,y)$.

$$Z_N(K,h) \overset{N\gg 1}{\approx} \sqrt{\frac{NK}{2\pi}} \max_y \left[e^{N\alpha(K,h,y)} \right] \qquad (7.64)$$

Let y_s be the value of y at which

$$\alpha(K,h,y_s) = \max_y \alpha(K,h,y) \qquad (7.65)$$

therefore

$$Z_N(K,h) \overset{N\gg 1}{\approx} \sqrt{\frac{NK}{2\pi}} e^{N\alpha(K,h,y_s)} \qquad (7.66)$$

When we are ample to compute the y_s we can do this approximation and

$$f_b(K,h) = \lim_{N\to\infty} \frac{1}{N}(-k_B T \log Z_N) = -k_B T \alpha(K,h,y_s) \qquad (7.67)$$

Looking for y_s we consider the condition $\frac{\partial \alpha}{\partial y} = 0$:

$$\frac{\partial \alpha}{\partial y} = \frac{\sinh(h+Ky)K}{\cosh(h+Ky)} - Ky = 0 \quad \Rightarrow y_s = \tanh(h+Ky_s) \qquad (7.68)$$

The last one is an implicit equation that can be solved graphically as a function of K and h.

The magnetization in the $N \to \infty$ limit is given by

$$
\begin{aligned}
m = -\left(\frac{\partial f}{\partial H}\right)_T &= \lim_{N\to\infty} \frac{1}{\beta N} \frac{\partial \ln Z_N(K,h)}{\partial H} \\
&= \frac{\partial \alpha(K,h,y_s)}{\partial h} + \frac{O(\log N)}{N} = \frac{2\sinh(Ky_s+h)}{2\cosh(ky_s+h)} \\
&= \tanh(Ky_s+h)
\end{aligned}
\tag{7.69}
$$

At the end $m \equiv y_s$

$$
m = \tanh(h + Km)
\tag{7.70}
$$

that is a self consistent equation. We have solved analitically this problem.

Chapter 8

Mean field theories of phase transitions adn variational mean field

8.1 Mean field theories

Increasing the dimension of the systems the effort to solve analitically the problems increase , in fact we have seen that

- In $D = 1$: many (simple) models can be solved exactly using techniques such as the transfer matrix method.

- In $D = 2$: few models can still be solved exactly (often with a lot of effort).

- In $D = 3$: almost no model can be exactly solved.

so, approximations are need. The most important and most used one is the *mean field approximation*. The idea is to try to simplify the problem by neglectic the correlation between the fluctuations of the order parameter. It is equivalent to a statistical indipendence of the microscopic degrees of freedom.

The mean field approximation has different names depending on the system considered:

- Magnetic: Weiss theory.

- Fluids: Van der Walls.

- Polymers: Flory's theory.

8.1.1 Mean field for Ising model

$$Z_N(T, H, \{J_{ij}\}) = \sum_{\{S\}} e^{\beta\left[\frac{1}{2}\sum_{\langle ij\rangle} J_{ij}S_iS_j + \sum_i H_iS_i\right]} = \exp(-\beta F_N(T, H, \{J_{ij}\})) \quad (8.1)$$

The magnetization per spin is $m \equiv \langle S_i\rangle$ and let us consider $H_i = H$ uniform. Consider the idenity

$$\begin{aligned}
S_iS_j &= (S_i - m + m)(S_j - m + m)\\
&= (S_i - m)(S_j - m) + m^2 + m(S_j - m) + m(S_i - m)
\end{aligned} \quad (8.2)$$

Remark. The term

$$(S_i - m)(S_j - m) = (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \tag{8.3}$$

measures correlation between fluctuations.

The mean field approximation consists in neglecting this term obtaining

$$S_i S_j \approx m^2 + m(S_i - m) + m(S_j - m) \tag{8.4}$$

We have:

$$\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j \overset{MF}{\approx} \frac{1}{2} \sum_{i,j} J_{ij} \left[-m^2 + m(S_i + S_j) \right] \tag{8.5}$$

The term

$$\frac{1}{2} \sum_{i,j} J_{ij} m(S_i + S_j) = \frac{2}{2} \sum_{i,j} J_{ij} m S_i \tag{8.6}$$

and assuming (*n.n.* = neirest neighbour)

$$\sum_{j \, n.n. \, \text{of} \, i} J_{ij} = z \hat{J}_i \simeq z \hat{J} \tag{8.7}$$

where z is the coordination number of the underlying lattice (hypercubic lattice $z = 2D$). Therefore, (8.6) became

$$\frac{2}{2} \sum_{i,j} J_{ij} m S_i = m \hat{J} z \sum_i S_i \tag{8.8}$$

$$-\mathcal{H} = \frac{1}{2} \sum_{\langle ij \rangle} J_{ij} S_i S_j + H \sum_i S_i \simeq -\frac{1}{2} N \hat{J} z m^2 + (\hat{J} z m + H) \sum_{i=1}^{N} S_i \tag{8.9}$$

Let us do the same story over j for the sum over i:

$$\begin{aligned} Z_N(T, H, \hat{J}) &= e^{-\frac{\beta m^2 N}{2} z \hat{J}} \sum_{\{S\}} e^{\beta(\hat{J} z m + H) \sum_i S_i} \\ &= e^{-\frac{\beta m^2 N}{2} z \hat{J}} \left(\sum_{S=\pm 1} \exp\left(\beta(\hat{J} z m + H) S \right) \right)^N \\ &= e^{-\frac{\beta m^2 N}{2} z \hat{J}} \left(2 \cosh[\beta(\hat{J} z m + H)] \right)^N \end{aligned} \tag{8.10}$$

The free energy per spin is

$$\begin{aligned} f_b(T, H, \hat{J}) &= -\frac{1}{N} k_B T \log Z_N(T, H, \hat{J}) \\ &= \frac{1}{2} \hat{J} z m^2 - k_B T \log\left[\cosh\left(\beta(\hat{J} z m + H) \right) \right] - k_B T \ln 2 \end{aligned} \tag{8.11}$$

Remark. We are replacing the interaction of the J with a field close to the S_i. We called $\hat{J} z m = H_{eff}$, the mean field!

In order to be a self-consistent equation has to satisfy the thermodynamic relation:

$$m = -\left(\frac{\partial f}{\partial H} \right)_T \quad \Rightarrow m = \tanh\left(\beta(\hat{J} z m + H) \right) \tag{8.12}$$

Remark. The results it is similar to the Ising with infinite range ($\hat{J} z \leftrightarrow J$).

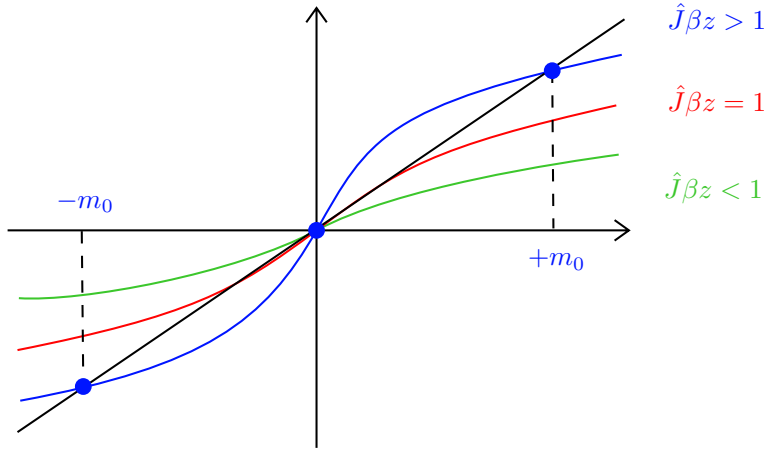**Figure 8.1**

If $H = 0$, we have

$$m = \tanh\Big(\beta(\hat{J}zm)\Big) \tag{8.13}$$

and the graphical solution is shown in Figure 8.1 (hyperbolic function).

In particular:

- case $\beta\hat{J}z > 1$: there are three solutsions, one at $m = 0$ and two symmetric at $m = \pm m_0$. Magnetization is $\neq 0 (= |m_0|)$ for $H = 0$ (*ordered phase*). The two solution are symmetric because they are related by the $\mathbb{Z}^2$ symmetry;

- case $\beta\hat{J}z < 1$: single solution at $m = 0$ (*disordered or paramagnetic phase*);

- case $\beta\hat{J}z = 1$: the three solutions coincide at $m = 0$.

The condition $\beta_c\hat{J}z = 1$, define the critical point. The critical temperature T_c is given by

$$\frac{z\hat{J}}{k_B T_c} = 1 \Rightarrow T_c = \frac{z\hat{J}}{k_B} \neq 0! \tag{8.14}$$

Remark. T_c depends on z and hence on D.

8.1.2 Free-energy expansion for $m \sim 0$

The critical point is characterized by the order parameter that is zero. Now we want to expand the free energy around the critical point. Let us put $H = 0$.

$$f(m, 0, T, \hat{J}) = \frac{1}{2}\hat{J}zm^2 - k_B T \ln\Big[\cosh\Big(\beta\hat{J}zm\Big)\Big] \tag{8.15}$$

Define $x \equiv \beta\hat{J}zm \simeq 0$, so

$$\cosh(x) = 1 + \underbrace{\frac{x^2}{2} + \frac{x^4}{4!}}_{t \simeq 0} + \dots \tag{8.16}$$

$$\log(1 + t) \simeq t - \frac{1}{2}t^2 \tag{8.17}$$

$$\log(\cosh x) \simeq \frac{x^2}{2} + \frac{x^4}{4!} - \frac{1}{2}\frac{x^4}{4} + O(x^6) = \frac{x^2}{2} - \frac{x^4}{12} + O(x^6) \tag{8.18}$$

This gives

$$f(m, 0, T, \hat{J}) = const + \frac{A}{2}m^2 + \frac{B}{4}m^4 + O(m^6) \tag{8.19}$$

with

$$A = \hat{J}z\left(1 - \beta\hat{J}z\right) \tag{8.20a}$$

$$B = \beta^3 \frac{(\hat{J}z)^4}{3} > 0 \tag{8.20b}$$

- case $\beta\hat{J}z > 1 \Rightarrow A < 0$: two stable symmetric minima at $m = \pm m_0$. Coexistence between the two ordered phases.

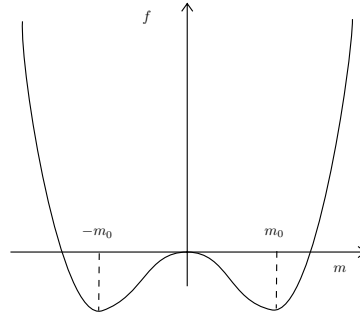**Figure 8.2**

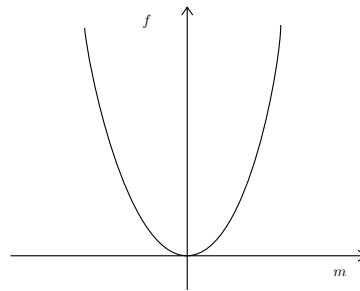- case $\beta\hat{J}z < 1 \Rightarrow A > 0$: one minimum at $m = 0$.

Figure 8.3

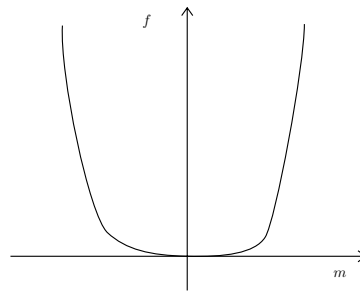- case $\beta\hat{J}z = 1 \Rightarrow A = 0$: 3 minima coincide at $m = 0$.

Figure 8.4

8.1.3   Mean field critical exponents

We have:

$$f(m, T, 0) \approx const + \frac{A}{2}m^2 + \frac{B}{4}m^4 + O(m^6) \tag{8.21}$$

with $B > 0$, so we do not need more term to find the minima of the solution. This is called stabilization. What is most important is the coefficient $A = \hat{J}z(1 - \beta\hat{J}z)$, that means that A can change sign.

β exponent

The β exponential observe the order parameter. Consider $H = 0, t \equiv \frac{T - T_c}{T_c}$ and $m \overset{t \to 0^-}{\sim} -t^\beta$. The condition of equilibrium is

$$\frac{\partial f}{\partial m} = 0 \tag{8.22}$$

which implies

$$\left.\frac{\partial f}{\partial m}\right|_{m=m_0} = Am_0 + Bm_0^3 = \left[\hat{J}z(1 - \beta\hat{J}z) + Bm_0^2\right]m_0 = 0 \tag{8.23}$$

Since $T_c = \frac{\hat{J}z}{k_B}$:

$$0 = \frac{k_B T_c}{T}(T - T_c)m_0 + Bm_0^3 \tag{8.24}$$

and $m_0 = 0$ implies

$$m_0 \simeq (T_c - T)^{1/2} \tag{8.25}$$

The mean field value is so $\beta = 1/2$.

δ exponent

Now, let us concentrate in the δ exponent. We are in the only case in which we are in $T = T_c$ and we want to see how the magnetization decrease: $H \sim m^\delta$.

Starting from the self-consistent equation

$$m = \tanh\left(\beta(\hat{J}zm + H)\right) \tag{8.26}$$

inverting it

$$\beta(\hat{J}zm + H) = \tanh^{-1} m \tag{8.27}$$

on the other hand, for $m \sim 0$

$$\tanh^{-1} m \simeq m + \frac{m^3}{3} + \frac{m^5}{5} + \ldots \tag{8.28}$$

Therefore, by substituting

$$H = k_B T\left(m + \frac{m^3}{3} + \ldots\right) - \hat{J}zm = \left(k_B T - \hat{J}z\right)m + k_B T\frac{m^3}{3} + \ldots$$
$$\simeq k_B(T - T_c)m + \frac{k_B T}{3}m^3 \tag{8.29}$$

At $T = T_c = \frac{\hat{J}z}{k_B}$, we have

$$H \sim k_B T_c \frac{m^3}{3} \tag{8.30}$$

The mean field value is $\delta = 3$.

α exponent

Consider the α exponent, for $H = 0$, $c_H \sim t^{-\alpha}$ and we have $t = (T - T_c)/T_c$. Compute the specific heat at $H = 0$. Consider first $T > T_c$, where $m_0 = 0$

$$f(m, H) = \frac{\hat{J}zm^2}{2} - \frac{1}{\beta} \ln \left(2 \cosh \left(\beta(\hat{J}zm + H) \right) \right) \tag{8.31}$$

If $m = 0$, $\cosh 0 = 1$ and

$$f = -k_B T \ln 2 \tag{8.32}$$

therefore

$$c_H = -T \left(\frac{\partial^2 f}{\partial T^2} \right) = 0 \tag{8.33}$$

The mean field value is $\alpha = 0$.

Remark. For $T < T_c$, $m = m_0 \neq 0$. This implies that $c_H \neq 0$, but still $f = -k_B T \ln A$ with $A = const$. We obtain $\alpha = 0$ also in this case.

$$m_0 = \pm \sqrt{-\frac{Jz}{2T_c}(T - T_c)} \tag{8.34}$$

γ exponent

Now we consider the γ exponent, for $H = 0$, $\chi \sim t^{-\gamma}$. Starting again from equation (8.26):

$$m = \tanh \left(\beta(\hat{J}zm + H) \right) \tag{8.35}$$

and developing it around $m \simeq 0$, as shown before we get

$$H = mk_B(T - T_c) + \frac{k_B T}{3} m^3 \tag{8.36}$$

$$\Rightarrow \chi_T = \frac{\partial m}{\partial H} = \frac{1}{\frac{\partial H}{\partial m}} \tag{8.37}$$

Since $\frac{\partial H}{\partial m} \simeq k_B(T - T_c) + K_B T m^2$, as $m \to 0$

$$\chi \sim (T - T_c)^{-1} \tag{8.38}$$

The mean field value is $\gamma = 1$.

Summary

The mean field critical exponents are

$$\beta = \frac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \alpha = 0 \tag{8.39}$$

Remark. In the mean field critical exponents the dimension D does not appear. T_c instead depends on the number of z of neirest neighbours and hence on the embedding lattice!

8.2   Mean field variational method

8.3   lesson

The ν exponent define the divergence of the correlation lengths. In order to do that in principle we should compute the correlation function, but which are the correlation we are talking about? The correlation or the fluctuation with to respect the average? In the ferromagnetic we have infinite correlation lengths, but it is not true because instead of that we consider the variation correlated! Which is the problem here? In meanfield we were neglecting correlation between fluctuation. We thought: let us compute negleting correlation. How we can computer the correlation function within the meanfield theory with thermal fluctuations? We look at the response of the system. Esperimentally what we can do? It is a magnetic field, but we cannot use homogeneous magnetic field. Another way to compute the correlation function without looking at thermal fluctuation it is by considering a non homogeneous magnetic field.

If I make a variation in H_i in the system, what happend in the H_j? This is an important point!

8.4   Mean field: variational approach

In quantum mechanics you have an energy:

$$E_\alpha = \langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle \geq E_0 \tag{8.40}$$

where ψ_α it is a trial function. We find the closest function. First of all let us call Φ a raondm variable and a function of it $f(\Phi)$. We can look at the expect value with repsect to the distribution function:

$$\langle f(\Phi) \rangle_p = \text{Tr}(p(\Phi)f(\Phi)) \tag{8.41}$$

Suppose $f(\Phi) = \exp[-\lambda\Phi]$, we have

$$\left\langle e^{-\lambda\Phi} \right\rangle_p \geq e^{-\lambda\langle\Phi\rangle_p} \quad \forall p \tag{8.42}$$

$$e^\Phi \geq 1 + \Phi \tag{8.43}$$

we have

$$e^{-\lambda\Phi} = e^{-\lambda\langle\Phi\rangle}e^{-\lambda[\Phi-\langle\Phi\rangle]} \geq e^{-\lambda\langle\Phi\rangle}(1 - \lambda(\Phi - \langle\Phi\rangle)) \tag{8.44}$$

we have

$$\rightarrow \left\langle e^{-\lambda\Phi} \right\rangle \geq e^{-\lambda\langle\Phi\rangle} \tag{8.45}$$

If $\rho(\Phi)$ is the probability distribution:

$$\text{Tr}(\rho(\Phi)) = 1 \quad \rho(\Phi) \geq 0 \quad \forall\Phi \tag{8.46}$$

$$e^{-\beta F_N} = Z_N = \text{Tr}_{\{\Phi\}} e^{-\beta\mathcal{H}[\{\Phi\}]} = \text{Tr}_{\{\Phi\}} \rho e^{-\beta\mathcal{H}-\ln\rho} = \left\langle e^{-\beta\mathcal{H}-\ln\rho} \right\rangle_\rho \tag{8.47}$$

therefore

$$e^{-\beta F_N} \geq e^{-\beta\langle\mathcal{H}\rangle_\rho - \langle\ln\rho\rangle_\rho} \tag{8.48}$$

$$F \leq \langle\mathcal{H}\rangle_\rho + k_B T \langle\ln\rho\rangle_\rho \tag{8.49}$$

whenever I'm able to write the last equation by using a ρ, then I minimize. This is the variational approach of statistical mechanics. The question is: which is the ρ

that minimize? The constrain that the ρ has to satisfty is the (8.46). The minimum is:

$$\bar{\rho} = \rho_{eq} = \frac{1}{Z} e^{-\beta \mathcal{H}} \tag{8.50}$$

Up to now everithing is exact. Let us now try to compute the Z by starting to the inequality (8.49). In general the ρ is a function of all the degree of freedom:

$$\rho = \rho(\Phi_1, \ldots, \Phi_N) \tag{8.51}$$

that is a N body problem. This is equivalent exactly when you have:

$$\psi_\alpha(\vec{r}_1, \vec{P}_1, \ldots, \vec{r}_N, \vec{P}_N) \tag{8.52}$$

So:

$$\rho \stackrel{MF}{\simeq} \prod_{\alpha=1}^{N} \rho^{(\alpha)}(\Phi_\alpha) \equiv \prod_{\alpha=1}^{N} \rho_\alpha \tag{8.53}$$

we asusme that the degree of freedom are indipendent (very strong!). For our spin model what is the Φ_α? It is the S_i. Now we have to compute the two averages in the (8.49) given the field. Remember that $\text{Tr}(\rho_\alpha) = 1$:

$$\text{Tr}_{\{\Phi\}}(\rho \ln \rho) = \text{Tr}\left(\prod_\alpha \rho_\alpha \left(\sum_\alpha \ln \rho_\alpha\right)\right) \stackrel{\text{to do}}{=} \sum_\alpha \text{Tr}(\rho_\alpha \ln \rho_\alpha) \tag{8.54}$$

we end up that

$$F_{MF} = \langle \mathcal{H} \rangle_{\rho_{MF}} + k_B T \sum_\alpha \text{Tr}^{(\alpha)}(\rho_\alpha \ln \rho_\alpha) \tag{8.55}$$

now we have to reduce the problem from a single distribution function to ... How parametrize ρ_α? The first approach is

1. $\rho_\alpha = \rho^{(1)}(\Phi_\alpha) \to \langle \Phi_\alpha \rangle_{\rho_\alpha}$

    we have the normalization $\text{Tr}^{(\alpha)} \rho_\alpha = 1$ and the self consistence condition: $\text{Tr}^{(\alpha)}(\rho_\alpha \Phi_\alpha) = \langle \Phi_\alpha \rangle$

Let us do it for the Ising model (Bragg-Williams): $\Phi_\alpha \to S_i = \pm 1$ and $\langle \Phi_\alpha \rangle \equiv m_i$:

$$\rho^{(1)} \equiv \rho^{(1)}(S_i) \to \begin{cases} \text{Tr}\, \rho_i^{(1)} = 1 \\ \text{Tr}\, \rho_i^1 S_i = m_i \end{cases} \tag{8.56}$$

The simplest function form with two parameters is the linear function, so

$$\rho^{(1)}(S_i) = a(1 - \delta_{S_i,1}) + b\delta_{S_i,1} \tag{8.57}$$

this is the simplest way we think to write something. This is the starting point. Given that since we have to satisfy we get an expression.

Conclusions

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