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LECTURE NOTES  
OF  
STATISTICAL MECHANICS

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COLLECTION OF THE LECTURES NOTES OF PROFESSOR ORLANDINI.

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# Contents

<b>Introduction</b>	<b>v</b>
<b>1 Recall of Thermodynamics</b>	<b>1</b>
1.1 A short recap of thermodynamics definitions . . . . .	1
1.2 Equilibrium states . . . . .	1
1.3 Equations of states . . . . .	3
1.4 Legendre transform and thermodynamic potentials . . . . .	4
1.5 Heltalpy . . . . .	6
1.6 Gibbs potential . . . . .	6
1.7 Grancanonical potential . . . . .	7
1.8 Response functions . . . . .	8
1.9 Response functions and thermodynamic stability . . . . .	10
<b>2 Equilibrium phases and thermodynamics of phase transitions</b>	<b>11</b>
2.1 Equilibrium phases as minima of Gibbs free energy . . . . .	11
2.2 First order phase transition and phase coexistence . . . . .	11
2.3 Second order phase transition . . . . .	13
2.4 Helmholtz free-energy . . . . .	14
2.5 Critical points . . . . .	14
2.6 Ferromagnetic system . . . . .	15
2.7 Lever Rule . . . . .	15
2.8 Thermodynamic of phase coexistence (one component system) . . . . .	16
2.9 Clausius-Clapeyron equation . . . . .	17
2.9.1 Application of C-C equation to the liquid-gas coexistence line . . . . .	18
2.10 Order parameter of a phase transition . . . . .	19
2.11 Divergence of the responde functions at the critical point . . . . .	20
2.12 Thermodynamic classification of the phase transitions . . . . .	20
2.12.1 Eherenfest classification . . . . .	21
2.12.2 Modern classification . . . . .	21
2.13 Critical exponents . . . . .	22
2.13.1 Law of the corresponding states . . . . .	22
2.13.2 Thermodynamic inequalities between critical exponents . . . . .	23
<b>3 Recall of statistical mechanics and theory of ensambles</b>	<b>25</b>
3.1 Statistical ensambles . . . . .	25
3.2 The canonical ensemble . . . . .	26
3.2.1 Energy fluctuations in the canonical ensemble . . . . .	28
3.3 Isothermal and isobaric ensemble . . . . .	29
3.3.1 Saddle point approximation . . . . .	30
3.4 Magnetic system . . . . .	31
3.5 Gran canonical ensemble . . . . .	31
<b>4 Statistical mechanics and phase transitions</b>	<b>33</b>

4.1	Statistical mechanics of phase transitions . . . . .	33
4.1.1	Magnetic system . . . . .	34
4.1.2	Fluid system (gran canonical) . . . . .	34
4.2	Thermodynamic limit with additional constraints . . . . .	35
4.2.1	Statistical mechanics and phase transitions . . . . .	35
4.3	Critical point and correlations of fluctuations . . . . .	36
4.4	Finite size effects and phase transitions . . . . .	38
4.5	Numerical simulations and phase transitions . . . . .	38
<b>5</b>	<b>Role of the models in statistical mechanics</b>	<b>41</b>
5.1	Role of the models . . . . .	41
5.2	Ising model (1925) . . . . .	41
5.2.1	D-dimensional Ising model . . . . .	41
5.2.2	Mathematical properties of the Ising model with neirest neigh- bours interactions . . . . .	43
5.2.3	Ising model and $\mathbb{Z}^2$ symmetry. . . . .	45
5.2.4	Lattice gas model . . . . .	46
5.3	Fluid system in a region $\Omega$ . . . . .	48
5.3.1	From the continuous to the lattice gas model . . . . .	49
5.4	Lesson ..... . . . .	51
5.5	Ising d=1 . . . . .	51
5.6	Transfer Matrix . . . . .	52
5.7	Correlation function . . . . .	54
	<b>Conclusions</b>	<b>57</b>
	<b>Bibliography</b>	<b>59</b>

# Introduction

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

- Brief recap of thermodynamics.
- Equilibrium phases and thermodynamics of the phase transitions.
- Statistical mechanics and theory of ensembles.
- Thermodynamic limit and phase transitions in statistical mechanics.
- Order parameter and critical point.
- The role of modelling in the physics of phase transitions.
- The Ising model.
- Exact solutions of the Ising model.
- Transfer matrix method.
- Role of dimension and range of interactions in critical phenomena (lower critical dimension).
- Approximations: *Meanfield theory Weiss* and *variational mean field*.
- Landau theory of phase transitions: the role of symmetries.
- Relevance of fluctuations: the *Ginzburg criterium* and the notion of the *upper critical dimension*.
- The Ginzburg-Landau model.
- Landau theory for non-homogeneous system. The  $\nu$  exponent.
- Gaussian fluctuations in the G-L theory.
- Widom's scaling theory.
- Kadanoff's theory of scaling.
- The theory of renormalisations group and the origin of *universality* in critical phenomena.
- Spontaneous symmetry breaking.

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 consider are

1. In equilibrium with an external bath at fixed temperature  $T$ .
2. Made by a (large) number  $N$  of degrees of freedom. 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 *axiomatic 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 characterize the system at equilibrium are the internal energy  $U$ , volume  $V$ , number of particles  $N$  and magnetization  $\vec{M}$  that "scale with the system". In general, the extensive variable are additive.

In thermodynamic, it is important the concept of walls and thermodynamic constraints 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 thermodynamics 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  $\vec{M}$ , etc .... If these variables are time independent, the system is in a *steady state*. If moreover there are no

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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  $\Delta t$  the system is at equilibrium. Therefore, consider a sequence of equilibrium states, the **quasi-static transformation** are described by the 1<sup>st</sup> *Law of thermodynamic*:

$$dU = \delta Q - \delta W \quad (1.1)$$

The variation of the internal energy of the systems depends by two factors,  $\delta w$  that is the work done by the system during a *quasi-static process* (infinitively slow), and  $\delta Q$  that is the heat absorbed by the system during the process. Remember that we write  $dU$  because it is a differential quantity, while the other quantities with the  $\delta$  are only small quantities. Therefore,  $dU$  is a function of state, the other are not. For example, for a simple fluid with a given pressure if we change the volume, the work done by the systems is  $\delta W = P dV$ . For a magnetized system, we can have  $\delta W = -\vec{H} \cdot d\vec{M}$ .

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 constraints.

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 *maximum 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

$$S = S(U, V, N) \quad (1.2)$$

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

The properties of  $S$  are:

- $S$  is an additive function with respect to the subsystems in which the system is partitioned:

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

- $S$  is differentiable and *monotonically increasing* with respect to the internal energy  $U$ . It means that  $\frac{\partial S}{\partial U}_{V,N} > 0$
- For each subsystem ( $\alpha$ ) we have:

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

This fundamental relation holds for each subsystem.

- $S$  is an *homogeneous function* of 1<sup>st</sup> order with respect to the extensive parameters, namely:

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

It means that  $S$  is an extensive quantity.

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

$$\left( \frac{\partial S}{\partial U} \right)_{V,N} > 0 \quad (1.6)$$



Therefore, we have  $(\frac{\partial S}{\partial U})_{V,N} \neq 0$  and it can be inverted locally. Afterwards,  $S = S(U, V, N)$  inverted in  $U$  gives the second fundamental relation

$$U = U(S, V, N) \quad (1.7)$$

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

By taking the differential of the fundamental relation

$$U = U(S, V, N_1, \dots, N_r) \quad (1.8)$$

one gets

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N_j}}_{\substack{T \\ \text{absolute} \\ \text{temperature}}} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N_j}}_{\substack{-P \\ \text{pressure}}} dV + \sum_{j=1}^r \underbrace{\left(\frac{\partial U}{\partial N_j}\right)}_{\substack{\mu_j \\ \text{electrochemical} \\ \text{potential}}} dN_j + \quad (1.9)$$

### 1.3 Equations of states

Now, we define another set of variables that are called *intensive variables*. The intensive variables are themselves functions of  $S, V, N$ . The **equations of state** are defined as:

$$T = T(S, V, N_1, \dots, N_r) \quad (1.10a)$$

$$P = P(S, V, N_1, \dots, N_r) \quad (1.10b)$$

$$\mu_j = \mu_j(S, V, N_1, \dots, N_r) \quad (1.10c)$$

*Observation 1.* If all the equations of state are known, the fundamental relation is determined a part from a constant. It means that the coefficients of the differential (1.9) are known.

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

$$PV = NK_b T$$

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

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - Nb) = NK_b T$$

Another equation of state for magnetic systems is the *Curie Law*:  $M = \frac{CH}{T}$ . We compute  $(\frac{\partial U}{\partial M})_{S,N} = H$ .

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

$$T(\lambda S, \lambda V, \lambda N) \stackrel{0}{=} \lambda T(S, V, N) \quad (1.11)$$

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

$$P(\lambda S, \lambda V, \lambda N) = \lambda P(S, V, N) \quad (1.12)$$

We keep  $S$  parameter separated from the other that are substituted by *generalised displacements* as  $V, N_1, \dots, N_r) \rightarrow X_j$ . The fundamental relation is

$$U = U(S, X_1, \dots, X_{r+1}) \quad (1.13)$$

We define:

$$\left(\frac{\partial U}{\partial S}\right) \equiv T \quad (1.14a)$$

$$\left(\frac{\partial U}{\partial X_j}\right) \equiv P_j \quad (1.14b)$$

The differential is written as the following:

$$dU = T dS + \sum_{j=1}^{r+1} P_j dX_j \quad (1.15)$$

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**:

$$S dT + \sum_{j=1}^{r+1} X_j dP_j = 0 \quad (1.16)$$

For a one-component simple fluid system, the equation (1.16) simplifies into

$$S dT - V dP + N d\mu = 0 \quad (1.17)$$

and dividing by the number of moles  $N$

$$d\mu = -s dT + v dP \quad (1.18)$$

that is the Gibbs-Duhem relation in *molar form*.

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

For a magnetic system we have  $dU = T dS + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} + \mu dN$ .

## 1.4 Legendre transform and thermodynamic potentials

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

In many situations it is convenient to change some extensive variables with their conjugate intensive ones that became independent and free to vary. We have new thermodynamic potentials. It works as following. Suppose we have the following function

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

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

$$X_k \rightarrow P_k \equiv \frac{\partial Y}{\partial X_k} \quad (1.19)$$

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

**Example 2.** Suppose we want to replace the entropy  $S$  with its conjugate derivative

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

One starts from the fundamental relation

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

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

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

By differentiating  $A$  we get

$$dA = dU - T dS - S dT$$

On the other hand

$$dU = T dS + \sum_j P_j dX_j$$

It implies that

$$dA = -S dT + \sum_j P_j dX_j$$

For such a system we have  $A = A(T, V, N_1, \dots, N_r)$ . Similarly for a magnetic system  $A = A(T, \vec{M}, N_1, \dots, N_r)$ .

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

$$A \equiv U - TS \quad (1.20)$$

In terms of heat and mechanical work, since

$$dU = \delta Q - \delta W \quad (1.21a)$$

$$dA = dU - d(TS) = \delta Q - T dS - S dT - \delta W \quad (1.21b)$$

Hence

$$\delta W = (\delta Q - T dS) - S dT - dA \quad (1.22)$$

On the other hand, for a *reversible transformation* we have:

$$\delta Q = T dS \quad (1.23a)$$

$$\delta W = -S dT - dA \quad (1.23b)$$

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

*Observation 2.* For an isothermal but *not reversible* (spontaneous) process we know the *II law of thermodynamics*

$$\delta Q \leq T dS$$

which implies

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

Hence, if  $\delta W = 0$  and  $dT = 0$ , we have  $dA \leq 0$ .

In a spontaneous (irreversible) process, the thermodynamic system, as a function of  $T, V, N$  etc, evolves towards a *minimum* of the Helmholtz free energy  $A = A(T, V, N_1, \dots, N_r)$ . In the case of a system with  $(P, V, T)$  we have:

$$dA = -S dT - P dV + \sum_j \mu_j dN_j \quad (1.24)$$

where

$$-S = \left( \frac{\partial A}{\partial T} \right)_{V, N_j} \quad (1.25a)$$

$$-P = \left( \frac{\partial A}{\partial V} \right)_{T, N_j} \quad (1.25b)$$

$$\mu_j = \left( \frac{\partial A}{\partial N_j} \right)_{T, V} \quad (1.25c)$$

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

$$dA = -S dT + \vec{H} \cdot d\vec{M} + \sum_j \mu_j dN_j \quad (1.26)$$

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

## 1.5 Hentalpy

The Hentalpy is the partial Legendre transform of  $U$  that replaces the volume  $V$  with the pressure  $P$  as independent variable. Therefore, consider  $U = U(S, V, N_1, \dots, N_r)$  and  $-P = \frac{\partial U}{\partial V}$ , we define the hentalpy as

$$H = U + PV \quad (1.27)$$

Note that the plus sign in the definition of the hentalpy is just because the minus of the  $P$ . Therefore:

$$\begin{aligned} dH &= dU + P dV + V dP \\ &= T dS - P dV + \sum_j \mu_j dN_j + P dV + V dP \\ &= T dS + V dP + \sum_j \mu_j dN_j \end{aligned} \quad (1.28)$$

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

## 1.6 Gibbs potential

The **Gibbs potential** is obtained by performing the Legendre transform of  $U$  to replace  $S$  and  $V$  with  $T$  and  $P$ . Therefore, we consider again  $U = U(S, V, N_1, \dots, N_r)$  and  $T = \frac{\partial U}{\partial S}$ ,  $-P = \frac{\partial U}{\partial V}$ , then we have:

$$G = U - TS + PV = A + PV \quad (1.29)$$

For a simple fluid system

$$\begin{aligned} dG &= dU - T dS - S dT + P dV + V dP \\ &= T dS - P dV + \sum_j \mu_j dN_j \\ &= -S dT + V dP + \sum_j \mu_j dN_j \end{aligned} \quad (1.30)$$

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

For a magnetic system, the Gibbs potential is defined as

$$G = A - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \quad (1.31)$$

and

$$\begin{aligned} dG &= dA - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} = d(U - TS) - d - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \\ &= dU - T dS - S dT - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot d\vec{\mathbf{H}} \\ &= T dS + \vec{\mathbf{H}} \cdot d\vec{\mathbf{H}} - T dS - S dT - d\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot d\vec{\mathbf{H}} \\ &= -S dT - \vec{\mathbf{H}} \cdot d\vec{\mathbf{H}} \end{aligned} \quad (1.32)$$

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

$$S = -\left(\frac{\partial G}{\partial T}\right)_{\vec{\mathbf{H}}} \quad (1.33a)$$

$$\vec{\mathbf{M}} = -\left(\frac{\partial G}{\partial \vec{\mathbf{H}}}\right)_T \quad (1.33b)$$

## 1.7 Grancanonical potential

The two intensive variables to become independent are  $T$  and  $\mu$ . The corresponding Legendre transform is

$$\Omega = U - TS - \sum_{i=1}^r \mu_i N_i = A - \sum_{i=1}^r \mu_i N_i \quad (1.34)$$

Differentiating this relation we obtain:

$$\begin{aligned} d\Omega &= dU - S dT - T dS - \sum_{ij} d\mu_j N_j - \sum_{i=1}^r \mu_i dN_i \\ &= (\delta Q - T dS) - \delta W - S dT - \sum_{j=1}^r d\mu_j N_j - \sum_{j=1}^r \mu_j dN_j \end{aligned} \quad (1.35)$$

Hence,  $\Omega = \Omega(T, P, \mu_j)$ . Internal energy  $U$  and entropy  $S$  are homogeneous function of the first order. A consequence of this fact is the relation called **Euler equation**:

$$U = TS - PV + \sum_j \mu_j N_j \quad (1.36)$$

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  $\frac{t(t+1)}{2}$  independent mixed derivatives.

**Example 3** (Internal energy).

$$dU = T dS - P dV + \mu dN \quad (1.37)$$

where  $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$  and  $-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$ . It implies that

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

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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 *Maxwell relations* obtained by the differential (1.37) with  $t = 2$ , for which we have  $t + 1 = 3$  and  $\frac{t(t+1)}{2} = 3$  ( $[S, V, N]$ ), are

$$(S, V) : \quad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad (1.38a)$$

$$(S, N) : \quad \left(\frac{\partial T}{\partial N}\right)_{V,S} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad (1.38b)$$

$$(V, N) : \quad -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \quad (1.38c)$$

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

$$dA = -S dT - P dV + \mu dN \quad (1.39)$$

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

$$(T, V) : \quad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \quad (1.40a)$$

$$(T, N) : \quad -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \quad (1.40b)$$

$$(V, N) : \quad -\left(\frac{\partial P}{\partial N}\right)_{V,T} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \quad (1.40c)$$

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

$$dG = -S dT - V dP + \mu dN \quad (1.41)$$

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

$$(T, P) : \quad -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad (1.42a)$$

$$(T, N) : \quad -\left(\frac{\partial S}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,N} \quad (1.42b)$$

$$(P, N) : \quad \left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \quad (1.42c)$$

## 1.8 Response functions

Aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variations of thermodynamic variables. In fact, 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.*

$$\alpha_P \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} \quad (1.43)$$

- *Molar heat capacity at constant pressure.*

$$c_P = \left( \frac{\delta Q}{dT} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P - S = \left( \frac{\partial G}{\partial T} \right)_P - T \left( \frac{\partial^2 G}{\partial T^2} \right)_P \quad (1.44)$$

- *Adiabatic compressibility.*

$$k_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S,N} = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial P^2} \right)_{S,N} - \frac{1}{V} \left( \frac{\partial^2 H}{\partial P^2} \right)_{S,N} \quad (1.45)$$

- *Isothermal compressibility .*

$$k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_{T,N} \quad (1.46)$$

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

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

$$c_V = \left( \frac{\delta Q}{dT} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = \left( \frac{\partial(-\partial A/\partial T)_{V,N}}{\partial T} \right)_{V,N} = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_{V,N} \quad (1.47)$$

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

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_T = -\left( \frac{\partial^2 G}{\partial H^2} \right)_T \quad (1.48)$$

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

$$\chi_{\alpha\beta} = \left( \frac{\partial M_\alpha}{\partial H_\beta} \right)_T, M_\alpha = -\left( \frac{\partial G}{\partial H_\alpha} \right)_T \Rightarrow \chi_{\alpha\beta} = \left( \frac{\partial^2 G}{\partial H_\beta \partial H_\alpha} \right)_T \quad (1.49)$$

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

**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

$$dG = -S dT + V dP$$

and the response function  $\alpha_P$  permit to write

$$\underbrace{\left( \frac{\partial S}{\partial P} \right)_{T,N}}_{\text{inaccessible to experiments}} = \underbrace{-V \alpha_P}_{\text{measurable}} \quad (1.50)$$

**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

$$dA = -S dT - P dV + \mu dN$$

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

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} \left(\frac{\partial V}{\partial P}\right)_{T,N} \left(\frac{\partial T}{\partial V}\right)_{P,N} = -1 \quad (1.51)$$

Hence

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_{V,N} &= \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_{T,N} \left(\frac{\partial T}{\partial V}\right)_{P,N}} = -\frac{\left(\frac{\partial V}{\partial T}\right)_{P,N}}{\left(\frac{\partial V}{\partial P}\right)_{T,N}} \\ &= \frac{-V\alpha_P}{-Vk_T} = \frac{\alpha_P}{k_T} \end{aligned} \quad (1.52)$$

## 1.9 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

$$\begin{cases} c_V \equiv \left(\frac{\delta Q}{dT}\right)_V \geq 0 \\ c_P \equiv \left(\frac{\delta Q}{dT}\right)_P \geq 0 \end{cases} \quad (1.53)$$

*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

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \geq 0 \quad (1.54)$$

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_M \geq 0 \quad (1.55)$$

*Remark.* In diamagnetic systems  $\chi_M$  can also be negative.

**Exercise 1.** By using Maxwell relations show that

$$c_P - c_V = \frac{TV\alpha^2}{k_T} = \frac{1}{Vk_T} T \left(\frac{\partial V}{\partial T}\right)_P^2 \quad (1.56a)$$

$$c_H - c_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T}\right)_H^2 \quad (1.56b)$$

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

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \quad (1.57)$$

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

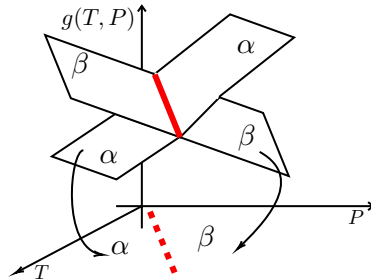
$$\frac{G}{N} \equiv g = g(T, P) \quad (2.1)$$

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  $\alpha$  the phase of a one-component system (say  $\alpha = \text{gas or liquid}$ ). Therefore, 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  $g_\alpha$  and  $g_\beta$ , 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:

$$g_\alpha(T, P) = g_\beta(T, P) \quad (2.2)$$

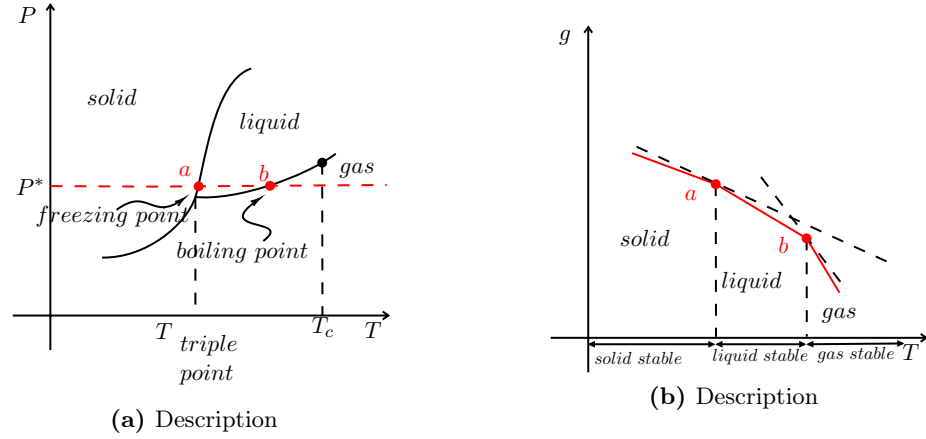


**Figure 2.1:** Description.

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).

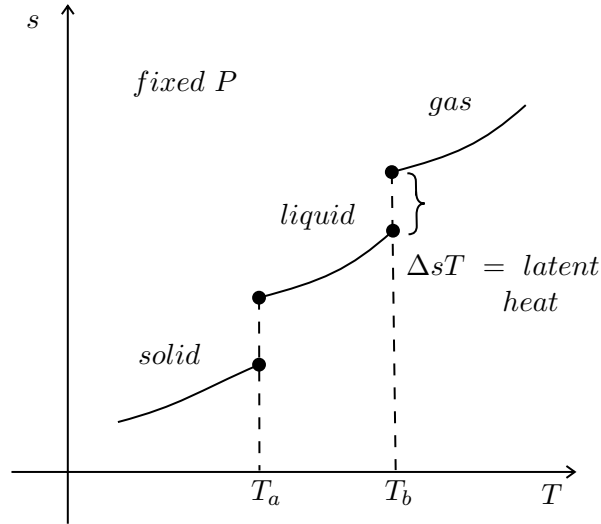
At the triple point  $g_{\text{solid}}(T_a, P^*) = g_{\text{liq}}(T_a)$  and  $g_{\text{liq}}(T_b) = g_{\text{gas}}(T_b, P^*)$  (see Figure 2.2b ). Note also that:

- 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  $P$ .



**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)  $v = \left(\frac{\partial g}{\partial P}\right)_T > 0$  :

$$\left(\frac{\partial^2 g}{\partial P^2}\right) = \left(\frac{\partial v}{\partial P}\right)_T = -vk_T < 0 \quad (2.3)$$

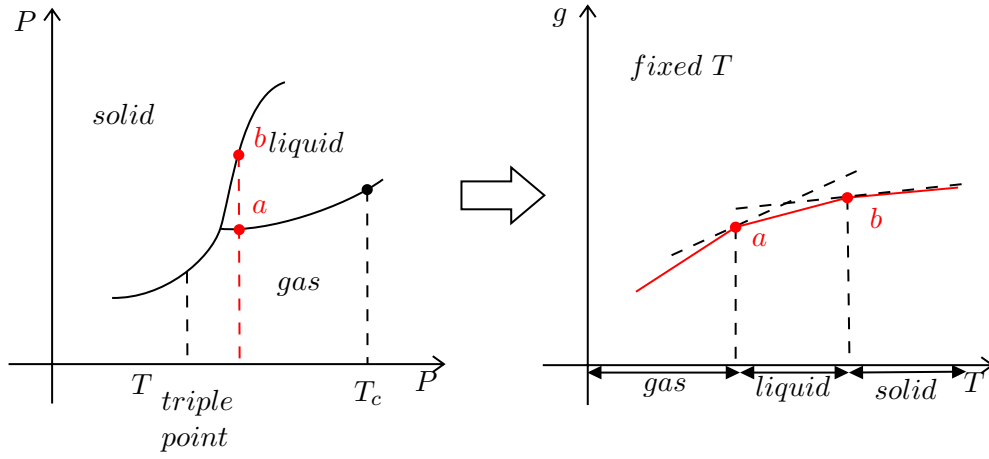


Figure 2.4: Description.

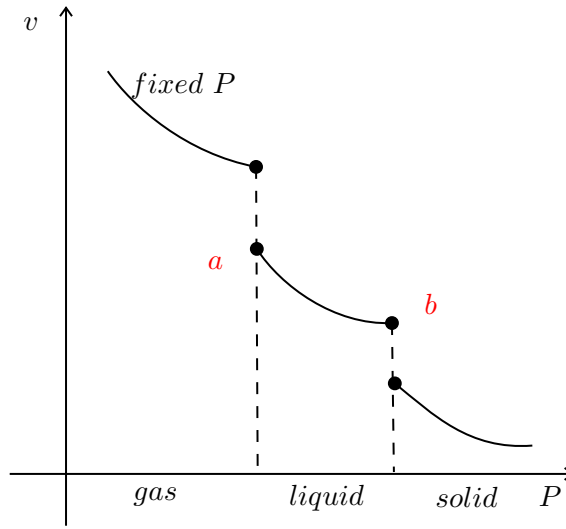


Figure 2.5: Description.

## 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:

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

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

This implies:

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

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 because 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

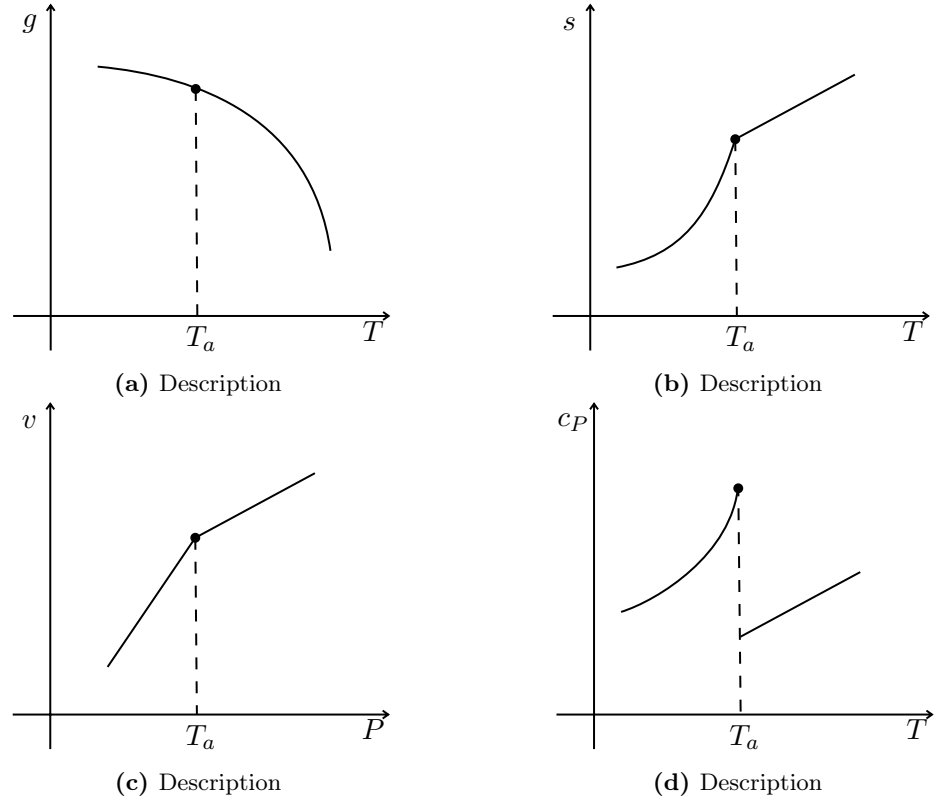


Figure 2.6: Description

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 pressure remains constant. At the coexistence line we see bubbles. It is the density that is changing locally, the bubbles become bigger and bigger and at the  $V_G$ , becomes 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

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

$A$  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

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

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

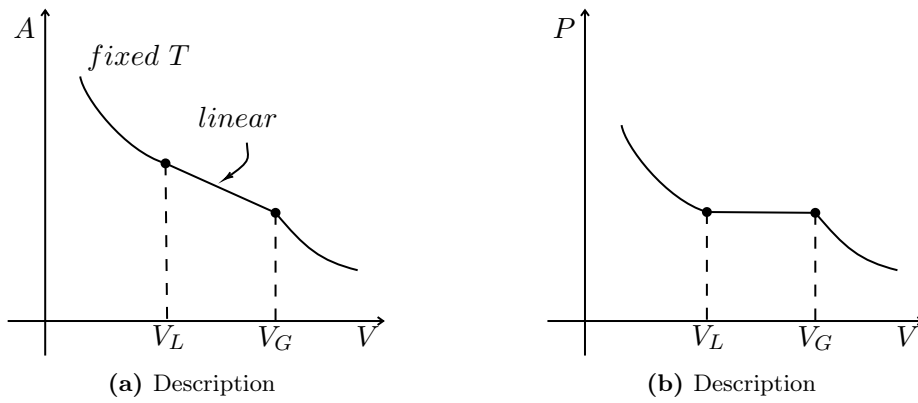


Figure 2.7: Description

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

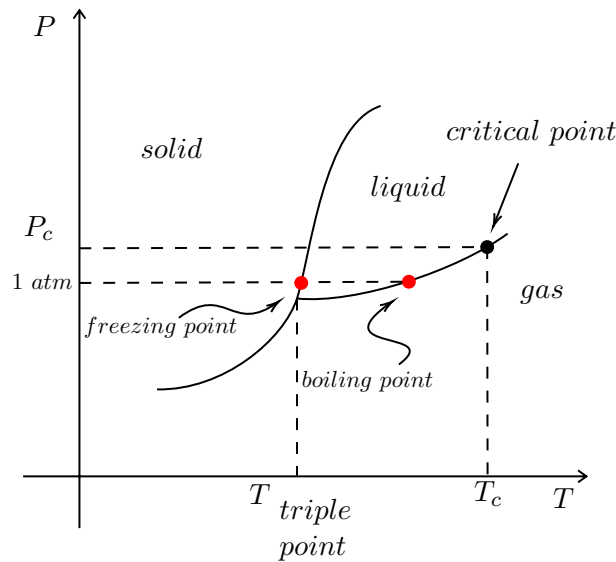


Figure 2.8: Description.

## 2.6 Ferromagnetic system

We can have a magnetization different from 0 even when there 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 continuously, 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 mixture 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:

$$v_D = \frac{N_A}{N} v_A + \frac{N_B}{N} v_B = x_A v_A + x_B v_B \quad (2.8)$$

**Lecture 3.**  
 Wednesday 16<sup>th</sup>  
 October, 2019.  
 Compiled:  
 Wednesday 6<sup>th</sup>  
 November, 2019.

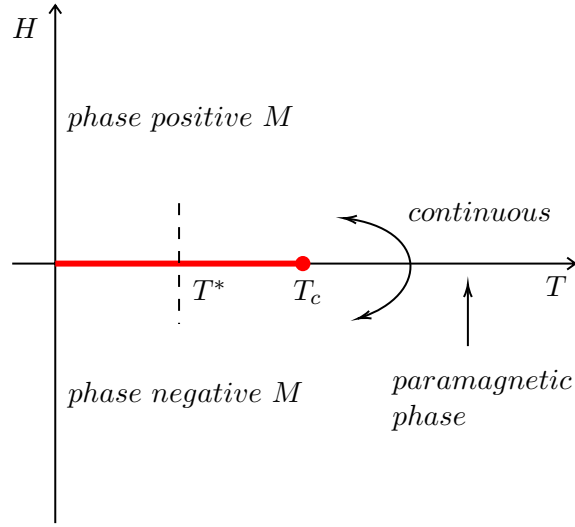


Figure 2.9: Description.

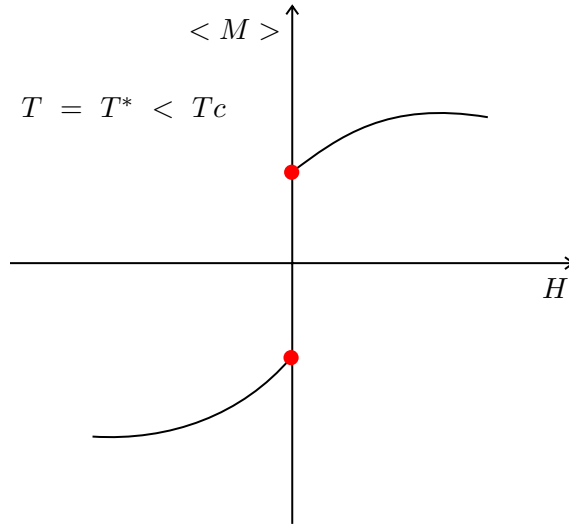


Figure 2.10: Description.

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**:

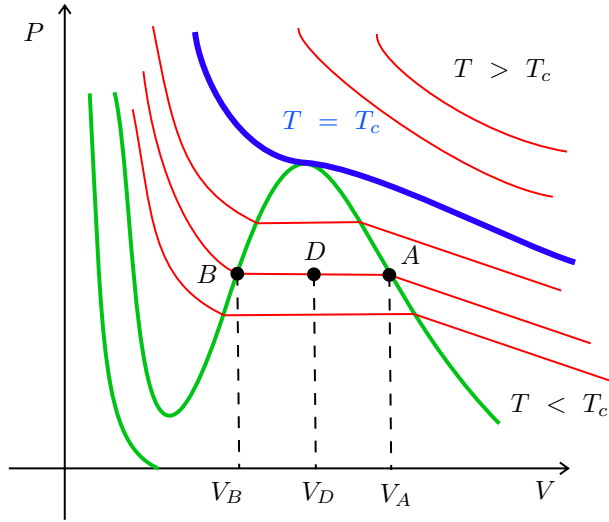
$$\frac{x_A}{x_B} = \frac{v_B - v_D}{v_D - v_A} \quad (2.9)$$

## 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  $\mu_1, \mu_2$ . The equilibrium condition is given by the maximum of the total entropy  $S = S_1 + S_2$  and gives the conditions

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 \quad (2.10)$$

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

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

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

Therefore, on the coexistence line it should hold the relation

$$g_1(T, P) = g_2(T, P) \quad (2.12)$$

## 2.9 Clausius-Clapeyron equation

Suppose to know the position on 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  $a$ . The idea is to compute the slope of the tangent of the coexistence curve, i.e.  $(dP/dT)$ . 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

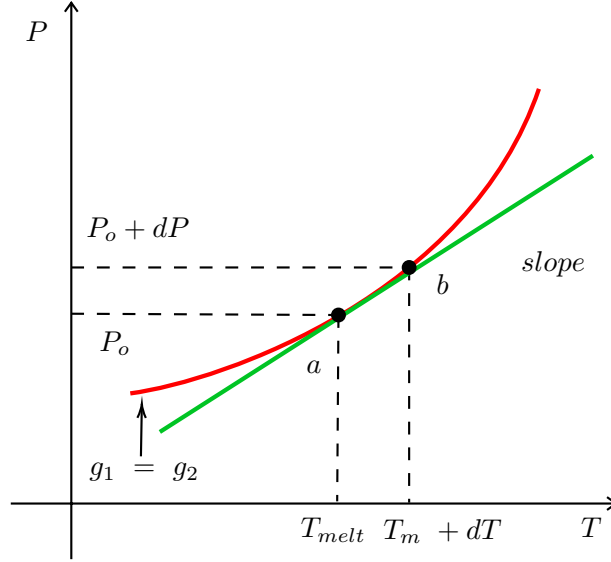
$$\begin{cases} g_1^{(a)} = g_2^{(a)} \\ g_1^{(b)} = g_2^{(b)} \end{cases} \quad (2.13)$$

Hence, if  $a$  and  $b$  are very close:

$$\begin{cases} dg_1 = g_1^{(b)} - g_1^{(a)} \\ dg_2 = g_2^{(b)} - g_2^{(a)} \end{cases} \quad (2.14)$$

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

$$\Rightarrow dg_1 = dg_2 \quad (2.15)$$



**Figure 2.12:** Description.

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

$$\begin{cases} dg_1 = -s_1 dT + v_1 dP = d\mu_1 \\ dg_2 = -s_2 dT + v_2 dP = d\mu_2 \end{cases} \quad (2.16)$$

taking the difference, one obtains

$$-(s_2 - s_1) dT + (v_2 - v_1) dP = 0 \quad (2.17)$$

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

$$\left( \frac{dP}{dT} \right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \frac{\Delta s}{\Delta v} \quad (2.18)$$

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

$$L_{12} = \Delta ST \quad (2.19)$$

### 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:

$$\left( \frac{dP}{dT} \right)_{coex} = \frac{s_2 - s_1}{v_2 - v_1} \quad (2.20)$$

Since for liquid-gas :

$$\left( \frac{dP}{dT} \right)_{coex} > 0 \Rightarrow \frac{s_2 - s_1}{v_2 - v_1} > 0 \quad (2.21)$$

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  $\Delta V$  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:

$$\left( \frac{dP}{dT} \right)_{coex} = \frac{\delta Q_{melt}}{T_{melt} \Delta v_{melt}} \quad \delta Q_{melt} = Q_{liq} - Q_{solid} > 0 \quad (2.22)$$



In general,  $\Delta v_m = v_{liq} - v_{solid} > 0$  which implies  $(dP/dT)_{coex} > 0$ . There are cases, however, where  $\Delta v_m = v_{liq} - v_{solid} < 0$  because  $\rho_{liq} > \rho_{solid}$  (for instance the  $H_2O$ , 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 coexistence ( $0 < T < 4$ ). This implies that  $dP/dT < 0$ .

**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:

$$\frac{dP}{dT} = \frac{\delta Q_m}{T\Delta v} = \frac{6.0110^3 J/mol}{273 \cdot (-1.7cm^3/mol)} = -1.29 \cdot 10^4 J/m^3 = -1.29bar/K \quad (2.23)$$

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

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

**Example 9** (Boiling point on Everest).

Consider  $P_{Everest} = 0.36atm$ ,  $\rho(T = 100^\circ C) = 0.598kg/m^3$  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:

$$\frac{dP}{dT} = \frac{L_{ge}}{T\Delta V} = \frac{L_{ge}\rho_g}{T} = \frac{2.25 \cdot 10^3 J/g \cdot 0.593kg/m^3}{373K} = \frac{3.6 \cdot 10^3 J}{K} \frac{kg}{g} \frac{1}{m^3} = 3.6 \cdot 10^3 Pa/K \quad (2.26)$$

$$\Rightarrow \Delta T \approx \Delta P/(3.6 \cdot 10^3 Pa/K) = 18^\circ C \rightarrow T_0 - T_{Everest} = 18^\circ C \Rightarrow T_{Everest} \approx 80^\circ C \quad (2.27)$$

## 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  $\vec{M} \rightarrow \vec{H}$  (magnetic field), while for *ferro electric* we have  $\vec{P} \rightarrow \vec{E}$  (electric field). For *liquid crystals*  $Q_{\alpha\beta} \rightarrow \vec{E}, \vec{H}$ , 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.

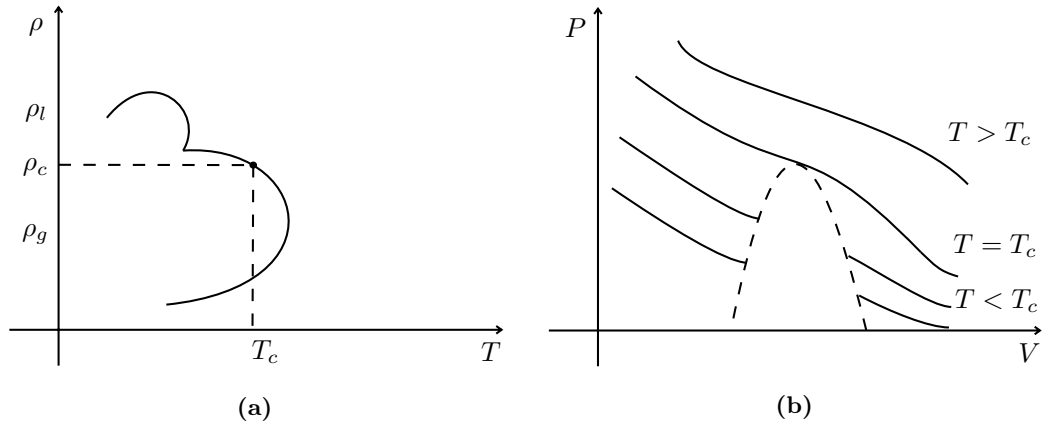


Figure 2.13: Description

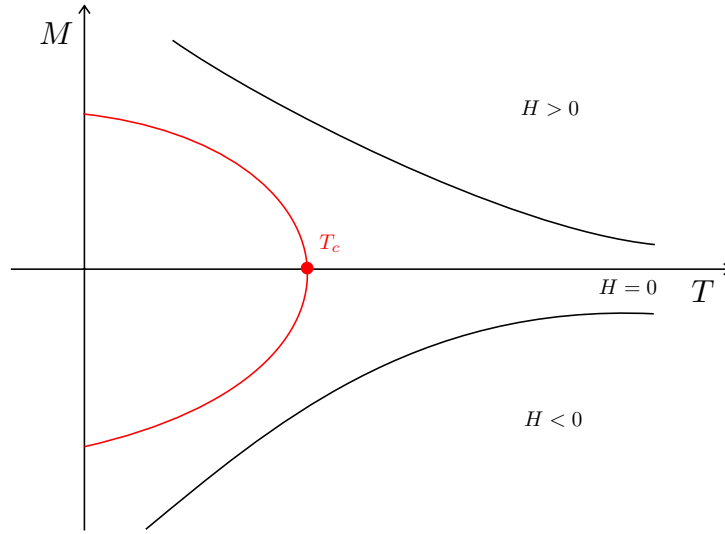


Figure 2.14: Description.

## 2.11 Divergence of the response functions at the critical point

While at the critical point the order parameter goes to zero continuously as  $T \rightarrow T_c^-$ , the response 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  $k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \rightarrow \infty$ . Similarly, in a magnetic system since the curve is like Figure 2.14, we have  $\chi_T = \left( \frac{\partial M}{\partial H} \right)_T \xrightarrow{T \rightarrow T_c} \infty$ .

## 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 Ehrenfest classification

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

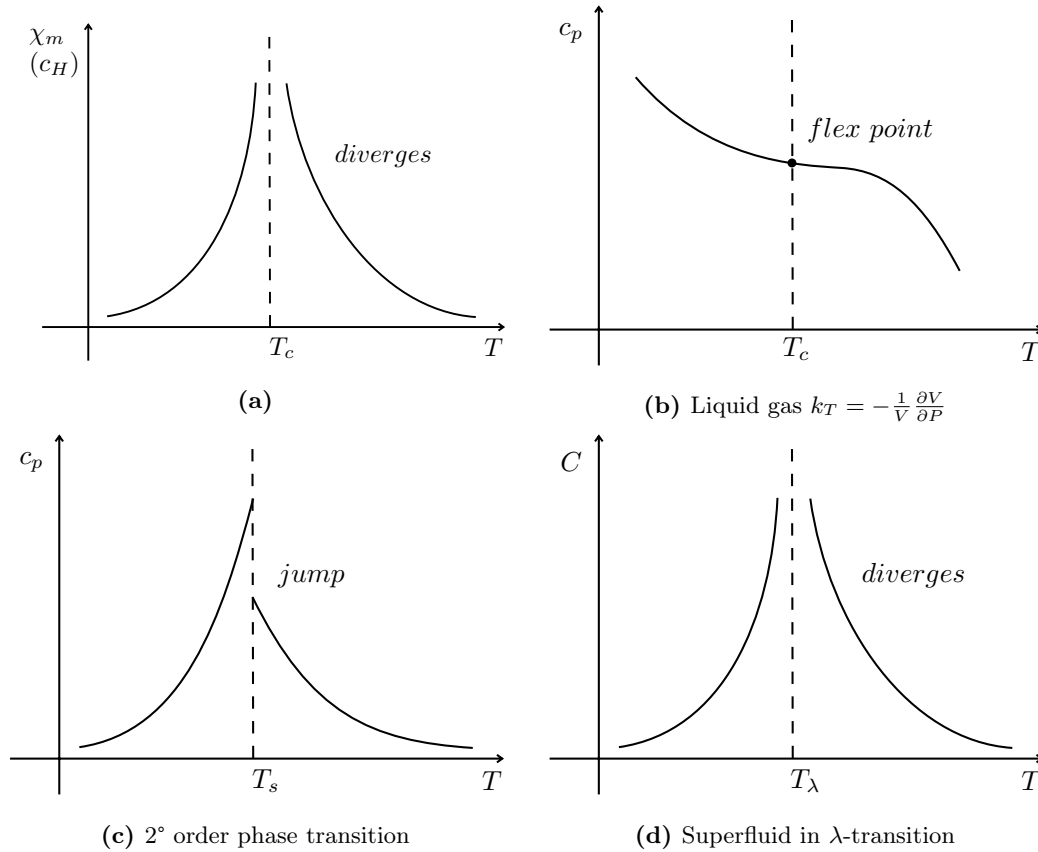
A phase transition is of order  $n$  if all the  $n-1$  derivatives are continuous and the  $n^{\text{th}}$  derivative displays a finite discontinuity.

**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  $\rho$  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  $\lambda$  transition) of the  $\text{He}_4$  (Figure 2.15d).



**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 singularities. 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 response 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*  $\lambda$  associated to the function  $F(t)$  is defined as:

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

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

$$F(t) \stackrel{t \rightarrow 0^{\pm}}{\sim} |t|^{\lambda_{\pm}} \quad (2.31)$$

More generally, for  $t \ll 1$ :

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

where all other terms are less important.

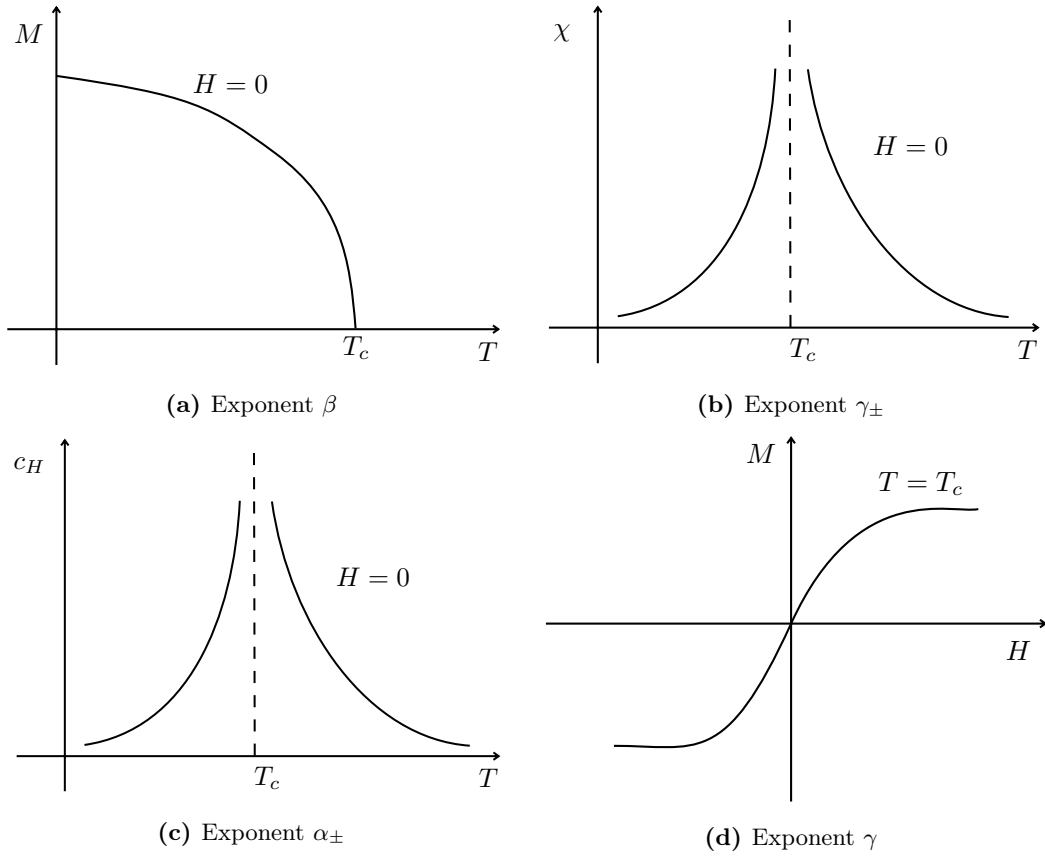
**Definition 2 (Thermodynamic critical exponents).**

- **Exponent  $\beta$**  : tells how the order parameter goes to zero. Consider Figure 2.16a, we have  $M \stackrel{t \rightarrow 0^-}{\sim} (-t)^{\beta}$ . 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  $\chi_T \stackrel{t \rightarrow 0^{\pm}}{\sim} |t|^{-\gamma_{\pm}}$ . In principle, the value of  $\gamma$  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  $\delta$** : 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  $T \rightarrow T_c$ . 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,  $\chi_e$ , Ne,  $N_2$ ,  $CO_2$  and  $O_2$ . By plotting  $T/T_c$  versus  $\rho/\rho_c$

**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  $t \rightarrow 0$ :

$$(\rho_l - \rho_c) \sim (-t)^{\beta} \quad (2.23)$$

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:

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

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

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

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

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

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

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

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

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

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

$$\alpha + 2\beta + \gamma \geq 2 \quad (2.39)$$

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

$$\Rightarrow \alpha + \beta(1 + \delta) \geq 2 \quad (2.40)$$

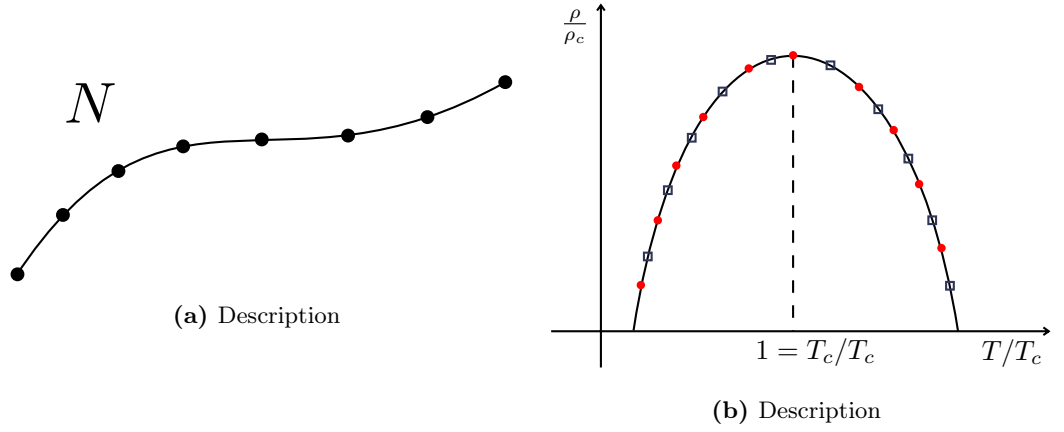


Figure 2.17

## Chapter 3

# Recall of statistical mechanics and theory of ensembles

### 3.1 Statistical ensembles

Statistical mechanics roughly speaking was born as a sort of theory from microscopic and try to compute the macroscopic length using thermodynamics. The problem is going from the continuous 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 equilibrium 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:

$$P_{\mathcal{C}} = \frac{1}{\Omega(E, V, N)} \quad (3.1)$$

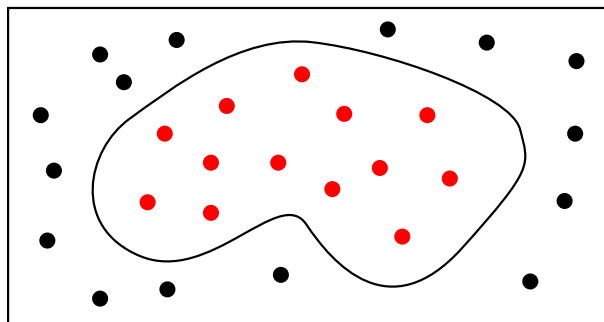


Figure 3.1: Description.

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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 show 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

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

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

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

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

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

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 ensembles). Note that  $V_S, N_S, V_B, N_B$  are fixed (no exchange of volume and particles). For reasuming, other quantities 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* (neglect interaction energy):

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

Let  $\mathcal{C}$  be 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:

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

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

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



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

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

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

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

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

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

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

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

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

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

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

$$\Delta \equiv x - x_0 = -E_{\mathcal{C}} \quad (3.13)$$

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

Therefore:

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

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

$$S_B \rightarrow N_B s_B \quad E_B \rightarrow N_B e_B \quad (3.16)$$

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

Let us consider the limit in which the system size is fixed while the one of the heat bath is going to  $\infty$ :

$$\lim_{N_B \rightarrow \infty} \frac{E_T}{N_B} = \frac{E + N_B e_B}{N_B} \rightarrow e_B \quad (3.18a)$$

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

On the other hand

$$\frac{ds_B}{de_B} \equiv \frac{1}{T_B} = \frac{1}{T} \quad (3.19)$$

which implies

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

Since the first term 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

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

*Observation 3.* 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:

$$\beta \equiv \frac{1}{k_B T} \quad (3.22)$$

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

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

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

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

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

$$A(T, V, N) = -k_B T \ln Q(T, V, N) \quad (3.25)$$

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

*Remark.*

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

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

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

### 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  $E$ .

$$\langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad (3.28)$$

On the other hand

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

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

$$\begin{aligned}
\langle (\delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle = Q^{-1} \left( \frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} - Q^{-2} \left( \frac{\partial Q}{\partial \beta} \right)_{N,V}^2 \\
&= \left( \frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{N,V} = - \left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_{N,V}
\end{aligned} \tag{3.31}$$

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 ensemble is *isothermal* and *isobaric*. All the assumptions 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  $N_B \rightarrow \infty$ .

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

Recalling that

$$\frac{dS}{dV} \Big|_E = \frac{P}{T} \quad \begin{cases} P_B \rightarrow P \\ T_B \rightarrow T \end{cases} \tag{3.38}$$

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

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*:

$$\begin{aligned}\Delta(T, P, N) &= \sum_V e^{-\beta PV} \left( \sum_{\substack{\mathbf{e} \\ V, N \text{ fixed}}} e^{-\beta E_{\mathbf{e}}} \right) \stackrel{\text{Laplace transform}}{=} \sum_V e^{-\beta PV} Q(T, V, N) \\ &= \underbrace{\sum_V \sum_E}_{\text{fluctuating variables}} e^{-\beta(E+PV)} \Omega(E, V, N)\end{aligned}\quad (3.41)$$

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

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

*Remark.*

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

### 3.3.1 Saddle point approximation

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

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

where

$$\left( \frac{dS(E^*, V^*, N)}{dE} \right)_{V, N} = \frac{1}{T} \quad \left( \frac{dS(E^*, V^*, N)}{dV} \right)_{E, N} = \frac{P}{T} \quad (3.45)$$

this implies

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

We define the *Gibbs free energy*:

$$G(T, P, N) = -k_B T \ln \Delta(T, P, N) \quad (3.47)$$

For classical systems (fluids)

$$\Delta(T, P, N) = \int_0^\infty dV e^{-\beta PV} \left[ \frac{1}{h^{3N} N!} \int d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta \mathcal{H}(p^N, r^N)} \right] \quad (3.48)$$

which implies

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

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

$$\beta P \equiv \frac{P}{T} = \frac{\partial S}{\partial V} \quad (3.50)$$

### 3.4 Magnetic system

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

$$P_{\mathcal{C}} \propto e^{S_B(E_T, M_T)/k_B - \frac{E_{\mathcal{C}}}{k_B} \frac{dS_B}{dE_B} - \frac{M_{\mathcal{C}}}{k_B} \frac{dS_B}{dM_B}} \quad (3.51)$$

Since  $\frac{dS_B}{dM_B} = -\frac{H_B}{T_B}$  and  $\frac{dS_B}{dE_B} = \frac{1}{T_B}$ :

$$\Rightarrow P_{\mathcal{C}} \propto \exp[-\beta(E_{\mathcal{C}} - H M_{\mathcal{C}})] \quad T_B \rightarrow T, H_B \rightarrow H \quad (3.52)$$

Normalization function:

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

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

### 3.5 Gran canonical ensemble

In this case  $N$  varies instead than  $V$ .

$$\begin{aligned} P_{\mathcal{C}} &= \exp\left[\frac{S_B(E_T - E_{\mathcal{C}}, N_T - N_{\mathcal{C}})}{k_B}\right] \\ &\sim \exp\left[\frac{S_B(E_T, N_T)}{k_B} - \frac{E_{\mathcal{C}}}{k_B} \frac{dS_B}{dE_B} - \frac{N_{\mathcal{C}}}{k_B} \frac{dS_B}{dN_B} + (\text{terms of order } \leq \frac{1}{V_B})\right] \\ &= \frac{\exp[-\beta E_{\mathcal{C}} + \beta \mu N_{\mathcal{C}}]}{\Theta(T, V, \mu)} \end{aligned} \quad (3.54)$$

where the *grancanonical partition function* is:

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

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 quantities.



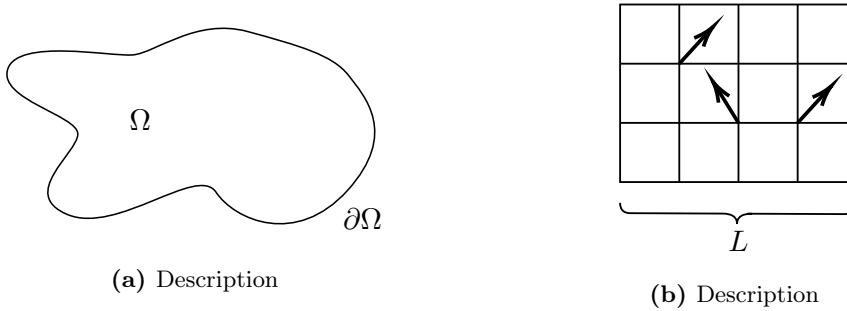
## Chapter 4

# 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.

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Wednesday 6<sup>th</sup>  
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**Figure 4.1:** Description

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

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

where  $d$  is the spatial dimension.

*Remark.* Space  $\Omega$  can be either *discrete* or *continuous*.

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

$$\mathcal{H}_\Omega = - \sum_n k_n \Theta_n \quad (4.2)$$

where

- $k_n$ : are the coupling constants. In general, but not always, they are *intensive thermodynamic variables*.
- $\Theta_n$ : is a linear of higher order combination of the dynamical microscopic degrees of freedom (local operators in quantum statistical mechanics).

- $k_n \Theta_n$ : 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:

$$\Theta_1 = \sum_i \vec{\mathbf{S}}_i \quad (4.3a)$$

$$\Theta_2 = \sum_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j \quad (4.3b)$$

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

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} \equiv \sum_{\vec{\mathbf{S}}_1} \sum_{\vec{\mathbf{S}}_2} \cdots \sum_{\vec{\mathbf{S}}_N} \quad (4.4)$$

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

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

#### 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

$$\{\mathcal{C}\} = \{(\vec{\mathbf{x}}_i, \vec{\mathbf{p}}_i)_{i=1, \dots, N}\} \quad (4.6)$$

and

$$\Theta_1 = \sum_i \left[ \frac{\vec{\mathbf{p}}_i^2}{2m_i} + U_1(\vec{\mathbf{x}}_i) \right] \quad (4.7a)$$

$$\Theta_2 = \frac{1}{2} \sum_{i>j} U(|\vec{\mathbf{x}}_i - \vec{\mathbf{x}}_j|) \quad (4.7b)$$

The trace operation is

$$\text{Tr} \equiv \sum_{\{\mathcal{C}\}} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{(\mathrm{d}\vec{\mathbf{p}}_i)(\mathrm{d}\vec{\mathbf{x}}_i)}{h^{dN}} \quad (4.8)$$

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

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

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

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

$$F_\Omega \propto V(\Omega \sim L^d) \quad (4.11)$$



In general, one can write

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

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

**Definition 3.** We define

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

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

For a system defined on a lattice we have

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

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

To get information on surface property of the system

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

## 4.2 Thermodynamic limit with additional constraints

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

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

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

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

These are analytic functions everywhere (it converges), therefore  $Z_\Omega$  is analytic for  $\Omega$  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 singularities we have to reach so precision in thermodynamic that we are not able to go exactly 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 of the onset of microscopic fluctuations 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

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

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

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

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

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

The thermodynamic response function  $\chi_T$  in statistical mechanics is related to the variance of the magnetization. We can relate the above expression 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

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

Hence

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

Let us assume the *translational symmetry*:

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

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

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

Given the translational invariance one can centre the system such that its centre of mass coincides with the origin

$$\vec{r}_{CM} \Rightarrow \vec{r}_0 \equiv \vec{0} \quad (4.27)$$

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

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

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

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

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

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

Meaning that for  $|\vec{r}| > \xi$  the fluctuations are uncorrelated. We define the  $\xi$  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  $\xi$  will diverge, there is not anymore the exponential and the integrall cannote be kepted finite.

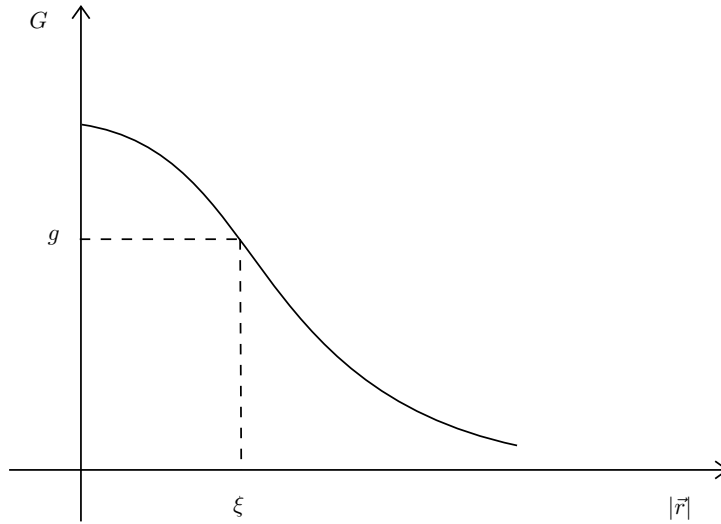
Let  $g$  be the value of  $G_c$  for  $|\vec{r}| < \xi$ :

$$k_B T \chi_T \leq V g \xi^3 \quad (4.31)$$

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

$$\frac{k_B T \chi_T}{V} < g \xi^3 \quad (4.32)$$

Hence if  $\chi_T$  diverges at the critical point it implies  $\xi \rightarrow \infty$ . In particular one can see



**Figure 4.2:** Description.

that for  $H = 0$  and  $T \rightarrow T_C^\pm$ :

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

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.  $t = 0$ )

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

where  $\mu$  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 instruments 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 correlation length  $\xi$  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  $\rho$  with respect to  $\rho_G$ ,  $\Delta\rho = \rho - \rho_G$ , due to the presence of denser droplets (liquid) in the continuum gas phase. These droplets will have different diameters, but the average size would be  $\xi$ , where it is the typical size of the liquid droplets. Clearly  $\xi = \xi[T]$  and, in proximity of the critical point  $\xi \stackrel{t \rightarrow 0}{\sim} |t|^{-\nu}$ .

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

As  $T \rightarrow T_c$ , where  $\xi$  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  $L \rightarrow \infty$ . 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  $\xi_0 = 10 \text{ \AA}$ , the lattice distance:

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

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

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

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  $\xi_0$  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 analytic solution and compute the energy. Try to extrapolate 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 behaviour, 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.

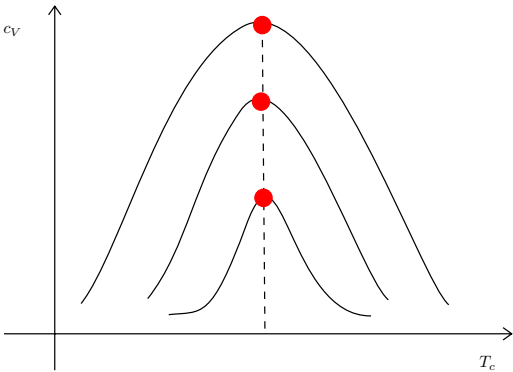


Figure 4.3: Description.



# 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 cannot describe the full physics of a specific system but they can reproduce its main features. Moreover these models can be studied numerically and, to some extent also 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 paramagnetic and a ferromagnetic phase. In  $d = 1$  the model was solved exactly by Ising. Unfortunately, he found that for  $T > 0$  the model does not display a phase transition. The wrong conclusion was that this model 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  $\{i\}_{i=1,\dots,N(\Omega)}$  and linear size  $L(\Omega)$ , we have  $N(\Omega) = L^D$ . The microscopic degrees of freedom are the spins  $S_i$  defined at

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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 anisotropic ferromagnet (along a given direction).

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

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

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

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

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

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 depends on the sign of  $J$ .

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

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

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

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

and the corresponding free-energy

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

The bulk limiting free energy is

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

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

$$\sum_{j \neq i} |J_{ij}| < \infty \quad (5.7)$$

*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

$$J_{ij} = A|\vec{r}_i - \vec{r}_j|^{-\sigma} \quad (5.8)$$

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

$$\sigma > D \quad (5.9)$$

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

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

### 5.2.2 Mathematical properties of the Ising model with nearest neighbours interactions

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

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ are nearest neighbours} \\ 0 & \text{otherwise} \end{cases} \quad (5.10)$$

The model is now very simple:

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

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

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

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

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

it is easy to show that:

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

where

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

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

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

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:

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

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

$$\frac{\partial^2 f_b}{\partial H^2} \leq 0 \quad (5.18)$$

This implies that

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

*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:

$$s \equiv -\frac{\partial f_b}{\partial T} \geq 0 \quad (5.20)$$

Let us consider a finite system

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

where we used the definition of the probability distribution

$$\rho_\Omega = \frac{e^{-\beta \mathcal{H}_\Omega}}{Z_\Omega} \quad (5.22)$$

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

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

□

All the other properties listed before (except (a)) are consequences 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 sequences  $\{g_k\}, \{h_k\}$ .

**Definition 4** (Hölder inequality). Given  $\{g_k\}, \{h_k\}$  with  $g_k, h_k \geq 0, \forall k$  and two non negative real numbers  $\alpha_1, \alpha_2$  such that  $\alpha_1 + \alpha_2 = 1$ , the following inequality holds

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

Consider now the partition function

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

it implies that

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

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

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

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

If we now apply the Hölder inequality we get

$$\begin{aligned} Z_\Omega(H_1 \alpha_1 + H_2 \alpha_2) &\leq \left( \text{Tr} \left( e^{\beta H_1 \sum_i S_i} G(S) \right)^{\alpha_1} \right) \left( \text{Tr} \left( e^{\beta H_2 \sum_i S_i} G(S) \right)^{\alpha_2} \right) \\ &= Z_\Omega(H_1)^{\alpha_1} Z_\Omega(H_2)^{\alpha_2} \end{aligned} \quad (5.29)$$

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

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

It implies

$$f_b(H_1 \alpha_1 + H_2 \alpha_2) \geq \alpha_1 f_b(H_1) + \alpha_2 f_b(H_2) \quad (5.31)$$

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

### 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  $\mathbb{Z}$  symmetry. Another interesting relation is the following:

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

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

this is true for all function of the spin.

We now consider the Hamiltonian of the Ising model:

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

Clearly

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

This is a spontaneous broken symmetry. Hence

$$\begin{aligned} Z_\Omega(-H, J, T) &= \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{S_i\})] \stackrel{(5.32)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(-H, J, \{-S_i\})] \\ &\stackrel{(5.34)}{=} \sum_{\{S_i=\pm 1\}} \exp[-\beta \mathcal{H}_\Omega(H, J, \{S_i\})] = Z_\Omega(H, J, T) \end{aligned} \quad (5.35)$$

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

$$F_\Omega(T, J, H) = F_\Omega(T, J, -H) \quad (5.36)$$

If we now take the thermodynamic limit we have

$$\Rightarrow f_b(T, J, H) = f_b(T, J, -H) \quad (5.37)$$

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

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

Therefore:

$$M(H) = -M(-H) \quad \forall H \quad (5.39)$$

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

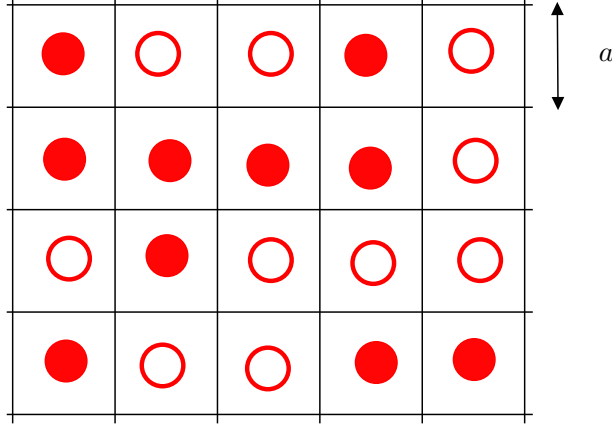
The magnetization of a finite system is, at  $H = 0$ , always zero. This is simply consequence of the symmetry argument shown above. It is only in the thermodynamic limit where the symmetry is spontaneously broken.

#### 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  $a \sim \text{\AA}$ ). The  $n_i$  is the occupation of the  $i$ -esim cell and it is

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

$$N_\Omega = \sum_{i=1}^{N_c} n_i \quad (5.41)$$



**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

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

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

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

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

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

The one body term:

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

while the two body term:

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

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

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

It implies

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

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

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

where

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

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

$$-J = \frac{U_2}{4} \quad (5.50c)$$

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

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

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 $\Omega$

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

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

In the gran-canonical ensemble

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

and the gran-canonical potential

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

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

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

$$\Rightarrow \sum_{N=0}^{\infty} \sim \sum_{N=0}^{N_{max}} \quad (5.55)$$

In the thermodynamic limit

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

with the constraint

$$\rho = \lim_{V \rightarrow \infty} \frac{\langle N \rangle}{V(\Omega)} = \text{const} \quad (5.57)$$

remember also that

$$d\omega_b(T, \mu) = -\sigma dT - p d\mu = -P \quad (5.58)$$

Now:

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

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

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

where

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

Therefore:

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

where

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

### 5.3.1 From the continuous to the lattice gas model

Let us divided  $\Omega$  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

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

where

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

$$\sum_i U_1(\vec{\mathbf{r}}_i) = \sum_i \int_{\Omega} d^D \vec{\mathbf{r}} U_1(\vec{\mathbf{r}}) \delta(\vec{\mathbf{r}}_i - \vec{\mathbf{r}}) = \int_{\Omega} d\vec{\mathbf{r}} U_1(\vec{\mathbf{r}}) \rho(\vec{\mathbf{r}}) \quad (5.66)$$

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

$$Q_N \propto \int \prod_{i=1}^N d^D \vec{\mathbf{r}}_i \rightarrow \sum_{\{n_{\alpha}\}} \quad (5.67)$$

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

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

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

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

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

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

$$\sum_{N=0}^{\infty} \sum'_{\{n_{\alpha}\}} f(n_{\alpha}) = \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=0}} f(n_{\alpha}) + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=1}} f(n_{\alpha}) \cdots + \sum'_{\substack{\{n_{\alpha}\} \\ \sum_{\alpha} n_{\alpha}=\infty}} f(n_{\alpha}) = \sum_{\{n_{\alpha}\}} f(n_{\alpha}) \quad (5.70)$$

with no restriction.

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

$$\mathcal{Z}_{\Omega}^{GC} \propto \sum_{\{n_{\alpha}\}} \exp \left[ -\beta \left( -\mu - \frac{D}{\beta} \log \frac{a}{\Lambda} \right) \sum_{\alpha=0}^{N_c} n_{\alpha} + \beta U_2 \sum_{\langle \alpha \beta \rangle} n_{\alpha} n_{\beta} + \dots \right] \quad (5.71)$$

$$\mathcal{Z}_{\Omega} = \text{Tr} e^{-\beta(\mathcal{H}_{\Omega} - \tilde{\mu}N)} = Z_{LG}(\tilde{\mu}) \quad (5.72)$$

where

$$\tilde{\mu} = \mu_{LG} = \mu_{phys} + Dk_B T \log \frac{a}{\Lambda} \quad (5.73)$$



## 5.4 Lesson .....

### 5.5 Ising d=1

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

$$Z_N(T) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp \left[ \overbrace{\beta J}^K \sum_{i=1}^{N-1} S_i S_{i+1} \right] \quad (5.74)$$

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

$$K \equiv \beta J, \quad h \equiv \beta H \quad (5.75)$$

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

$$Z_{N+1}(T) = \sum_{S_{N+1}=\pm 1} \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} e^{K(S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N)} e^{K S_N S_{N+1}} \quad (5.76)$$

This sum is just involve this term:

$$\sum_{S_{N+1}=\pm 1} e^{K S_N S_{N+1}} = e^{K S_N} + e^{-K S_N} = 2 \cosh(K S_N) = 2 \cosh(K) \quad (5.77)$$

$$Z_{N+1}(T) = (2 \cosh(K)) Z_N(T) \quad (5.78)$$

$$Z_N(T) = (2 \cosh(K)) Z_{N-1}(T) \quad (5.79)$$

In general, we get:

$$\Rightarrow Z_N(T) = Z_1 (2 \cosh(K))^{N-1} \quad \text{with} \quad Z_1 = \sum_{S_1=\pm 1} 1 = 2 \quad (5.80)$$

therefore

$$Z_N(T) = 2(2 \cosh(K))^{N-1} \quad (5.81)$$

$$F_N(T) = -k_B T \ln Z_N(T) = -k_B T \ln 2 - k_B T (N-1) \ln 2 \cosh(K) \quad (5.82)$$

$$f_b \equiv \lim_{N \rightarrow \infty} \frac{1}{N} F_N = -k_B T \ln 2 \cosh \left( \frac{J}{k_B T} \right) \quad (5.83)$$

The function goes as Figure 3.

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

$$\exp[k S_i S_{i+1}] = \cosh(K) + S_i S_{i+1} \sinh(K) = \cosh(K) [1 + S_i S_{i+1} \tanh(K)] \quad (5.84)$$

It means that

$$Z_N(T) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp \left[ K \sum_{i=1}^{N-1} S_i S_{i+1} \right] \Rightarrow \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \prod_{i=1}^{N-1} [\cosh(K) (1 + S_i S_{i+1} \tanh(K))] \quad (5.85)$$

$$= (\cosh K)^{N-1} \sum_{\{S\}} \prod_{i=1}^{N-1} (1 + S_i S_{i+1} \tanh K) \quad (5.86)$$

In principle there will be a generic term written as this

$$\sum_{\substack{S_{i_e} = \pm 1 \\ e=1, \dots, M}} (\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_{M+1}} = 0 \quad (5.87)$$

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

$$(5.86) = 2^N (\cosh K)^{N-1} \quad (5.88)$$

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

$$(\tanh K)^M S_{i_1} S_{i_1+1} S_{i_2} S_{i_2+1} \dots S_{i_M} S_{i_{M+1}} S_j \quad (5.89)$$

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

$$\langle S_j \rangle = 0 \quad (5.90)$$

**Lecture 7.**  
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## 5.6 Transfer Matrix

Today we introduce a general technique used in many fields as graph theory: the transfer matrix. If you are able to diagonalize the transfer matrix, you can use trick as eigenvalues and eigenvectors.

Consider the Ising model in a circle, as in Figure 1. We are introducing the bulk

$$S_{N+1} = S_1 \quad (5.91)$$

$$\beta \mathcal{H} = k \sum_{i=1}^N S_i S_{i+1} + h \sum_{i=1}^N S_i \quad \text{with} \quad k \equiv \beta J, h \equiv H\beta \quad (5.92)$$

$$Z_N(k, h) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \dots \sum_{S_N=\pm 1} \left[ e^{k S_1 S_2 + \frac{h}{2}(S_1 + S_2)} \right] \dots \left[ e^{k S_N S_1 + \frac{h}{2}(S_N + S_1)} \right] \quad (5.93)$$

Suppose you have a sort of  $\sum_j M_{ij} P_{jk}$ , what we have done is doing something like that. We can rewrite this formally:

$$\rightarrow Z_N = \sum_{S_1=\pm 1} \dots \sum_{S_N=\pm 1} \langle S_1 | \mathbb{T} | S_2 \rangle \langle S_2 | \mathbb{T} | S_3 \rangle \dots \langle S_N | \mathbb{T} | S_1 \rangle \quad (5.94)$$

where  $\mathbb{T}$  is a 2x2 matrix and

$$\langle S | \mathbb{T} | S' \rangle = \exp \left[ k S S' + \frac{h}{2} (S + S') \right] \quad (5.95)$$

For example:

$$\langle +1 | \mathbb{T} | +1 \rangle = \exp[k + h] \quad (5.96)$$

$$\langle +1 | \mathbb{T} | -1 \rangle = \exp[-k] \quad (5.97)$$

The matrix has the form:

$$\mathbb{T} = \begin{pmatrix} e^{k+h} & e^{-k} \\ e^{-k} & e^{k-h} \end{pmatrix} \quad (5.98)$$

$$|S_i^{(+)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (5.99)$$

$$|S_i^{(-)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (5.100)$$

Therefore the bra is:

$$\langle S_i^{(+)}| = (1^*, 0) \quad (5.101)$$

$$\langle S_i^{(-)}| = (0, 1^*) \quad (5.102)$$

Now:

$$\sum_{S_i=\pm 1} |S_i\rangle \langle S_i| = \mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (5.103)$$

Therefore:

$$\rightarrow Z_N = \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \langle S_1| \mathbb{T} |S_2\rangle \langle S_2| \mathbb{T} |S_3\rangle \cdots |S_i\rangle \langle S_i| \mathbb{T} |S_{i+1}\rangle \cdots \quad (5.104)$$

$$\rightarrow Z_N(k, h) = \sum_{S_1=\pm 1} \langle S_1| \mathbb{T}^N |S_1\rangle = \text{Tr}[\mathbb{T}^N] \quad (5.105)$$

this is exactly the trace of the matrix. We can find a unitary transformation:

$$\mathbb{T}_D = \mathbb{P} \mathbb{T} \mathbb{P}^{-1} \quad (5.106)$$

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

$$\rightarrow Z = \text{Tr}[\mathbb{P}^{-1} \mathbb{P} \mathbb{T} \mathbb{P}^{-1} \mathbb{P} \mathbb{T} \cdots \mathbb{P}^{-1} \mathbb{P} \mathbb{T} \mathbb{P}^{-1} \mathbb{P}] \quad (5.107)$$

$$\rightarrow = \text{Tr}[\mathbb{P}^{-1} \mathbb{T}_D^N \mathbb{P}] = \text{Tr}[\mathbb{P} \mathbb{P}^{-1} \mathbb{T}_D^N] = \text{Tr}[\mathbb{T}_D^N] \quad (5.108)$$

Now:

$$Z_N(k, h) = \text{Tr}[\mathbb{T}_D^N] = \lambda_+^N + \lambda_-^N, \quad \lambda_+ \geq \lambda_- \quad (5.109)$$

We have  $S_i = +1, 0, -1$ , therefore it can assume three different values. This is a *deluted* ising model.

Let us suppose there are  $(n+2)$  possible values:

$$\langle S_i^{(3)}| = (0, 0, 1^*, 0, \dots) \quad (5.110)$$

$$|S_i^{(3)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \quad (5.111)$$

$$\sum_{S_i} |S_i\rangle \langle S_i| = \mathbb{1}, \quad \mathbb{1} \in (n+2) \times (n+2) \quad (5.112)$$

$$\mathbb{S}_i = \sum_{S_i} |S_i\rangle S_i \langle S_i| \quad (5.113)$$

Now  $\{\lambda_+, \lambda_-, \lambda_1, \dots, \lambda_n\}$ , with  $\lambda_+ > \lambda_- \geq \lambda_1 \geq \dots \geq \lambda_n$ .

$$Z_N(\{k\}, h) = \lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \quad (5.114)$$

$$\mathbb{T} = \mathbb{P} \mathbb{T}_D \mathbb{P}^{-1} = \sum_i |t_i\rangle \lambda_i \langle t_i| \quad (5.115)$$

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

$$F_N() = -k_B T \log Z_N() \quad (5.116)$$

In general, looking at the thermodynamic limit:

$$f_b(\{k\}, h) = \lim_{N \rightarrow \infty} \frac{1}{N} F_N = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T) \log \left[ \lambda_+^N + \lambda_-^N + \sum_{i=1}^n \lambda_i^N \right] \quad (5.117)$$

$$\rightarrow = \lim_{N \rightarrow \infty} \frac{-k_B T}{N} \log \left[ \lambda_+^N \left( 1 + \frac{\lambda_-^N}{\lambda_+^N} + \sum_i \left( \frac{\lambda_i}{\lambda_+} \right)^N \right) \right] = -k_B T \log \lambda_+ \quad (5.118)$$

So we have obtained

$$f_b = -k_B T \log \lambda_+ \quad (5.119)$$

This is simply because  $\lambda_+$  is the largest.

**Theorem 5.6.1** (Perron-Frobenius). *Let  $A$  be a  $m \times m$  matrix. If  $A$  is finite ( $m < \infty$ ) and  $A_{ij} > 0, \forall i, j$ , ( $A_{ij} = A_{ij}(\vec{x})$ ) therefore  $\lambda_+$  has the following properties:*

1.  $\lambda_+ \in \mathbb{R}^+$
2.  $\lambda_+ \neq$  from  $\{\lambda_i\}_{i=1, \dots, m-1}$
3.  $\lambda_+$  is a analytic function of its arguments

Try to change  $A_{ij} > 0$  or the hypothesis that  $A$  is finite and see what is obtained.

## 5.7 Correlation function

Now we calculate the two points correlation function. We want the fluctuation respect to the average:

$$\Gamma_R = \langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle \quad (5.120)$$

we expect from physics that

$$\Gamma_R \underset{R \rightarrow \infty}{\sim} \exp[-R/\xi] \quad (5.121)$$

$$\xi^{-1} = \lim_{R \rightarrow \infty} \left[ -\frac{1}{R} \log [\langle S_1 S_R \rangle - \langle S_1 \rangle \langle S_R \rangle] \right] \quad (5.122)$$

$$\langle S_1 S_R \rangle_N = \frac{1}{Z_N} \sum_{\{S\}} S_1 S_R \exp[-\beta \mathcal{H}] \quad (5.123)$$

$$= \frac{1}{Z_N} \sum_{\{S\}} S_1 \langle S_1 | \mathbb{T} | S_2 \rangle \dots \langle S_{R-1} | \mathbb{T} | S_R \rangle S_R \langle S_R | \mathbb{T} | S_{R+1} \rangle \dots \langle S_N | \mathbb{T} | S_1 \rangle \quad (5.124)$$

$$= \frac{1}{Z_N} \sum_{S_1, S_R} S_1 \langle S_1 | \mathbb{T}^{R-1} | S_R \rangle S_R \langle S_R | \mathbb{T}^{N-R+1} | S_1 \rangle \quad (5.125)$$

$$\mathbb{T}^{R-1} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i^{R-1} \langle t_i| \quad (5.126)$$

$$\mathbb{T}^{N-R+1} = \sum_{i=1}^{n+2} |t_i\rangle \lambda_i^{N-R+1} \langle t_i| \quad (5.127)$$

$$\langle S_1 | \mathbb{T}^{R-1} | S_R \rangle = \sum_{i=1}^{n+2} \langle S_i | t_i \rangle \lambda^{R-1} \langle t_i | S_R \rangle \quad (5.128)$$

$$\sum_{\{S\}} S_1 S_R e^{-\beta \mathcal{H}} = \sum_{S_1 S_R} S_1 \sum_{i=1}^{n+2} \langle S_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | S_R \rangle S_R \sum_{j=1}^{n+2} \langle S_R | t_j \rangle \lambda_j^{N-R+1} \langle t_j | S_1 \rangle \quad (5.129)$$

Define:

$$\mathbb{S}_1 = \sum_{S_1} |S_1\rangle S_1 \langle S_1| \quad (5.130)$$

$$\mathbb{S}_R = \sum_{S_R} |S_R\rangle S_R \langle S_R| \quad (5.131)$$

$$\rightarrow = \sum_{ij} \langle t_j | \mathbb{S}_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | \mathbb{S}_R | t_j \rangle \lambda_j^{N-R+1} \quad (5.132)$$

Last time we computed the lamnbda function, the fluctuation of the transfer matrix:

$$\langle s_1 s_R \rangle_N = \frac{\sum_{ij} \langle t_j | S_1 | t_i \rangle \lambda_i^{R-1} \langle t_i | S_R | T_j \rangle \lambda_j^{N-R+1}}{\sum_{k=1}^n \lambda_k^N} \quad (5.133)$$

$$\mathbb{s}_i = \sum_{s_i} |s_i\rangle S_i \langle s_i| \quad (5.134)$$

$$\mathbb{T} | t_i \rangle = \lambda_i | t_i \rangle \quad (5.135)$$

For the Ising model:

$$\sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (5.136)$$

$$\langle s_1 s_R \rangle_N = \frac{\sum_{ij} \langle t_j | S_1 | t_i \rangle \lambda_i^{R-1} / \lambda_+ \langle t_i | S_R | T_j \rangle \lambda_j^{N-R+1} / \lambda_T^{N-R+1}}{\sum_{k=1}^n \lambda_k^N / \lambda_+^N} \quad (5.137)$$

You keep the sum and the one that survives are  $j = +, k = +$ :

$$\lim_{N \rightarrow \infty} \langle s_1 s_R \rangle_N = \sum_{i=\pm}^n \left( \frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | s_1 | t_i \rangle \langle t_i | s_R | t_+ \rangle \quad (5.138)$$

remember that  $\lambda_+ > \lambda_T \geq \lambda_1 \dots \lambda_n$

$$\Rightarrow \langle t_+ | \mathbb{s}_1 | t_+ \rangle \langle t_+ | s_R | t_+ \rangle + \sum_{i \neq +}^n \left( \frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | s_1 | t_i \rangle \langle t_i | s_R | t_+ \rangle \quad (5.139)$$

$$\Gamma_R = \langle s_1 s_R \rangle - \langle s_1 \rangle \langle s_R \rangle \quad (5.140)$$

$$\lim_{N \rightarrow \infty} \langle \mathbb{s}_i \rangle_N = \langle t_+ | \mathbb{s}_1 | t_+ \rangle \quad (5.141)$$

Because of (??):

$$\Gamma_R = \sum_{i \neq +}^n \left( \frac{\lambda_i}{\lambda_+} \right)^{R-1} \langle t_+ | s_1 | t_i \rangle \langle t_i | s_R | t_+ \rangle \quad (5.142)$$

$$\xi^{-1} = \lim_{N \rightarrow \infty} \left\{ -\frac{1}{R-1} \log |\langle s_1 s_R \rangle \langle s_1 \rangle \langle s_R \rangle| \right\} = -\log \left( \frac{\lambda_-}{\lambda_+} \right) - \lim_{R \rightarrow \infty} \frac{1}{R-1} \log \langle s_1 s_R \rangle - \langle s_1 \rangle \langle s_R \rangle \quad (5.143)$$

$$\xi^{-1} = -\log \left( \frac{\lambda_-}{\lambda_+} \right) \quad (5.144)$$

**Lecture 8.**

Wednesday 6<sup>th</sup>

November, 2019.

Compiled:

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Let us try to apply this general result to the classical Ising model.

$$\mathbb{T} = \begin{pmatrix} \exp(k+h) & \exp(-k) \\ \exp(-k) & \exp(k-h) \end{pmatrix} \quad (5.145)$$

Calculate the eigenvalues:

$$|\mathbb{T} - \lambda \mathbb{1}| = 0 = (e^{k+h} - \lambda)(e^{k-h} - \lambda) - e^{-2k} = 0 \quad (5.146)$$

Calculate the two eigenvalues:

$$\lambda_{\pm} = e^k \cosh(h) \pm \sqrt{e^{2k} \sinh^2(h) + e^{-2k}} \quad (5.147)$$

$$f_b = -k_B T \log \lambda_+ = -k k_B T - k_B T \log \left( \cosh(h) + \sqrt{\sinh^2(h) + e^{-4k}} \right) \quad (5.148)$$

remember  $k \equiv \beta J, h \equiv \beta H$ .

Suppose we are looking for the  $T \rightarrow 0$  limit, with  $H$  fixed and  $J$  fixed, in that case we have  $k \rightarrow \infty, h \rightarrow \infty$ .

$$e^{-4k} \xrightarrow{k \rightarrow \infty} 0 \quad (5.149)$$

$\sqrt{\sinh^2 h} \approx \sinh h$  and  $\cosh(h) + \sinh h \approx \frac{2e^h}{2} e^h$ :

$$f \xrightarrow[k \rightarrow \infty]{h \rightarrow \infty} -k k_B T - k_B T \log e^h \approx -J - H \quad \text{const} \quad (5.150)$$

So if  $T \rightarrow \infty, h \rightarrow 0, k \rightarrow 0$ :

$$f_B \approx -J - k_B T \ln 2 \quad (5.151)$$

The important is that it goes linearly as in Figure 1.

$$m = -\frac{\partial f_b}{\partial H} = -\frac{1}{k_B T} \frac{\partial f_b}{\partial h} = \frac{\sinh h + \frac{2 \sinh h \cosh h}{\sqrt{\sinh^2 h + e^{-4k}}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4k}}} \quad (5.152)$$

$$\chi = \frac{\partial m}{\partial H} = \frac{1}{k_B T} \frac{\partial m}{\partial h} \quad (5.153)$$

Just look for  $h = 0$  ( $\rightarrow \sinh h = 0$  and  $\cosh h = 1$ ):

$$\xi^{-1} = -\log \left[ \frac{1 - e^{-2k}}{1 + e^{-2k}} \right] = -\log \left[ \frac{1}{\coth k} \right] \quad (5.154)$$

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.

## 5.8 Classica Heisenberg model

The spin are vector or modulus one, so they are versor. Figure 2  $\vec{\mathbf{s}}_i \in \mathbb{R}^3$  with the constraint  $|\vec{\mathbf{s}}_i| = 1 \rightarrow \hat{\mathbf{s}}_i$ .

At  $H = 0$ :

$$-\beta \mathcal{H}(\{\vec{\mathbf{S}}_i\}) = k \sum_{i=1}^N \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1} (\longrightarrow \sum_i \vec{\mathbf{h}} \cdot \vec{\mathbf{S}}_i) \quad (5.155)$$

this is a  $O(3)$  symmetric. Compute:

$$Z_N(k) = \sum_{\{\vec{\mathbf{S}}\}} e^{-\beta \mathcal{H}} = \text{Tr}(\mathbb{T}^N) \quad (5.156)$$

$$\langle \vec{\mathbf{S}}_i | \mathbb{T} | \vec{\mathbf{S}}_{i+1} \rangle = e^{k \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_{i+1}} \quad (5.157)$$

$$\mathbb{T}_D = \mathbb{P}^{-1} \mathbb{T} \mathbb{P} \quad (5.158)$$

$$\mathbb{T} |t_i\rangle = \lambda_i |t_i\rangle \quad (5.159)$$

$$\mathbb{T} = \sum_i |t_i\rangle \lambda_i \langle t_i| \quad (5.160)$$

$$\exp[k \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2] = \langle \vec{\mathbf{S}}_1 | \mathbb{T} | \vec{\mathbf{S}}_2 \rangle = \sum_{i \in \text{eigenval}} \lambda_i \langle \vec{\mathbf{S}}_1 | t_i \rangle \langle t_i | \vec{\mathbf{S}}_2 \rangle = \sum_i \lambda_i f_i(\vec{\mathbf{S}}_1) f_i^*(\vec{\mathbf{S}}_2) \quad (5.161)$$

$$e^{k \vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2} \iff e^{i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \quad (5.162)$$

$$e^{i \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l (i)^l j_l(qr) Y_{lm}(\hat{\mathbf{q}}) Y_{lm}^*(\hat{\mathbf{r}}) \quad (5.163)$$

$$j_l(qr) = -\frac{(i)^l}{2} \int_0^\pi \sin(\theta) e^{iqr \cos(\theta)} P_l(\cos(\theta)) d\theta \quad (5.164)$$

where  $P_l(\cos(\theta))$  are the Legendre polynomial of order  $l$ .

$$qr = -ik |\vec{\mathbf{S}}_1| |\vec{\mathbf{S}}_2| = -ik \quad (5.165)$$

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

$$\lambda_i = \lambda_{lm}(k) = 4\pi (i)^l j_l(-ik) \quad (5.166)$$

note that there is not  $m$  dependence If  $l = 0$ :

$$\lambda_+ = \lambda_0(k) = 4\pi j_0(-ik) = 4\pi \frac{\sin k}{k} \quad (5.167)$$

$$\lambda_- = \lambda_1(k) = 4\pi i j_1(-ik) = 4\pi \left[ \frac{\cosh k}{k} - \frac{\sinh k}{k^2} \right] \quad (5.168)$$





# Conclusions



# Bibliography