UNIVERSITÀ DEGLI STUDI DI PADOVA

Dipartimento di Fisica e Astronomia "Galileo Galilei"

Corso di Laurea in Physics of Data

Transcription of the lessons

Models of theoretical physics

Professore

Prof. Amos Maritan

Student

Alice Pagano

Contents

Introduction

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

- Brief recap of thermodinamics.

- Equilibrium phases and thermodynamics of the phase transitions.

- Statistical mechanics and theory of ensambles.

- Thermodinamic 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 *Geinzburg criterium* and the notion of the *upper critical dimension.*

- The Ginzburg-Landau model.

- Landau theory for non-homogeneous system. The ν exponent.

- Gaussian fluctuations in the G-L theory.

- Widom's scaling theory.

- Kadauoff'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 dreedom. For instance, we remind that $1\,\text{mol} \approx N_A \sim 10^{23}$ elementary units.

Thermodynamic is a macroscopic theory of matter at equilibrium. It starts either from experimental observations or from *assiomatic assumptions* and establishes rigorous relations between macroscopic variables (**observables**) to describe systems at equilibrium.

One of the first important concept is the one of **extensive variables**. For instance, the extensive variables that caracterize the system at equilibrium are the internal energy U, volume V V, number of particles N and magnetization $\vec{\mathbf{M}}$ that "scale with the system". In general, the extensive variable are additive.

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

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

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

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

1.2 Equilibrium states

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

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

macroscopic currents, the system is at *equilibrium.* Therefore, we describe a system by characterizing all the extesnive variables at equilibrium.

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

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

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

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

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

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

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

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

- S is sidderentiable and *monotonically increasing* with respect to the internal energy U. It means that $\frac{\partial S}{\partial U}_{V,N} > 0$

- For each subsystem (α) we have:

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

  This fundamental relation holds for each subsystem.

- S is an *homogeneous function* of 1st order with respect to the extensive parameters, namely:
$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N), \quad \forall \lambda > 0 \tag{1.5}$$

  It means that S is an extensive quantity.

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

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

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

$$U = U(S, V, N) \tag{1.7}$$

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

By taking the differential of the fundamental relation

$$U = U(S, V, N_1, \ldots, N_r) \tag{1.8}$$

one gets

$$\mathrm{d}U = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N_j}}_{\substack{T \\ \text{absolute} \\ \text{temperature}}} \mathrm{d}S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N_j}}_{\substack{-P \\ \text{pressure}}} \mathrm{d}V + \sum_{j=1}^{r} \underbrace{\left(\frac{\partial U}{\partial N_j}\right)}_{\substack{\mu_j \\ \text{elettrochemical} \\ \text{potential}}} \mathrm{d}N_j + \tag{1.9}$$

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:

$$T = T(S, V, N_1, \ldots, N_r) \tag{1.10a}$$
$$P = P(S, V, N_1, \ldots, N_r) \tag{1.10b}$$
$$\mu_j = \mu_j(S, V, N_1, \ldots, N_r) \tag{1.10c}$$

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

$$PV = NK_bT$$

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

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

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

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

$$T(\lambda S, \lambda V, \lambda N) \overset{0}{=} \lambda T(S, V, N) \tag{1.11}$$

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

$$P(\lambda S, \lambda V, \lambda N) = \lambda P(S, V, N) \tag{1.12}$$

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

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

We define:

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

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

The differential is written as the following:

$$dU = T\,dS + \sum_{j=1}^{r+1} P_j\,dX_j \tag{1.15}$$

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**:

$$S\,dT + \sum_{j=1}^{r+1} X_j\,dP_j = 0 \tag{1.16}$$

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

$$S\,dT - V\,dP + N\,d\mu = 0 \tag{1.17}$$

and dividing by the number of moles N

$$d\mu = -s\,dT + v\,dP \tag{1.18}$$

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

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

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

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 $Y = Y(X_0, X_1, \ldots, P_k, \ldots, X_{r+1})$, where

$$X_k \to P_k \equiv \frac{\partial Y}{\partial X_k} \tag{1.19}$$

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

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

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

One starts form the fundamental relation

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

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

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

By differentiating A we get

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

On the other hand

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

It implies that

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

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

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

$$A \equiv U - TS \tag{1.20}$$

In terms of heat and mechanical work, since

$$\mathrm{d}U = \delta Q - \delta W \tag{1.21a}$$
$$\mathrm{d}A = \mathrm{d}U - \mathrm{d}(TS) = \delta Q - T\,\mathrm{d}S - S\,\mathrm{d}T - \delta W \tag{1.21b}$$

Hence

$$\delta W = (\delta Q - T\,\mathrm{d}S) - S\,\mathrm{d}T - \mathrm{d}A \tag{1.22}$$

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

$$\delta Q = T\,\mathrm{d}S \tag{1.23a}$$
$$\delta W = -S\,\mathrm{d}T - \mathrm{d}A \tag{1.23b}$$

If the reversible transformation is also *isothermal*, $\mathrm{d}T = 0$ and $\mathrm{d}A = \mathrm{d}W$. It is reminiscent of a potential energy.

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

$$\delta Q \leq T\,\mathrm{d}S$$

which implies

$$(\delta W)_{\mathrm{IRR}} = \delta Q - T\,\mathrm{d}S - \mathrm{d}A \leq -\mathrm{d}A\,.$$

Hence, if $\delta W = 0$ and $\mathrm{d}T = 0$, we have $\mathrm{d}A \leq 0$.

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

$$\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V + \sum_j \mu_j\,\mathrm{d}N_j \tag{1.24}$$

where

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

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

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

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

$$dA = -S\,dT + \vec{\mathbf{H}} \cdot d\vec{\mathbf{M}} + \sum_j \mu_j\,dN_j \tag{1.26}$$

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

1.5   Heltalpy

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

$$H = U + PV \tag{1.27}$$

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

$$\begin{aligned}
dH &= \boxed{dU} + P\,dV + dP\,V \\
&= \boxed{T\,dS - P\,dV + \sum_j \mu_j\,dN_j} + P\,dV + V\,dP \\
&= T\,dS + V\,dP + \sum_j \mu_j\,dN_j
\end{aligned} \tag{1.28}$$

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

1.6   Gibbs potential

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

$$G = U - TS + PV = A + PV \tag{1.29}$$

For a simple fluid system

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

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

For a magnetic system, the Gibbs potential is defined as

$$G = A - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \tag{1.31}$$

and

$$
\begin{aligned}
\mathrm{d}G &= \mathrm{d}A - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} = \mathrm{d}(U - TS) - \mathrm{d} - \vec{\mathbf{M}} \cdot \vec{\mathbf{H}} \\
&= \boxed{\mathrm{d}U} - T\,\mathrm{d}S - S\,\mathrm{d}T - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot \mathrm{d}\vec{\mathbf{H}} \\
&= \boxed{T\,\mathrm{d}S + \vec{\mathbf{H}} \cdot \mathrm{d}\vec{\mathbf{H}}} - T\,\mathrm{d}S - S\,\mathrm{d}T - \mathrm{d}\vec{\mathbf{M}} \cdot \vec{\mathbf{H}} - \vec{\mathbf{M}} \cdot \mathrm{d}\vec{\mathbf{H}} \\
&= -S\,\mathrm{d}T - \vec{\mathbf{H}} \cdot \mathrm{d}\vec{\mathbf{H}}
\end{aligned}
\tag{1.32}
$$

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

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

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

1.7 Grancanonical potential

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

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

Differentiating this relation we obtain:

$$
\begin{aligned}
\mathrm{d}\Omega &= \mathrm{d}U - S\,\mathrm{d}T - T\,\mathrm{d}S - \sum_{ij}\mathrm{d}\mu_j\,N_j - \sum_{i=1}^{r}\mu_i\,\mathrm{d}N_i \\
&= (\delta Q - T\,\mathrm{d}S) - \delta W - S\,\mathrm{d}T - \sum_{j=1}^{r}\mathrm{d}\mu_j\,N_j - \sum_{j=1}^{r}\mu_j\,\mathrm{d}N_j
\end{aligned}
\tag{1.35}
$$

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

$$U = TS - PV + \sum_j \mu_j N_j \tag{1.36}$$

Instead, the **Maxwell relations** are relations between the mixed derivatives of the thermodynamic potentials. They can be obtained from the expressions of $\mathrm{d}U$, $\mathrm{d}H$, $\mathrm{d}A$, $\mathrm{d}G$ and $\mathrm{d}\Omega$ and from the Schwarz theorem on mixed partial derivatives. Due to Schwarz theorem, if a thermodynamic potential depends on $t + 1$ variables there will be $\frac{t(t+1)}{2}$ indipendent mixed derivatives.

Example 3 (Internal energy)**.**

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N \tag{1.37}$$

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

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

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

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

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

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

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

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

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

$$dA = -S\,dT - P\,dV + \mu\,dN \tag{1.39}$$

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

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

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

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

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

$$dG = -S\,dT - V\,dP + \mu\,dN \tag{1.41}$$

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

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

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

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

1.8   Response functions

Aim of most experiments is to measure the response of a thermodynamic system write respect to controlled variatious 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.*

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

- *Molar heat capacity at constant pressure.*

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

- *Adiabatic compressibility.*

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

- *Isothermal compressibility .*

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

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.

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

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

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_{T \ M=-\frac{\partial G}{\partial H}\big|_T} = -\left(\frac{\partial^2 G}{\partial H^2}\right)_T \tag{1.48}$$

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

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

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

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 α_P permit to write

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

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

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

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

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

Hence

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

$$= \frac{-V\alpha_P}{-Vk_T} = \frac{\alpha_P}{k_T} \tag{1.52}$$

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

$$\begin{cases} c_V \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_V \geq 0 \\ c_P \equiv \left(\frac{\delta Q}{\mathrm{d}T}\right)_P \geq 0 \end{cases} \tag{1.53}$$

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

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

Similar considerations for a magnetic system, gives

$$c_H \geq 0, \quad c_M \geq 0, \quad \chi_M \geq 0 \tag{1.55}$$

Remark. In diamangetic systems χ_M can also be negative.

Exercise 1. By using Maxwell relations show that

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

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

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

$$\begin{cases} c_P \geq c_V \geq 0 \\ c_H \geq c_M \geq 0 \end{cases} \tag{1.57}$$

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

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

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

2.2 First order phase transition and phase coexistence

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

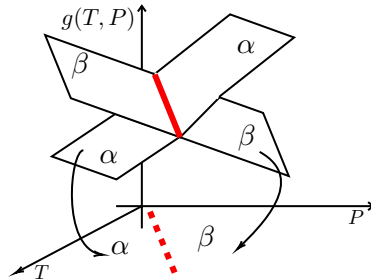$$g_\alpha(T, P) = g_\beta(T, P) \tag{2.2}$$

Figure 2.1: Description.

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

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

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

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

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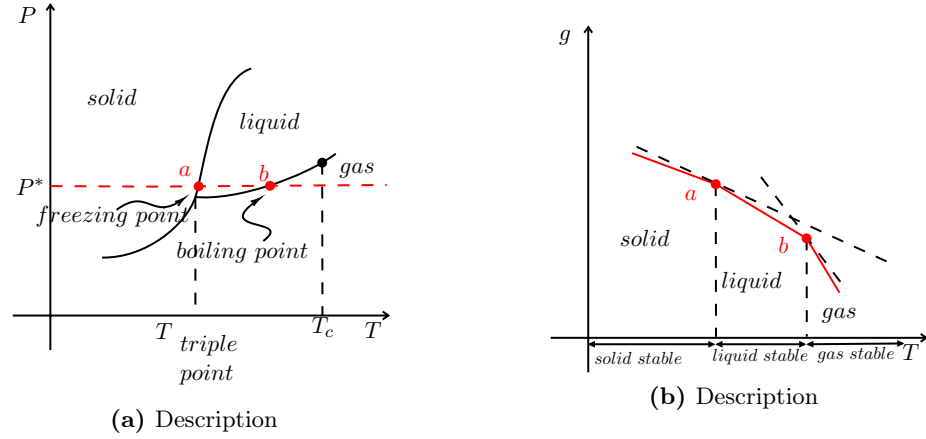

(a) Description

(b) Description

Figure 2.2: Description

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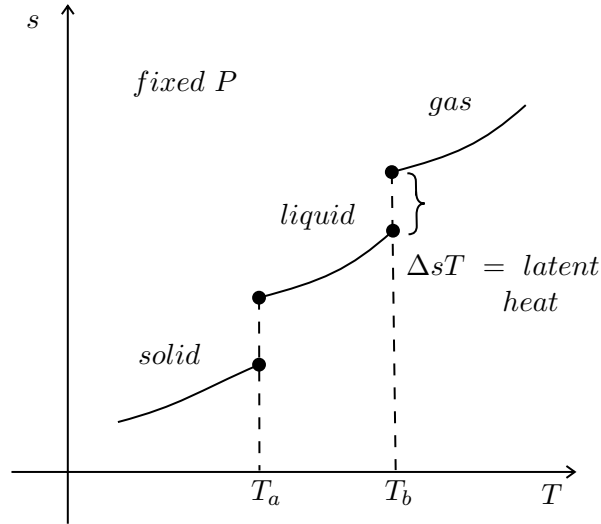

Figure 2.3: Description.

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

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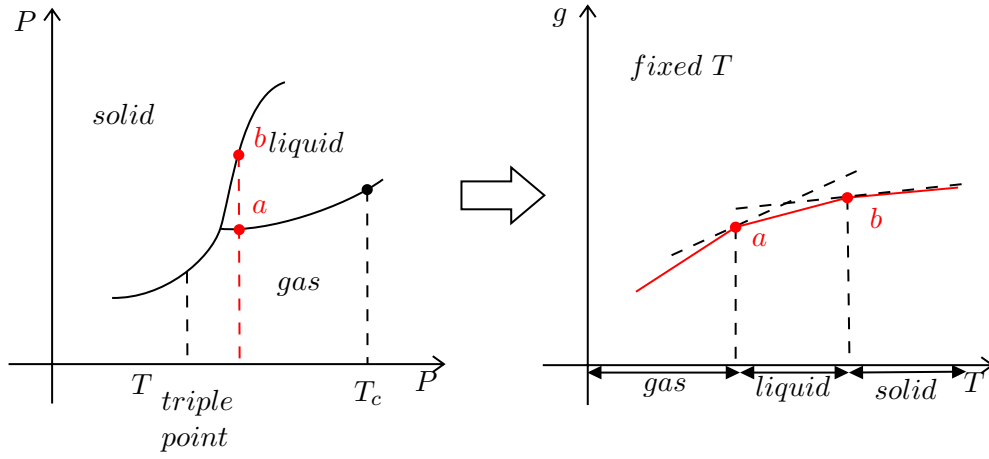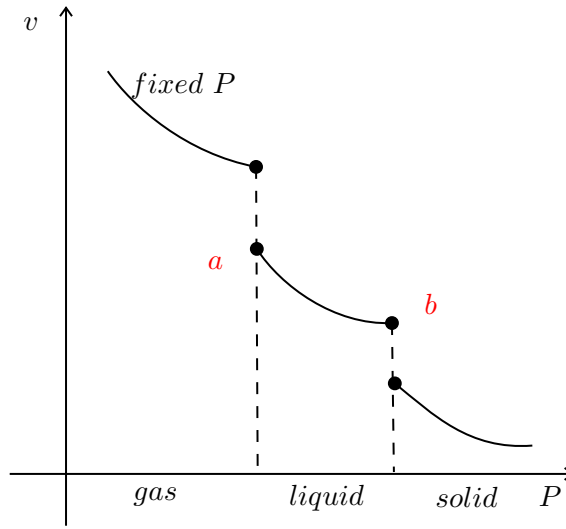
Figure 2.4: Description.

Figure 2.5: Description.

2.3 Second order phase transition

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

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

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

This implies:

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

An example is *superconductivity*.

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

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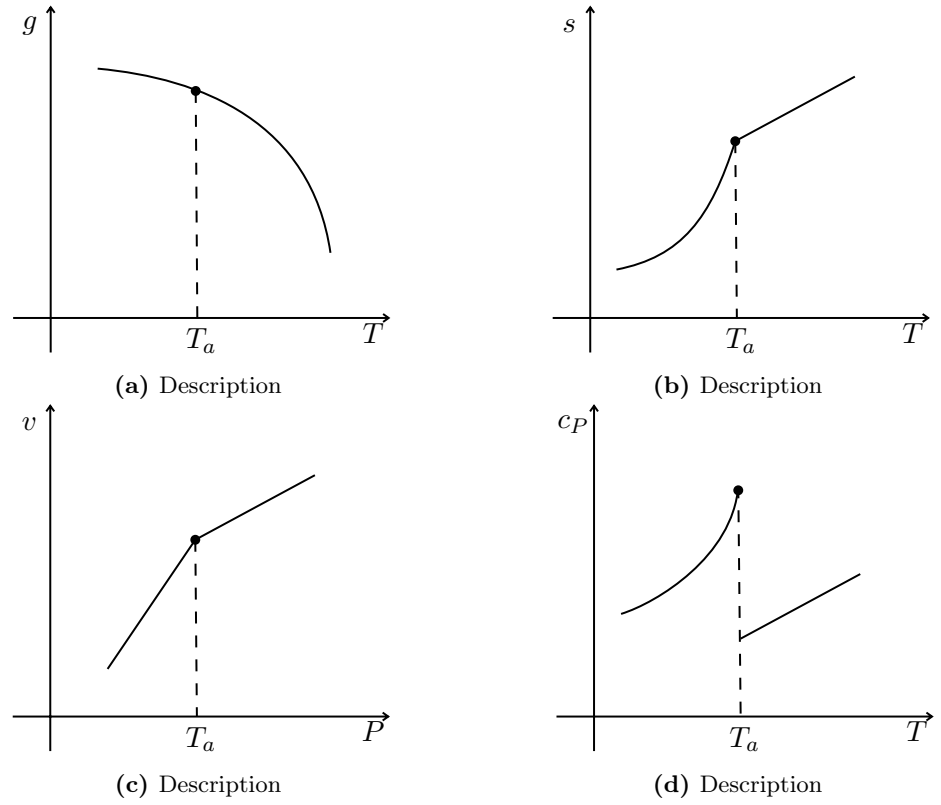
(a) Description

(b) Description

(c) Description

(d) Description

Figure 2.6: Description

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

2.4   Helmholtz free-energy

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

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

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

2.5   Critical points

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

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

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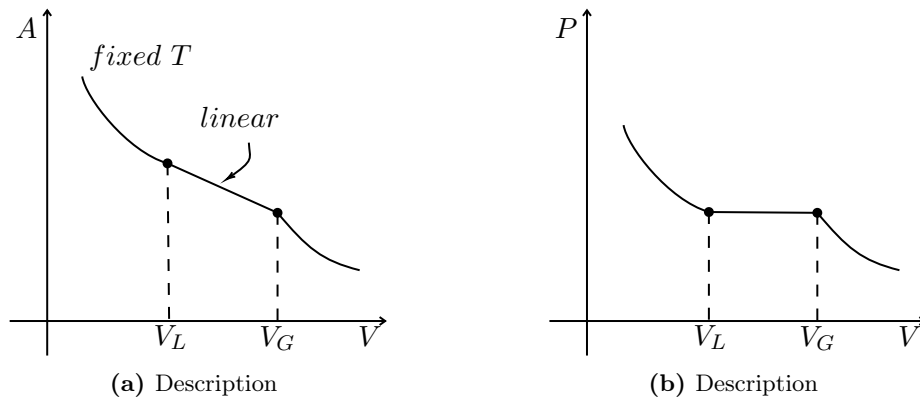
(a) Description **(b)** Description

Figure 2.7: Description

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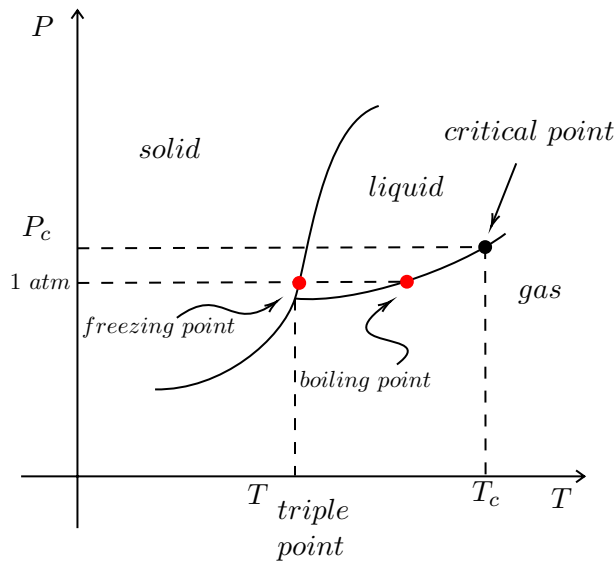

Figure 2.8: Description.

2.6 Ferromagnetic system

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

2.7 Lever Rule

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

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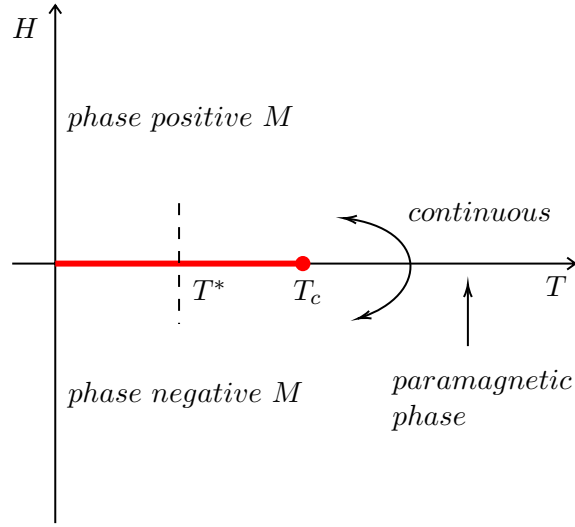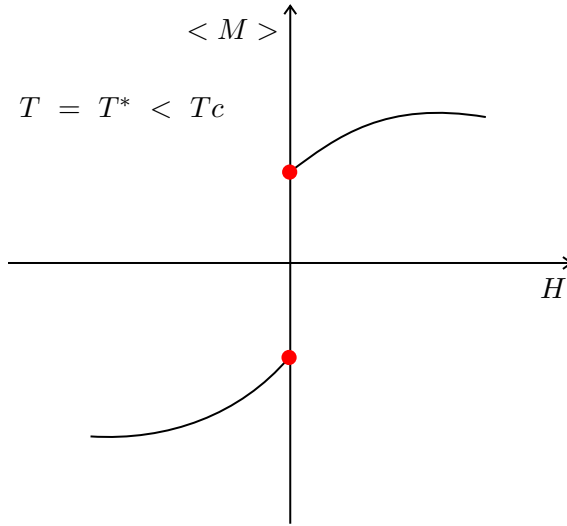
Figure 2.9: Description.

Figure 2.10: Description.

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

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

2.8 Thermodynamic of phase coexistence (one component system)

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

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

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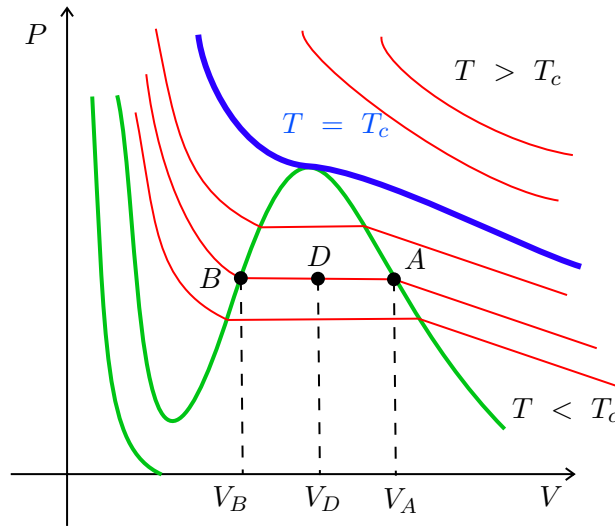
Figure 2.11: Description.

the Gibbs per mole is

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

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

Therefore, on the coexistence line it should hold the relation

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

2.9 Clausius-Clapeyron equation

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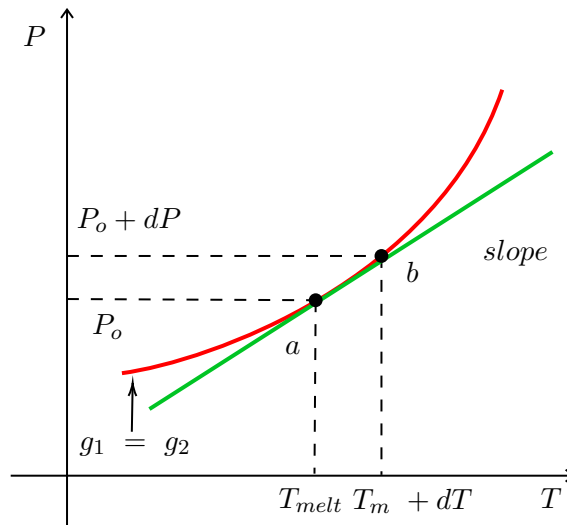

Figure 2.12: Description.

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

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

Hence, if a and b are very close:

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

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

$$\Rightarrow \mathrm{d}g_1 = \mathrm{d}g_2 \tag{2.15}$$

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

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

taking the difference, one obtains

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

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

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

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

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

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

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

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

Since for liquid-gas :

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

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

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

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

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

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

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

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

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

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

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

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

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.
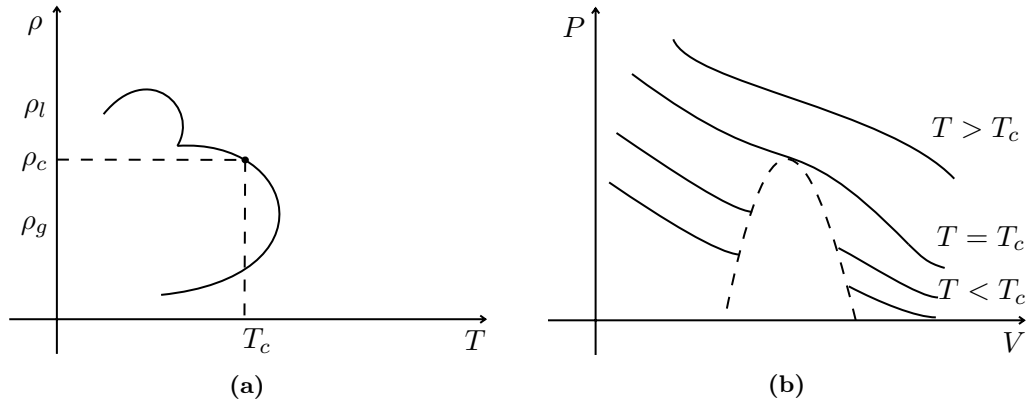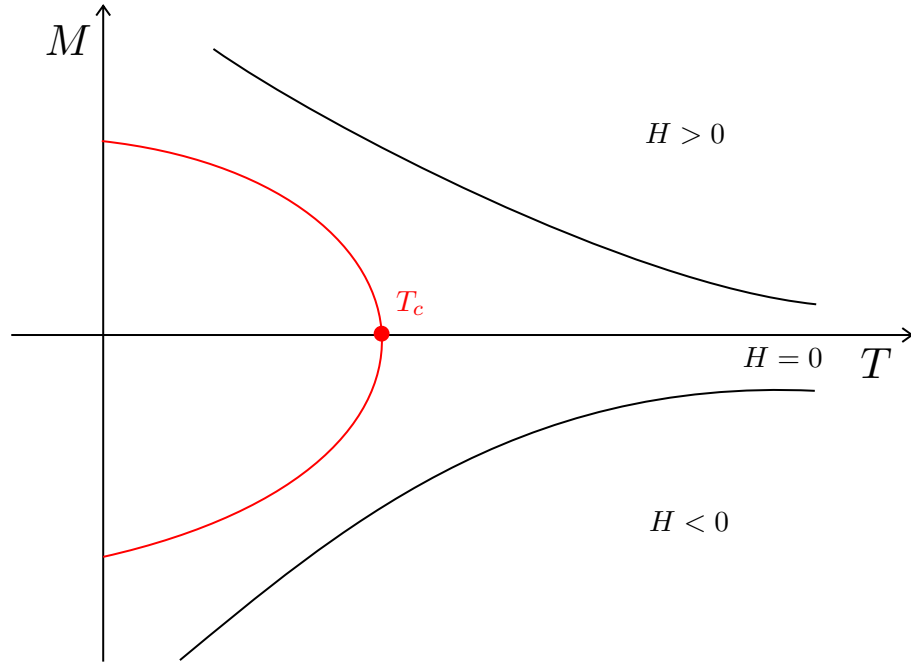
Figure 2.13: Description

Figure 2.14: Description.

2.11   Divergence of the responde functions at the critical point

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

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

2.12   Thermodynamic classification of the phase transitions

Thermodynamically one can distinguish two kinds of phase transitions:

1. Ones who develop latent heat.

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

transition.

2.12.1 Eherenfest classification

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

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

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

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

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

Second order transition but with divergence. Consider the fluid-superfluid transition (or λ transition) of the He$_4$ (Figure 2.15d).

(a)

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

(c) 2° order phase transition

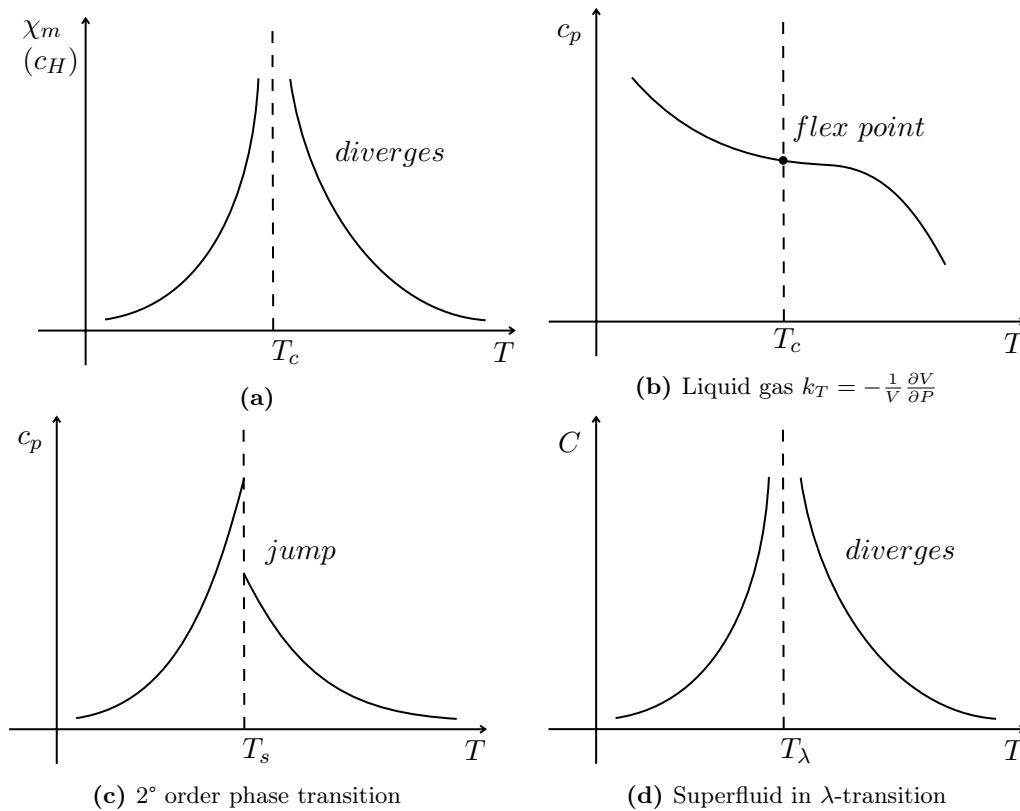**(d)** Superfluid in λ-transition

Figure 2.15: Description

2.12.2 Modern classification

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

2.13   Critical exponents

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

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

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

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

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

More generally, for $t \ll 1$:

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

where all other terms are less important.

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

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

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

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

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

2.13.1   Law of the corresponding states

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

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

(a) Exponent β

(b) Exponent $\gamma_{\pm}$

(c) Exponent $\alpha_{\pm}$
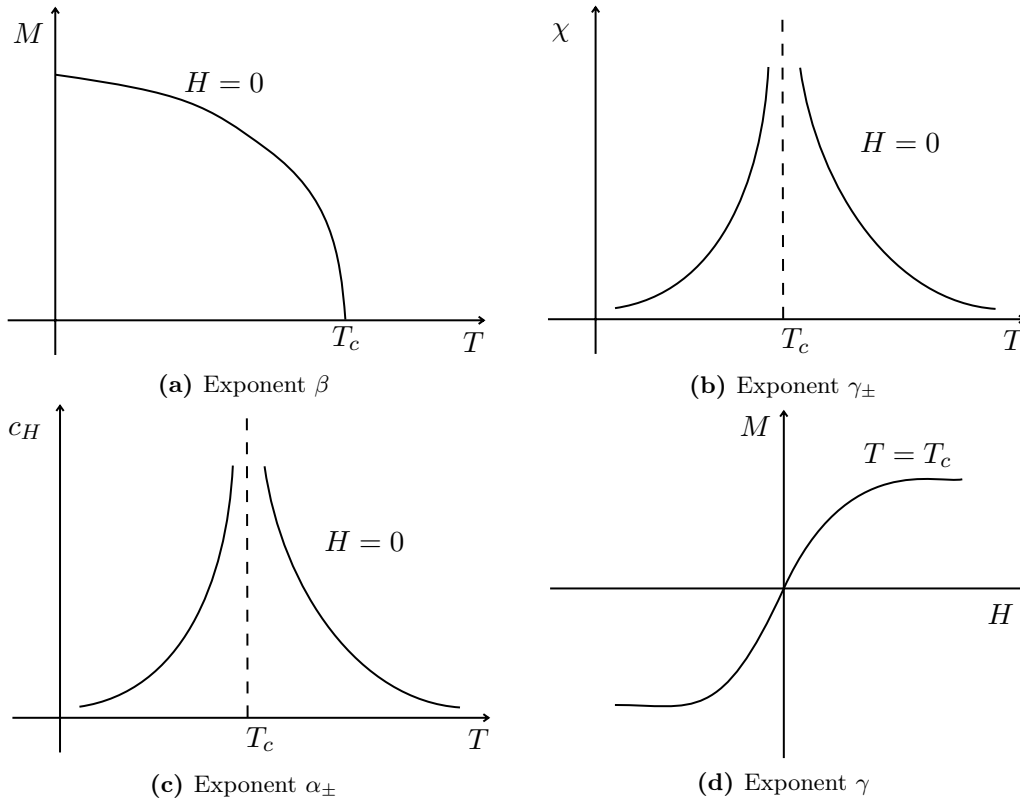
(d) Exponent γ

Figure 2.16: Description

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

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

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

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

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

2.13.2 Thermodynamic inequalities between critical exponents

Rushbrocke inequality

Remember the relation between response functions:

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

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

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

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

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

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

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

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

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

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

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

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

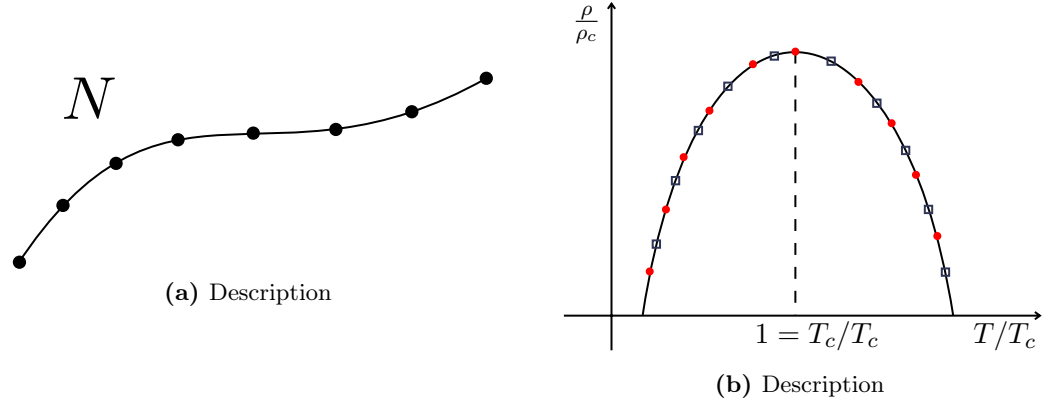$$\Rightarrow \alpha + \beta(1 + \delta) \geq 2 \tag{2.40}$$

(a) Description

(b) Description

Figure 2.17

Chapter 3

Recall of statistical mechanics and theory of ensambles

3.1 Statistical ensambles

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

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

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

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

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

Therefore, we call a single configuration of a given microstate $\mathcal{C}$. A configuration is just when you have the spatial part, because momentum can be obtained by integrating. Suppose you want to compute the probability of a given configuration $\mathcal{C}$, $P_{\mathcal{C}}$, because there is equal probability:
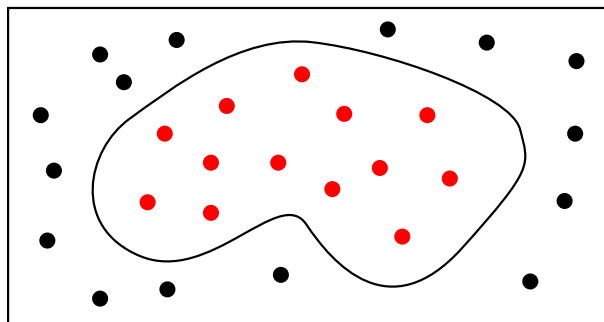
$$P_{\mathcal{C}} = \frac{1}{\Omega(E, V, N)} \tag{3.1}$$

Figure 3.1: Description.

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

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

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

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

$$(3.3)$$

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

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

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

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

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

3.2   The canonical ensemble

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$f(E_B) = f(E_T) + \left.\frac{\mathrm{d}f}{\mathrm{d}E_B}\right|_{E_B = E_T} (E_B - E_T) + \dots \tag{3.14}$$

Therefore:

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

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

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

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

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

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

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

On the other hand

$$\frac{\mathrm{d}s_B}{\mathrm{d}e_B} \equiv \frac{1}{T_B} = \frac{1}{T} \tag{3.19}$$

which implies

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

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

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

Observation 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:

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

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

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

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

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

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

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

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

Remark.

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

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

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

3.2.1   Energy fluctuations in the canonical ensemble

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

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

On the other hand

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

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

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

Since

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

we have

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

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

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

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

3.3   Isothermal and isobaric ensemble

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

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

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

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

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

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

Recalling that

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

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

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

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

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

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

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

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

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

Remark.

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

3.3.1   Saddle point approximation

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

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

where

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

this implies

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

We define the *Gibbs free energy*:

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

For classical systems (fluids)

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

which implies

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

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

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

3.4 Magnetic system

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

$$P_c \propto e^{S_B(E_T, M_T)/k_B - \frac{E_c}{k_B}\frac{dS_B}{dE_B} - \frac{M_c}{k_B}\frac{dS_B}{dM_B}} \tag{3.51}$$

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

$$\Rightarrow P_c \propto \exp[-\beta(E_c - HM_c)] \qquad T_B \to T, H_B \to H \tag{3.52}$$

Normalization function:

$$\Delta(T, H, N) = \sum_c e^{-\beta(E_c - HM_c)} = \sum_{E,M} e^{-\beta E + \beta MH}\Omega(E, M) \tag{3.53}$$

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

3.5 Gran canonical ensemble

In this case N varies instead than V.

$$
\begin{aligned}
P_c &= \exp\left[\frac{S_B(E_T - E_c, N_T - N_c)}{k_B}\right] \\
&\sim \exp\left[\frac{S_B(E_T, N_T)}{k_B} - \frac{E_c}{k_B}\frac{dS_B}{dE_B} - \frac{N_c}{k_B}\frac{dS_B}{dN_B} + (\text{terms of order} \le \frac{1}{V_B})\right] \\
&= \frac{\exp[-\beta E_c + \beta \mu N_c]}{\Theta(T, V, \mu)}
\end{aligned}
\tag{3.54}
$$

where the *grancanonical partition function* is:

$$\Theta(T, V, \mu) = \sum_N \sum_{\substack{c \\ V,N\text{fixed}}} e^{-\beta(E_c - \mu N)} = \sum_{N=0}^{\infty} z^N \Big(\sum_{\substack{c \\ V,N\text{fixed}}} e^{-\beta E_c}\Big) \tag{3.55}$$

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

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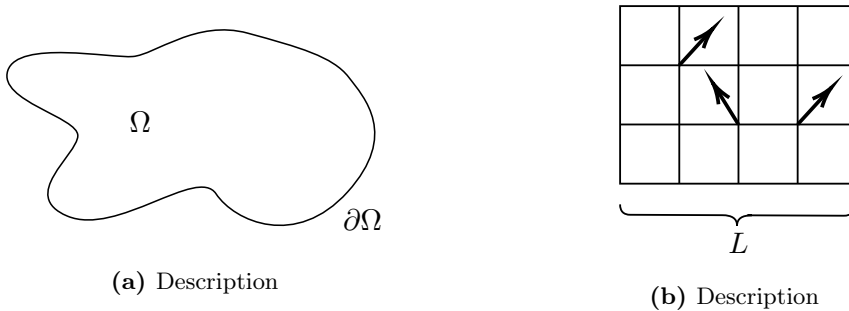

(a) Description

(b) Description

Figure 3.2: Description

3.6 Lezione...da sistemare

Suppose a system Ω carachterzied by $V(\Omega)$ and that have a boundary $\partial\Omega$ carachterized by $S(\Omega)$ (Figure 3.2a). L is the characteristic lenght, and we have $V(\Omega) \propto L^d$

and $S(\Omega) \propto L^{d-1}$ in d dimension:

$$\mathcal{H}_\Omega(C) = -\sum_n \underbrace{k_n \Theta_n(C)}_{\text{must satisfy symmetry}} \tag{3.56}$$

It is important that in principle the term satisfies the symmetry of the system. This is a master rule!

For instance, consider the magnetic system. In a bravais lattice we put a spin up (+1) or down (-1). We can define the vector $\vec{\mathbf{S_i}}$ as the *spin at i-esim site* (Figure 3.2b) with $1 \leq i \leq N(\Omega)$. A configuration is the orientation of the spin in each site $C = \{\vec{\mathbf{S_1}}, \ldots, \vec{\mathbf{S_N}}\}$. In this case

$$k_1 \Theta_1(C) = k_1 \sum_i \vec{\mathbf{S_i}} \tag{3.57a}$$

$$k_2 \Theta_2(C) = \frac{1}{2} \sum_{ij} \vec{\mathbf{S_i}} \cdot \vec{\mathbf{S_j}} k_2(i,j) \tag{3.57b}$$

Now, we sum over all configurations, but first of all define the trace operation:

$$\text{Tr} \equiv \sum_{\{C\}} = \sum_{\vec{\mathbf{S_1}}} \sum_{\vec{\mathbf{S_2}}} \cdots \sum_{\vec{\mathbf{S_N}}} \tag{3.58}$$

$$Q_\Omega(T, \{k_n\}) = \text{Tr}\left(e^{-\beta \mathcal{H}(C)}\right) \tag{3.59}$$

All the configuration are $\{C\} = \{(\vec{\mathbf{r_i}}, \vec{\mathbf{p_i}})_{i=1,\ldots,N}\}$ we have:

$$\Theta_1(C) = \sum_i \left[\frac{\vec{\mathbf{p_i}}^2}{2m} + U_1(\{\vec{\mathbf{r}}_i\})\right] \tag{3.60}$$

$$\Theta_2(C) = \frac{1}{2} \sum_{ij} U(|\vec{\mathbf{r_i}} - \vec{\mathbf{r_j}}|) \tag{3.61}$$

We have:

$$\text{Tr} \equiv \sum_{\{C\}} = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\vec{\mathbf{r_i}}\, d\vec{\mathbf{p_i}}}{h^{3N}} \tag{3.62}$$

$$\mathcal{L} = \text{Tr}\left(e^{-\beta(\mathcal{H}_\Omega - \mu N)}\right) \tag{3.63}$$

Let us write:

$$F_\Omega[T, \{k_n\}] = -k_B \ln Z_N(T, \{k_n\}) \tag{3.64}$$

with $F_\Omega \propto V(\Omega) \sim L^d$ In general, we can write:

$$F_\Omega = V(\Omega) \underbrace{f_b}_{\substack{\text{bulk} \\ \text{free energy} \\ \text{density}}} + S(\Omega) f_s + O(L^{d-2}) \tag{3.65}$$

We have:

$$f_b[T, \{k_n\}] = \lim_{V(\Omega) \to \infty} \frac{F_\Omega(T, \{k_n\})}{V(\Omega)} \tag{3.66}$$

$$f_s[T, \{k_n\}] = \lim_{V(\Omega) \to \infty} \frac{F_\Omega - V(\Omega) f_b}{S(\Omega)} \tag{3.67}$$

Therefore, spin

$$f_b = \lim_{N(\Omega) \to \infty} \frac{F_N}{N} \qquad \substack{V \to \infty \\ N \to \infty} \quad \rho \quad \text{fixed} \tag{3.68}$$

One interesting things is to prove the existence of the limit. Given that, the questions is: can we describe the thermodynamics singularities underneat the phase transition? This is not completely clear. The partition function of a given Ω is an analitic function (it converges):

$$Z(\Omega) = \mathrm{Tr}\left(e^{-\beta \mathcal{H}_\Omega}\right) \tag{3.69}$$

There is no way in you can produce singularities out of this. The singularities will develop in the thermodynamic limits. The next question is the following: there are singularities that come out in the thermodynamic limit, for reach singulariities you have to reach so precision in thermodynamic that you are not able to go extactly into the critical point. Next: how you can relate singularities in the behaviour of the system geometrically?

Conclusions

Bibliography