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

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

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.*

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

- *Adiabatic compressibility.*

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

- *Isothermal compressibility .*

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

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.

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

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

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

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

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

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

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

and the response function α_P permit to write

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

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:

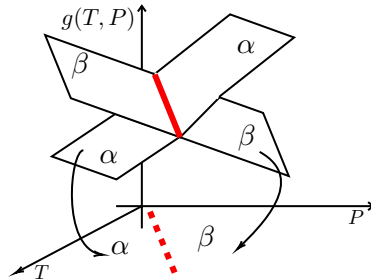$$g_\alpha(T, P) = g_\beta(T, P) \tag{2.2}$$

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.
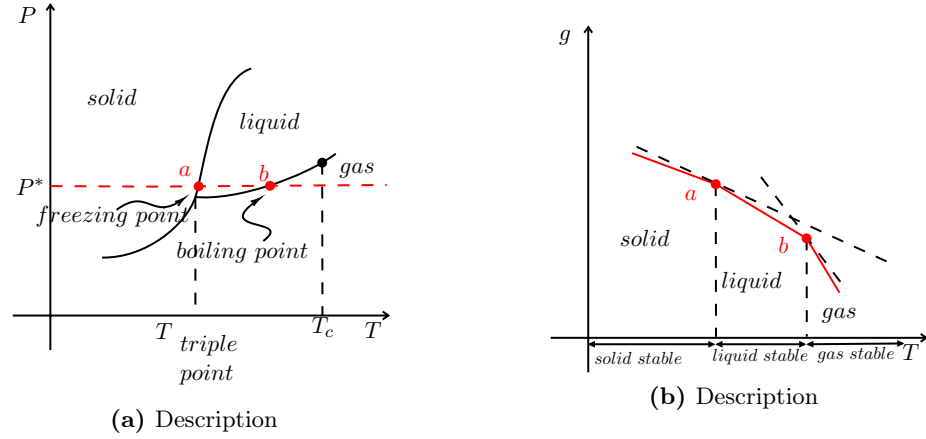

(a) Description

(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*.
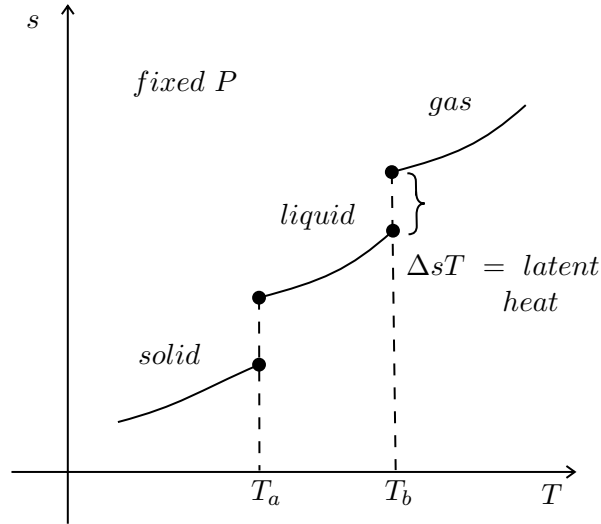
Figure 2.3: Description.

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

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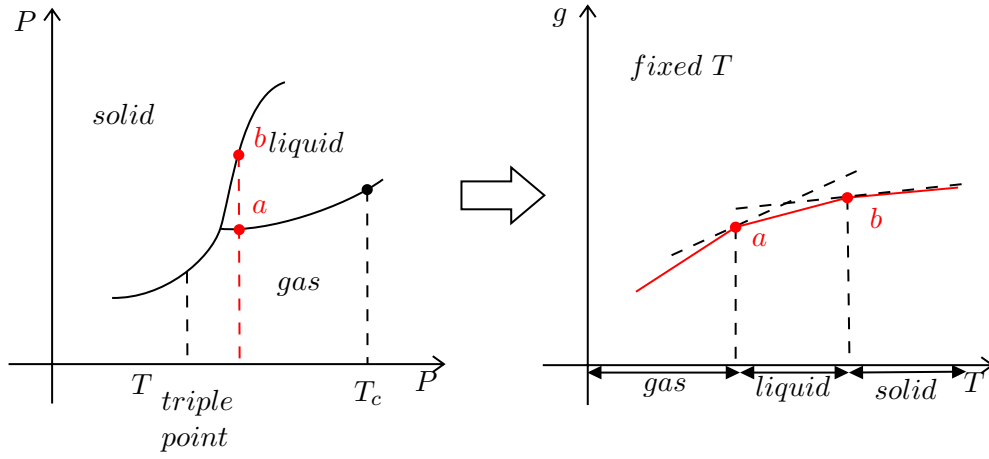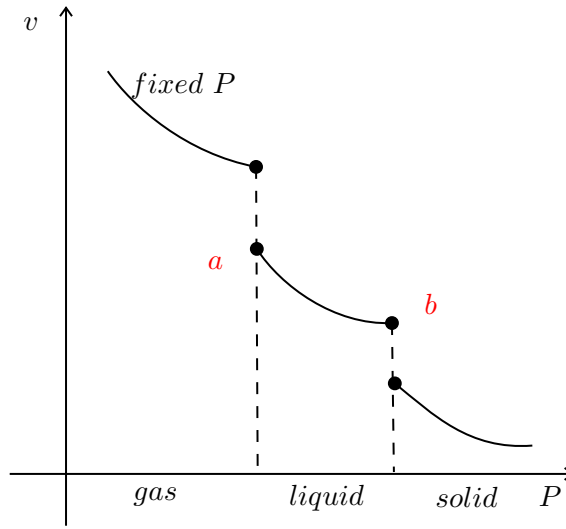
Figure 2.4: Description.

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
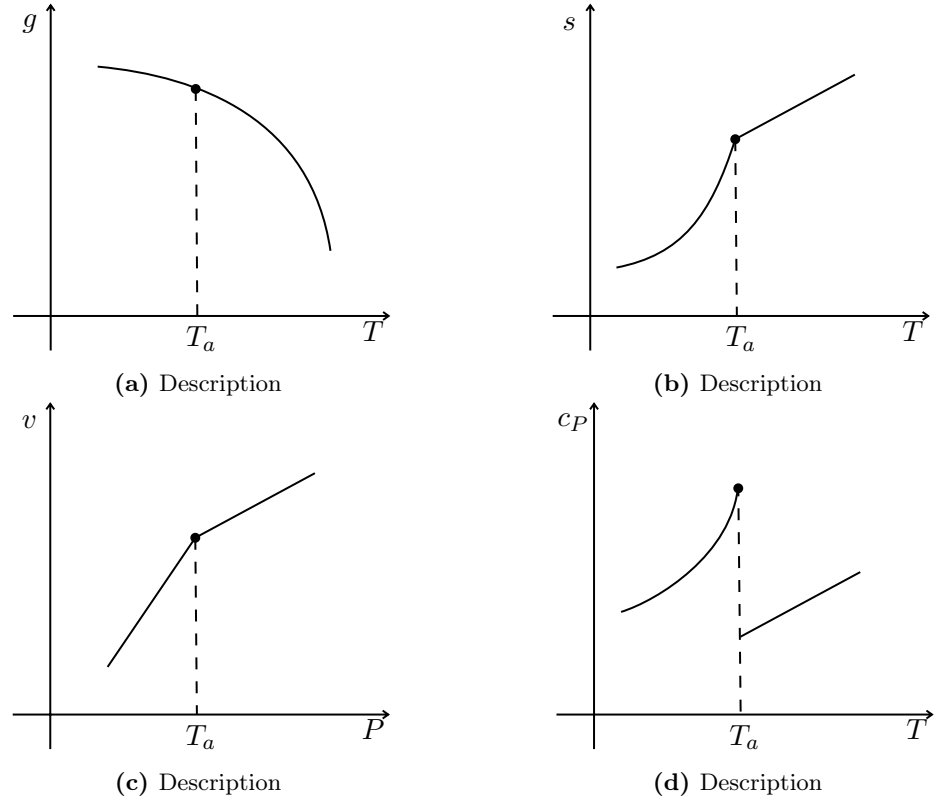
(a) Description

(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
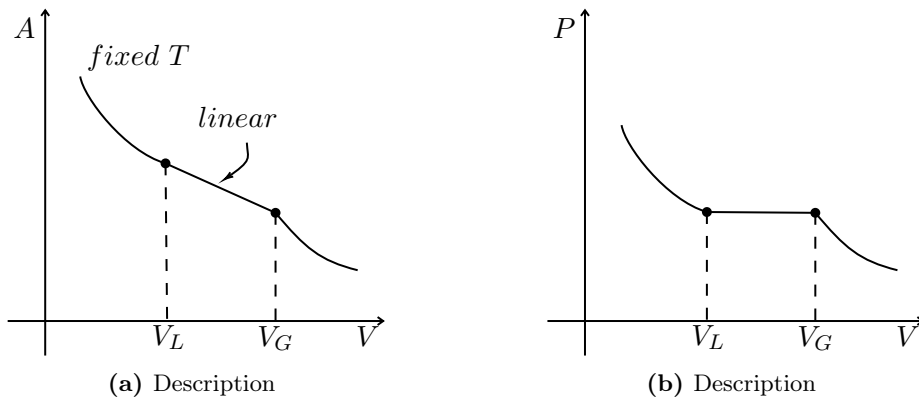
(a) Description   **(b)** Description

Figure 2.7: Description

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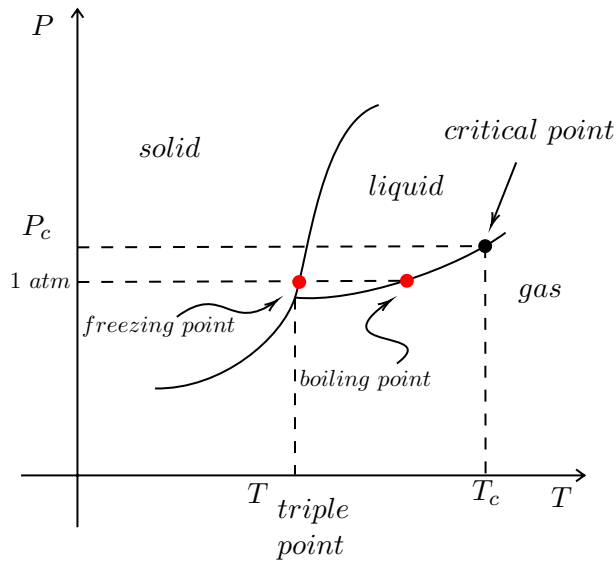

Figure 2.8: Description.

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.
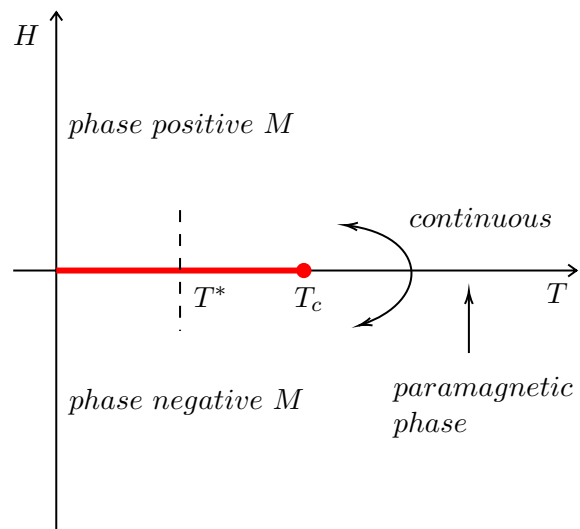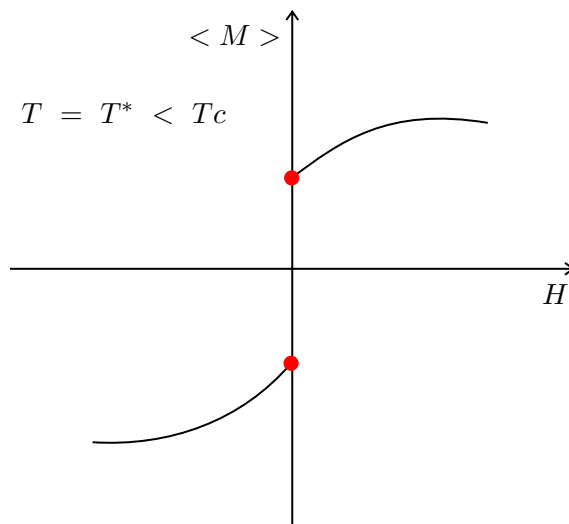
Figure 2.9: Description.

Figure 2.10: Description.

Conclusions

Bibliography