



Advanced Statistical Physics

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III

Introduction to Quantum Criticality



Fundamental Concepts

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1. Start with What, Why and How.

This course will be dealing primarily with the physics of 10^{23} particle systems such as gases, liquids and solids. Through out the history, characterizing many-body systems was challenging due to the many interactions present in many-body systems that induces phenomena which are hard to predict by relying only on the full knowledge we have on one particle. Thus, it is impossible for us to keep track of 10^{23} particles, so what do we do ?

One useful strategy is to aim at understanding the collective behavior of many-particles systems by making use of basic physical laws to develop new methods of analysis that can bring out the essential characteristics of these complex systems. This is the approach of “statistical physics”, which is a beautiful theory that uses the microscopic laws of physics to describe nature on a macroscopic scale.

Before going into the details and to have a bird eyes view on the theory of statistical physics, we begin by asking and answering three fundamental questions : *What, Why* and *How*.

1.1 *What* is statistical physics ?

The complexity of studying many-body systems discussed earlier is a double-edged sword. On one side, it is in fact true, that it is extremely hard to write and solve the Schrödinger equation for a system of 10^{23} particles. From the other side, this sheer complexity offers a way to fight back. Because of the large number of particles in many-body systems, using statistical arguments becomes possible and effective. This does not mean that all issues disappear, but many problems do become simple by applying statistical approaches or probability theory. In a nutshell, “statistical physics is probability theory applied to physical systems”.

1.2 *Why* do we study statistical Physics ?

The techniques of statistical physics or statistical mechanics have been proved to be powerful and substantial at understanding the deeper laws of physics. As a matter of fact, the tools of statistical mechanics provides a rational understanding of “Thermodynamics”, by allowing the calculation of the basic thermodynamic quantities such as : the free energy and the entropy and also transport

properties, the conduction of heat and electricity. Moreover, the key that solved the problem of the black body radiation, which led to the discovery of quantum physics, was developed via arguments of statistical mechanics; from these two examples, it is clear that statistical mechanics is very ubiquitous in physics.

1.3 How to describe systems using statistical physics ?

Earlier, we discussed that statistical arguments applies effectively when the system in question consists of very many particles. To illustrate the idea, consider the following experiment of throwing 100 dice from a cup into a table, how can we describe the outcome of such an experiment ?

The beauty of statistical physics lies in its very basic formalism, the necessary ingredients that we will be using whenever we consider experiments of this kind are the following:

- A method for determining the state of the system, that is a procedure for describing the outcome of the experiment.
- In realistic experiments, we usually don't have access to the detailed information on each dice (i.e. initial position, velocity and orientation of the dice), we tackle this hardship by introducing probabilities over an "ensemble" of many such experiments conducted under the same conditions.
- Statistical physics is constructed via *a priori* postulates, which we verify their validity by experimental observations. An example would be the fact that the probabilities of appearance of any face of a uniform dice are all equal.
- Having the basic postulates all set and done, the theory of probability allows the calculation of the probability associated with each outcome of any experiment.

1.3.1 Specification of the state of the system

The description of a system of particles at a microscopic level can be done via the notion of *micro-state*, which is a certain configuration a particular system takes at some instant. For macroscopic systems, practically we can not speak of micro-states as these systems are of the order of the Avogadro number ($N = 10^{23}$), and to determine the micro-states, one need to know $3N$ positions and $3N$ momentum coordinates to completely specify the system, which is, practically, an impossible task. Furthermore, at the macroscopic level we are not interested in knowing the positions of individual particles, but rather we want to answer basic questions such as : the content of the box, its color, is it wet ? is it cold ? what happens when we heat it up ?

We constrain then our discussion on *micro-states* at a theoretical level to make the connection between the microscopic and macroscopic world and to introduce statistical physics ideas.

To assimilate the idea of *micro-states*, we take a simple ubiquitous example of the hydrogen atom, a system that is heavily studied in physics and chemistry. The energy levels of the hydrogen atom are given by :

$$\epsilon_n = -\frac{13.6}{n^2} \text{eV}$$

Where n is a positive integer called *the quantum number*. For a given energy state ϵ_n , there can be many possible configurations given by other quantum numbers l, m, s, s_z related by the following laws:

- $0 \leq l \leq n - 1$, where l is an integer related to the angular momentum of the electron.
- $-l \leq m \leq +l$, m is the magnetic quantum number related to the projection of the angular momentum on the z -axis.
- $s = \frac{1}{2}$ is the spin quantum number.

- $-\frac{1}{2} \leq s_z \leq +\frac{1}{2}$, s_z is the projection of the spin on the z -axis, which, in this case, can take only two values $-\frac{1}{2}$ or $+\frac{1}{2}$.

Up to this point, the *micro-state* is a particular configuration given by the ensemble (n, l, m, s, s_z) , which describes the system completely at the microscopic level.

Classical description : The notion of phase space

The microscopic world is described adequately using the theory of quantum mechanics, however we can encounter physical problems where a description through classical mechanics, which in general is inadequate, can be a useful approximation and sufficient to understand the general behavior of many-body systems.

In classical mechanics, specifying the position and the momentum coordinate (x, p) results in a complete description of the system, that is a knowledge of the position and the momentum at any time of a classical system provides a way, through the laws of classical mechanics, to predict the values of (x, p) at any other time. Thus we can introduce the phase space representation of classical systems. As an example, take a single particle in one dimension, we can represent geometrically this system by drawing cartesian axes labeled by x and p , as shown in Fig. 1.3.1.

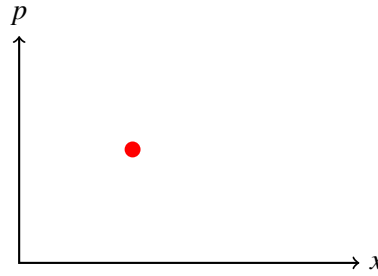


Figure 1.3.1: Phase space representation of a one dimensional particle. Each couple of (x, p) is associated to a point in the phase space (i.e. the red point). The time evolution of (x, p) is equivalent to the movement of the point through the phase space.

Classical mechanics predicts an infinite number of micro-states, in order to make the possible states countable, we subdivide the 2-dimensional phase space into small cells of area $\delta x \delta p = h_0$, where h_0 is small constant having the dimension of angular momentum (Planck constant). Classical micro-states are the configurations that lies in a particular phase space cell, which in classical mechanics corresponds to an infinite number of possibilities. The state of the system lies in the interval between $[x, x + \delta x]$ and between $[p, p + \delta p]$, it is clear that the accuracy of this specification can be increased by decreasing the size of the cell, that is decreasing the magnitude of h_0 . If we apply some constraint to our system that limits the access to only an area S of the phase space, the number of *accessible* micro-states is then : $\frac{S}{\delta x \delta p}$.

But there is a catch, quantum mechanic imposes a limit to the accuracy of determining the position x and the momentum p simultaneously, a limit that is expressed via the *Heisenberg uncertainty* which states the the uncertainties δx and δp cannot exceed the Planck constant “ h_0 ”, that is :

$$\delta x \delta p \geq \frac{h_0}{2\pi}$$

Choosing a cell of area smaller than the Planck constant results in a specification of the state of the system more than what the theory of quantum mechanics allows, which is physically meaningless. The generalization of the above discussion is straightforward, an arbitrary complex system can be described using $2f$ parameters, f coordinates (x_1, \dots, x_f) and f momenta (p_1, \dots, p_f) . The set of

numbers $(x_1, \dots, x_f, p_1, \dots, p_f)$ can be seen as points in $2f$ -dimensional phase space, which again can be subdivided into small cells of volume $\delta x_1 \dots \delta x_f \delta p_1 \dots \delta p_f = h_0^f$. The state of the system can be determined by stating over which range the coordinate $x_1, \dots, x_f, p_1, \dots, p_f$ can be found.

Quantum description

Quantum mechanics provides the necessary formalism to describe the basic constituents of any complex system (i.e. atoms, electrons ... etc.). The wave function $\psi_k(x_1, \dots, x_f)$ in quantum mechanics is the key tool to describe the particles, where f is the number of degrees of freedom which when specified results in a complete description of the quantum state of the system at any time t and at any other time t' , through the laws of quantum mechanics.

To illustrate, take a single and fixed particle having a spin $s = \frac{1}{2}$. The state of this system in a quantum mechanics description is specified by the projection of the spin on the z -axis which can take values of $+\frac{1}{2}$ or $-\frac{1}{2}$. In other terms, we say that the particle points either up or down.

1.3.2 Statistical ensemble

In realistic scenarios, a complete specification of the system either at a classical or a quantum level, is out of hand or is of little interest for us. In general, our aim is not on a single system, but rather on an *ensemble* consisting of very large number of identical systems, all prepared to the same conditions. The systems in this ensemble will, in general, be in different states and characterized by different macroscopic parameters (i.e. temperature, pressure, ..., etc). Our aim is to predict the probability of occurrence in the ensemble of various values of this parameter on the basis of some postulates.

A simple example, where we apply the essence of the idea, is *flipping coins*. Take an ensemble of 100 biased coins, and we ask what is the probability to find Head and what is the probability of find Tail.

A concrete example is a system of three fixed particles, each having a spin $s = \frac{1}{2}$ and a magnetic moment along the z -axis of μ when it points up and $-\mu$ when it points down. The system interacts with an external magnetic field H along the z -axis. The energy of a particle is $-\mu H$ when it points up and $+\mu H$ when it points down. The state of i^{th} particle can be specified by the quantum number m_i (the projection of the spin on the z -axis), which can take two values $m_i = \pm \frac{1}{2}$. The state of the whole system can be determined by knowing the values of m_1, m_2 and m_3 as presented in the following table, where we enumerate the possible states of the system.

State index r	Quantum numbers m_1, m_2, m_3	Total magnetic moment	Total energy
1	+++	3μ	$-3\mu H$
2	++-	μ	$-\mu H$
3	+ - +	μ	$-\mu H$
4	- + +	μ	$-\mu H$
5	+ - -	$-\mu$	$+\mu H$
6	- + -	$-\mu$	$+\mu H$
7	- - +	$-\mu$	$+\mu H$
8	- - -	-3μ	$+3\mu H$

Sometimes we may have access to some information about the system, for example its energy. In this case, the system will be in a state compatible with the available information. These state are

known by *the accessible states*. Consider again the previous example of the three fixed particles, if the system has an energy of $-\mu H$ and if this is the only piece of information we have, the state of the system will be either in the 2nd, 3rd or 4th state as illustrated in the table.

1.3.3 Basic postulates

At this point, we can state some fundamental assumptions of statistical physics that will help us make theoretical progress.

Postulate 1 : Equiprobability

“For an isolated system in equilibrium, all accessible states are equally likely.”

If this is not the case, the system is out of equilibrium and will evolve to satisfy the equiprobability postulate. If we have only some partial information on the system, such as the energy, there is no *a priori* reason to favourize a micro-state over the other. This first fundamental postulate is prominent and does not violate the laws of mechanics. The validity of the postulate can be verified by making theoretical predictions based on it and by checking whether these predictions goes along with the experimental observations.

In the previous example, where we assumed that the three particles system has a fixed energy, we found that the system can be in any of the following configurations :

$$(+ + -), (+ - +), (- + +)$$

The equiprobability postulate assures that at equilibrium, the system is equally likely to be in any of these three configurations.

Postulate 2 : Ergodic hypothesis

“The mean over time of any parameter is equal to the average of this parameter taken over an ensemble of systems.”

Over the flow of time, the system changes its micro-state from one to the other as a result of small interactions between its particles. If we observe the system in one instant of time, he will be in only one micro-state. However, if we look long enough (infinite duration), one expects that the system will swap over all its micro-state and will stay an equal duration in all its micro-states. This is the ergodic hypothesis and it is just another reformulation of the first postulate because it supposes the equiprobability of micro-states. Then, instead of observing only one system, we track, in a given instant, an ensemble of many identical systems.

As an example, consider a fair dice : it has six accessible states with probability $\frac{N_i}{N}$ each. We consider $N = 10^3$ trials, at the end of the experiment we will have N_1 of the first outcome, N_2 of the second outcome, ..., etc, so that $N_1 + N_2 + \dots + N_6 = 10^3$. The probability to obtain the outcome i is $\frac{N_i}{N}$, as $N \rightarrow \infty$ the probability of each outcome tends to $\frac{1}{6}$. Instead of looking at one dice, we repeat the same experiment many times to calculate the probability distribution, which is essentially taking the mean in time over one dice.

1.3.4 Probability calculations

A complete description of systems at equilibrium is done via the postulates we introduced above. Consider an isolated system at equilibrium, where its energy is known to be in some range between E and $E + \delta E$. To make use of probability theory, we aim on an assembly of many copies of this system, all of which they satisfy the energy range condition. Let $\Omega(E)$ be the total number of state in this range. Suppose that among these states there is a certain number $\Omega(E, y_k)$ of states for which some parameter y (i.e. magnetic field, pressure) takes the value y_k . Using the equi probability

postulate, we can say the probability $P(y_k)$ that the parameter y takes the value y_k is :

$$P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)}$$

We can also calculate the mean of this parameter by taking the average over the system in the ensemble :

$$\langle y \rangle = \sum_k P(y_k) y_k$$

Throughout out this course, these kind of calculation, which are simple in principle, will be very frequent and important in discussing the properties of systems at equilibrium.

2. Statistical Thermodynamics

“The history of thermodynamics is a story of people and concepts. The cast of characters is large. At least ten scientists played major roles in creating thermodynamics, and their work spanned more than a century. The list of concepts, on the other hand, is surprisingly small; there are just three leading concepts in thermodynamics: energy, entropy, and absolute temperature.” William H. Cropper

In the previous section, we focused on the basic ideas that provides an analysis at the microscopic level of many-particle systems. In the following, we will take step back and focus on a theory that does not care for the atoms, and applies to macroscopic systems. Thermodynamics describes the relationships between observable macroscopic phenomena such as the temperature T , the pressure P and the volume V . Classical thermodynamics is not as fundamental as the statistical description and as we will see later, all the laws of thermodynamics can be reconstructed from statistical physics.

2.1 Laws of classical thermodynamics

Classical thermodynamics is based on statements that does not take into account for the microscopic properties systems i.e. the atoms. Theses statements is what we call the “thermodynamical laws”.

Zeroth law

If two systems A and B are in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other

The 0th law defines the concept of temperature. When thermodynamics was first being developed, no one was certain exactly what “temperature” really was. It was strictly an empirical measurement. Suppose that systems A and C are known to be in a state (p_1, V_1) and (p_3, V_3) respectively. An equilibrium state, is where a relationship between (p_1, V_1) and (p_3, V_3) exists. Then, in order to check the equilibrium hypothesis we put the systems A and B in thermal contact to see if their state will change and reach a thermal equilibrium.

The constraint that determines when A and C are in equilibrium, is given by the function :

$$F_{AC} = (p_1, V_1; p_3, V_3),$$

which can be solved to give the volume for the system C :

$$V_3 = f_{AC}(p_1, V_1; p_3).$$

The same reasoning is valid when B and C are in equilibrium, the constraint is given by :

$$F_{BC} = (p_2, V_2; p_3, V_3),$$

which can be solved to give the volume for the system C :

$$V_3 = f_{BC}(p_2, V_2; p_3).$$

Then :

$$f_{AC}(p_1, V_1; p_3) = f_{BC}(p_2, V_2; p_3),$$

which means that there exist a constraint that relates the system A and B that does not depend on p_3 , because it cancels out on both sides of the previous equality :

$$F_{AB} = (p_1, V_1; p_2, V_2).$$

Then, the relationship between states of A and B emerges after the cancellation of p_3 , given by :

$$\theta_A(p_1, V_1) = \theta_B(p_2, V_2),$$

where $\theta(p, V)$ is the “temperature” of the system and the function $T = \theta(p, V)$ is the “equation of state”.

First law

An isolated system at equilibrium is characterized by a macro-state which has a constant internal energy $\bar{E} = \text{constant}$.

If the system is allowed to change macrostates (not isolated), the change in the internal energy is given by :

$$\Delta\bar{E} = -W + Q,$$

where $-W$ is the work done by the system and $+Q$ is the heat absorbed by the system.

The first law reflects the conservation of energy. But once again, remember that the founders of classical thermodynamics did not know exactly what *heat* was. The fact that it was a form of energy, and that it participated in the conservation of energy, had to be discovered through experiment.

Second law

In any thermodynamic process, the total entropy “ S ” either increases or remains constant, but never decreases.

The second law of thermodynamics reflects a deep truth about the nature of the universe we live in, that is there are many processes (macroscopic) in nature that cannot be reversed and that there is a preferred direction of time. Things fall apart. Words cannot be unsaid.

Third law

The entropy “ S ” has a limiting property that : as $T \rightarrow 0_+$, $S \rightarrow S_0$.

Where S_0 is a constant independent of all the parameters of the system.

2.2 Thermodynamical quantities

Consider a closed system composed of two parts A and B, the thermodynamical variables of the whole system (E, V, N) , obeys the following : $V = V_1 + V_2$, $E = E_1 + E_2$ and $N = N_1 + N_2$.

An equilibrium state requires the entropy, "S", to be maximized over any changes in (E, V, N) . Then, we can write :

$$dS = dS_1 + dS_2 = \left(\frac{\partial S_1}{\partial E_1}\right) dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right) dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial E_2}\right) dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right) dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2.$$

Since we are interested in the equilibrium state ($dS = 0$), we have : $dV_1 + dV_2 = 0$, $dE_1 + dE_2 = 0$ and $dN_1 + dN_2 = 0$. Which leads to :

$$dS = \left[\left(\frac{\partial S_1}{\partial V_1}\right) - \left(\frac{\partial S_2}{\partial V_2}\right) \right] dV_1 + \left[\left(\frac{\partial S_1}{\partial E_1}\right) - \left(\frac{\partial S_2}{\partial E_2}\right) \right] dE_1 + \left[\left(\frac{\partial S_1}{\partial N_1}\right) - \left(\frac{\partial S_2}{\partial N_2}\right) \right] dN_1 = 0.$$

Therefore :

$$\text{at constant } N \text{ and } E: \left(\frac{\partial S_1}{\partial V_1}\right) = \left(\frac{\partial S_2}{\partial V_2}\right) = \frac{P}{T},$$

$$\text{at constant } V \text{ and } N: \left(\frac{\partial S_1}{\partial E_1}\right) = \left(\frac{\partial S_2}{\partial E_2}\right) = \frac{1}{T},$$

$$\text{at constant } E \text{ and } V: \left(\frac{\partial S_1}{\partial N_1}\right) = \left(\frac{\partial S_2}{\partial N_2}\right) = -\frac{\mu}{T}.$$

Where P is the pressure, T is the temperature and μ is the chemical potential. If T is not uniform, energy flows will occur. If P is not uniform, the relative volume of the two subsystems will change. If μ is not uniform, mass transport will take place.

Further progress can be achieved when specifying the equation of the state which relates different thermodynamical variables at equilibrium. The equation of state varies from a system to another and most often they are determined experimentally. In the case of the ideal gas, we have :

$$PV = NRT.$$

In general, equations of state are unknown. Instead, one has access to differential equations of state of the form :

$$dP = \left(\frac{\partial P}{\partial V}\right)_{N,T} dV + \left(\frac{\partial P}{\partial T}\right)_{N,V} dT$$

and :

$$dE = \left(\frac{\partial E}{\partial V}\right)_{N,T} dV + \left(\frac{\partial E}{\partial T}\right)_{N,V} dT$$

A knowledge of the (T, V) dependencies of these derivatives results in deriving the equation of state and some other important thermodynamical quantities, such as :

$$\text{heat capacity at constant volume : } C_V = T \left(\frac{\partial S}{\partial T}\right)_V,$$

$$\text{heat capacity at constant pressure : } C_P = T \left(\frac{\partial S}{\partial T}\right)_P.$$

Now, consider a homogeneous system with r constituents with N_1, N_2, \dots, N_r particles. We can expand the derivative of the internal energy in terms of (S, V, N_r) as :

$$dE = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}}_T dS + \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{-P} dV + \sum_{j=1}^r \underbrace{\left(\frac{\partial E}{\partial N_j}\right)_{S,V}}_{\mu_j} dN_j.$$

Which leads to :

$$dE = TdS - PdV + \sum_{j=1}^r \mu_j dN_j.$$

In the case of a homogeneous system with one constituent, we find :

$$dE = TdS - PdV,$$

which is also equal to :

$$dE = TdS - PdV = \delta Q + \delta W,$$

From the definition of the internal energy we can introduce the concept of “*the enthalpy*” and “*the free energy*” (which will be central to the analysis of phase transitions later on), can be defined :

$$H = E + PV = TS + \sum_{j=1}^r \mu_j N_j,$$

$$dH = TdS + VdP + \sum_{j=1}^r \mu_j dN_j$$

and :

$$F = E - TS = -PV + \sum_{j=1}^r \mu_j N_j,$$

$$dF = -SdT - PdV + \sum_{j=1}^r \mu_j dN_j$$

2.3 Thermodynamics through statistical relations

Thermodynamics can also be summarized through statistical physics. For this aim, we start with the notion of *entropy*, which precedes *the temperature* and even *the energy*.

Consider a closed system of N particles at equilibrium; if $\Omega(N, E, V)$ is the total number of configurations, then the equiprobability postulate states that the probability of finding the system in any of its accessible states is :

$$P = \frac{1}{\Omega(N, E, V)}.$$

All states of the same energy occur with equal probability. Then, through Boltzmann’s formula (although it is not a general formula), we can build our first connection between the entropy and the $\Omega(N, E, V)$, which relates the thermodynamics laws to the microscopic knowledge of the system :

$$S = k_b \ln \Omega(N, E, V),$$

where k_b is the Boltzmann constant.

The temperature, is basically the change of the energy required for changing the entropy of the system by 1 bit (this will be stressed out, when we discuss the entropy and information), can be derived also from $\Omega(N, E, V)$ by taking the derivative of the entropy with respect to the energy. Thus, we write :

$$\beta = \frac{1}{k_b T} = \frac{\partial \ln \Omega(N, E, V)}{\partial E}$$

At this point, it is very clear how the knowledge of the number of configurations (number of states) $\Omega(N, E, V)$ is crucial for calculating the thermodynamical quantities. To illustrate the idea, consider

an ideal gas, since for such a system the interaction between the potential energy U is null between the molecules. Then :

$$\Omega^{\text{Ideal gas}}(N, E, V) \propto V^N f(E),$$

where $f(E)$ is a function of the energy *only*. Thus, we have :

$$\ln \Omega = N \ln V + \ln f(E) + \text{constant},$$

Then, the pressure P can be calculated by taking the derivative with respect to the volume V :

$$P = \frac{N}{\beta V} = \frac{N}{V} k_b T.$$

This is the equation of state for an idea gas.

The mean energy of an ideal gas has an interesting property, which can obtained by noticing :

$$\beta = \frac{\partial \ln f(\bar{E})}{\partial E}.$$

Thus, it follows that, for an ideal gas $\beta = \beta(\bar{E})$ or $\bar{E} = \bar{E}(T)$. The mean energy of an ideal gas depends solely on the temperature. An expected result we say, since for an ideal gas, the interaction between the molecules is negligible so increasing the volume would not effect the energy of the system, while the internal energies of the molecules is distance independent, which preserves the total energy of the system.

3. A crash course on statistical mechanics

“With thermodynamics, one can calculate almost everything crudely; with kinetic theory, one can calculate fewer things, but more accurately; and with statistical mechanics, one can calculate almost nothing exactly.” Eugene Paul Wigner

The present chapter is brief summary of the beauty of statistical mechanics, in which we show how statistical relations takes part in :

- Constructing general probability statements which can describe situations of physical interest.
- The calculations of important macroscopic quantities such as the entropy and specific heats, from a knowledge of the microscopic properties of the system in question.
- Very wide applications.

3.1 The heroes

Every theory has its good and bad guys, in statistical physics we have on our side *ensembles* which are representatives of situations of our physical interest. The most trivial situation a researcher or scientist start with, is the case of an isolated system.

3.1.1 The microcanonical ensemble

Consider an isolated system consisting of N particles in a specified volume V , whose energy lies between E and $E + \delta E$. To impose probability statements, we consider an assembly of many such system following the same constraint on N , V and the energy range. Then, at equilibrium the system can be found equally likely in any of its accessible states. Thus, the probability to found the system in a state r with energy E_r is :

$$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{Otherwise} \end{cases} \quad (3.1.1)$$

where C is a constant which can be determinated by the normalization condition $\sum P_r = 1$. An ensemble that follows the probability distribution (3.1.1) to describe isolated systems, is called *the microcanonical ensemble*.

3.1.2 The canonical ensemble

Now, we consider a system A in contact with a heat reservoir A' where $A \ll A'$, for example A could be a spin- $\frac{1}{2}$ particle placed between two parallel walls (A') with infinite height. For these kind of systems, we impose two constraints :

- The distinguishability of the system A .
- The additivity of the energies (weak interactions between A and A'), so that the combined energy E_r (which is not fixed) of the system and that of the reservoir E' is a constant. That is, $E_r + E' = E^0$.

Then, we ask the following : what is the probability P_r of finding system A in any one particular microstate r of energy E_r ?

If the system is in a definite state r with energy E_r , then A' will have an energy of $E' = E^0 - E_r$. Thus, the number of accessible states for the whole system is $\Omega(E^0 - E_r)$. Then, following the fundamental statistical postulate, the probability of finding the A in the microstate r is :

$$P_r = C' \Omega(E^0 - E_r),$$

where C' is a constant independent of r , which can be obtained by the normalization condition. The system A having many few degrees of freedom in comparison to A' ($A \ll A'$), implies that $E_r \ll E^0$. Then, we can expand slowly varying logarithm of $\Omega(E^0 - E_r)$ as :

$$\ln \Omega(E^0 - E_r) = \ln \Omega(E^0) - \underbrace{\left[\frac{\partial \ln \Omega}{\partial E'} \right]}_{\beta} E_r \dots$$

where we neglect higher-order terms. The derivative $\frac{\partial \ln \Omega}{\partial E'} = \beta = (kT)^{-1}$ is evaluated at the fixed energy $E' = E^0$, meaning that it is a constant independent of the energy E_r of A . β in fact characterize the temperature of the heat bath . Then :

$$\begin{aligned} \ln \Omega(E^0 - E_r) &= \ln \Omega(E^0) - \beta E_r \\ \Omega(E^0 - E_r) &= \Omega(E^0) e^{-\beta E_r}, \end{aligned}$$

it follows that :

$$P_r = C e^{-\beta E_r}.$$

Again C is another constant independent of r . Probabilities have to be normalized, so :

$$\begin{aligned} \sum_r P_r &= 1, \\ C^{-1} &= \sum_r e^{-\beta E_r}, \end{aligned}$$

Leading to :

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad (3.1.2)$$

This expression is central in statistical physics, the exponential factor $e^{-\beta E_r}$ is called the “*Boltzmann factor*” and the probability distribution (3.1.2) is the “*canonical distribution*”. Any ensemble describing systems interacting with a heat bath characterized with a temperature T , following the canonical distribution (3.1.2), is called the “*canonical ensemble*”.

Application : Paramagnetism

Paramagnetism is a phenomenon due to atoms or molecules having a permanent magnetic momentum μ , which can generally stem from the spin of unpaired electrons in atomic orbitals, the magnetic momentum of electrons of an incomplete atomic sub-level, or the superposition of the two phenomena.

Consider a substance containing N_0 magnetic atoms (each atom have a spin $s = \frac{1}{2}$) per unit volume, placed in an external magnetic field H . We assume that each atom interact weakly with the other atoms and that the substance is at absolute temperature T . Then, what is the mean magnetic momentum $\bar{\mu}_H$ of such an atom ?

According the quantum mechanics, the spin of each atom can either point up or down, so that we have only two energy levels for each atom :

$$E_{\uparrow} = -\mu H \quad \text{and} \quad E_{\downarrow} = +\mu H.$$

Then, following (3.1.2) the probability of finding the atom in these two energy configuration is :

$$P_{\uparrow} = \frac{e^{-\beta E_{\uparrow}}}{e^{-\beta E_{\uparrow}} + e^{+\beta E_{\downarrow}}} \quad \text{and} \quad P_{\downarrow} = \frac{e^{+\beta E_{\downarrow}}}{e^{-\beta E_{\uparrow}} + e^{+\beta E_{\downarrow}}}.$$

At this point, we introduce a new quantity $y = \frac{\mu H}{kT}$. Then, the mean value $\bar{\mu}_H$ is :

$$\bar{\mu}_H = \frac{P_{\uparrow}\mu + P_{\downarrow}(-\mu)}{P_{\uparrow} + P_{\downarrow}} = \mu \frac{e^y - e^{-y}}{e^y + e^{-y}} = \mu \tanh y$$

The *magnetization* M_0 , or the mean magnetic moment per unit volume in the direction of H is :

$$M_0 = N_0 \bar{\mu}_H \quad (3.1.3)$$

Now, we study the limiting cases of the magnetization, that is for high temperatures ($y \ll 1$) and for $T \rightarrow 0$ ($y \gg 1$).

- **High temperatures** : $y \ll 1$

In this case, $\tanh y \approx y$. Then :

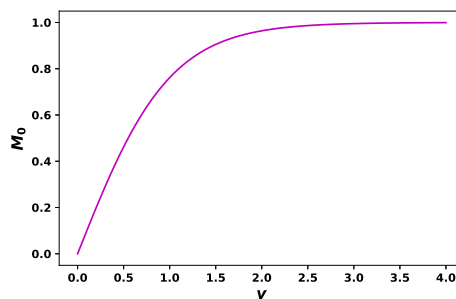
$$M_0 \approx N_0 y = N_0 \underbrace{\frac{\mu^2}{kT}}_{\chi} H = \chi H, \quad (3.1.4)$$

where χ is called the “*magnetic susceptibility*” of the substance and it is independent of H . The fact that $\chi \propto T^{-1}$ is called *Curie’s law*.

- **Low temperatures** : $y \gg 1$ In this limit, $\tanh y \approx 1$. Then, the magnetization of the substance reaches a saturation stage, as :

$$M_0 \rightarrow N_0 \mu, \quad (3.1.5)$$

which is completely independent of the magnetic field H . A summary of the previous results is shown in Figure. 6.1.1



3.1.3 Other ensembles

Previously, with the canonical ensemble we supposed that the system is exchanging the energy E with a heat bath. Now, imagine the system exchanging the energy E and some quantity X . Following the reasoning of the canonical ensemble, the probability P_r of finding the system A in a microstate r is :

$$P_r(E_r, X_r) \propto \Omega(E^0 - E_r, X^0 - X_r),$$

again, we suppose that $A \ll A'$ so that $E_r \ll E^0$ and $X_r \ll X^0$. Thus,

$$\ln \Omega(E^0 - E_r, X^0 - X_r) = \ln \Omega(E^0, X^0) - \left[\frac{\partial \ln \Omega}{\partial E'} \right]_0 E_r - \left[\frac{\partial \ln \Omega}{\partial X'} \right]_0 X_r \dots$$

Then :

$$\Omega(E^0 - E_r, X^0 - X_r) = \Omega(E^0, X^0) e^{-\beta E_r - \alpha X_r}$$

Finally :

$$P_r \propto e^{-\beta E_r - \alpha X_r} \quad (3.1.6)$$

A particular example is *the grand canonical ensemble*, in which $X = N$, meaning that the system can exchange the energy E and the particles N . The parameter β is the temperature of the ensemble, and $\alpha = \frac{-\mu}{kT}$, where μ is *the chemical potential* of the reservoir.

3.2 Our lord and savior “Z”

Statistical physics has a dear friend that we've been trying our best to hide so far. This friend, is our greatest ally in order to grasp the physical situations of our interest.

3.2.1 Connections with thermodynamics

The mean energy of a system described using the canonical distribution (3.1.2) is given by :

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}, \quad (3.2.1)$$

where we perform the sum over all accessible states r of the system. From now on, our friend will make his debut.

Notice that the formula (3.2.1), can be rewritten in much simpler form by using the fact that :

$$\sum_r e^{-\beta E_r} E_r = - \sum_r \frac{\partial}{\partial \beta} (e^{-\beta E_r}) = - \frac{\partial}{\partial \beta} Z,$$

where :

$$Z = \sum_r e^{-\beta E_r}. \quad (3.2.2)$$

Then, the mean energy (3.2.1) reduces to :

$$\bar{E} = - \frac{1}{Z} \frac{\partial}{\partial \beta} Z = - \frac{\partial \ln Z}{\partial \beta}. \quad (3.2.3)$$

The quantity (3.2.2) is a sum over states, called **the partition function**. Z is used as symbol for the partition function due to its name in German “*Zustandssomme*”.

The partition function is, as we will see later on, the most important quantity in statistical physics. In fact, the sole goal of statistical mechanics is to calculate the partition function as all important physical quantities can be expressed via Z . That is why it is considered as our greatest ally.

The dispersion in energy can also be computed :

$$\overline{(\Delta E)^2} = \overline{E^2} - \bar{E}^2,$$

where

$$\overline{E^2} = \frac{\sum_r e^{-\beta E_r} E_r^2}{\sum_r e^{-\beta E_r}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}.$$

Notice that :

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta} + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

Then :

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (3.2.4)$$

Or

$$\overline{(\Delta E)^2} = kT^2 \left(\frac{\partial \bar{E}}{\partial T} \right)_{V,N} = kT^2 C_V, \quad (3.2.5)$$

where C_V is the heat capacity at constant volume.

We saw that the pressure can be given in term of the energy as :

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

then the mean value of the pressure is :

$$\bar{P} = \sum_r P_r \mathcal{P}(E_r) = \frac{1}{Z} \sum_r \left(\frac{\partial E_r}{\partial V} \right) e^{-\beta E_r}.$$

In fact, we can write $\frac{\partial}{\partial V} e^{-\beta E_r} = -\beta e^{-\beta E_r} \frac{\partial}{\partial V} E_r$. Then :

$$\bar{P} = \frac{1}{\beta Z} \frac{\partial Z}{\partial V} \quad (3.2.6)$$

Suppose now that the number of particle is fixed, the partition function depends on only the temperature T (β) and the volume V :

$$Z = Z(T, V)$$

Then, we can write :

$$\begin{aligned} d \ln Z &= \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial V} dV \\ &= -\bar{E} d\beta + \beta \bar{P} dV, \end{aligned}$$

while

$$d(\beta \bar{E}) = \bar{E} d\beta + \beta d\bar{E}.$$

It follows then :

$$d(\ln Z + \beta \bar{E}) = \beta \bar{P} dV + \beta d\bar{E},$$

furthermore, we have :

$$d\bar{E} = T dS - \bar{P} dV.$$

Thus :

$$d(\ln Z + \beta \bar{E}) = \beta T dS = \frac{dS}{k}.$$

Finally, the entropy is:

$$S = k(\ln Z + \beta \bar{E}), \quad (3.2.7)$$

at the limit $\beta \rightarrow \infty$ ($T \rightarrow 0$), $S \rightarrow k \ln c$, where c is a constant which is consistent with the third law of thermodynamics.

The entropy equation (3.2.7), can also be written as : $TS = kT \ln Z + \bar{E}$. Then the free energy is :

$$F = \bar{E} - TS = -kT \ln Z. \quad (3.2.8)$$

Application : The one dimensional harmonic oscillator

The 1D harmonic oscillator is a famous model in physics, it is used to describe any physical situation where the potential energy is a quadratic function of the coordinate, such as the vibration of molecule around its position of equilibrium.

Quantum mechanics imposes the discreteness of energy spectrum of the 1D harmonic oscillator, the energy levels of such a system is given by :

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad \text{where} \quad n = 0, 1, 2, \dots$$

The partition function is then :

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta \left(n + \frac{1}{2}\right) \hbar \omega} \\ &= e^{-\beta \frac{\hbar \omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega}. \end{aligned}$$

Time for change of variables, we put $r = e^{-\beta \hbar \omega}$. Then, using the property of geometric series, we have :

$$Z = e^{-\beta \frac{\hbar \omega}{2}} \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{1}{e^{\beta \frac{\hbar \omega}{2}} - e^{-\beta \frac{\hbar \omega}{2}}} = \frac{1}{2 \sinh(-\beta \frac{\hbar \omega}{2})}.$$

Then, the thermodynamical quantities can be easily calculated :

$$\begin{aligned} \bar{E} &= -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar \omega}{2} \coth\left(\beta \frac{\hbar \omega}{2}\right), \\ S &= k(\ln Z + \beta \bar{E}) = k \left[-\ln \left(2 \sinh \left(\frac{\hbar \omega}{2kT} \right) \right) + \frac{\hbar \omega}{2kT} \coth \left(\frac{\hbar \omega}{2kT} \right) \right], \\ F &= -kT \ln Z = kT \ln \left(2 \sinh \left(\frac{\hbar \omega}{2kT} \right) \right) \end{aligned}$$

3.3 Statistics of Ideals Gases

Ideal gases are systems consisting of a bunch of particles flying around and that do not interact with each other (negligible mutual interactions). The goal of this section is to construct a complete description of ideal gas, which cannot be achieved without a knowledge on the symmetry requirements and the statistical distribution functions.

3.3.1 Symmetries

Consider a gas consisting of N identical particles in a container of volume V . The coordinate and the state of each particle is given respectively by X_i and s_i . The wave function of the whole gas is then :

$$\Psi = \Psi_{\{s_1, \dots, s_N\}}(X_1, X_2, \dots, X_N) \quad (3.3.1)$$

Classical treatment

Particles can be described either using classical or quantum mechanics. Although, in general, the classical approach is inadequate, here in the case of ideal gases where the temperature is not so close to the absolute zero which is the quantum realm, will be a useful approximation to understand the behavior of ideal gases.

In a classical treatment, the particles are considered **distinguishable**, and any number of particles can be in the same state s . This description does not impose any symmetry requirement on the wave function when we interchange two particles. This is the so called “*Maxwell-Boltzmann statistics*” and as we will see later, this approach is wrong from a quantum mechanical point of view, but it is useful for comparison.

Quantum approach

Quantum mechanics distinguishes particles into two categories : bosons and fermions, where each class obeys its own statistics. This imposes some symmetry requirements on the wave function (3.3.1) when we interchange two particles and does not create a new state of the whole gas. What quantum mechanics really cares about in characterizing identical particles is not the identifiability of particles as it consider them **indistinguishable** (it implies also that it does not care about which particles occupies which state), but rather **how** many particles there are in each state s .

- **Bosons**

Particles with integral spin number e.g. 0, 1, 2, ... such as “photons” are called “*bosons*”. The wave function Ψ of the bosons remain unchanged after interchanging two particles, it is said to be “*symmetric*”.

$$\Psi(\dots X_i \dots X_j \dots) = \Psi(\dots X_j \dots X_i \dots). \quad (3.3.2)$$

Particles following (3.3.2) are said to obey “**Bose-Einstein statistics**”(BE statistics). Note that the particles are considered indistinguishable, and that there is no restriction on how many particles occupy a single state s .

- **Fermions**

Fermions are particles having a half-integer spin i.e. $\frac{1}{2}, \frac{3}{2}, \dots$ an example would be the case of an electron. The wave function of the fermions changes its sign after interchanging two particles, thus it is a *anti-symmetric* wave function.

$$\Psi(\dots X_i \dots X_j \dots) = -\Psi(\dots X_j \dots X_i \dots). \quad (3.3.3)$$

This change of sign is what will lead us to the famous “*Pauli exclusion principle*”. How is that ?

Suppose two particles i and j occupy the same state s , are interchanged. Then, we have :

$$\Psi(\dots X_i \dots X_j \dots) = \Psi(\dots X_j \dots X_i \dots).$$

Taking into account the symmetry requirement (3.3.3), imply that :

$$\psi = 0 \quad \text{when } i \text{ and } j \text{ are in the same state } s.$$

This is the so-called “*Pauli exclusion principle*”. When dealing with fermions one need to keep in mind that there can never be more than one particle in a given state s .

Particles following (3.3.3) are said to obey the “**Fermi-Dirac statistics**”(FD statistics).

Illustration

Imagine a gas of two particles A and B , each particle can be in one of three possible states $s = 1, 2, 3$. Taking into account the symmetry requirement we discussed earlier, let us count the possible states of the gas.

- **Maxwell-Boltzmann statistics :**

The particles are distinguishable, then :

1	2	3
AB
...	AB	...
...	...	AB
A	B	...
B	A	...
A	...	B
B	...	A
...	A	B
...	B	A

Each particle can be in any one of the three states. Thus, there exist $3^2 = 9$ possible states of the whole gas.

- **Bose-Einstein statistics :**

The particles are now indistinguishable, which means that $A = B$, Then :

1	2	3
AA
...	AA	...
...	...	AA
A	A	...
A	...	A
...	A	A

There exist $3 + 3 = 6$ possible states of the whole gas.

- **Fermi-Dirac statistics :**

The particles are again indistinguishable, but only one particle can occupy a single state s . Then :

1	2	3
A	A	...
A	...	A
...	A	A

There exist only 3 possible states of the whole gas.

3.3.2 Statistical distribution functions

Consider a gas of identical particles characterized by a volume V , temperature T and a number of possible quantum states R . Each particle can be in quantum state labeled by r with an energy ϵ_r and the number of particles occupying the state r is n_r .

Since we are dealing with ideal gases, the total energy of the gas is given by :

$$E_R = n_1\epsilon_1 + n_2\epsilon_2 + \dots = \sum_r n_r\epsilon_r,$$

where the sum is over all possible quantum states r . When the total number of particles in the gas is known to be N , we have : $\sum_r n_r = N$.

Now, we call for our dear friend “ Z ”, the partition function, with which we can calculate the thermodynamic quantities :

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)},$$

where the sum now runs over all possible states R of the gas. Then, the mean number of particles in a state s is :

$$\begin{aligned} \bar{n}_s &= \frac{\sum_R n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}}{\sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}} \\ &= \frac{1}{Z} \sum_R \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \right) e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} \\ &= -\frac{1}{\beta Z} \frac{\partial Z}{\partial \epsilon_s}, \end{aligned}$$

or :

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} \quad (3.3.4)$$

Maxwell-Boltzmann statistics

The Maxwell-Boltzmann statistics takes into account the distinguishability of particles, as a result the partition function given by :

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}, \quad (3.3.5)$$

need to consider this property. If there is a total of N particles and for given values $\{n_1, n_2, \dots\}$, there are :

$$\frac{N!}{n_1!n_2!\dots},$$

possible way in which we can arrange n_1 particles in the first state, n_2 in the second state, \dots . Thus, the partition function (3.3.5) can be written as :

$$Z = \sum_{n_1, n_2, \dots} \frac{N!}{n_1!n_2!\dots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}, \quad (3.3.6)$$

where we sum again over all values $n_r = 0, 1, 2, \dots$, subjected to the restriction :

$$\sum_r n_r = N.$$

The partition function (3.3.6) is then :

$$Z = \sum_{n_1, n_2, \dots} \frac{N!}{n_1! n_2! \dots} \left(e^{-\beta \varepsilon_1} \right)^{n_1} \left(e^{-\beta \varepsilon_2} \right)^{n_2} \dots, \quad (3.3.7)$$

or :

$$\ln Z = N \ln \left(\sum_r e^{-\beta \varepsilon_r} \right). \quad (3.3.8)$$

Then, the mean number of particles in a state s is :

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_s} = -\frac{1}{\beta} N \frac{-\beta e^{-\beta \varepsilon_s}}{\sum_r e^{-\beta \varepsilon_r}},$$

or

$$\bar{n}_s = N \frac{e^{-\beta \varepsilon_s}}{\sum_r e^{-\beta \varepsilon_r}}. \quad (3.3.9)$$

The distribution (3.3.9) is called : the **Maxwell-Boltzmann distribution**.

Photon statistics

Now, we will consider that the total number N is not fixed, this is a *special* case of the Bose-Einstein statistics. The partition function is given by :

$$Z = \sum_R e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots)},$$

the summation is over all values $n_r = 0, 1, 2, \dots$ for each r . Then :

$$\begin{aligned} Z &= \sum_{n_1, n_2, \dots} e^{-\beta n_1 \varepsilon_1} e^{-\beta n_2 \varepsilon_2} e^{-\beta n_3 \varepsilon_3} \dots \\ &= \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \varepsilon_1} \right) \left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \varepsilon_2} \right) \left(\sum_{n_3=0}^{\infty} e^{-\beta n_3 \varepsilon_3} \right) \dots \end{aligned}$$

Notice that each sum is just an infinite geometric series. Thus, the partition function can be written as :

$$\begin{aligned} Z &= \left(\frac{1}{1 - e^{-\beta \varepsilon_1}} \right) \left(\frac{1}{1 - e^{-\beta \varepsilon_2}} \right) \left(\frac{1}{1 - e^{-\beta \varepsilon_3}} \right) \dots \\ \ln Z &= -\sum_r \ln \left(1 - e^{-\beta \varepsilon_r} \right). \end{aligned}$$

Using (3.3.4), we find the mean number of particles in the state s :

$$\bar{n}_s = \frac{1}{e^{\beta \varepsilon_s} - 1}. \quad (3.3.10)$$

This is called the “**Planck distribution**”.

Fermi-Dirac statistics

Now, we return to the case where the total number N of particles is fixed : $\sum_r n_r = N$. Recall that the mean of the number of particles can be written as :

$$\bar{n}_s = \frac{\sum_R n_s e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}{\sum_R e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}} \quad (3.3.11)$$

$$= \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s} \sum_{n_1 \dots n_2}^{(s)} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}{\sum_{n_s} e^{-\beta n_s \epsilon_s} \sum_{n_1 \dots n_2}^{(s)} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}. \quad (3.3.12)$$

Fixing the number of particles means that when a particle occupy a state s , the sum $\sum^{(s)}$ in (3.3.12) runs over the remaining $(N - 1)$ particles. Then, Let :

$$Z_s(N) = \sum_{n_1, n_2, \dots}^{(s)} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad \text{with} \quad \sum_r^{(s)} n_r = N, \quad \text{the state } s \text{ is omitted from the sum.}$$

Summing over $n_s = 0, 1$ in (3.3.12), yield to :

$$\bar{n}_s = \frac{0 + e^{-\beta \epsilon_s} Z_s(N-1)}{Z_s(N) + e^{-\beta \epsilon_s} Z_s(N-1)} \quad (3.3.13)$$

$$= \frac{1}{\left[\frac{Z_s(N)}{Z_s(N-1)} \right] e^{-\beta \epsilon_s} + 1}. \quad (3.3.14)$$

To proceed we need a relation between $Z_s(N)$ and $Z_s(N-1)$, if $\Delta N \ll N$ we can write :

$$\ln Z_s(N - \Delta N) = \ln Z_s(N) - \frac{\partial Z_s}{\partial N} \Delta N = \ln Z_s(N) - \alpha_s \Delta N, \quad \text{where} \quad \alpha_s = \frac{\partial Z_s}{\partial N},$$

or

$$Z_s(N - \Delta N) = Z_s(N) e^{-\alpha_s \Delta N}. \quad (3.3.15)$$

At this point, we introduce an approximation : $\alpha_s = \alpha$. The motivation is that, since we are summing over many states, the coefficient α_s should be independent of the choice of s . Then, we have :

$$\alpha = \frac{\partial \ln Z_s}{\partial N}.$$

Thus, taking into account $\Delta N = 1$, (3.3.14) can be written as :

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1}. \quad (3.3.16)$$

α can be determined by either the condition $\sum_r \bar{n}_r = N$, or by noticing that the free energy F can be written as $F = -\frac{1}{kT} \partial \ln Z$. Then, we have :

$$\alpha = -\frac{1}{kT} \frac{\partial F}{\partial N} = -\frac{\mu}{kT} = -\beta \mu,$$

where μ is the chemical potential. Then, we have :

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}. \quad (3.3.17)$$

This is called the **Fermi-Dirac distribution**.

Bose-Einstein statistics

The reasoning we followed to derive the FD distribution, can be extended to the BE statistics as well. In this case, the sum (3.3.12) ranges over all values of the numbers n_1, n_2, \dots such that $n_r = 0, 1, 2, 3, \dots$ and taking into account the the total number of particles in fixed. Then, we have :

$$\bar{n}_s = \frac{0 + e^{-\beta\epsilon_s} Z_s(N-1) + 2e^{-2\beta\epsilon_s} Z_s(N-2) + \dots}{Z_s(N) + e^{-\beta\epsilon_s} Z_s(N-1) + e^{-2\beta\epsilon_s} Z_s(N-2) + \dots}$$

Using (3.3.15) and the approximation $\alpha_s = \alpha$, we get :

$$\bar{n}_s = \frac{Z_s(N) (0 + e^{-\beta\epsilon_s} e^{-\alpha} + 2e^{-2\beta\epsilon_s} e^{-2\alpha} + \dots)}{Z_s(N) (1 + e^{-\beta\epsilon_s} e^{-\alpha} + 2e^{-2\beta\epsilon_s} e^{-2\alpha} + \dots)},$$

or in a more compact form :

$$\bar{n}_s = \frac{\sum_s n_s e^{-n_s(\alpha + \beta\epsilon_s)}}{\sum_s e^{-n_s(\alpha + \beta\epsilon_s)}}.$$

Thus :

$$\bar{n}_s = \frac{1}{e^{(\beta\epsilon_s + \alpha)} - 1}. \quad (3.3.18)$$

$\alpha = -\beta\mu$ is again the chemical potential and the formula (3.3.18) represents the “**Bose-Einstein statistics**”.

Remarks

- **BE vs FD statistics :**

Systems obeying BE or FD statistics behave differently, especially at the limit $T \rightarrow 0$. Consider for instance a gas consisting of a fixed number N of particles and suppose that the lowest energy of a single particle is ϵ_1 .

BE statistics is fine with having multiple particles in the same state, so to reach the lowest energy of the whole gas (at $T \rightarrow 0$), all the particles need to be placed in their lowest-lying state of energy ϵ_1 .

However, FD statistics allows only one particle to occupy a given state. Then, in order to reach the lowest energy state of the whole gas, one need to populate all the single-particle states starting from the state of the lowest energy ϵ_1 until all the particles are accommodated. The gas as a whole is in its state of lowest energy, but there are particles that have a very high energy compared to ϵ_1 .

- **Classical limit of quantum statistics:**

The classical limit can be reached at high temperatures ($\beta \rightarrow 0$). How this limit affects BE and FD statistics ?

As $\beta \rightarrow 0$ in Equations (3.3.17) and (3.3.18), large energies ϵ_r contribute to the sum. To prevent this sum from exceeding N , α must become large enough to that each ϵ_r is sufficiently small. That is $e^{\alpha + \beta\epsilon_r} \gg 1$, then FD and BE statistics reduces to :

$$\bar{n}_r = e^{-\alpha - \beta\epsilon_r},$$

α can be determined by the condition :

$$\sum_r e^{-\alpha - \beta\epsilon_r} = e^{-\alpha} \sum_r e^{-\beta\epsilon_r} = N$$

$$\bar{n}_r = N \frac{e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}}.$$

Then, in the classical limit BE and FD statistics reduces to MB statistics.



Phase Transitions and Critical Phenomena

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4. Introduction

In our everyday life, we use water in different forms that ranges from liquid, ice to steam. These forms are called *phases* which are states (of minimum free energy) of water upon some macroscopic condition. While changing the external parameters of a system, such as the temperature and the pressure, we can jump from a phase to another and this is what we call a *phase transition*. A phenomenon that is captured by an abrupt change of the properties of the substance which is reflected by a singularity in the thermodynamical quantities (i.e. the free energy) of the system or in its derivatives.

The transformation from liquid to gas, from a paramagnetic substance to a ferromagnetic material or from a normal metal to a superconductor are prominent examples of phase transitions. Our goal in this part of the course is to describe systematically phase transitions, how they occur in nature, in practice and how to classify them. We will also present a simple lattice model- the Ising model- which is considered the *drosophila* of statistical mechanics and we will not shrink from using it because of its simplicity and its important results.

4.1 The liquid-gas transition.

The different phases of matter arises as a consequence of interactions among a large number of atoms or molecules at a given thermodynamical condition, to illustrate the phenomenon we use the phase diagram of water depicted in Fig. 4.1.1. The diagram represent in the P - T plan the different phases of water : solid, liquid and gas, while the solid lines separate the phases and the coexistence zones. The AB curve, called the “**sublimation curve**”, separates the solid and the vapor phases, while they coexist along the curve. The BD line, called the “**fusion curve**”, represents the coexistence zone of the solid and the liquid phases. The BC branch, is the “**vaporization curve**”, where the liquid phase coexists with the vapor phase.

The phase diagram of water has two interesting points: the first is, B, where all the phases coexist and is called “*the triple point*”. For water, the value of the triple point is 273.16 K. The other one is C, called the critical point, at this point the density of the liquid and the gas are equal, so we cannot distinguish the two phases. After crossing the point C, water transits continuously from liquid to gas.

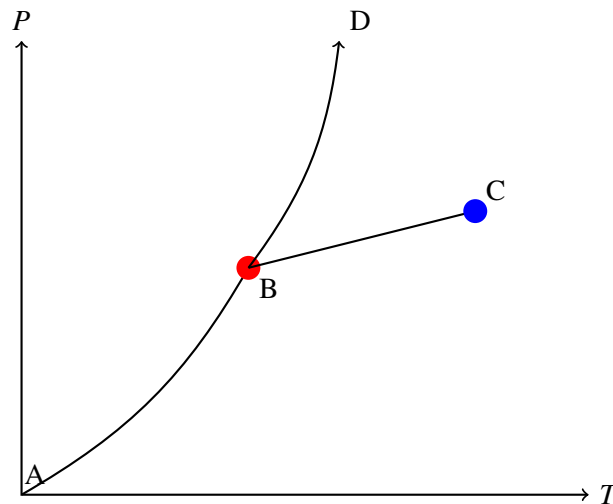


Figure 4.1.1: Phase diagram of water.

4.2 The ferromagnetic transition.

The ferromagnetic-paramagnetic transition is another good example of phase transitions, which happens experimentally when we heat up a ferromagnetic material above *the Curie temperature*, where ferromagnetism is destroyed and paramagnetism takes place.

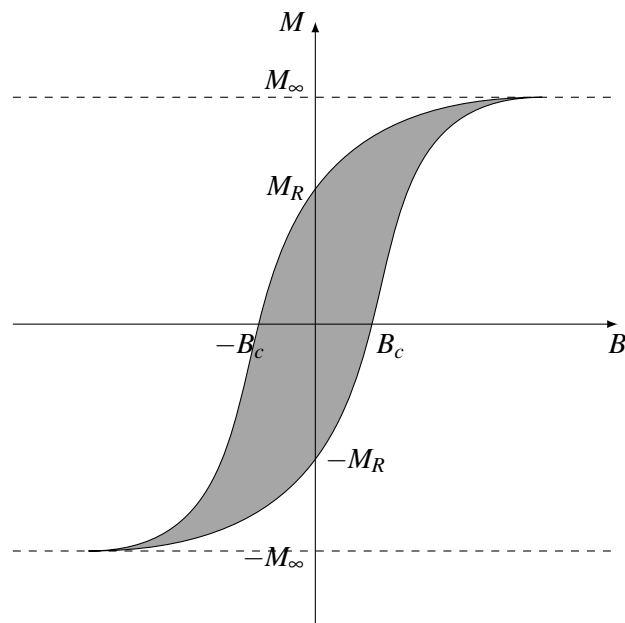


Figure 4.2.1: Hysteresis cycle

When a magnetic field B interacts with a ferromagnetic material, its magnetization M increase and saturates to a value M_∞ . Decreasing the magnetic field, decreases the magnetization but it does not vanish when B is zero, but rather it reaches a value M_R called *retentive magnetization*. To destroy the magnetization completely, a *coercive* magnetic field $-B_c$ is needed and decreasing the magnetic field further and further the magnetization reaches another saturation point M_∞ . Finally, increasing the magnetic field takes the magnetization to another retentive point $-M_R$ and to another point

where it vanishes at B_c . We say that the magnetization form a **Hysteresis cycle** represented in Fig. 4.2

Ferromagnetism can be understood via Weiss' hypothesis, which states that ferromagnetic materials has a *domain* structure, small on a macroscopic level and big on a microscopic level. Each domain has it own spontaneous magnetization which reaches a maximum value when we apply a magnetic field B below the Curie temperature, and because each domain will be oriented in a different direction, on a macroscopic level the material is far from reaching a saturation magnetization. The phase diagram of a ferromagnetic material is represented in Fig. 4.2.

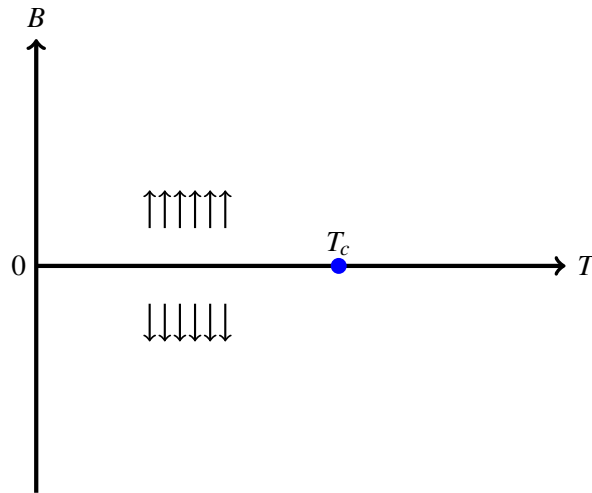


Figure 4.2.2: Phase diagram of a ferromagnetic material.

5. How Phase Transitions Occur in Principle

5.1 Preliminaries.

Phase transitions are studied through the behavior of the thermodynamical quantities of the system, mostly we choose the free energy F . Functions of free energy are often a convex or a concave function of thermodynamic parameters.

5.1.1 Concavity and Convexity.

$f(x)$ is a convex function of x if :

$$f\left(\frac{x_1 + x_2}{2}\right) \leq \frac{f(x_1) + f(x_2)}{2} \quad \text{for all } x_1 \text{ and } x_2.$$

Which means that the chord joining the points $f(x_1)$ and $f(x_2)$ lies above of $f(x)$ for all x in $x_1 < x < x_2$. Likewise, $f(x)$ is a concave function of x if :

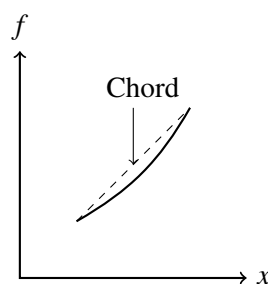


Figure 5.1.1: Convex function.

$$f\left(\frac{x_1 + x_2}{2}\right) \geq \frac{f(x_1) + f(x_2)}{2} \quad \text{for all } x_1 \text{ and } x_2.$$

That is the chord joining the points $f(x_1)$ and $f(x_2)$ lies below of $f(x)$ for all x in $x_1 < x < x_2$. If the function is differentiable and the derivative $f'(x)$ exists, then a tangent to a convex (concave)

function always lies below (above) the function except at the point of tangent. While for the second derivative $f''(x)$, if it exists, then for a convex (concave) function $f''(x) \geq 0$ (≤ 0) for all x .

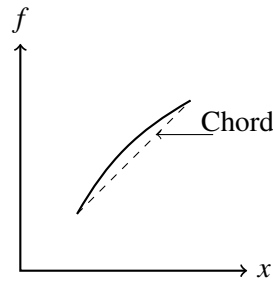


Figure 5.1.2: Concave function

The specific heat and the susceptibility (for magnetic materials) are positive thermodynamical response function, which implies that the free energy F is convex. This is a direct consequence of Le Chatelier's principle for stable equilibrium which states that : if a system is in thermal equilibrium any small spontaneous fluctuation in the system parameter, the system gives rise to certain processes that tends to restore the system back to equilibrium.

5.1.2 Existence of the Thermodynamic limit.

The goal of statistical mechanics is to compute the partition function Z , as it links to all the thermodynamical quantities. The free energy is :

$$F_{\Omega} = -k_b T \log Z_{\Omega},$$

all the necessary information on the thermodynamics of the system Ω is encoded in the derivatives of the free energy F_{Ω} , including bulk effects, surface effects and finite size effects. However, when Ω is finite, there is no information about phase transitions or phases as this phenomena occurs *theoretically* in the thermodynamic limit that is $\Omega \rightarrow \infty$.

The existence of the thermodynamic limit is not trivial as it fails to exist for some systems. In order for this limit to exist, the system must satisfy some certain properties so that a uniform bulk behaviour can exist. To see this, consider a charged system at $T = 0$ in 3 dimensions, the interaction between two particles separated by a distance r is given by Coulomb's law :

$$U(r) = A/r,$$

with A being a constant. Then, the energy for a spherical system of radius R is :

$$\begin{aligned} E &= \int_0^R \left(\frac{4}{3} \pi r^3 \rho \right) \frac{A}{r} 4\pi r^2 \rho dr \\ &= A \frac{(4\pi)^2}{15} \rho^2 R^5. \end{aligned}$$

The energy per unit volume is then : $\varepsilon = A \frac{(4\pi)^2}{15} \rho^2 R^2$, which diverges as $R \rightarrow \infty$. Thus, inverse square law forces like gravity and electrostatics are too long-ranged to permit thermodynamic behaviour. A result that is a consequence of only allowing charges of one sign, if we have positive and negative charges the interaction is no long ranged.

A more general case is where the interaction potential is of the form :

$$U(r) = A/r^m,$$

in this case, the energy per unit volume of a unit sphere in d -dimensions is :

$$\varepsilon \sim R^{d-m}.$$

Taking the limit $R \rightarrow \infty$, the system is stable only when $m > d$. The thermodynamic limit exist then only when $m > d$.

5.1.3 Phase boundaries and Phase transitions.

Consider a finite system Ω , who's Hamiltonian can be written as :

$$H_{\Omega} = -k_b T \sum_n K_n \theta_n,$$

where K_n are coupling constants and θ_n are local operators that encodes information on the dynamical degrees of freedom.

The free energy is an extensive quantity, that is $F_{\Omega} \propto V(\Omega)$. Then, for finite systems we have :

$$F_{\Omega} = V(\Omega)f_b + S(\Omega)f_s + O(L^{d-2}),$$

where f_b is the bulk free energy per unit volume and f_s is the surface free energy per unit area. Phases and phase boundaries can be defined when $f_b[K]$ exists. Suppose we have D coupling constants, then the phase diagram has K_1, K_2, \dots, K_D axes and the dimension of the phase diagram is D . $f_b[K]$ is analytic almost everywhere, the possible locations of non-analyticities of $f_b[K]$ are points, lines, planes and hyperplanes, etc, having a dimentionality D_s . Thus we can define the codimension C , which is an invariant quantity for each type of singular location :

$$C = D - D_s$$

Then, a phase is just a region of analycity of $f_b[K]$ and loci of codimension $C = 1$ is called a phase boundary.

$f_b[K]$ can be used also to classify phase transitions :

- **First order phase transitions**

If one or more $\partial f_b / \partial K_i$ are discontinuous across a phase boundary, the transition is first order.

- **Continous phase transitions**

If the first derivative of $f_b[K]$ is countinuous across the phase boundary, the transition is said to be countinuous phase transitions (or a second order phase transition)

5.2 The Ising model.

Models are a way to describe approximately our reality, in statistical physics and in particular in the study of phase transitions, we come across different models such as : the Ising model, the Heisenberg model, the Potts model, the Baxter model ... etc. These models are systems for which the partition function can be found exactly and through out this course we will be dealy primarily with the Ising model, a simple model describe ferromagnets or antiferromagnets which was solved in a *tour de force* back in 1944 by Lars Onsager, but to this day the 3 dimensional Ising model is not yet solved exactly.

The Ising model was first studied by Lenz and Ising in 1925, they showed that in one dimension and at finite temperatures ($T > 0$) the model has no phase transitions. Then, they concluded *incorrectly* that for higher dimensions and finite temperatures, the model exhibit no phase transitions, and so the model could not describe real magnetic systems.

The degrees of freedom in the Ising model are classical spin variables S_i that resides in a d -dimension lattice of sites $\{i\}$ labelled $1 \dots N(\Omega)$ and taking only two values ± 1 . The spins interacts with each other through *the exchange interaction* J_{ij}, K_{ijk}, \dots which couples two spins, three spins, ... etc. The spins also interacts with an external magnetic field H_i which, in general, varies from site to site. Thus, the Ising model can be written as :

$$-H_\Omega = \sum_{i \in \Omega} H_i S_i + \sum_{ij} J_{ij} S_i S_j + \sum_{ijk} K_{ijk} S_i S_j S_k + \dots \quad (5.2.1)$$

In the following, we will restrict ourselves only to two spins interactions, so that Eq. 5.2.1 becomes:

$$-H_\Omega = \sum_{i \in \Omega} H_i S_i + \sum_{ij} J_{ij} S_i S_j \quad (5.2.2)$$

Phase transitions arises only in the thermodynamic limit, for this limit to exist the exchange energy need to satisfy the following conditions :

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

That is, the exchange interaction J_{ij} between S_i and S_j has to get weaker and weaker as the distance between them gets bigger in the lattice.

The free energy is given by :

$$F_\Omega(T, H_i, J_{ij}) = -k_b T \log \text{Tr} e^{-\beta H_\Omega}$$

Thermodynamical properties can be calculated through F_Ω , for example the magnetization at site i is :

$$\begin{aligned} \frac{\partial F_\Omega}{\partial H_i} &= -k_b T \frac{1}{\text{Tr} e^{-\beta H_\Omega}} \text{Tr} \frac{S_i}{k_b T} e^{-\beta H_\Omega} \\ &= -\langle S_i \rangle_\Omega \end{aligned}$$

5.2.1 Symmetries

Investigating the symmetries of spin models is helpful as it provides insights on the physical properties of the model, for instance we can show the impossibility of phase transitions in finite systems using a symmetry argument.

Spin-reversal symmetry

The Ising model is Z_2 symmetric. That is a rotation of π of all the spins, leave the system energy unchanged. Mathematically, this implies that :

$$H_\Omega(H, J, S_i) = H_\Omega(-H, J, -S_i).$$

Thus :

$$\begin{aligned} Z_\Omega(-H, J, T) &= \sum_{S_i = \pm 1} e^{-\beta H_\Omega(-H, J, S_i)} \\ &= \sum_{S_i = \pm 1} e^{-\beta H_\Omega(-H, J, -S_i)} \\ &= \sum_{S_i = \pm 1} e^{-\beta H_\Omega(H, J, S_i)} \\ &= Z_\Omega(H, J, T). \end{aligned}$$

The free energy is then :

$$F(H, J, T) = F(-H, J, T)$$

Sub-lattice symmetry

This symmetry emerges at zero magnetic field ($H = 0$). We divide the lattice into two interpenetrating lattices A and B . The spins of lattice A interacts only with the ones in the lattice B . The Hamiltonian is :

$$H_{\Omega}(0, J, S_i^A, S_i^B) = -J \sum_{\langle ij \rangle} S_i^A S_j^B$$

The sub-lattice symmetry implies that :

$$\begin{aligned} H_{\Omega}(0, -J, S_i^A, S_i^B) &= H_{\Omega}(0, J, -S_i^A, S_i^B) \\ &= H_{\Omega}(0, J, S_i^A, -S_i^B). \end{aligned}$$

Now, we ask how this symmetry affects the partition function. In zero field we write :

$$\begin{aligned} Z_{\Omega}(0, -J, T) &= \text{Tr} e^{-\beta H_{\Omega}(0, -J, T)} \\ &= \sum_{S_i^A} \sum_{S_j^B} e^{-\beta H_{\Omega}(0, -J, S_i^A, S_j^B)} \\ &= \sum_{S_i^A} \sum_{S_j^B} e^{-\beta H_{\Omega}(0, J, -S_i^A, S_j^B)} \\ &= \sum_{S_i^A} \sum_{S_j^B} e^{-\beta H_{\Omega}(0, J, S_i^A, S_j^B)} \\ &= Z_{\Omega}(0, J, T). \end{aligned}$$

Then, the free energy satisfies the following :

$$F(0, J, T) = F(0, -J, T).$$

The sub-lattice symmetry implies that the thermodynamics of the ferromagnetic Ising model and that of the anti-ferromagnetic Ising model are the same at zero magnetic field.

5.3 Existence of Phase Transition

The phase diagram is a guide map of the different phases a system or a model has. One strategy to construct the phase diagram is through *the energy-entropy argument*. We study the free energy at high and low temperatures and if the macroscopic states of the system obtained by the two limits are different, then we conclude that at least one phase transition has occurred at some temperature.

5.3.1 Zero temperature Phase Diagram

Consider the Ising model in d -dimensions at $T = 0$. The problem of calculating the free energy is reduced to finding just the internal energy E of the system. Now suppose that we have available the energy configurations of our system, that is we know the configuration that minimize the energy, the ground state, of our system with respect to some coupling constant $[K]$, and we know the first excited state ... and so on. We probe our system in some interval of $[K]$, and it may happen that when our system crosses a set of values $[K_c]$ the first excited state become the ground state of the system. This is generally what happens with first order phase transitions and this phenomena is called **level-crossing** depicted in Fig. 5.3.1.

It is important to note here, that this mechanism occurs not necessarily at the thermodynamic limit. Here, the non-analyticity roots back to taking the limit $\beta \rightarrow \infty$ and not $N \rightarrow \infty$.

However, the long range order is possible at $T = 0$, because the free energy has only one term that depends on J , which forces the ground states to have two configurations, either all up spins or all down spins. We conclude then that phase transitions can occur only at zero temperature in the one dimensional Ising model.

5.3.3 2D Phase Diagram

We consider again a domain of flipped spins, in a background of spins with long range order, but this time the domain in two dimensional. What is the energy difference ? and what is the entropy? Since each flipped spin costs an amount of energy of $2J$, then the internal energy change of a domain of length L is $\Delta E = 2JL$. The entropy can be estimated by enumerating the different possibilities of the domain wall, it turns out that this number is proportional to the coordinate number of the lattice z . The entropy is then $\Delta S = k_b L \log(z - 1)$ and the free energy is:

$$\Delta F = 2JL - (\log(z - 1)) k_b T L.$$

A scenario where the second term of the free energy is dominant, corresponds to the case where thermal fluctuations exceeds some critical temperature of the model, which means that long range order cannot exist. Accordingly, we anticipate at $T > T_c$ a disordered, paramagnetic phase with zero magnetization. When $T < T_c$, the term involving the interaction between the spins is dominant which support long-range order and the **spontaneous** magnetization can be non-zero in this regime.

5.3.4 Spontaneous Symmetry Breaking

The impossibility of phase transitions can be seen immediately from the spin-reversal symmetry of the Ising model. We know that the free energy satisfies the following :

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

and the magnetization satisfies :

$$\begin{aligned} N(\Omega)M_\Omega(H) &= -\frac{\partial F_\Omega(H)}{\partial H} \\ &= -\frac{\partial F_\Omega(-H)}{\partial H} \\ &= \frac{\partial F_\Omega(-H)}{\partial -H} \\ &= -N(\Omega)M_\Omega(-H). \end{aligned}$$

Then :

$$M_\Omega(H) = -M_\Omega(-H),$$

we are interested in the zero field case, thus:

$$M_\Omega(0) = -M_\Omega(-0) = 0.$$

This **impossibility theorem**, shows that the magnetization in $H = 0$ should be zero, a result that contradicts our previous finding. What has gone wrong ?

Our line of thoughts in deriving the impossibility theorem is indeed correct, but works only for finite systems and it fails for the thermodynamic limit. When $N \rightarrow \infty$ the free energy develops a discontinuity in its first derivative, and knowing the fact that $F(H)$ is a convex function, the condition $F(H) = F(-H)$ does not imply $M(0) = 0$, for that to happen we need to add the assumption of the

smoothness of the free energy at $H = 0$ and that the left and right derivatives are equal. The smoothness of F follows if :

$$F(H) = F(0) + O(H^p) \quad p > 1$$

and

$$\lim_{\varepsilon \rightarrow 0} \frac{F(+\varepsilon) - F(0)}{\varepsilon} = \lim_{\varepsilon \rightarrow 0} \frac{F(-\varepsilon) - F(0)}{\varepsilon} = 0$$

We can then turn around the impossibility theorem and still satisfy the analytical properties of the free energy by writing :

$$F(H) = F(0) - M_s |H| + O(H^p) \quad p > 1$$

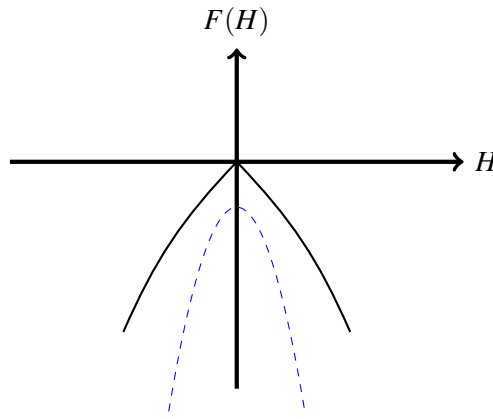


Figure 5.3.2: The free energy as function of H for a finite system (dashed line) and for an infinite system (solid line)

which is not differentiable at $H = 0$, but still hold the convexity property as depicted Fig. 5.3.2. Thus :

$$\frac{\partial F}{\partial H} = \begin{cases} -M_s + O(H^{p-1}), & H > 0 \\ -M_s + O(H^{p-1}), & H < 0. \end{cases}$$

As $|H| \rightarrow 0$, we have :

$$M = -\frac{\partial F}{\partial H} = \begin{cases} M_s, & H > 0 \\ -M_s, & H < 0. \end{cases}$$

The spontaneous magnetization is given by :

$$\pm M_s = \lim_{H \rightarrow 0^\pm} -\frac{\partial F}{\partial H}.$$

An important remark to rise, is that taking the limit :

$$\lim_{N(\Omega) \rightarrow \infty} \lim_{H \rightarrow 0} \frac{1}{N(\Omega)} \frac{\partial F_\Omega(H)}{\partial H} = 0 \quad \text{and} \quad \lim_{H \rightarrow 0} \lim_{N(\Omega) \rightarrow \infty} \frac{1}{N(\Omega)} \frac{\partial F_\Omega(H)}{\partial H} \neq 0$$

are not equal, that is the thermodynamic limit and taking $H \rightarrow 0$ do not commute.

Even though the Hamiltonian is invariant under spin reversal, the expectation values do not follow this symmetry, so that $\langle S_i \rangle \neq 0$ and :

$$M = \lim_{N \rightarrow \infty} \frac{1}{N(\Omega)} \sum_i \langle S_i \rangle \neq 0.$$

These phenomena is what we call **spontaneous symmetry breaking** . The use of the word “spontaneous” so we can distinguish this particular case from the case where the magnetization appears due to an external magnetic field.

6. How Phase Transitions Occur in Practice

In the previous chapter, we have introduced the basics of phase transitions and now it is time to put these ideas into practice. This chapter is about a method introduced by Kramers, called the **transfer matrix** which reduces the problem of finding the partition function to solving the eigenvalue system of a certain matrix. We also introduce Weiss' mean field theory and its limitations.

6.1 Transfer Matrix

We start with the Ising model in one dimension with nearest neighboring interactions:

$$-H_{\Omega} = H \sum_{i \in \Omega} S_i + \sum_{\langle ij \rangle} J_{ij} S_i S_j, \quad J > 0.$$

Let $h = \beta H$ and $K = \beta J$, and suppose periodic boundary conditions, that is $S_{N+1} = S_1$. Then, the partition function is :

$$\begin{aligned} Z_N(h, K) &= \text{Tr} \exp \left[h \sum_i S_i + K \sum_i S_i S_{i+1} \right] \\ &= \sum_{S_1} \dots \sum_{S_N} \left[e^{\frac{h}{2}(S_1+S_2)+KS_1S_2} \right] \cdot \left[e^{\frac{h}{2}(S_2+S_3)+KS_2S_3} \right] \dots \left[e^{\frac{h}{2}(S_N+S_1)+KS_NS_1} \right]. \end{aligned}$$

Each term in the partition function can be written as a matrix T :

$$T_{S_1 S_2} = e^{\frac{h}{2}(S_1+S_2)+KS_1S_2},$$

whose elements are :

$$T = \begin{pmatrix} T_{1,1} & T_{1,-1} \\ T_{-1,1} & T_{-1,-1} \end{pmatrix} = \begin{pmatrix} e^{h+K} & e^{-K} \\ e^{-K} & e^{-h+K} \end{pmatrix} \quad (6.1.1)$$

the partition function can be re-written in terms of the matrix T as :

$$Z_N(h, K) = \sum_{S_1} \dots \sum_{S_N} T_{S_1 S_2} T_{S_2 S_3} \dots T_{S_N S_1}.$$

Thus :

$$Z_N(h, K) = \text{Tr}(T^N),$$

since T is real and symmetric, we diagonalize it by writing :

$$T' = S^{-1}TS,$$

where S is a matrix whose rows and columns are eigenvectors of T . Then :

$$T' = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix},$$

where λ_1 and λ_2 are the eigenvalues of T . The cyclic property of the trace operation implies that $\text{Tr}(T') = \text{Tr}(T)$, so that :

$$\text{Tr}(T^N) = \lambda_1^N + \lambda_2^N.$$

Assuming that $\lambda_1 > \lambda_2$, we have :

$$Z_N(h, K) = \lambda_1^N \left(1 + \left[\frac{\lambda_2}{\lambda_1} \right]^N \right),$$

and taking the thermodynamic limit $N \rightarrow \infty$, we get :

$$Z_N(h, K) \approx \lambda_1^N (1 + O(e^{-\alpha N})),$$

where $\alpha = \log\left(\frac{\lambda_1}{\lambda_2}\right)$ is a positive constant. From the expression of the partition function, we notice that only the largest eigenvalue of the transfer matrix is relevant in the thermodynamic limit. Then, the free energy can be calculated using only λ_1 and we write :

$$\lim_{N \rightarrow \infty} \frac{F_N(h, K, T)}{N} = -k_B T \log(\lambda_1).$$

Solving Eq. 6.1.1, we obtain :

$$\lambda_{1,2} = e^K \left[\cosh h \pm \sqrt{\sinh^2 h + e^{-4K}} \right].$$

The free energy of the one dimensional Ising model in an external magnetic field is :

$$\frac{F_N(h, K, T)}{N} = -J - k_B T \log \left[\cosh h + \sqrt{\sinh^2 h + e^{-4K}} \right] \quad (6.1.2)$$

Theorem 6.1.1 — Perron's Theorem. For an $N \times N$ matrix ($N < \infty$) A , with positive entries A_{ij} for all (i, j) , the largest eigenvalue satisfies the following :

1. real and positive
2. non-degenerate
3. an analytic function of A_{ij}

Perron's theorem can be used to prove that in one dimension there are no $T > 0$ phase transitions in the systems controlled by finite-ranged interactions. From one side, inspecting Eq. 6.1.2 leads to the conclusion that to have non-zero temperature phase transitions, λ_1 should be either non-analytic, degenerate ($\lambda_1 = \lambda_2$), or $\lambda_1 = 0$. On the other side, the transfer matrix for 1D systems with sufficiently short-ranged interactions satisfy the Perron's theorem, that is $\lambda_1 \neq 0$, $\lambda_1 \neq \lambda_2$ and λ_1 in analytic.

Thus, we immediately conclude that there are no finite temperature phase transitions in the 1D Ising model.

What happens at $T = 0$ ($K \rightarrow \infty$) ? the largest eigenvalue of the transfer matrix becomes :

$$\lambda_1 = e^K \left[\cosh h + \sqrt{\sinh^2 h (1 + O(e^{-4K}))} \right] = e^{K+|h|}.$$

Then, the free energy and the magnetization are given by :

$$F = -Nk_B T (K + |h|) + O(T^2) = -N(J + |H|),$$

$$M = -\frac{1}{N} \frac{\partial F}{\partial H} = \begin{cases} 1 & H > 0; \\ -1 & H < 0, \end{cases}$$

the non-analytic behaviour of the magnetization at $T = 0$ is obtained without taking the thermodynamic limit. In fact, the non-analyticity of the magnetization originates from the term $\sqrt{h^2} = |h|$ where for non-zero temperatures this term equals $\sqrt{h^2 + \varepsilon^2}$ which is analytic at $h = 0$ as long as $\varepsilon \neq 0$.

We move to the case of zero magnetic field, that is $h = 0$, our goal is to calculate the specific heat C_V and the magnetic susceptibility χ_T . In this case, the largest eigenvalue can be written as :

$$\lambda_1 = e^K (1 + e^{-2K}) = 2 \cosh K,$$

the partition function is $Z = (2 \cosh K)^N$ as $N \rightarrow \infty$ and the free energy is :

$$F = -k_B T N [K + \log(1 + e^{-2K})],$$

with limits :

$$F/N = \begin{cases} -J & T \rightarrow 0 (K \rightarrow \infty); \\ -k_B T \log 2 & T \rightarrow \infty (K \rightarrow 0). \end{cases}$$

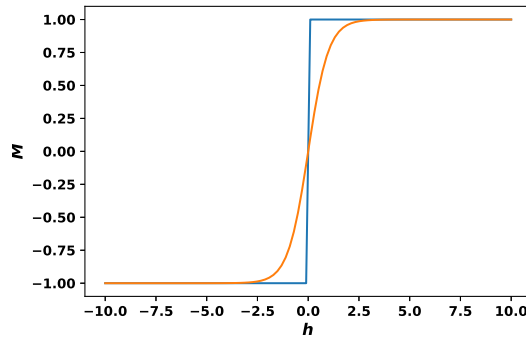


Figure 6.1.1: Magnetization plotted with respect to the magnetic field. Blue line correspond to $T = 0$, while the orange line is for a non-zero temperature.

The specific heat is :

$$C_V = \frac{\partial E}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial E}{\partial \beta}$$

$$= \frac{1}{k_B T^2} \frac{\partial^2 Z}{\partial \beta^2}$$

$$= \frac{NJ^2}{k_B T^2} \operatorname{sech}^2 \left(\frac{J}{k_B T} \right).$$

The heat capacity does not show any singularity, however it exhibit a peak at $J \sim k_B T$, a phenomena known as **Schottky anomaly**.

From Eq. 6.1.2 the magnetization can be obtained immediately :

$$M = -\frac{1}{Nk_B T} \frac{\partial F}{\partial h}$$

$$= \frac{\sinh h}{\sqrt{\sinh^2 h + e^{-4K}}},$$

the rate of change of the magnetization with respect to the magnetic field is called the magnetic susceptibility, given by :

$$\chi = \frac{\partial M}{\partial H},$$

for small field ($h \rightarrow 0$), it reduces to:

$$\chi \sim \begin{cases} \frac{1}{k_B T}, & T \rightarrow \infty (\text{Curie's law}); \\ \frac{e^{\frac{2J}{k_B T}}}{k_B T}, & T \rightarrow 0 \end{cases}$$

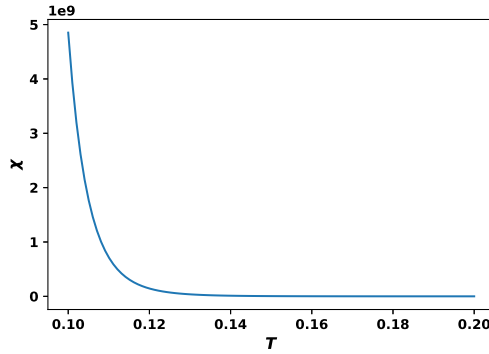


Figure 6.1.2: Magnetic susceptibility vs temperature at zero magnetic field.

6.2 Correlation Functions

A correlation in its simplest form, that is between two systems A and B , is the information we get about system B while knowing system A . In statistical mechanics, a correlation functions is a measure of order in a system, more concretely they describe how microscopic variables, such as spin and density, co-vary with one another across space and time.

The two point correlation function is defined as :

$$G(i, j) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \langle S_i S_j \rangle, \quad (\text{For } T > 0 \text{ and } h = 0 : \langle S_i \rangle = \langle S_j \rangle = 0).$$

As we consider the spin to be sensitive to only its first neighbor, $G(i, j)$ can be written as:

$$G(i, j) = \langle S_i S_{i+1} \rangle \langle S_{i+1} S_{i+2} \rangle \langle S_{i+2} S_{i+3} \rangle \dots \langle S_{N-1} S_N \rangle.$$

Nearest neighbors correlation function $\langle S_i S_{i+1} \rangle$ can be calculated by :

$$\langle S_i S_{i+1} \rangle = \frac{1}{Z} \sum_{\{S\}} S_i S_{i+1} e^{K S_i S_{i+1}} = \frac{\partial \log Z}{\partial K},$$

the partition function for nearest neighbors is :

$$Z = \sum_{S_i = \pm 1} e^{KS_i S_{i+1}} = 2(e^K + e^{-K}) = 2^2 \cosh(K).$$

Then :

$$\langle S_i S_{i+1} \rangle = \tanh(K) = \tanh(\beta J).$$

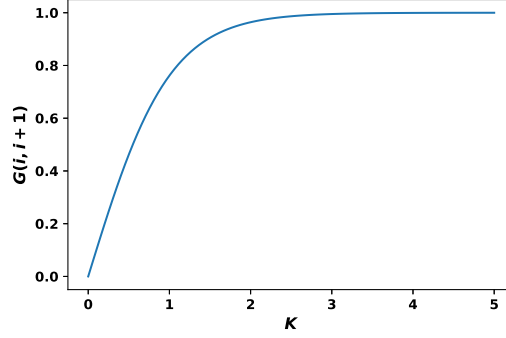


Figure 6.2.1: Nearest neighbour correlation function vs temperature. For high temperatures ($K \rightarrow 0$) the two spins are less correlated, while for low temperatures ($K \rightarrow \infty$) the spins are highly correlated

It is straightforward, to generalize the result beyond $\langle S_i S_{i+1} \rangle$. The correlation function $G(i, i+j)$ is :

$$\begin{aligned} G(i, i+j) &= \langle S_i S_{i+j} \rangle \\ &= \tanh(K_i) \tanh(K_{i+1}) \dots \tanh(K_{i+j-1}) \\ &= (\tanh(K))^j, \end{aligned}$$

an expected result, because of the translation invariance of the system, that is $G(i, i+j)$ depends only on the distance between the spins “ j ”. We say that the correlation function satisfies $G(i, i') = G(i-i')$, which is the case of systems with periodic boundary conditions, continuous systems and also for finite systems as long as i and i' are not on the boundary.

The existence of long range order can be deduced from the behaviour of the correlation function. For $T = 0$, the correlation function $G(i, i+j) = 1$, this a perfectly correlated state that exhibit long range order. Switching on the temperature ($T >$) reduces the magnitude of $G(i, i+j)$ and it decays exponentially as :

$$G(i, i+j) = e^{-j \log(\coth K)} = e^{-j/\xi},$$

where $\xi = \frac{1}{\log(\coth K)}$ is called : **the correlation length**, which measures the length over which the spins are correlated. As we approach the transition temperature of the 1D Ising model ($T \rightarrow 0$), the correlation length diverges to infinity (ξ diverges exponentially fast), while it approaches zero at high temperatures.

Through the transfer matrix formalism, one can notice that :

$$\left(\frac{\lambda_1}{\lambda_2} \right)_{h=0} = \frac{e^K + e^{-K}}{e^K - e^{-K}} = \coth(K),$$

on the other hand :

$$\xi^{-1} = \log(\coth K).$$

Then, we prove a general result relating the eigenvalues of the transfer matrix and the correlation length :

$$\xi^{-1} = \log \left(\frac{\lambda_1}{\lambda_2} \right). \quad (6.2.1)$$

A clear indication of a phase transition is a divergence in the correlation length, for that to happen we need $\lambda_1 = \lambda_2$ (the largest eigenvalue need to be degenerate). This is a general result.

6.3 Weiss' Mean Field Theory

We end this chapter with a discussion on “mean field theory”. A theory used frequently for treating interacting statistical mechanical systems. The idea is simple, in general for an N particle system, we replace the interaction between the particles by a mean potential or mean field. With this approximation we forget about the fluctuations of the system and we focus only its mean behaviour. Such a theory would be effective only when the fluctuations of the system are weak, which is not the case around the critical point.

As usual, we call again for the Ising model in d dimensions :

$$H_\Omega = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i.$$

Suppose we are dealing with an ensemble of independent spins, that is $J = 0$. The partition function for such a system is :

$$Z_\Omega(0, H) = \left[2 \cosh \left(\frac{H}{k_B T} \right) \right]^N,$$

the magnetization is :

$$M = -\frac{1}{N} \frac{\partial F}{\partial H} = \tanh \left(\frac{H}{k_B T} \right).$$

Weiss tried to understand the case when $J \neq 0$, by supposing that each spin is immersed in a effective field H_{eff} created by the magnetic moment of all the other spins. This magnetic moment is unknown to us, so in the end each spin experiences two magnetic fields : the externally applied field and the effective field.

In this approach, the Ising model can be written as :

$$H_\Omega = - \sum_i S_i H_i,$$

where

$$H_i = \underbrace{H}_{\text{magnetic field}} + \underbrace{\sum_j J_{ij} \langle S_j \rangle}_{\text{the mean field}} + \underbrace{\sum_j J_{ij} (S_j - \langle S_j \rangle)}_{\text{the fluctuations}}$$

We ignore the fluctuation term, and we write H_i for a d -dimensional hypercubic lattice as :

$$H_i = H + 2dJm,$$

where $2d$ is the coordination number of each site of the lattice and m is the mean field sensed by the spin. Then, the magnetization is :

$$M = \tanh \left(\frac{H + 2dJm}{k_B T} \right),$$

when $H = 0$, the critical temperature is :

$$T_c = 2dJ/k_B.$$

The equation of state can be obtained by putting $\tau = T_c/T$ and we find :

$$M = \tanh\left(\frac{H}{k_B T} + m\tau\right) = \frac{\tanh\left(\frac{H}{k_B T}\right) + \tanh m\tau}{1 + \tanh\left(\frac{H}{k_B T}\right)\tanh m\tau},$$

then :

$$\tanh\left(\frac{H}{k_B T}\right) = \frac{m - \tanh m\tau}{1 - m \tanh m\tau}, \quad (6.3.1)$$

for weak H and small m , we can expand Eq. 6.3.1 as :

$$\frac{H}{k_B T} \approx m(1 - \tau) + m^3 \left(\tau - \tau^2 + \frac{\tau^3}{3} + \dots \right) + \dots \quad (6.3.2)$$

For zero magnetic field and when $T \rightarrow T_c^-$, we have :

$$m^2 \approx 3 \frac{T_c - T}{T} + \dots$$

As $m \propto \left(\frac{T_c - T}{T}\right)^\beta$, we can extract immediately the critical exponent of the ferromagnetic transition, $\beta = 1/2$. The critical isotherm is the curve in the H - M plan corresponding to $T = T_c$. Near the critical point, it is described by a critical exponent δ :

$$H \sim M^\delta.$$

Setting $\tau = 1$ in Eq. 6.3.2, we find $\delta = 3$. That is :

$$\frac{H}{k_B T} \sim M^3.$$

The isothermal magnetic susceptibility also diverges near T_c :

$$\chi_T = \frac{\partial m}{\partial H},$$

from Eq. 6.3.2, we get :

$$\frac{1}{k_B T} = \chi_T(1 - \tau) + 3m^2 \chi_T \left(\tau - \tau^2 + \frac{1}{3} \tau^3 \right).$$

$M = 0$ for $T > T_c$, then :

$$\chi_T = \frac{1}{k_B} \frac{1}{T - T_c} + \dots \quad (6.3.3)$$

$$\sim |T - T_c|^{-\gamma}. \quad (6.3.4)$$

The critical exponent that characterizes the divergence in the isothermal susceptibility is $\gamma = 1$. For $T < T_c$,

$$m = \sqrt{3} \left(\frac{T_c - T}{T} \right)^{1/2} + \dots$$

which yields to :

$$\chi_T = \frac{1}{2k_B} \frac{1}{T - T_c} + \dots$$

Below the transition temperature, the isothermal susceptibility diverges with $\gamma = 1$.

The critical exponent α of the specific heat can also be calculated, for that we write the free energy in the mean field approximation as :

$$F_m = -k_B T \ln [2 \cosh(\beta J 2dm)],$$

knowing that $\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots$ and that $m = 0$ for $T > T_c$ while $m = \left(3\frac{T_c-T}{T}\right)^{1/2}$ for $T < T_c$. Taking the second derivative of the free energy with respect to the temperature leads to :

$$C = \begin{cases} \frac{3}{2}k_B N & T < T_c \\ 0 & T > T_c. \end{cases}$$

Since $C \sim \left|\frac{T_c-T}{T}\right|^{-\alpha}$, the critical exponent α must be zero.

Now, we derive an important relationship between the isothermal magnetic susceptibility and the correlations functions. For that, we start from the partition function given by :

$$Z = \text{Tr} \exp \left[H\beta \sum_i S_i + \beta J \sum_{\langle ij \rangle} S_i S_j \right],$$

then :

$$\begin{aligned} \sum_i \langle S_i \rangle &= \frac{1}{\beta Z} \frac{\partial Z}{\partial H}, \\ \sum_i \langle S_i S_j \rangle &= \frac{1}{\beta^2 Z} \frac{\partial^2 Z}{\partial H^2}. \end{aligned}$$

On the other side :

$$\begin{aligned} \chi_T &= \frac{\partial m}{\partial H} = \frac{1}{\beta N} \frac{\partial^2 \log Z}{\partial H^2} \\ &= \frac{1}{N} k_B T \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial H^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial H} \right)^2 \right] \\ &= \frac{1}{N} (k_B T)^{-1} \left[\sum_{ij} \langle S_i S_j \rangle - \left(\sum_i \langle S_i \rangle \right)^2 \right] \\ &= \frac{1}{N} (k_B T)^{-1} \sum_{ij} G(r_i - r_j) \\ &= (k_B T)^{-1} \sum_i G(x_i) \\ &= (a^d k_B T)^{-1} \int_{\Omega} d^d r G(r). \end{aligned}$$

This result relates the divergence in χ_T with the two point correlation function G . Then, G have to reflect the divergence in χ_T , in general we have :

$$G(r) \sim \frac{e^{-|r|/\xi}}{|r|^{(d-1)/2} \xi^{(d-3)/2}}, \quad \text{for } |r| \gg \xi.$$

Combining this result with the equation describing the divergence of the isothermal susceptibility yields to :

$$\begin{aligned} \left(\frac{T_c - T}{T} \right)^{-1} &\sim \int \frac{r^{d-1} e^{-r/\xi}}{r^{(d-1)/2} \xi^{(d-3)/2}} dr \\ &\sim \int \left(z^{(d-1)/2} e^{-z} dz \right) \xi^2, \end{aligned}$$

with $z = r/\xi$. Thus :

$$\xi \sim \left(\frac{T_c - T}{T} \right)^{-\nu}, \quad (6.3.5)$$

with $\nu = 1/2$. The last critical exponent we mention is η , which describe how the point correlation function behave at long distances at the critical point. $G(r)$ for long distances near the critical point is given by : $G(r) \sim r^{-(d-2+\eta)}$, with $\eta = 0$. In principal η can be non zero.

Exponent	Mean Field	Experiment	2D Ising	3D Ising
α	0	0.110-0.116	0	0.110
β	1/2	0.316-0.327	1/8	0.325 ± 0.0015
γ	1	1.23-1.25	7/4	1.2405 ± 0.0015
δ	3	4.6-4.9	15	4.82
ν	1/2	0.625 ± 0.010	1	0.630
η	0	0.016 - 0.06	1/4	0.032 ± 0.003

Table 6.1: Critical exponents for the Ising universality class

Can we trust mean field theory ? from Tab. 6.1, we see the discrepancy between the critical exponents obtained by the mean field approximation and the experimental result while the exponents of the 3D Ising model are in accordance with experience. This is due to the mean field approximation, from one hand the exponents in the approximation do not depend on the dimension, while from the table it is clear that the critical exponents depend on the dimensionality of the system. On the other hand, the approximation supposes that the spins do not interact and each spin feels the same field due to all the other spins, and this contradicts the essence of magnetism, which is due to the long range cooperative behavior of spins. The mean field approximation is clearly not a good choice for magnetic systems.

The critical exponents satisfy the scaling relations obtained by thermodynamic considerations, they are given by :

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2, \\ \gamma &= \beta(\delta - 1), \\ \gamma &= \nu(2 - \eta). \end{aligned}$$

The precision of the mean field approximation increases as we increase the dimension of the system. In fact, from the scaling relation $2 - \alpha = d\nu$, where d is the dimension of the system, we can deduce the critical dimension at which we get precise results from the mean field approximation. Since $\alpha = 0$ and $\nu = 1/2$, d_c must be 4.



7. Landau Theory of Phase Transitions

We've seen in the previous chapter Weiss' approach to criticality in magnetic systems, which is based on an expansion of the equation of the state in terms of the order parameter, a quantity that we will define shortly, the theory was successful to some extent in describing the critical behaviour of the Ising model. In the same spirit, Landau proposed a theory based on simple hypotheses for all phase transitions. Landau theory of phase transitions consist of *guessing* a quantity called the **Landau potential**, where its minima with respect to the order parameter should describe the thermodynamic properties of the system at the critical point.

7.1 The order parameter

The order parameter m is a quantity used to describe phase transitions, it is zero (non-zero) in the disordered (ordered) phase. The definition of the order parameter is not always trivial as there are systems for which this quantity can not be defined. Depending on the nature of the system, the order parameter can be a scalar, vector or a tensor.

The order parameter of the ferromagnetic-paramagnetic transition is, in general, a vector : the magnetization M . It is zero above the Curie temperature while it has non zero values below this transition temperature. For the liquid-gas transition, the order parameter is the difference between the density of liquid and that of the gas, that is $\rho_l - \rho_g$. Then, the order parameter of this system is a scalar.

7.2 Landau Theory

Landau theory of phase transitions consists of writing a function L called *Landau free energy* or *Landau functional* in terms of the order parameter η and the coupling constants $\{K_i\}$. In this decomposition, we keep only the terms that are compatible with the symmetry of the system and we assume that thermodynamic functions of the system can be calculated by differentiation of L . Landau free energy has the following constraints :

1. L has to follow the symmetries of the system.

2. Near T_c , L is a analytic function of η and $[K]$. We can write :

$$L = \sum_{n=0}^{\infty} a_n([K])\eta^n.$$

3. $\eta=0$ in the disordered phase, while it is small and non zero in the ordered phase near T_c . Thus, for $T > T_c$ we solve the minimum equation for L by $\eta = 0$ and for $T < T_c$ $\eta \neq 0$ solves the minimum equation. For a homogeneous system we can write :

$$L = \sum_{n=0}^4 a_n([K])\eta^n. \quad (7.2.1)$$

Where we suppose that all the necessary information about the physics of phase transitions appear at this order as it did for Weiss' theory.

Using Eq. 7.2.1, we have at equilibrium :

$$\frac{\partial L}{\partial \eta} = a_1 + 2a_2\eta + 3a_3\eta^2 + 4a_4\eta^3 = 0. \quad (7.2.2)$$

For $T > T_c$, the order parameter η is zero. Then, $a_1 = 0$. In fact, the system is invariant under change of η by $-\eta$, that is L is an even function : $L(\eta) = L(-\eta)$. Thus :

$$L = a_0([K], T) + a_2([K], T)\eta^2 + a_4([K], T)\eta^4. \quad (7.2.3)$$

Each term in Landau's free energy has it own role. $a_0([K], T)$ represents the value L in the disordered phase ($\eta = 0$ for $T > T_c$), it describes the degrees of freedom of the system that cannot be understood via the order parameter. For a_2 and a_4 expanding in temperature near T_c , we obtain :

$$\begin{aligned} a_4 &= a_4^0 + (T - T_c)a_4^1 + \dots \\ a_2 &= a_2^0 + \frac{(T - T_c)}{T_c}a_2^1 + O\left((T - T_c)^2\right), \end{aligned}$$

Since $\partial^2 L / \partial \eta^2 = 1/\chi = 0$ as $T \rightarrow T_c$, one has $a_2^0 = 0$ and :

$$a_2 = \frac{(T - T_c)}{T_c}a_2^1 + O\left((T - T_c)^2\right).$$

The extension to the case $H \neq 0$ for the Ising ferromagnet is immediate. The order parameter in the Ising model is the magnetization M , that is $\eta = M$. The additional energy in the Hamiltonian due to the magnetic field is $-H \sum_i S_i = -HNM$. Thus, Landau free energy can be written as :

$$L = a \left(\frac{T - T_c}{T_c} \right) \eta^2 + \frac{1}{2} b \eta^4 - H \eta. \quad (7.2.4)$$

The coefficient a and b can be obtained from a microscopic analysis.

7.3 Continuous Phase Transitions

We present in Fig. 7.3.1 the variation of Landau free energy with respect to the order parameter η . The case $H = 0$ is when the continuous phase transition occur. For $T > T_c$, L has a minimum at $\eta = 0$. When $T = T_c$ Landau potential has zero curvature at $\eta = 0$ while $\eta = 0$ is still the global

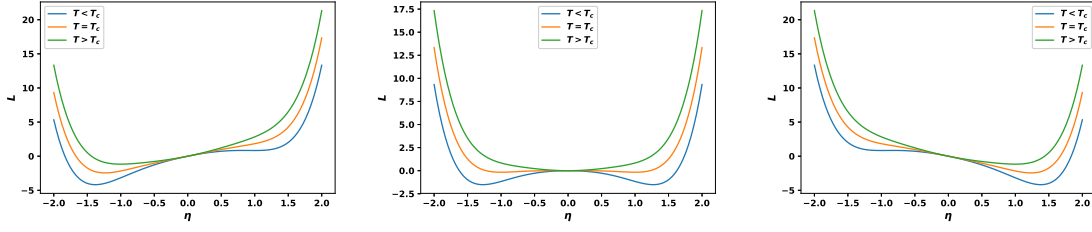


Figure 7.3.1: Landau free energy for different values of T and H . From left to right : $H < 0$, $H = 0$ and $H > 0$.

minimum. For $T < T_c$, Landau free energy shows two degenerate minima at $\eta = \pm n_s(T)$. Solving Eq. 7.2.2 for η we can read off the critical exponent β . We have :

$$\eta = 0 \quad \text{or} \quad \eta = \sqrt{-\frac{at}{b}},$$

then, for $T < T_c$ $\beta = 1/2$.

Landau potential is zero for $t > 0$ and for $t < 0$ we can write :

$$L = -\frac{1}{2} \frac{a^2 t^2}{b}.$$

The critical exponent α of the heat capacity can be extracted by writing : $C_V = -T \partial^2 L / \partial T^2$, then : which shows that the heat capacity exhibit a discontinuity and that $\alpha = 0$.

Switching on the magnetic field allows us to calculate the other critical exponents. Taking the derivative with respect to H in Eq. 7.2.4 gives :

$$at\eta + b\eta^3 = \frac{1}{2}H. \quad (7.3.1)$$

On the critical isotherm, $t = 0$ thus $H \propto \eta^3$ and we read the critical exponent $\delta = 3$. The isothermal susceptibility χ_T can be computed by taking the derivative of Eq. 7.3.1 with respect to H . That is :

$$\chi_T = \frac{\partial \eta(H)}{\partial H} = \frac{1}{2(at + 3b\eta(H)^2)}, \quad (7.3.2)$$

where $\eta(H)$ is a solution of Eq. 7.3.1. For $t > 0$, we have $\eta = 0$, then $\chi_T \propto t^{-1}$ while for $t < 0$, we have $\eta = (-at/b)^{1/2}$ and $\chi_T \propto t^{-1}$. Thus, the critical exponent is $\gamma = 1$.

7.4 First Order Phase Transitions

The symmetry requirement prevented the Landau free energy in Eq. 7.2.3 of having a cubic term in η . In general, what is the effect of this term in Landau potential ? We first write L as :

$$L = at\eta^2 + \frac{1}{2}b\eta^4 + C\eta^3 - H\eta. \quad (7.4.1)$$

Where a and b are positive. A derivative of L with respect to η at equilibrium and at zero magnetic field ($H = 0$) gives :

$$\eta = \begin{cases} 0, \\ -c \pm \sqrt{c^2 - at/b}, \end{cases} \quad \text{with } c = 3C/4b.$$

The solution $\eta \neq 0$ is real when the argument of the square root is positive, i.e. $\sqrt{c^2 - at/b} > 0$. That is, $t < t^* = bc^2/a$. When $t < t^*$, in addition to the minimum $\eta = 0$, L develops a secondary minimum and a maximum. Reducing t further, below a value t_1 , the value of the order parameter which minimizes L **jumps discontinuously** from $\eta = 0$ to a non-zero value and the secondary minimum becomes the global minimum of L . This is a first order phase transition.

A sufficient but not necessary condition of the occurrence of continuous phase transitions is that there are no cubic terms in the potential. In general, the cubic term causes a first order phase transition.

