

As said, this first approximation is reasonable if either

1. ρ is small enough. It implies that $|\vec{r}_i - \vec{r}_j| \gg 1$ and hence $\Phi_{ij} \ll 1$.
2. Sufficiently high T such that $\Phi(|\vec{r}_i - \vec{r}_j|)/k_B T \ll 1$. What is important it is the ration between β and Φ_{ij} .

In either cases we have $\exp(-\beta\Phi_{ij}) \rightarrow 1$ and $f_{ij} \rightarrow 0$. By keeping only linear terms, the configurational contribution to the partition function will be

$$\begin{aligned} Q_N(V, T) &= \int_V d\vec{r}_1 \dots d\vec{r}_N \left(1 + \sum_{i,j>i} f_{ij} + \dots \right) = V^N + \sum_{i,j>i} \int_V d\vec{r}_1 \dots \int_V d\vec{r}_N f_{ij} \\ &= V^N + V^{N-2} \sum_{i,j>i} \int_V d\vec{r}_i d\vec{r}_j f_{ij} + \dots \end{aligned}$$

We are summing up over all configurations ij . Let us try to compute the double integral, with the definition of a new variable $\vec{r} = \vec{r}_i - \vec{r}_j$:

$$\int_V d\vec{r}_i \int_V d\vec{r}_j f_{ij}(|\vec{r}_i - \vec{r}_j|) \stackrel{\text{translational symmetry}}{=} \int_V d\vec{r}_i \int_V d\vec{r} f(\vec{r}) = V \int_V d\vec{r} f(|\vec{r}|) \equiv -2B_2 V$$

Hence,

$$B_2 \equiv -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) \quad (1)$$

From this we see precisely how the virial coefficient, which as we have already stated can be experimentally measured, is related to the microscopic properties of the interaction between the particles, represented by the Mayer function f . It can also be shown that all the virial coefficients can be expressed in terms of integrals of products of Mayer functions: higher order coefficients involve the computation of increasingly difficult integrals, which can however be visualized in terms of graphs.

What we have seen now is how the cluster expansion works in general. Let us now apply it in order to find the virial expansion for real gases. From what we have found, the configurational partition function of the system becomes:

$$Q_N(V, T) = V^N - V^{N-1} 2B_2(T) \sum_{i,j>i} 1 + \dots$$

The remaining sum is equal to $N(N-1)/2$: in fact, for any of the N values that i can assume, j can have $N-1$ values. These are all the possible connections (bonds) between pairs of particles (i, j) with $j > i$. Hence,

$$Q_N(V, T) = V^N - V^{N-1} B_2(T) N(N-1) + \dots \quad (2)$$

and, considering that $N-1 \approx N$ for large N , the complete partition function of the system will be:

$$Z_N(V, T) = \left(\frac{V^N}{N! \Lambda^{3N}} \right) \left(1 - \frac{N^2}{V} B_2(T) + \dots \right) \quad (3)$$

We recognise in this expression that $(1 - B_2 N^2/V + \dots)$ is the correction χ to the ideal gas partition function that we have mentioned earlier; therefore, the free energy of the system will be:

$$F_N = F_N^{ideal} - k_B T \ln \left[1 - \frac{N^2}{V} B_2(T) + \dots \right] \quad (4)$$

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and its pressure:

$$P_N = -\left(\frac{\partial F_N}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V} \left(1 + \frac{\frac{N}{V} B_2}{1 - \frac{N^2}{V} B_2}\right) = \frac{Nk_B T}{V} \left(\frac{1 - \frac{N^2}{V} B_2 + \frac{N}{V} B_2}{1 - \frac{N^2}{V} B_2}\right)$$

Expanding the denominator for $\frac{N}{V} B_2 \ll 1$ $\rho \ll 1$, one gets

$$P_N \simeq \frac{Nk_B T}{V} \left(1 + \frac{N}{V} B_2 + \dots\right) \quad (5)$$

here we see the correction to the ideal gas.

Remark. The equation (5) gives an important relation between experimentally accessible observables as P_N and microscopic quantities such as $f(\vec{r})$ (and hence $\Phi(\vec{r})$) through the estimate of B_2 . Therefore, it is important computing B_2 , because one time we have this we have the expansion. Or if we wish, by doing the fit of data at different temperature we obtain B_2 from the experiment and we can see f_{ij} .

The expansion in Eq.(5) contains only low-order terms in the density N/V , so strictly speaking it is valid only for low densities. To consider higher order terms in the virial expansion we need to consider higher order products of the f_{ij} . However, we can use a "trick" in order to extend its range; in fact, remembering that the McLaurin expansion $(1 - x)^{-1} = 1 + x + \dots$, from the Eq.(5) we can write:

$$\frac{PV}{Nk_B T} \approx 1 + \rho B_2 + \dots \simeq \frac{1}{1 - B_2 \rho}$$

and now re-expand $(1 - B_2 \rho)^{-1}$, so that we can express all the virial coefficients in terms of the first one:

$$\frac{1}{1 - B_2 \rho} \simeq 1 + B_2 \rho + (B_2)^2 \rho^2 + (B_2)^3 \rho^3 + \dots$$

Hence,

$$\frac{P}{k_B T} = \rho + B_2 \rho^2 + (B_2)^2 \rho^3 + (B_2)^3 \rho^4 + \dots$$

Identifying the coefficients for each power we get, in the end:

$$B_3 \approx (B_2)^2, \quad B_4 \approx (B_2)^3, \quad \dots, \quad B_n \approx (B_2)^{n-1}$$

This is the approximation of higher order virial coefficients with powers of B_2 .

Remark. One question at the exam can be: let us compute virial expansion of a gas in a potential.

0.0.1 Computation of virial coefficients for some interaction potentials Φ

Let us now see this method in action by explicitly computing some coefficients B_2 for particular interaction potentials.

Hard sphere potential

The particles are interacting (it is not ideal!) and there is a size that is the range of the potential. As a first trial, we use a hard sphere potential similar (see Figure 1) to the one we have seen for the derivation of the Van der Waals equation:

$$\Phi(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (6)$$

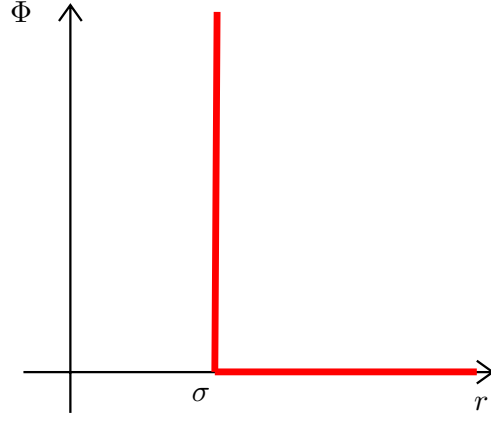


Figure 1: Plot of the hard sphere potential $\Phi(r)$.

(the difference with what we have seen in Van der Waals equation is that now the potential is purely repulsive, and has no attractive component).

In this case,

$$f(\vec{r}) = e^{-\beta\Phi(r)} - 1 = \begin{cases} -1 & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (7)$$

Therefore, from the definition of B_2 and shifting to spherical coordinates:

$$B_2(T) = -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) = -\frac{1}{2} 4\pi \int_0^{+\infty} dr r^2 [e^{-\beta\Phi(r)} - 1] = 2\pi \int_0^\sigma dr r^2 = \frac{2}{3}\pi\sigma^3$$

Hence,

$$\Rightarrow B_2^{HS}(T) = \frac{2}{3}\pi\sigma^3 \quad (8)$$

this is the second virial coefficient for a hard sphere gas. As expected B_2^{HS} does not depend on temperature (purely repulsive interaction). Finally, for hard spheres we have:

$$PV = Nk_B T \left(1 + \frac{2}{3}\pi\sigma^3 \frac{N}{V} \right) \quad (9)$$

Note that the excluded volume interaction (hard sphere term) increases the product PV with respect to the ideal gas.

Square wall potential

We now use a slight refinement of the previous potential:

$$\Phi(\vec{r}) = \begin{cases} +\infty & |\vec{r}| < r_0 \\ -\varepsilon & r_0 < |\vec{r}| < r_0 + \delta \\ 0 & |\vec{r}| > r_0 + \delta \end{cases} \quad (10)$$

This can be seen as a hard sphere potential where the spheres have an attractive shell of thickness δ . We thus have:

$$f(\vec{r}) = \begin{cases} -1 & |\vec{r}| < r_0 \\ e^{\beta\varepsilon} - 1 & r_0 < |\vec{r}| < r_0 + \delta \\ 0 & |\vec{r}| > r_0 + \delta \end{cases} \quad (11)$$

so that:

$$\begin{aligned}
B_2 &= -\frac{1}{2} \int f(|\vec{r}|) d\vec{r} = -\frac{1}{2} \int 4\pi r^2 f(r) dr = \\
&= -2\pi \left[\int_0^{r_0} (-r^2) dr + \int_{r_0}^{r_0+\delta} (e^{\beta\varepsilon} - 1) r^2 dr \right] = \\
&= -2\pi \left\{ -\frac{r_0^3}{3} + \frac{e^{\beta\varepsilon} - 1}{3} [(r_0 + \delta)^3 - r_0^3] \right\} = B_2^{\text{h.s.}} - \frac{2}{3}\pi (e^{\beta\varepsilon} - 1) [(r_0 + \delta)^3 - r_0^3]
\end{aligned}$$

where B_2^{HS} is the first virial coefficient of the hard sphere potential we have previously seen. Now, if the temperature is sufficiently high, namely $\beta\varepsilon \ll 1$, we can approximate $e^{\beta\varepsilon} - 1 \approx \beta\varepsilon$, so that:

$$B_2 = B_2^{\text{HS}} - \frac{2}{3}\pi\beta\varepsilon r_0^3 \left[\left(1 + \frac{\delta}{r_0}\right)^3 - 1 \right] \quad (12)$$

For the sake of simplicity, defining:

$$\lambda \equiv \left(1 + \frac{\delta}{r_0}\right)^3 - 1$$

we will have, in the end:

$$\frac{PV}{Nk_B T} = 1 + B_2\rho = 1 + \left(B_2^{\text{HS}} - \frac{2}{3} \frac{\pi\varepsilon}{k_B T} r_0^3 \lambda \right) \rho \quad (13)$$

so in this case B_2 actually depends on the temperature.

Lennard-Jones potential

This potential is a quite realistic representation of the interatomic interactions. It is defined as:

$$\Phi = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (14)$$

which contains a long-range attractive term (the one proportional to $1/r^6$, which can be justified in terms of electric dipole fluctuations) and a short-range repulsive one (proportional to $1/r^{12}$, which comes from the overlap of the electron orbitals, i.e. Pauli excluded principle). This potential is plotted in Figure 2. The minimum is in $r_{\min} = 2^{1/\sigma}$. We can play with the range of attraction by changing σ or by changing the ε .

With this interaction potential, the first virial coefficient is:

$$B_2(T) = -2\pi \int_0^\infty r^2 \left[e^{-\frac{4\varepsilon}{k_B T} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]} - 1 \right] dr$$

which is not analytically computable. However, it can be simplified defining the variables

$$x = \frac{r}{\sigma}, \quad \tau = \frac{k_B T}{\varepsilon}$$

so that, integrating by parts $\int f'g = fg - \int g'f$ where $f' = x^2g = \exp[-()]$, we obtain

$$\begin{aligned}
B_2(T^*) &= \frac{2}{3}\pi\sigma^3 \frac{4}{\tau} \int_0^\infty x^2 \left(\frac{12}{x^{12}} - \frac{6}{x^6} \right) e^{-\frac{4}{\tau} \left(\frac{1}{x^{12}} - \frac{1}{x^6} \right)} dx \\
&= A \int_0^\infty \left(\frac{12}{x^{16}} - \frac{6}{x^4} \right) e^{-\frac{4}{\tau} \left(\frac{1}{x^{12}} - \frac{1}{x^6} \right)} dx
\end{aligned}$$

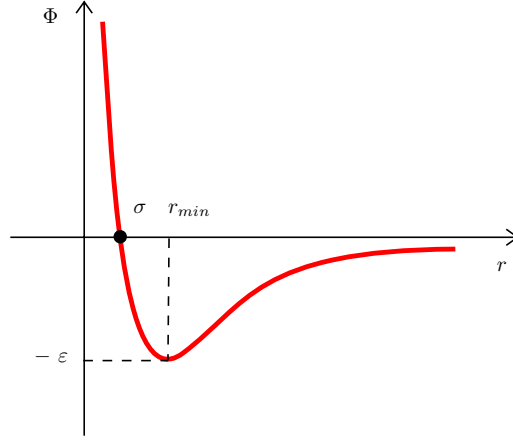


Figure 2: Plot of the Lennard-Jones potential Φ .

Now, we can expand the exponential and integrate term by term; this gives an expression of B_2 as a power series of $1/\tau$:

$$B_2(\tau) = -2A' \sum_{n=0}^{\infty} \frac{1}{4n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{1}{\tau}\right)^{\frac{2n+1}{4}} \quad (15)$$

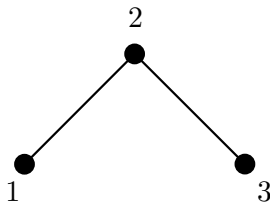
where Γ is the Euler function and A' is a constant. Note that the attractive part of the Lennard-Jones potential has introduced in B_2 a dependence on the temperature.

0.0.2 Higher order terms in the cluster expansion

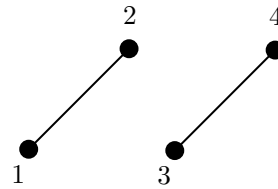
Let us consider again the formal expansion

$$\prod_i \left(\prod_{j>i} (1 + f_{ij}) \right) = 1 + \sum_{i,j>i} f_{ij} + \sum_{\substack{i \\ j>i \\ l>k \\ k>i \\ (ij) \neq (kl)}} f_{ij} f_{kl} + \dots$$

The problem with this expansion is that it groups terms quite different from one another. For example the terms $f_{12}f_{23}$ and $f_{12}f_{34}$. Indeed the first term corresponds to a diagram as in Figure 3a, while the second to two disconnected diagrams as in Figure 3b.



(a) Diagram of $f_{12}f_{23}$.



(b) Diagram of $f_{12}f_{34}$.

Figure 3

Another problem of the above expansion is that it does not recognize identical clusters formed by different particles. For example the terms $f_{12}f_{23}$ and $f_{12}f_{14}$ contribute in the same way to the partition function. It is then convenient to follow a diagrammatic approach similar to the Feynman approach in the reciprocal space.

For the linear term f_{ij} the only diagram is given by Figure 4. As we have seen this has multiplicity

$$\frac{N(N-1)}{2}$$

and the integral is of the form

$$\int f_{12} d\vec{r}_1 d\vec{r}_2 = V \int f(\vec{r}) d\vec{r} = -2VB_2$$

For the term $f_{ij}f_{kl}$ we can have the case as in Figure 5, that has multiplicity

$$\frac{N(N-1)}{2} \frac{(N-1)(N-3)}{2} \frac{1}{2}$$

and the integral is of the form

$$\int f_{12}f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

i.e. involving 4-particles

$$\begin{aligned} & \int f(|\vec{r}_1 - \vec{r}_2|)f(|\vec{r}_3 - \vec{r}_4|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 = \\ & = V^2 \left(\int f(\vec{r}) d\vec{r} \right)^2 = 4V^2 B_2^2 \end{aligned}$$

The next case is for instance as in Figure 6. This involves 3 particles. The multiplicity of this diagram is

$$\frac{N(N-1)(N-2)}{3!} \times 3$$

The integral is of the form

$$\begin{aligned} & \int f_{12}f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \simeq V \left(\int dr f(r) \right)^2 = \\ & = \int f(|\vec{r}_1 - \vec{r}_2|)f(|\vec{r}_2 - \vec{r}_3|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \quad (16) \\ & = V \left(\int f(\vec{r}) d\vec{r} \right)^2 = 4VB_2^2 \end{aligned}$$

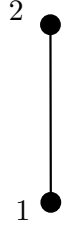


Figure 4

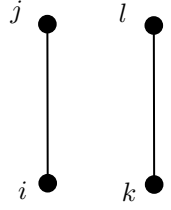


Figure 5

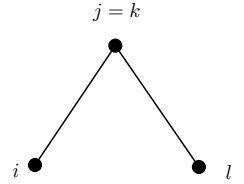


Figure 6

Another interesting diagram is the one in Figure 7. Its multiplicity is

$$\frac{N(N-1)(N-2)}{3!}$$

The associated integral involves 3 particles and it is of the form

$$\begin{aligned} \int f_{12} f_{23} f_{31} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 &= \\ &= \int f(|\vec{r}_1 - \vec{r}_2|) f(|\vec{r}_2 - \vec{r}_3|) f(|\vec{r}_3 - \vec{r}_1|) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \\ &= \int f(|\vec{r}_1 - \vec{r}_2|) f(|\vec{r}_2 - \vec{r}_3|) f(|\vec{r}_3 - \vec{r}_1|) d\vec{r}_2 d\vec{r}_{21} d\vec{r}_{23} \end{aligned}$$

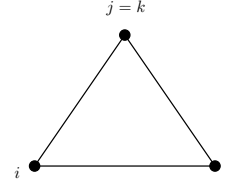


Figure 7

On the other hand $\vec{r}_{13} = \vec{r}_{23} - \vec{r}_{21}$, which implies

$$f(|\vec{r}_3 - \vec{r}_1|) = f(|\vec{r}_{23} - \vec{r}_{21}|)$$

Hence,

$$\int f(|\vec{r}_{12}|) f(|\vec{r}_{23}|) f(|\vec{r}_{31}|) d\vec{r}_{21} d\vec{r}_{23} d\vec{r}_2 = \int f(|\vec{r}_{12}|) f(|\vec{r}_{23}|) f(|\vec{r}_{23} - \vec{r}_{21}|) d\vec{r}_{21} d\vec{r}_{23} d\vec{r}_2$$

Let us call this integral

$$\int f_{12} f_{23} f_{31} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \equiv 3!V(B_3 - 2B_2^2) \quad (17)$$

The configurational partition function with the terms in Eq.16 and Eq.17 becomes

$$\begin{aligned} Q_N(V, T) &= V^N - V^N \frac{N(N-1)}{V} B_2 + V^N \frac{N(N-1)(N-2)(N-3)}{8V^2} (4B_2^2) + V^N \frac{N(N-1)(N-2)}{2V^2} 4B_2^2 \\ &= V^N \left(1 + \frac{N(N-1)}{V} B_2 + \frac{N(N-1)(N-2)(N-3)}{2V^2} B_2^2 + \frac{N(N-1)(N-3)}{V^2} B_3 \right) \end{aligned} \quad (18)$$

Let us now face the problem in a slightly different ways. Let us remind that

$$Q_N(V, T) = \sum_{\text{diagrams}} \int \prod_{kl} f_{kl} d^{3N}r \quad (19)$$

where the sum is over all possible diagrams, i.e. all possible ways in which ones can draw edges between pairs of points (k, l) . For each such diagrams I have to product between all edge and then integrate over the configurational space (N points).

Let us now consider only *connected* diagrams for i sites. In other words given i points (i particles) from a system of N points and I consider all the possible ways I can connect these i points (an example is shown in Figure 8).

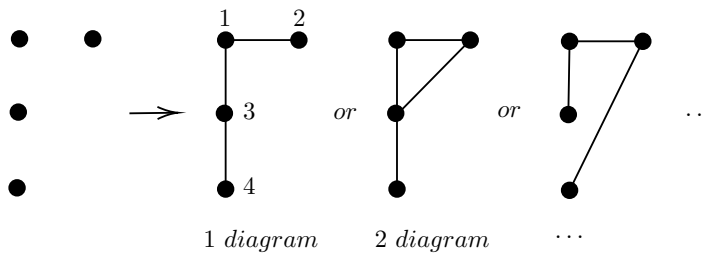


Figure 8: Example of connected diagrams for $i = 4$ sites.

For each diagram we take the product $\prod_{kl} f_{kl}$ and then integrate over the position of the i points (i particles). For a fixed diagram:

$$\int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 \dots d\vec{r}_i$$

Example 1: Diagram for $i = 4$ sites

For example the diagram 1 in Figure 8 gives the contribution

$$\int f_{12} f_{13} f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

The diagram 2 gives

$$\int f_{12} f_{13} f_{23} f_{34} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

and so on.

Finally, we sum over all these connected diagrams of i points:

$$\sum_{\text{connected diagrams}} \int \prod_{lk \in \text{diagram}} f_{lk} d\vec{r}_1 \dots d\vec{r}_i$$

the results is what we call $(i!V B_i)$ and defines B_i . Let us analyze what happens for different values of i points:

- case $i = 1$: clearly $B_1 = 1$;
- case $i = 2$: just one edge, hence we have just one connected diagram. The integral becomes:

$$\int f_{12} d\vec{r}_1 d\vec{r}_2 = -2V B_2$$

- case $i = 3$: the connected diagrams are shown in Figure 9.

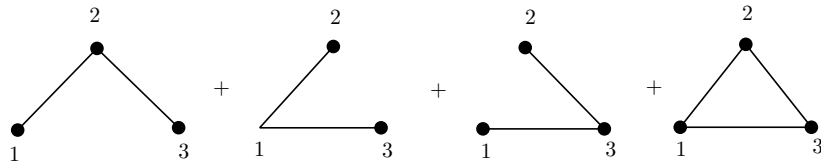


Figure 9: Connected diagrams for $i = 3$ points.

$$\begin{aligned} & \sum_{\substack{\text{connected diagrams} \\ \text{of } i = 3 \text{ points}}} \int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \\ &= \underbrace{\int f_{12} f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 + \int f_{12} f_{13} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 + \int f_{13} f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3}_{3V(\int f(\vec{r})d\vec{r})^2} \\ &+ \underbrace{\int f_{12} f_{23} f_{13} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3}_{3!V(B_3 - 2B_2^2)} \end{aligned}$$

Hence,

$$\sum_{\substack{\text{connected diagrams} \\ \text{of } i = 3 \text{ points}}} \int \prod_{kl \in \text{diagram}} f_{kl} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = 3V(-2B_2)^2 + 6V(B_3 - 2B_2) \\ = 6VB_3 = 3!VB_3$$

Eventually, for the partition function we have to sum over all possible clusters. One possible procedure is:

1. given the N points we can partition them into connected clusters. For all i points we can make m_i clusters of that size i .

$$\sum_i i m_i = N$$

For each cluster of size i we have a term $(i!VB_i)$. If there are m_i of them we have a weight $(i!VB_i)^{m_i}$.

2. Now, we have to count in how many ways we can make the partition of N in a set of $\{m_i\}$ clusters. Clearly if we permute the label of the N vertices we have possible different clusters. In principle, this degeneracy is proportional to $N!$. On the other hand, if one changes the order of the labels within a cluster (in $i!$ ways) this does not change the cluster and since there are m_i clusters of size i we have to divide by $(i!)^{m_i}$.

Moreover, since there are m_i clusters one can swap them (in $m_i!$ ways). The degeneracy is $\frac{N!}{m_i!(i!)^{m_i}}$. Therefore,

$$Q_N(V, T) = \sum_{\{m_i\}} \prod_i \frac{N!}{m_i!(i!)^{m_i}} (i!VB_i)^{m_i} \quad (20)$$

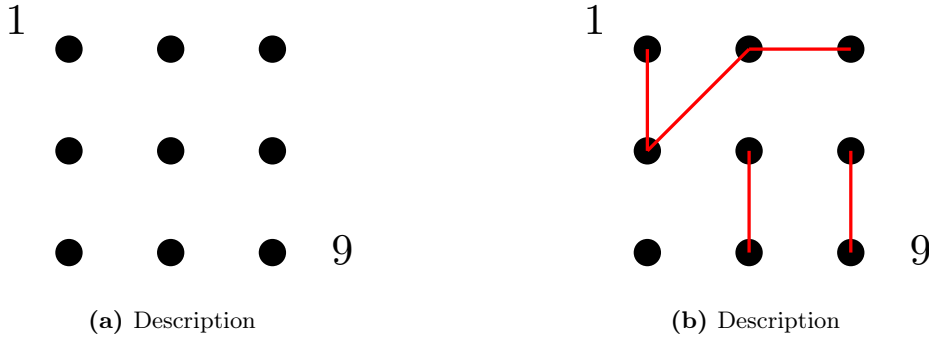


Figure 10

Exercise 1: $N = 9$ points

Consider the $N = 9$ points in Figure 10a.

1. Partition these points into clusters, as in Figure 10b.

For this partition $\{m_i\}$ we have $m_4 = 1, m_2 = 2, m_1 = 1$. Now, the cluster of size 4 can be connected in a given different ways $(4!VB_4)^1$.

2. Compute the degeneracy of this case (More on Huang chapter 10).

Chapter 1

Landau theory of phase transition for homogeneous systems

1.1 Introduction to Landau theory

Landau theory is a phenomenological mean field theory of phase transitions that aims at describing the occurrence of phase transitions in a unitary framework (no spatial variation of the order parameter). Landau theory is based on some assumptions, which we now introduce:

1. Existence of an uniform order parameter η . Remember the definition of the order parameter:

$$\eta = \begin{cases} 0 & T \geq \bar{T} \text{ (disordered phase)} \\ \neq 0 & T < \bar{T} \text{ (ordered phase)} \end{cases}$$

Well known examples are

$$\begin{cases} \eta \rightarrow m \\ \eta \rightarrow \rho_L - \rho_G \end{cases}$$

2. There exists a function \mathcal{L} called Landau free energy¹, which is an analytic function of the coupling constants $\{K_i\}$ of the system and of the order parameter η :

$$\mathcal{L} = \mathcal{L}(\eta)$$

3. The form of \mathcal{L} must satisfy the underlying symmetry of the system.
4. The equilibrium states of the system are the global minima of \mathcal{L} with respect to η .

We also assume that the thermodynamic properties of the system can be obtained by differentiating \mathcal{L} , just like we can do with thermodynamic potentials².

Note also that the general formulation of the Landau theory does not depend on the dimensionality of the system (although we will see that once a system has been chosen some details can depend on it).

Remark. Since \mathcal{L} is analytic it can be formally expanded in power of η , for $\eta \sim 0$.

$$\mathcal{L}(\eta) \approx a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + \dots \quad (1.1)$$

¹To be more precise, \mathcal{L} is the Landau free energy density; the "real" Landau free energy should be $L = V\mathcal{L}$.

²Strictly speaking, Landau free energy is not really a thermodynamic potential: the correct interpretation of \mathcal{L} is that it is a coarse grained free energy (not the exact one).

1.2 Landau theory for the Ising model

To make things more clear, let us now consider the Ising model without any external field and see how we can determine the form of \mathcal{L} from the general assumptions we have introduced. In this case η is a scalar (magnetization).

1.2.1 Costruction of \mathcal{L}

First of all, since the equilibrium configurations of the system must be minima of \mathcal{L} :

$$\frac{\partial \mathcal{L}}{\partial \eta} = a_1 + 2a_2\eta + 3a_3\eta^2 + \dots = 0$$

where we have chosen to stop the expansion at the three order. Now, since this equation must hold for all T and for $T > \bar{T}$ ³ we have $\eta = 0$, we see that $a_1 = 0$.

Considering now the constraint on the symmetries of the system, in absence of phase transitions for finite systems we have seen that the Ising model is invariant under parity (\mathbb{Z}^2 symmetry), i.e. its Hamiltonian is simultaneously even in H and $\{S_i\}$:

$$\mathcal{H}(H, \{S_i\}) = \mathcal{H}(-H, \{-S_i\})$$

Thus, in absence of external fields ($H = 0$) the Hamiltonian of the Ising model is even; this means that also \mathcal{L} must be invariant under parity, namely an even function of η :

$$\mathcal{L}(-\eta) = \mathcal{L}(\eta)$$

Therefore all the odd terms of the expansion are null:

$$a_{2k+1} = 0 \quad \forall k \in \mathbb{N}$$

Finally, since we have assumed that \mathcal{L} is an analytic function of η then its expansion cannot contain terms proportional to $|\eta|$.

In conclusion, the minimal expression for $\mathcal{L}(\eta)$ that describes the equilibrium phase diagram of an Ising-like system is:

$$\mathcal{L}(\eta) \simeq a_0(J, T) + a_2(J, T)\eta^2 + a_4(J, T)\eta^4 + O(\eta^6) \quad (1.2)$$

where the coefficients of the expansion a_0, a_2, a_4, \dots are functions of the physical parameters, J and T . However, \mathcal{L} can be further simplified and we can also explicitly show its dependence on the temperature. In fact, first of all we can note that a_0 is the value of \mathcal{L} in the paramagnetic state (when $T > \bar{T}$, $\eta = 0$):

$$\mathcal{L}(\eta = 0) = a_0$$

and so for simplicity we can set $a_0 = 0$ (it's just a constant shift in the energy, what matters is the free-energy difference).

Moreover, in order to have $\eta = \bar{\eta} \neq 0 < \infty$ for $T < \bar{T}$ (thermodynamic stability) we should impose that the coefficient of the highest power of η is always positive. In this case:

$$a_4(J, T) > 0$$

Indeed if this condition is violated \mathcal{L} reaches its absolute minimum for $\eta \rightarrow \pm\infty$, which makes no sense physically! The Landau free energy results

$$\mathcal{L}(\eta) \simeq a_2\eta^2 + a_4\eta^4, \quad \text{with } a_4 > 0 \quad (1.3)$$

³For $T > \bar{T}$ (critical point) we expect a paramagnetic phase.

Finally, fixing J and expanding the coefficients a_2 and a_4 as a function of the reduced temperature $t \equiv \frac{T-\bar{T}}{\bar{T}}$ (in T near \bar{T}), we obtain

$$a_2 \sim a_2^0 + \frac{T-\bar{T}}{\bar{T}} \frac{a}{2} + \dots, \quad a_4 \sim \frac{b}{4} + \dots$$

in the expansion of a_4 we have neglected any explicit dependence on $T - \bar{T}$ because as we will see it will not dominate the behaviour of the thermodynamics near \bar{T} . Moreover, by choosing $a_2^0 = 0$ the sign of a_2 is determined by the one of t . In particular, at $T = \bar{T}$, one has $a_2 = 0$.

We finally have that the form of the Landau free energy for the Ising model is given by:

$$\mathcal{L} = \frac{a}{2} t \eta^2 + \frac{b}{4} \eta^4 + O(\eta^6) \quad (1.4)$$

Remark. Does not matter the coefficient in green in front, so in the next part of the course we will change it. If it is written in this way we have always $a > 0$. We have also $b > 0$.

Note that, in presence of an external magnetic field h , one should consider the Legendre transform of \mathcal{L} obtaining its Gibbs version:

$$\mathcal{L}_G = \frac{a}{2} t \eta^2 + \frac{b}{4} \eta^4 - h \eta \quad (1.5)$$

we have inserted a field coupled with the order parameter.

1.2.2 Equilibrium phases

Let us now see what does the Landau theory for the Ising model predict. First of all, in the absence of external fields we have that the equilibrium states are determined by:

$$\frac{\partial \mathcal{L}}{\partial \eta} = 0 \quad \Rightarrow \quad at\eta + b\eta^3 = \eta(at + b\eta^2) = 0 \quad (1.6)$$

Hence, the minima are

$$\bar{\eta} = \begin{cases} 0 & t > 0 \text{ (i.e. } T > \bar{T}) \\ \pm \sqrt{\frac{-at}{b}} & t < 0 \text{ (i.e. } T < \bar{T}) \end{cases} \quad (1.7)$$

and at $T = \bar{T}$ the 3 solutions coincide!

Let us consider the two different cases:

- Case $t > 0$ ($T > \bar{T}$): the only global minimum of \mathcal{L} is the solution $\bar{\eta} = 0$. The second derivative of \mathcal{L} with respect to η is

$$\frac{\partial^2 \mathcal{L}}{\partial \eta^2} = at + 3b\eta^2$$

which results ≥ 0 for $\bar{\eta} = 0$ and in the case $t > 0$. It implies that $\eta = \bar{\eta}$ is a global minima, as in Figure 1.1a.

- Case $t < 0$ ($T < \bar{T}$): there are 3 solutions, $\bar{\eta} = 0$ and $\bar{\eta} = \pm \sqrt{-\frac{at}{b}}$. Let us see wheter they are minima or local maxima.

$$\left. \frac{\partial^2 \mathcal{L}}{\partial \eta^2} \right|_{\bar{\eta}=0} = at < 0 \quad \Rightarrow \quad \bar{\eta} = 0 \text{ local maxima (no equilibrium)}$$

$$\left. \frac{\partial^2 \mathcal{L}}{\partial \eta^2} \right|_{\bar{\eta} = \pm \sqrt{-\frac{at}{b}}} = at + 3b \left(-\frac{at}{b} \right) = -2at$$

since $t < 0$, we have $-2at > 0$ and hence $\bar{\eta} = \pm \sqrt{-\frac{at}{b}}$ are two minima!

$$\mathcal{L} \left(\bar{\eta} = \pm \sqrt{-\frac{at}{b}} \right) = -\frac{a^2 t^2}{2b} + \frac{a^2 t^2}{4b} = -\frac{a^2 t^2}{4b} < 0$$

Hence, the two minima have the same value are related by the group symmetry \mathbb{Z}^2 ($\bar{\eta} \rightarrow -\bar{\eta}$).

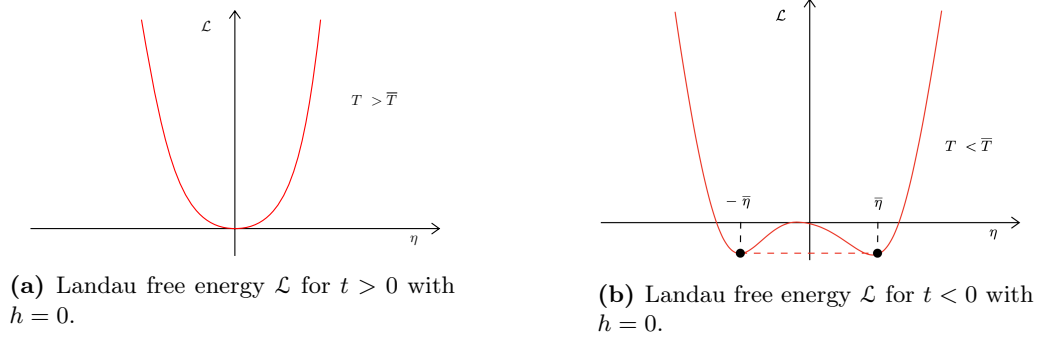


Figure 1.1

1.3 Critical exponents in Landau's theory

Let us therefore see what critical exponents does the Landau theory for the Ising model predict. Let us define $t \equiv \frac{T - \bar{T}}{\bar{T}}$.

Exponent β

This is immediately determined from what we have just seen: in fact, $\eta \sim t^\beta$ for $h = 0$, $t \rightarrow 0^-$. Since $t < 0$, the minima of \mathcal{L} are

$$\bar{\eta} = \pm \sqrt{-\frac{at}{b}} \Rightarrow \beta = \frac{1}{2}$$

as expected.

Exponent α

The specific heat at zero field of the system is $C_H = -T \frac{\partial^2 \mathcal{L}}{\partial T^2}$. In particular, we have $C_H \sim t^{-\alpha}$ for $h = 0$, $|t| \rightarrow 0$. As we have seen:

- if $t > 0$: $\mathcal{L}(\bar{\eta} = 0) = 0$.
- if $t < 0$: $\mathcal{L}_{min} = \mathcal{L} \left(\bar{\eta} = \pm \sqrt{-\frac{at}{b}} \right) = -\frac{a^2 t^2}{4b}$.

Hence,

$$\mathcal{L}_{min} = \begin{cases} 0 & t > 0 \\ -\frac{a^2 t^2}{4b} & t < 0 \end{cases}$$

Therefore:

$$c_H = -T \frac{\partial^2 \mathcal{L}}{\partial T^2} = -T \frac{\partial^2}{\partial T^2} \left(-\frac{a^2}{4b\bar{T}^2} (T - \bar{T})^2 \right)$$

We have

$$\frac{\partial}{\partial T} \left[-\frac{a^2}{4b\bar{T}^2} (T - \bar{T})^2 \right] = -\frac{a^2}{2b\bar{T}^2} (T - \bar{T})$$

$$\frac{\partial^2}{\partial T^2} = \frac{\partial}{\partial T} \left[-\frac{a^2}{2b\bar{T}^2} (T - \bar{T}) \right] = -\frac{a^2}{2b\bar{T}^2}$$

Hence, the specific heat at zero field results

$$c_H = \begin{cases} 0 & T > \bar{T} \\ \frac{a^2}{2b\bar{T}^2} T & T < \bar{T} \end{cases}$$

We have $t \rightarrow 0^-$ if and only if $T \rightarrow \bar{T}^-$, which implies $c_H \rightarrow \frac{a^2}{2b\bar{T}}$ that is constant. Hence, in both cases:

$$\alpha = 0$$

Exponent δ

Let us remind that $h \sim \eta^\delta$ at $T = \bar{T}$. Considering now also an external field, the state equation of the system will be given by the differentiation of \mathcal{L} :

$$\frac{\partial \mathcal{L}}{\partial \eta} = a\eta + b\eta^3 - h = 0$$

Hence, the condition of equilibrium is

$$h = a\eta + b\eta^3 \quad (1.8)$$

This tells us that, for fixed h , the extreme points of \mathcal{L} are given by the values of η that satisfies Eq.(1.8) (see Figure 1.2).

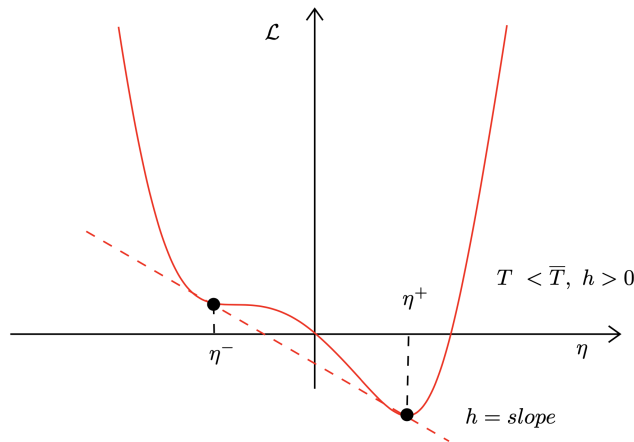


Figure 1.2: Plot of the Landau free energy for $t < 0$ with an external field $h > 0$.

At the critical point $T = \bar{T}$ ($t = 0$) we have $h \sim \eta^3$. Therefore:

$$\delta = 3$$

Exponent γ

Let us remind that $\chi_T \sim t^{-\gamma}$ for $h = 0$, $|t| \rightarrow 0$. If we now differentiate the state equation (1.8) with respect to h we get:

$$at \frac{\partial \eta}{\partial h} + 3b\eta^2 \frac{\partial \eta}{\partial h} = 1$$

Since $\chi = \frac{\partial \eta}{\partial h}$, we have

$$\chi = \frac{1}{at + 3b\eta^2}$$

If we now set $h = 0$, then for:

- $t > 0$: we will have $\bar{\eta} = 0$ and thus $\chi_T = \frac{1}{at}$.
- $t < 0$: we will have $\bar{\eta} = \pm \left(-\frac{at}{b}\right)^{1/2}$ and thus $\chi_T = -\frac{1}{2at}$.

In both cases $\chi_T \sim 1/t$ and thus:

$$\gamma = \gamma' = 1$$

Summary

In summary, the Landau theory for the Ising model gives the following (mean field) values of the critical exponents

$$\beta = \frac{1}{2}, \quad \alpha = 0, \quad \delta = 3, \quad \gamma = 1 \quad (1.9)$$

which, as we expected, are identical to those we have found within Weiss mean field theory. Moreover, Landau theory does not depend on the system dimension d (as expected since is a mean field theory) but only on its symmetries.

Remark. For a $O(n)$ (vector) model the order parameter η becomes a vector field $\vec{\eta}$ with n components and

$$\mathcal{L}_G(\vec{\eta}) = \frac{a}{2} t \vec{\eta} \cdot \vec{\eta} + \frac{b}{4} (\vec{\eta} \cdot \vec{\eta})^2 - \vec{h} \cdot \vec{\eta} + O((\vec{\eta} \cdot \vec{\eta})^3) \quad (1.10)$$