

**Lecture 15.**  
 Wednesday 4<sup>th</sup>  
 December, 2019.  
 Compiled:  
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$$e^{-\beta \sum_{i,j>i} \Phi_{ij}} = \prod_i \left( \prod_{j>i} (1 + f_{ij}) \right) = 1 + \sum_{i,j>i} f_{ij} + \sum_{\substack{i,j>i \\ k,l>k \\ k \geq i \\ (i,j) \neq (k,l)}} f_{ij} f_{kl} + O(f^3) \quad (1)$$

where

$$f_{ij} \equiv e^{-\beta \Phi_{ij}} - 1 \quad (2)$$

The  $f_{ij}$  will be small enough when  $T$  is very large or  $\Phi_{ij}$  is small enough because you are in small density. What is important it is the ration between  $\beta$  and  $\Phi_{ij}$ .

In the case  $\Phi_{ij} \ll 1$  you keep other terms contributions. In the other cases you can keep the linear term.

The partition function is:

$$Q_N(V, T) = \int_V d\vec{r}_1 \dots d\vec{r}_N \left( 1 + \sum_{i,j>i} f_{ij} + \dots \right) = V^N + V^{N-2} \sum_{i,j>i} \int d\vec{r}_i d\vec{r}_j f_{ij} + \dots \quad (3)$$

We are summing up over all configurations  $ij$ . Let us try to compute the term in the integral:

$$\int d\vec{r}_i d\vec{r}_j f_{ij} = \int d\vec{r}_i d\vec{r}_j f(|\vec{r}_i - \vec{r}_j|) = V \int_V d\vec{r} f(|\vec{r}|) \equiv -2b_2 V \quad (4)$$

so, what is important it is the relative distance.  $\vec{r}$  gives us the position from the center we have choosen.

$$b_2 \equiv -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) \quad (5)$$

Rewrite again the partition function:

$$Q_N(V, T) = V^N - V^{N-1} N(N-1) b_2 \quad (6)$$

$$Z_N(V, T) = \left( \frac{V^N}{N! \Lambda^{3N}} \right) \left( 1 - \frac{N^2}{V} b_2 + \dots \right) \quad (7)$$

*Remark.* I do not care about the  $(N-1)$  term, because  $N$  is big enough!

The free energy is:

$$F_N = F_N^{\text{ideal}} - k_B T \ln \left[ 1 - \frac{N^2}{V} b_2 + \dots \right] \quad (8)$$

$$P_N = - \left( \frac{\partial F_N}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \left( 1 + \frac{\frac{N}{V} b_2}{1 - \frac{N}{V} b_2} \right) \approx \frac{N k_B T}{V} \left( 1 + \frac{N}{V} b_2 + \dots \right) \quad (9)$$

here you see the ideal gas and the correction to the ideal gas.

Therefore, it is important computing  $b_2$ , because one time you have this you have the expansion. Or if you wish, by doing the fit of data at different temperature you obtain  $b_2$  from the experiment and you see  $f_{ij}$ . You can use macroscopic to obtain information about the potential in the microscopic.

In principle, from the expansion I realized that for example in a generic expansion

$$(1-x)^{-1} = 1 + x + \dots \quad (10)$$

so, the our expansion is something like this.

$$\frac{PV}{N k_B T} \approx 1 + \rho b_2 \simeq \frac{1}{1 - b_2 \rho} \approx 1 + b_2 \rho + \underbrace{(b_2)^2 \rho^2}_{b_3 \approx b_2^2} + \underbrace{(b_2)^3 \rho^3}_{b_4 \approx b_2^3} \quad (11)$$

**Example 1.** Exam: let us compute virial expansion of a gas in a potential.

The simple one is the hardcore potential.

### Gas of hard spheres

The particles are interacting (it is not ideal!) and there is a size that is the range of the potential.

$$\Phi(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (12)$$

(insert plot of that potential!)

Hence,

$$e^{-\beta\Phi} = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma \end{cases} \quad (13)$$

$$\Rightarrow b_2 = -\frac{1}{2} \int_V d\vec{r} f(|\vec{r}|) = -\frac{1}{2} 4\pi \int dr r^2 [e^{-\beta\Phi} - 1] = 2\pi \int_0^\sigma dr r^2 = \frac{2}{3} \pi \sigma^3 \quad (14)$$

There is no condensation in the gas spheres. The pressure is increased because of therm. It is very easy, but it is interesting for introducing attraction. Let us say, that the potential is not anymore zero but is  $-\varepsilon$  when it is in the case  $r \geq \sigma$ . Or consider a case in which it is  $-\varepsilon$  between  $[\sigma, 2\sigma]$ , then it goes to zero. (Insert graphics of these last potentials!!!!).

We can consider a Lennard-Jones potential:

$$\Phi = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (15)$$

(insert graphics of the Lennard-Jones potential!!!!). The minimum is in  $r_{min} = 2^{1/\sigma}$ . You can play with the change of attraction by changing  $\sigma$  or by changin the  $\varepsilon$ . What it is important is that for the Lennard-Jones we have

$$b_2 \stackrel{LJ}{=} b_2(T) \quad (16)$$

We have pairs  $ij$  or  $kl$  (insert picture). For instance, 12 and 34:

$$\int_V d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 f_{12} f_{34} = V^2 \left( \int dr f(r) \right)^2 \quad (17)$$

$$\frac{N(N-1)}{2} \left[ \frac{(N-2)(N-3)}{2} \right] \frac{1}{2} \quad (18)$$

If we have 123(insert picture) (three particles involved) the integral is:

$$\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 f_{12} f_{23} \simeq V \left( \int dr f(r) \right)^2 \quad (19)$$

In the case (insert picture) were 123 are all interacting we have

$$\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 f_{12} f_{23} f_{31} \simeq V (b_3 - 2b_2^2) \quad (20)$$

## 0.1 Landau mean field of phase transition

Assumptions:

1. Existence of an order parameter  $\eta$ . Remember the definition of the order parameter:

$$\eta = \begin{cases} 0 & T \geq \bar{T} \text{ (disordered or symmetric phase)} \\ \neq 0 & T < \bar{T} \text{ (ordered symmetry is broken)} \end{cases} \quad (21)$$

2. The *free energy* is an analytic function of the order parameter  $\eta$ . It is because you are doing the expansion close to...etc etc. Therefore,  $\mathcal{L} = \mathcal{L}(\eta)$ .
3. Form of  $\mathcal{L}$  must satisfy the symmetries of the system.
4. Equilibrium states are the ones that minimise  $\mathcal{L}$ . Absolute minima.

$$\mathcal{L}(\eta) \approx a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + \dots \quad (22)$$

In this case  $\eta$  is scalar.

If  $\mathbb{Z}^2$  symmetry we have:

$$\mathcal{L}(-\eta) = \mathcal{L}(\eta) \quad (23)$$

We are interested in the minima. Since we want  $\eta = 0$  to be a solution we want  $a_1 = 0, a_3 = 0 \dots$ . Therefore, in  $\mathbb{Z}^2$  symmetry:

$$\mathcal{L}(\eta) \simeq a_0 + a_2\eta^2 + a_4\eta^4 + O(\eta^6) \quad (24)$$

$$a_0 = a_0(J, T) \quad (25a)$$

$$a_2 = a_2(J, T) \quad (25b)$$

$$a_4 = a_4(J, T) \quad (25c)$$

if  $T > \bar{T}$ ,  $\eta = 0$  it implies  $\mathcal{L}(\eta = 0) = a_0$ . Therefore,

$$\mathcal{L}(\eta) \simeq a_2\eta^2 + a_4\eta^4 \quad (26)$$

The term  $a_4$  it is positive and fixed.

Expand in  $t \equiv \frac{T-\bar{T}}{\bar{T}}$ , when  $T = \bar{T} \rightarrow a_2 = 0$ . The Landau free energy in the minimal form is:

$$\mathcal{L} = \frac{a}{2} t\eta^2 + \frac{b}{4} \eta^4 \quad (27)$$

*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  $b > 0$ .

For the Gibbs version (that can be useful):

$$\mathcal{L} = \frac{a}{2} t\eta^2 + \frac{b}{4} \eta^4 - h\eta \quad (28)$$

we insert a field coupled with the order parameter.

Suppose to look for  $h = 0$ , the equilibrium states are the minima

$$\frac{\partial \mathcal{L}}{\partial \eta} = 0 \Rightarrow at\eta + b\eta^3 = 0 \quad (29)$$

so

$$\eta(at + b\eta^2) = 0 \Rightarrow \eta = 0, \eta = \pm \sqrt{\frac{-at}{b}} \quad (30)$$

(insert plot of  $(\eta, \mathcal{L})$  for  $t > 0$  and  $t < 0$  ).

The solutions in the case  $t < 0$  are correlated by the  $\mathbb{Z}^2$  symmetry. The free energy is like the: (plot of  $x^4$  ..... vedere da qualcuno, era un grafico già visto e fatto).

We have  $h \sim \eta^\delta$  for  $T = \bar{T}$ .

$$\frac{\partial \mathcal{L}}{\partial \eta} = 0 \quad \Rightarrow \quad h = at\eta + b\eta^3 \quad (31)$$

that is an equation of state.

$$\chi = \frac{\partial \eta}{\partial h} \quad (32)$$

it implies

$$\chi = \frac{1}{at + 3b\eta^2} \quad (33)$$

You have to proceed in this way.