Lecture 15. Wednesday 4th December, 2019. Compiled: Wednesday 4th December, 2019.

$$e^{-\beta\sum_{i,j>i}\Phi_{ij}} = \prod_i \left(\prod_{j>i}(1+f_{ij})\right) = 1 + \sum_{i,j>i} f_{ij} + \sum_{\substack{i,j>i\\ k,l>k\\ k\geq i\\ (i,j)\neq(k,l)}} f_{ij}f_{kl} + O(f^3) \tag{1}$$

where

$$f_{ij} \equiv e^{-\beta\Phi_{ij}} - 1 \tag{2}$$

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

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

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

$$\int \mathrm{d}\vec{\mathbf{r}}_i\,\mathrm{d}\vec{\mathbf{r}}_j\, f_{ij} = \int \mathrm{d}\vec{\mathbf{r}}_i\,\mathrm{d}\vec{\mathbf{r}}_j\, f(|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j|) = V\int_V \mathrm{d}\vec{\mathbf{r}}\, f(|\vec{\mathbf{r}}|) \equiv -2b_2V \tag{4}$$

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

$$b_2 \equiv -\frac{1}{2}\int_V \mathrm{d}\vec{\mathbf{r}}\, f(|\vec{\mathbf{r}}|) \tag{5}$$

Rewrite again the partition function:

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

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

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

The free energy is:

$$F_N = F_N^{il} - k_BT\ln\left[1 - \frac{N^2}{V}b_2 + \dots\right] \tag{8}$$

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

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 ypu 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

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

so, the our expansion is something like this.

$$\frac{PV}{Nk_BT} \approx 1 + \rho b_2 \simeq \frac{1}{1-b_2\rho} \tag{11}$$