Chapter 1

Non ideal fluids: Mean field theory, Van der Walls, Virial expansion and Cluster expansion

1.1 Mean field theory for fluids

Fluid system of N particles with position vectors $\{\vec{r}_i\}_{i=1,\dots,N}$. The configurational (grancanonical) partition function is (we can do Gaussian integrals)

$$Q_N(T) = \int_V \prod_{i=1}^N \mathrm{d}\vec{r}_i \exp\left[-\beta\Phi(\{\vec{r}\}) - \beta\sum_{i=1}^N \psi_{ext}(\vec{r}_i)\right] \qquad (1.1)$$

where ψ_{ext} is a one body potential, but we do not consider it because is not the aim of our problem.

In general,

$$\Phi(\{\vec{r}_i\}) = \sum_{i,j>i} U_2(\vec{r}_i, \vec{r}_j) + \sum_{i,j,\mu} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_\mu) + \dots \qquad (1.2)$$

but we forgot about U_3 that is the three body interaction.

We consider

$$U_2(\vec{r}_i, \vec{r}_j) \to U_2(|\vec{r}_i - \vec{r}_j|) \qquad (1.3)$$

Therefore,

$$Q_N(T) = \int_V \prod_{i=1}^N \mathrm{d}\vec{r} \exp\left[-\beta\sum_{i,j>i} U_2(|\vec{r}_i - \vec{r}_j|)\right] \qquad (1.4)$$

Now, we replace all this story with just a field, it is a sort of average of the interactions. Doing the mean field assumption for U_2, we obtain

$$\sum_{i,j>1} U_2(|\vec{r}_i - \vec{r}_j|) \to \sum_i \Phi_{MF}(\vec{r}_i) \qquad (1.5)$$

In particular, the **mean field approximation** consists in substituting the multi-body interaction potential $\Phi(\{\vec{r}_i\})$ with an effective one body potential $\Phi(\vec{r})$ withing which all the particles move.

$$\Phi(\{\vec{r}_i\}) = \sum_i \Phi_{MF}(\vec{r}_i) \qquad (1.6)$$

As said, for simplicity consider $\psi_{ext} = 0$, hence

$$Q_N(T) \simeq \left[\int_V \prod_{i=1}^N d\vec{r} \exp[-\beta \Phi_{MF}(\vec{r})] \right]^N \tag{1.7}$$

Remark. The integral depends on the form of $\Phi_{MF}(\vec{r})$.

If one assumes the *spatial isotropy*, what it is important is not anymore the vector but only the distance; hence, it is important just the integral over the modulus:

$$\Phi_{MF}(\vec{r}) = \Phi_{MF}(|\vec{r}|) = \Phi_{MF}(r) \tag{1.8}$$

In general

$$\Phi_{MF}(r) = \begin{cases} \infty & r < r_0 \quad \text{repulsion} \\ u < 0 & r > r_0 \quad \text{attraction} \end{cases} \tag{1.9}$$
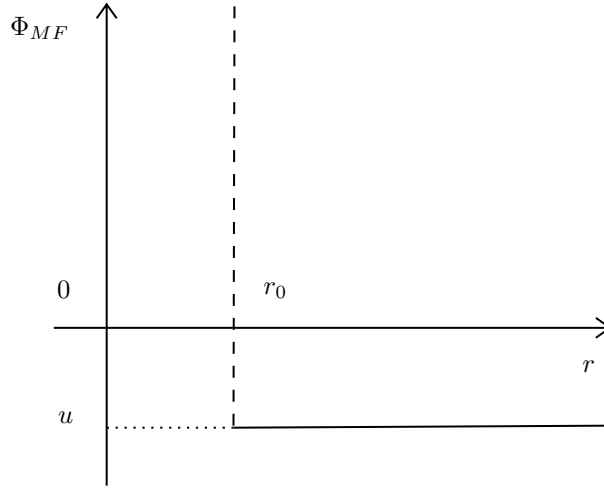
as plotted in Figure 1.1. Moreover,

Figure 1.1: Plot of the potential $\Phi_{MF}(r)$.

$$Q_N^{MF}(T) = \left[V_{ex} e^{-\infty} + (V - V_{ex}) e^{-\beta u} \right]^N \tag{1.10}$$

where $V_{ex} \simeq r_0^3$ is the volume not accessible by the particle.

$$Q_N^{MF}(T) = \left[(V - V_{ex}) e^{-\beta u} \right]^N \tag{1.11}$$

The free energy is

$$F_N^{MF}(T) = -Nk_BT[\ln(V - V_{ex}) - \beta u] \tag{1.12}$$

The pressure is

$$P_N^{MF} = -\left. \frac{\partial F_N^{MF}}{\partial V} \right|_T = \frac{Nk_BT}{V - V_{ex}} - N\left(\frac{\partial u}{\partial V}\right)_T \tag{1.13}$$

Remark. In general, the deep u can go up and down depending on the V: $u = u(V)$. This is becous u is the attractive well of the mean field potential and, for $r \geq r_0$ must be proportional to the fluid density

$$u \sim -N/V$$

where the minus sign means attraction. On the other hand, also V_{ex}, the volume not accessible, must be proportional to N,

$$V_{ex} = bN \quad \Rightarrow u = -a\frac{N}{V}$$

where b is the volume of a single particle.

Inserting the last term in (1.13), we obtain the *Van der Walls equation of state*:

$$P_N^{MF}(V,T) = \frac{Nk_BT}{V-bN} - a\left(\frac{N}{V}\right)^2 \tag{1.14}$$

1.2   Equation of state and critical point

Let us define the specific volume

$$v \equiv \frac{1}{\rho} = \frac{V}{N} \tag{1.15}$$

Hence,

$$P = \frac{K_BT}{v-b} - \frac{a}{v^2} \tag{1.16}$$

We have this effect because it is a mean field, so the curve in Figure 1.2a it is replaced by the curve in Figure 1.2b.

(a) Description

(b) Description

Figure 1.2
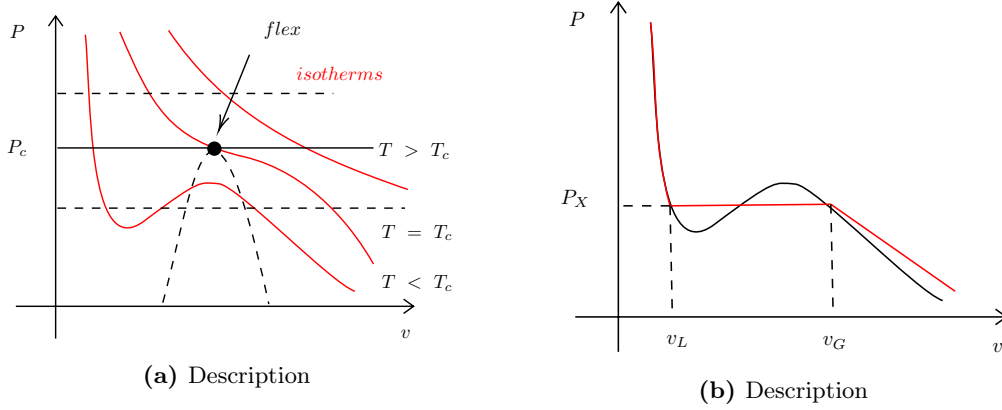
For $T < T_c$ the equation $P(v) = const$ has 3 distinct solutions. For $T > T_c$ only one solution $\in \mathbb{R}$.

- The *inflection point condition* at $T = T_c$ is

$$\frac{\partial P}{\partial v} = \frac{\partial^2 P}{\partial v^2} = 0 \tag{1.17}$$

  and these are the critical point conditions. The second in particular means that there is a flex point. Let us pay attention to it, indeed it is a standard way to find critical points. We obtain $v_c = 3b$:

$$P_c = \frac{a}{27b^2}, \quad k_BT_c = \frac{8a}{27b} \tag{1.18}$$

  and

$$\frac{P_c v_c}{k_BT_c} = \frac{3}{8} \approx 0.375 \tag{1.19}$$

- Another way to find the critical point consists in noticing that at $T = T_c$, the 3 solutions coincide. Let us rewrite the equation of state

$$P = \frac{v^2 k_BT - a(v-b)}{v^2(v-b)} \tag{1.20}$$

as

$$v^3 - \left(b + \frac{k_B T}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0 \tag{1.21}$$

Since at $T = T_c$ the 3 solutions coincide, equation (1.21) must be of the form

$$(v - v_c)^3 = 0 \quad \Rightarrow v^3 - 3v^2 v_c + 3v v_c^2 - v_c^3 = 0 \tag{1.22}$$

and, by identifying its coefficients with the ones in (1.21) one gets

$$v_c^3 = \frac{ab}{P_c}, \quad 3v_c^2 = \frac{a}{P_c}, \quad 3v_c = b + \frac{k_B T_c}{P_c} \tag{1.23}$$

Giving

$$v_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad k_B T_c = \frac{8a}{27b} \tag{1.24}$$

From the relations (1.24), it is clear that it is sufficient to estimate the a and b coefficients of a gas using the equation of state at T sufficiently high to estimate its critical values, v_c, T_c and P_c. Moreover, one can show that

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} \approx 0.375 \tag{1.25}$$

It is an universal ratio whose value does not depends on either a or b.

1.2.1 Law of the correspondent states

The universal value of the ratio $\frac{P_c v_c}{k_B T_c}$ suggests a deeper correspondence between different fluid systems.

Let us rewrite the Van der Walls equation of state (1.14) in adimensional form

$$\pi \equiv \frac{P}{P_c}, \quad \nu \equiv \frac{v}{v_c}, \quad \tau \equiv \frac{T}{T_c} \tag{1.26}$$

The result is

$$\left(\pi + \frac{3}{\nu^2}\right)(3\nu - 1) = 8\tau \tag{1.27}$$

Remark. When rescaled by P_c, v_c and T_c, the thermodynamic variables P, v and T of the Van der Walls fluids, follow the same equation of state! The Van der Walls theory describes the law of correspondent states found experimentally.

1.3 Region of coexistence and Maxwell construction

In real fluids, for $T < T_c$ ($\tau < 1$), there is a first order liquid-gas transition with coexistence between vapor and liquid phase and non analiticity of the thermodynamic potential. In particular, an isotherm for $T < T_c$ is the one in Figure 1.2b. How this is described by the mean-field (i.e. Van der Walls) theory?

The Van der Walls isotherm is given by the graphic in Figure 1.3. The liquid phase goes into a phase region that is not thermodinamycally stable.

How can we remove the non physical regions of the Van der Walls equation of state and describe coexistence? The solution is the Maxwell (or equal area) construction.
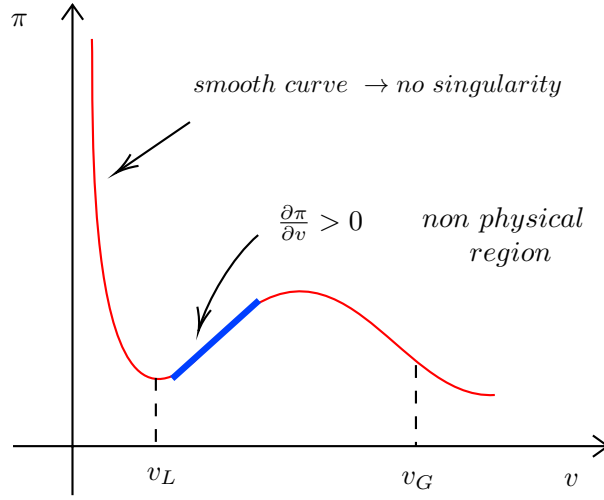
Figure 1.3: Description.

1.3.1 Equal area or Maxwell construction

Remark. The coexistence regions are characterised by having the same pressure (mechanical equilibrium) and same temperature (thermal equilibrium).

Since

$$\mu \equiv \frac{G}{N} = \frac{F + PV}{N} \tag{1.28}$$

we have

$$d\mu = -\frac{S}{N}\, dT + \frac{V}{N}\, dP \tag{1.29}$$

Along an isotherm ($T = const$), $dT = 0$, which implies

$$d\mu = \frac{V}{N}\, dP \tag{1.30}$$

At the coexistence $dP_{coex} = 0$, hence

$$d\mu = 0 \tag{1.31}$$

is the physical condition.

Now, let us consider a Van der Walls isotherm at $T < T_c$, as in Figure 1.4.

Remark. For Van der Wall $dP \neq 0$!

The physical coexistence condition $d\mu_{phy}$ implies

$$0 = \int_1^2 d\mu = \mu(2) - \mu(1) \stackrel{Van\,der\,Walls}{=} \frac{1}{N} \int_{P_G}^{P_L} dP\, V \tag{1.32}$$

The integral can be partitioned in two parts

$$0 = \int_{P_G}^{P_L} dP\, V \quad \Rightarrow \int_{P_G}^{P_x} dP\, V = -\int_{P_x}^{P_L} dP\, V \tag{1.33}$$

Remark. The equal area condition gives the value of P_x of the coexistence line!
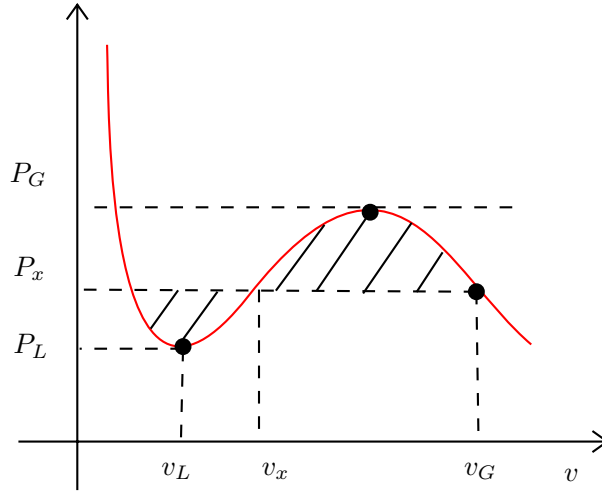
Figure 1.4: Description.

1.4   Critical exponents of Van der Walls

β exponent

The equation of state is

$$\left(\pi + \frac{3}{\nu^2}\right)(3\nu - 1) = 8\tau \tag{1.34}$$

where

$$\pi = \frac{P}{P_c}, \quad \nu = \frac{v}{v_c}, \quad \tau = \frac{T}{T_c} \tag{1.35}$$

Let us consider

$$\begin{cases} t \equiv \tau - 1 = \frac{T - T_c}{T_c} \\ \Phi = \nu - 1 = \frac{v - v_c}{v_c} \end{cases} \tag{1.36}$$

we want the deviation from the critical point. Close to the critical point $\tau \sim \nu \sim 1$ and $t \sim \Phi \sim 0$.

We now expand the equation of state with respect to t and Φ

$$\left(\pi + \frac{3}{(1 + \Phi)^2}\right)(3(\Phi - 1) - 1) = 8(t + 1) \tag{1.37}$$

$$\Rightarrow \pi = \frac{8(t + 1)}{2(\Phi + 1) - 1} - \frac{3}{(1 + \Phi)^2} \tag{1.38}$$

Expanding for $\Phi \sim 0$,

$$(1 + \Phi)^\alpha \simeq 1 + \Phi \tag{1.39}$$

To do:

$$\pi \simeq 1 + 4t - 6t\Phi - \frac{3}{2}\Phi^3 + O(t\Phi^2, \Phi^4) \tag{1.40}$$

Remark. Since we will get $\Phi \sim t^{1/2}$ the truncation of the expansion is justified a posteriori.

In order to get the values of $v_G(P)$ and $v_L(P)$ at coexistence, we use the Maxweel construction

$$\int_{P_G}^{P_L} v \, dP = 0 \tag{1.41}$$

$$\int_{v_L}^{v_G} v \, \mathrm{d}P = 0 \tag{1.42}$$

Rewrite it with respect to the rescaled variables $\pi = \frac{P}{P_c}$ and $\nu = \frac{v}{v_c}$, if $\Phi = \nu - 1$ we have

$$\mathrm{d}P = P_c \, \mathrm{d}\pi \tag{1.43}$$

Let us consider $T < T_c$ fixed, if and only if $t < 0$ (but small)

$$\pi = \pi(v) = \pi(\Phi) \tag{1.44}$$

$$\pi \simeq 1 + 4t - 6t\Phi - \frac{3}{2}\Phi^3 + O(t\Phi^2, \Phi^4) \tag{1.45}$$

$$\Rightarrow \mathrm{d}\pi \simeq -6t \, \mathrm{d}\Phi - \frac{q}{2}\Phi^2 \, \mathrm{d}\Phi \tag{1.46}$$

$$\Rightarrow \mathrm{d}P = P_c\left[-6t \, \mathrm{d}\Phi - \frac{q}{2}\Phi^2 \, \mathrm{d}\Phi\right] \tag{1.47}$$

The equation (1.42) implies

$$\int_{\Phi_c}^{\Phi_g} \Phi\left(-6t - \frac{q}{2}\Phi^2\right) \mathrm{d}\Phi = 0 \tag{1.48}$$

It must be true for all $t \ll 1$.

Remark.

$$\int_c^g 1 \, \mathrm{d}P = 0 \tag{1.49}$$

since we are at coexistence!

$$\Rightarrow -3\Phi_g^2\left[t + \frac{\Phi_g^2}{g}\right] + 3\Phi_c^2\left[t + \frac{\Phi_c^2}{g}\right] = 0 \tag{1.50}$$

if and only if $\Phi_g^2 = \Phi_c^2$, hence if and only if

$$\Phi_g = \pm\Phi_c \tag{1.51}$$

On the other hand,

$$\Phi_g = \frac{v_g - v_c}{v_c}, \quad \Phi_l = \frac{v_l - v_c}{v_c} \tag{1.52}$$

$$\Rightarrow \Phi_g = -\Phi_l \tag{1.53}$$

If we now insert Φ_g and Φ_l in the expression of π, we get

$$\Phi_g \to \pi = 1 + 4t - 6t\Phi_g - \frac{3}{2}\Phi_g^3 \tag{1.54a}$$

$$\Phi_l \to \pi = 1 + 4t + 6t\Phi_g + \frac{3}{2}\Phi_g^3 \tag{1.54b}$$

The two expression of π must be equal since we are at coexistence. Solving with respect to Φ_g we get

$$\Phi_g = 2\sqrt{-t} \sim \left(\frac{T_c - T}{T_c}\right)^{1/2} \tag{1.55}$$

which implies

$$\beta = \frac{1}{2} \tag{1.56}$$

1.5 Theory of weakly interacting fluids

If the gas is not ideal but made by weakly interacting particles, it is possible to follow a *perturbative approach*. Let us consider N particles in region Ω of volume V. Particles interact by a two-body interacting potential

$$U_2(\vec{r}_i, \vec{r}_j) = \Phi(|\vec{r}_i - \vec{r}_j|) \tag{1.57}$$

hence,

$$\Rightarrow U(\{\vec{r}\}) = \frac{1}{2} \sum_{i,j} \Phi(|\vec{r}_i - \vec{r}_j|) \tag{1.58}$$

The Hamiltonian we are considering is

$$\mathcal{H}_\Omega(\{\vec{r}\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i,j>i} \Phi(|\vec{r}_i - \vec{r}_j|) \tag{1.59}$$

In the canonical ensemble

$$Z_\Omega(N, V, T) = \frac{1}{N! \Lambda^{3N}} Q_N(V, T) \tag{1.60}$$

where

$$Q_N(V, T) = \int_V d\vec{r}_1 \int_V d\vec{r}_2 \cdots \int_V d\vec{r}_N \exp[-\beta U(\{\vec{r}\})] \tag{1.61}$$

Remark. For ideal gases $U = 0$, so

$$Q_N(V, T) = V^N \quad \rightarrow Z_N^{ideal} = \frac{V^N}{N! \Lambda^{3N}} \tag{1.62}$$

and the dependence on T is exclusively due to $\Lambda = \Lambda(T)$ (i.e. kinetic energy).

Now, suppose $U \neq 0$, but small! We can say that we can assume that our $Q_N(V, T)$ it would be the ideal version times a new function

$$Q_N(V, T) \simeq V^N \chi(N, V, T) \tag{1.63}$$

Remark. If Φ is only repulsive, χ does not depend on T.

In conclusion, we obtain

$$F_N = F_N^{ideal} - k_B T \ln \chi_N \tag{1.64}$$

remaThe correction χ due to particle-particle interaction depends on the particle density ρ.

$$\begin{cases} \rho_{small} \Rightarrow U = 0 \\ \rho_{high} \Rightarrow U \neq 0 \text{ and not negligible} \end{cases} \tag{1.65}$$

This suggests that the equation of state of a weakly interacting gas can be expanded formally in powers of ρ. This is known as *virial expansion*.

For the ideal gas:

$$\frac{P}{k_B T} = \rho \tag{1.66}$$

This is the ideal gas, now start to add the other terms of the expansion

$$\rightarrow \frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots + O(\rho^n) \tag{1.67}$$

this is a *virial expansion* and it is one of the most used. The coefficient B are called the *virial coefficients*. The equation (1.67) was first introduced as a formula to fit

experimental data. Indeed, making a fit, you will obtain the virial coefficients. This is what physicist have done for years. Then, mapping the coefficient with the real world experiments, we can find some macroscopical parameters.

The formula (1.67) can be also obtained rigorously from a perturbation approach to the partition function (see later).

Which is the virial expansion of a Van der Walls (i.e. mean field) gas?

1.6 Van der Walls and virial expansion

Consider the Van der Walls equation of state

$$\frac{P}{k_B T} = \frac{N}{V - bN} - \frac{aN^2}{k_B T V^2} \tag{1.68}$$

Let us factorize N/V,

$$\frac{P}{k_B T} = \left(\frac{N}{V}\right)\left(1 - b\frac{N}{V}\right)^{-1} - \frac{a}{k_B T}\left(\frac{N}{V}\right)^2 \tag{1.69}$$

Expanding in power of (N/V),

$$\Rightarrow \frac{P}{k_B T} = \left(\frac{N}{V}\right) + \left(\frac{N}{V}\right)^2 \left(b - \frac{a}{k_B T}\right) + \left(\frac{N}{V}\right)^3 b^2 + \left(\frac{N}{V}\right)^4 b^3 + \dots$$

$$= \rho + \left(b - \frac{a}{k_B T}\right)\rho^2 + b^2\rho^3 + b^3\rho^4 + \dots \tag{1.70}$$

Therefore,

$$B_2(T)^{VdW} = b - \frac{a}{k_B T} \qquad B_3^{VdW} = b^2 \tag{1.71}$$

where in $B_2(T)^{VdW}$ the first term is repulsive on excluded volume and the second one is the attraction term. In B_3^{VdW} we note that the term is always positive.

1.6.1 Boyle's temperature T_B

The Boyle's temperature is the T at which the second coefficient is zero:

$$B_2^{VdW}(T_B) = 0 \tag{1.72}$$

so we have removed the most important coefficient. The competing effects of repulsion and attraction are cancelled out.

We have the Van der Walls temperature T_B^{VdW}

$$T_B^{VdW} = \frac{a}{bk_B} \tag{1.73}$$

to be compared with T_c^{VdW} that is

$$T_c^{VdW} = \frac{8a}{27b^3} \tag{1.74}$$

We notice that $T_c^{VdW} \ll T_B$. It is clear that the Boyle's temperature must be much greater than the critical one.

We now obtain the formal virial expansion by starting from the microscopic system and performing a perturbation expansion of the Boltzmann weights for small values of U.

Remark. Consider a polymer, the transition point called the θ point is when the second coefficient is zero, as the case described above, but it is interesting in polymer kind of system (lesson).

1.7 Cluster expansion technique for weakly interacting gases

Now, we try to do some calculation of this virial coefficients, starting from the model microscopical. Let us start from the partition function

$$
\begin{aligned}
Q_N &= \int_V d\vec{r}_1 \cdots \int_V d\vec{r}_N \, e^{-\beta U(\{\vec{r}\})} \\
&= \int_V d\vec{r}_1 \cdots \int_V d\vec{r}_N \, e^{-\beta \sum_{i,j>i} \Phi_{ij}}
\end{aligned}
\tag{1.75}
$$

where

$$
\Phi_{ij} \equiv \Phi(|\vec{r}_i - \vec{r}_j|)
\tag{1.76}
$$

Definition 1 (Mayer function). The *Mayer function* is something that is smaller in that given point

$$
f(|\vec{r}|) \equiv \exp[-\beta \Phi(|\vec{r}|)] - 1
\tag{1.77}
$$

with $f_{ij} \equiv f(|\vec{r}_i - \vec{r}_j|)$.

Remark. Note: if $\beta\Phi(r) \ll 1$, we have $f(r) \ll 1$.

Hence,

$$
\begin{aligned}
\Rightarrow e^{-\beta \sum_{i,j>i} \Phi_{ij}} &= \prod_i \left(\prod_{j>i} (1 + f_{ij}) \right) \\
&= \underbrace{(1 + f_{12})(1 + f_{13}) \ldots (1 + f_{1N})}_{i=1} \ldots \underbrace{(1 + f_{23})(1 + f_{24}) \ldots (1 + f_{2N})}_{i=2} \ldots \\
&= (1 + f_{12} + f_{13} + f_{12}f_{13})(1 + f_{14}) \ldots (1 + f_{23}) \\
&= 1 + \sum_i \sum_{k>i} f_{ij} + \sum_j^N \sum_{k \geq i} \sum_{l>k} \sum_{j>i} \sum_{(ij)\neq(lk)} f_{ik} f_{kl} + O(f^3)
\end{aligned}
\tag{1.78}
$$

where

$$
f_{ij} \equiv e^{-\beta \Phi_{ij}} - 1
\tag{1.79}
$$

Higher order terms contain products of $3, 4, \ldots f_{ij}$ terms. For simplicity, let us consider first only linear terms. Hence, the solution is given by considering only the linear term. This is the cluster expansion.