Proof:

$$\frac{1}{2!}(I)^2 = \frac{1}{2!}\left(\frac{N(N-1)}{2V^2}\underbrace{\int d^3r_1\, d^3r_2\, f_{12}(r_{12})}_{vV}\right)^2 = \frac{1}{8}\frac{N^2(N-1)^2 v^2}{V^2}$$

$$= \left(\frac{N^4}{8} - \frac{N^3}{4} + \frac{N^2}{8}\right)\frac{v^2}{V^2}$$

$$(II) = \frac{N(N-1)(N-2)(N-3)}{8V^4}\int d^3r_1 \cdots d^3r_4\, f_{12} f_{34} \leftarrow$$

$$= \left(\frac{N^4}{8} - \frac{3N^3}{4} + \frac{11}{8}N^2 - \frac{3N}{4}\right)\frac{v^2}{V^2}$$

$$\frac{N(N-1)(N-2)}{2V^3}\int d^3r_1\, d^3r_2\, d^3r_3\, f_{12} f_{23}$$

$$= \left(\frac{N^3}{2} - \frac{3N^2}{2} + N\right)\frac{v^2}{V^2}$$

1PI = one-particle irreducible

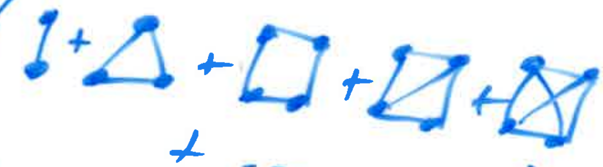
≡ connected diagrams, and <u>remain</u> connected if you remove any one dot and all the lines connected to that one dot.

e.g.  $= \dfrac{N(N-1)(N-2)}{6\, V^3} \int d^3r_1\, d^3r_2\, d^3r_3\, f_{12}(r_{12}) f_{23}(r_{23}) f_{31}(r_{31})$

$$Z = Z_{ideal} \cdot Z_c$$

Z_c ← configuration integral

$$F = -k_B T \ln(Z) = -k_B T \ln(Z_{ideal}) - k_B T \ln(Z_c)$$

$= -N k_B T \ln\left(\dfrac{V}{N v_Q}\right) - k_B T \Big($  $+ \cdots \Big)$

$\underbrace{\qquad\qquad\qquad}_{1PI}$

Evaluate  for a given $u_{12}(r_{12})$

 $= \dfrac{\overbrace{N(N-1)}^{N^2}}{2V^2} \int d^3r_1\, d^3r_2\, f_{12}(r_{12})$

$= \dfrac{N^2}{2V^2} \underbrace{\left[\int d^3r_{cm}\right]}_{V} \underbrace{\int d^3r\, f_{12}(r)}_{v}$

change variable
$\vec{r}_{cm}$ center of mass
$\vec{r} = \vec{r}_2 - \vec{r}_1$
relative coordinate
cf. lecture 24.

$$I = \frac{1}{2}\frac{N^2}{V^2} V \int d^3r\, f(r)$$

$$d^3r = r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

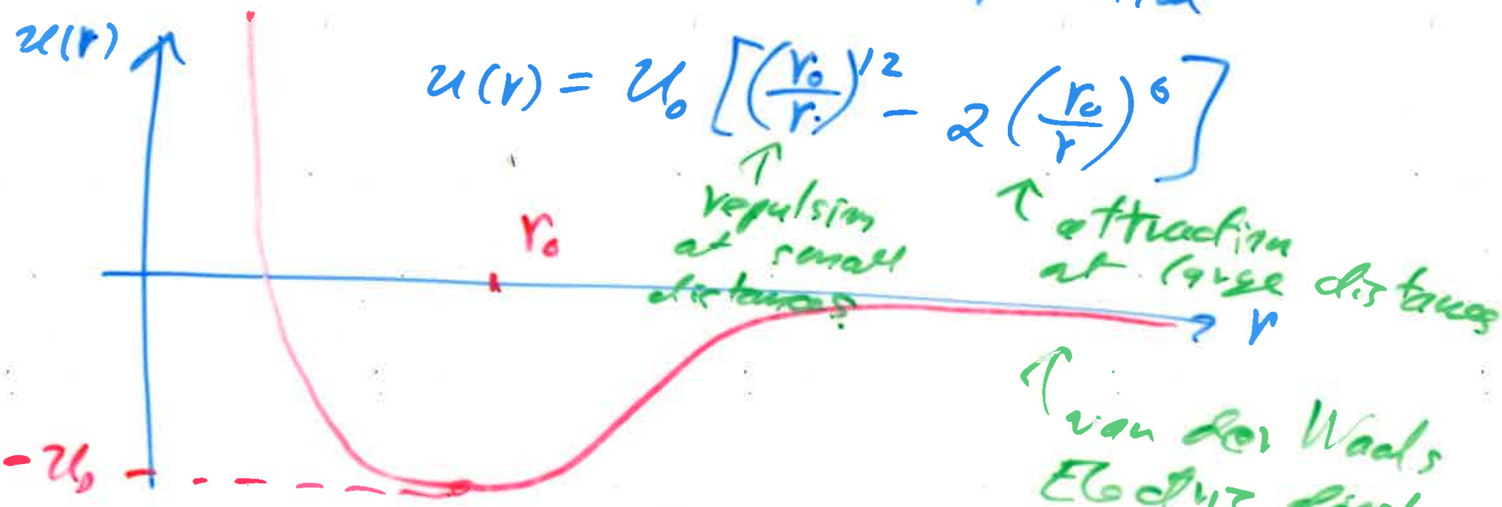
$$f(r) = e^{-\beta u(r)} - 1$$

$$I = \frac{1}{2}\frac{N^2}{V}(4\pi)\int_{r=0}^{\infty} r^2\left[e^{-\beta u(r)} - 1\right] dr$$

Now we need a $u(r)$ potential energy:

e.g. Lennard-Jones (6-12) potential

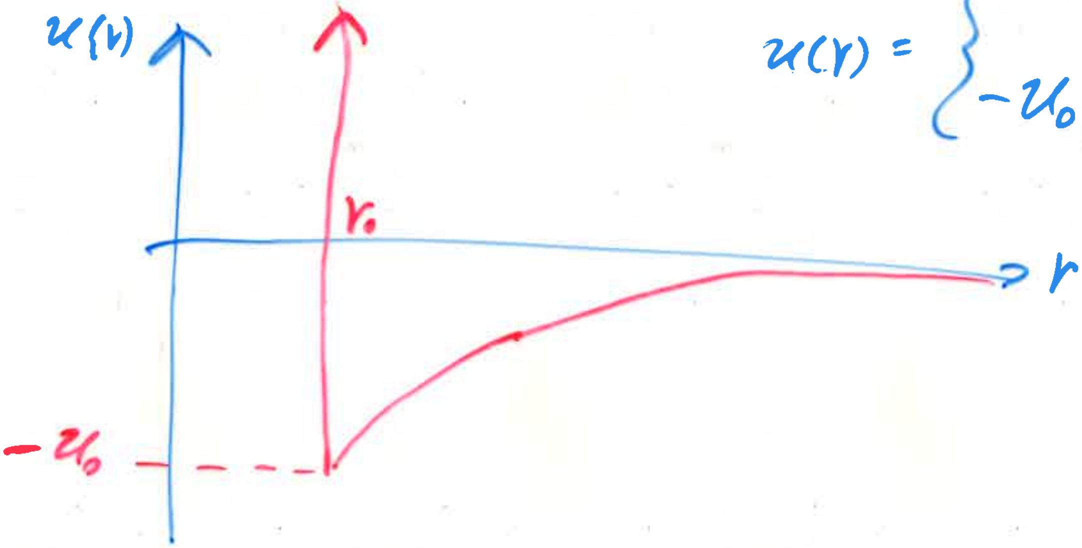
$$u(r) = u_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$



$(x^2 - 2x)$

Coulomb potential $u \sim \frac{1}{r}$, Mayer f-expansion does not converge $\longrightarrow$ use ring expansion.

e.g. Hard core potential energy.



$$u(r) = \begin{cases} \infty & r < r_0 \\ -u_0\left(\frac{r_0}{r}\right)^6, & r > r_0 \end{cases}$$

\# Dots "n" → n^{th} Virial Coefficent