Class Assignment 1

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CASE 1: Considering Homogenous rho i.e. taking rho(r_1) = rho(r_2) = N/V

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Q – USE $U(\vec{r}_N) = \sum_{i=1}^{N}\sum_{j>i}^{N} U(r_{ij})$

IDENTICAL BEHAVIOUR OF PAIRS
$$U(\vec{r}_N) = \frac{N(N-1)}{2} U(\vec{r}_{12}) \quad \forall \vec{r}_{12}$$

EXPRESS U_{EXCESS} IN TERMS OF $g_N^2(\vec{r}_1, \vec{r}_2)$

Ans – $$U_{EXCESS} = \langle U(\vec{r}_N)\rangle = \frac{1}{Z_N}\int_{r_N} U(\vec{r}_N)\, e^{-\beta U(\vec{r}_N)}\, d\vec{r}_N$$

$$= \frac{1}{Z_N}\int_{\vec{r}_N} \frac{N(N-1)}{2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_N$$

$$= \frac{\iint_{\vec{r}_1 \vec{r}_2} \frac{N(N-1)}{2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 d\vec{r}_2 \int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}{\int_{\vec{r}_N} e^{-\beta U(\vec{r}_N)}\, d\vec{r}^N}$$

$$= \frac{\iint_{\vec{r}_1 \vec{r}_2} \frac{N(N-1)}{2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}$$

$$= \frac{N(N-1)}{2} \frac{\iint_{\vec{r}_1 \vec{r}_2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 d\vec{r}_2}{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 d\vec{r}_2} \qquad \text{— (1)}$$

$$* \quad g_N^2(\vec{r}_1, \vec{r}_2) = \frac{e_N^2(\vec{r}_1, \vec{r}_2)}{\prod_{i=1}^{2} e_N^1(\vec{r}_i)} = \frac{\frac{N!}{(N-2)!}\left(\frac{1}{Q_N h^{3N} N!}\right)\int_{\vec{p}^N}\int_{\vec{r}^{N-2}} e^{-\beta H(\vec{r}^N, \vec{p}^N)}\, d\vec{r}^{N-2} d\vec{p}^N}{\prod_{i=1}^{2} e_N^1(\vec{r}_i)}$$

substituting Q_N

$$g_N^2(\vec{r}_1,\vec{r}_2) = \frac{1}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)} \times \frac{\frac{N!}{(N-2)!}\cancel{\left(\frac{1}{h^{3N}N!}\right)\int_{\vec{p}^N} e^{-\beta\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}} d\vec{p}^N} \int_{\vec{r}_{N-2}} e^{-\beta U(\vec{r}_N)} d\vec{r}_{N-2}}{\frac{1}{\cancel{h^{3N}}N!}\int_{\vec{r}_N} e^{-\beta U(\vec{r}_N)} d\vec{r}_N \cancel{\int_{\vec{p}^N} e^{-\beta\sum\frac{\vec{p}_i^{\,2}}{2m}} d\vec{p}^N}}$$

$$= \frac{1}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)} \frac{N(N-1)\int_{\vec{r}_{N-2}} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_{N-2}}{\int_{\vec{r}_N} e^{-\beta\frac{N(N-2)}{2}U(\vec{r}_{12})} d\vec{r}_N}$$

$$= \frac{N(N-1)}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)} \cdot \frac{e^{-\beta\frac{N(N-2)}{2}U(\vec{r}_{12})} \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}{\iint_{\vec{r}_1,\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}$$

$$= \frac{N(N-1)\, e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \times \left\{\iint_{\vec{r}_1,\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2\right]^{-1}}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)}$$

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$$= \frac{N(N-1)}{\rho^2} \frac{e^{-\beta \frac{(N)(N-1)}{2} U(\vec{r}_{12})}}{\left(\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2\right)}$$

(assuming homogenous $\rho = \rho_N^1(\vec{r}_1) = \rho_N^2(\vec{r}_2)$)

now,

$$\iint_{\vec{r}_1 \vec{r}_2} g_N^2(\vec{r}_1, \vec{r}_2) \frac{\rho^2}{2} U(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2 = \frac{N(N-1)}{2} \frac{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{(N)(N-1)}{2} U(\vec{r}_{12})} U(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2}{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2}$$

~~us~~ right hand side $= U_{EXCESS}$ from (V)

$$\therefore \; U_{EXCESS} = \frac{\rho^2}{2} \iint_{\vec{r}_1 \vec{r}_2} g_N^2(\vec{r}_1, \vec{r}_2) U(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2$$

also as, ~~we know~~ $\rho = N/V$

$$U_{EXCESS} = \frac{N^2}{2V^2} \iint_{\vec{r}_1 \vec{r}_2} U(\vec{r}_{12}) g_N^2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

CASE 2: **NOT** Considering Homogenous rho i.e. taking rho(r_1) = rho(r_2) = N/V

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Q – USE $U(\vec{r}_N) = \sum_{i=1}^{N} \sum_{j>i}^{N} U(r_{ij})$

IDENTICAL BEHAVIOUR OF PAIRS

$$U(\vec{r}_N) = \frac{N(N-1)}{2} U(\vec{r}_{12}) \quad \forall \vec{r}_{12}$$

EXPRESS U_{EXCESS} IN TERMS OF $g_N^2(\vec{r}_1, \vec{r}_2)$

Ans – $U_{EXCESS} = \langle U(\vec{r}_N) \rangle = \frac{1}{Z_N} \int_{\vec{r}_N} U(\vec{r}_N)\, e^{-\beta U(\vec{r}_N)} d\vec{r}_N$

$$= \frac{1}{Z_N} \int_{\vec{r}_N} \frac{N(N-1)}{2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_N$$

$$= \frac{\iint_{\vec{r}_1 \vec{r}_2} \frac{N(N-1)}{2} U(\vec{r}_{12}) e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2 \int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}{\int_{\vec{r}_N} e^{-\beta U(\vec{r}_N)} d\vec{r}_N}$$

$$= \frac{\iint_{\vec{r}_1 \vec{r}_2} \frac{N(N-1)}{2} U(\vec{r}_{12}) e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}_{N-2}} d\vec{r}_{N-2}}}$$

$$= \frac{N(N-1)}{2} \frac{\iint_{\vec{r}_1 \vec{r}_2} U(\vec{r}_{12}) e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2}{\iint_{\vec{r}_1 \vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2} \qquad \text{— (1)}$$

$$* \quad g_N^2(\vec{r}_1, \vec{r}_2) = \frac{\rho_N^2(\vec{r}_1, \vec{r}_2)}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)} = \frac{\frac{N!}{(N-2)!} \left(\frac{1}{Q_N h^{3N} N!}\right) \int_{\vec{p}^N} \int_{\vec{r}_{N-2}} e^{-\beta H(\vec{r}_N, \vec{p}_N)} d\vec{r}_{N-2} d\vec{p}_N}{\prod_{i=1}^{2} \rho_N^1(\vec{r}_i)}$$

substituting Q_N

$$g^2_N(\vec{r}_1,\vec{r}_2) = \frac{1}{\prod_{i=1}^{2} \rho^1_N(\vec{r}_i)} \times \frac{\frac{N!}{(N-2)!}\left(\cancel{\frac{1}{h^{3N}N!}}\right) \cancel{\int_{\vec{p}^N} e^{-\beta\sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m}} d\vec{p}^N} \int_{\vec{r}^{N-2}} e^{-\beta U(\vec{r}^N)} d\vec{r}^{N-2}}{\cancel{\frac{1}{h^{3N}N!}} \int_{\vec{r}^N} e^{-\beta U(\vec{r}^N)} d\vec{r}^N \cancel{\int_{\vec{p}^N} e^{-\beta\sum\frac{\vec{p}_i^2}{2m}} d\vec{p}^N}}$$

$$= \frac{1}{\prod_{i=1}^{2} \rho^1_N(\vec{r}_i)} \; \frac{N(N-1) \int_{\vec{r}^{N-2}} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}^{N-2}}{\int_{\vec{r}^N} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}^N}$$

$$= \frac{N(N-1)}{\prod_{i=1}^{2} \rho^1_N(\vec{r}_i)} \cdot \frac{e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \cdot \cancel{\int_{\vec{r}^{N-2}} d\vec{r}^{N-2}}}{\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2 \cdot \cancel{\int_{\vec{r}^{N-2}} d\vec{r}^{N-2}}}$$

$$= \frac{N(N-1)\, e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \times \left\{\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2\right\}^{-1}}{\prod_{i=1}^{2} \rho^1_N(\vec{r}_i)}$$

$$= \frac{N(N-1)\, e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \times \left(\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2\right)^{-1}}{\frac{\frac{N!}{(N-1)!}\int_{\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 \cdot \frac{N!}{(N-1)!}\int_{\vec{r}_1} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_2}{\left(\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2\right)^2 \times 1}}$$

$$= \frac{\cancel{N}(N-1)}{N^{\cancel{2}}}\; e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \frac{\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2}{\int_{\vec{r}_1} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 \int_{\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_2}$$

$$g^2_N(\vec{r}_1,\vec{r}_2) = \frac{(N-1)}{N}\, e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} \frac{\iint_{\vec{r}_1\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 d\vec{r}_2}{\int_{\vec{r}_1} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_1 \int_{\vec{r}_2} e^{-\beta\frac{N(N-1)}{2}U(\vec{r}_{12})} d\vec{r}_2} \longrightarrow (2)$$

$$\Rightarrow \int_{\vec{r}_1}\int_{\vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1\, d\vec{r}_2 = \frac{g_N^2(\vec{r}_1,\vec{r}_2) \times \int_{\vec{r}_1} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 \int_{\vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_2}{\frac{(N-1)}{N}\, e^{-\beta N \frac{N-1}{2} U(\vec{r}_{12})}}$$

substituting this in (1),

$$V_{EXCESS} = \frac{\cancel{N}(N-1)}{2} \frac{\int_{\vec{r}_1}\int_{\vec{r}_2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1\, d\vec{r}_2}{\frac{\cancel{N} \times g_N^2(\vec{r}_1,\vec{r}_2) \int_{\vec{r}_1} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1 \int_{\vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_2}{(N-1)\, e^{-\beta N \frac{(N-1)}{2} U(\vec{r}_{12})}}}$$

$$V_{EXCESS} = \frac{1}{g_N^2(\vec{r}_1,\vec{r}_2)} \cancel{\{K\}}\, F(\vec{r}_1,\vec{r}_2)$$

where,
$$F(\vec{r}_1,\vec{r}_2) = \frac{(N-1)^2}{2} \left(\frac{\int_{\vec{r}_1}\int_{\vec{r}_2} U(\vec{r}_{12})\, e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1\, d\vec{r}_2}{\int_{\vec{r}_1} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_1} \right) \times \left(\frac{e^{-\beta N \frac{(N-1)}{2} U(\vec{r}_{12})}}{\int_{\vec{r}_2} e^{-\beta \frac{N(N-1)}{2} U(\vec{r}_{12})}\, d\vec{r}_2} \right)$$