Correlation Functions

* Interactions between particles leads to correlations between their motions in coordinate space (true for quantum or classical systems)

* For simplicity, let's just consider systems w/ binary (pairwise) interactions

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} u(|\vec{r}_i - \vec{r}_j|)$$

$$= \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} u(|\vec{r}_i - \vec{r}_j|) \equiv U(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)$$

* The key tool to study spatial correlations is the two-particle correlation function, which is closely related to a generalization of the notion of a single particle density

$$\boxed{n_1(\vec{r}) \equiv \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \right\rangle}$$

1-particle density

(Not being too precise whether this is a QM or CM system, or the particular ensemble)

e.g., $$n_1^{CE}(\vec{r}) = \frac{1}{Z_{CE}} \sum_n e^{-\beta E_n^N} \left\langle \Psi_n^N \middle| \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \middle| \Psi_n^N \right\rangle$$

for QM system in Canonical Ensemble

e.g. $$n_1^{GCE} = \frac{1}{Z_{GCE}} \sum_{N=0}^{\infty} \sum_{n} e^{-\beta(E_n^N - \mu N)} \langle \Psi_n^N | \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) | \Psi_n^N \rangle$$

for a QM sys. in the Grand Canonical

* Clearly see that

$$\boxed{\begin{aligned} \int d^3\vec{r}\, n_1(\vec{r}) &= N \quad (CE) \\ &= \langle N \rangle \quad (GCE) \end{aligned}}$$

* In the following, our notation will be for that of the CE, though many of the formulas go thru to the GCE with suitable modification (e.g., $\langle N \rangle_{CE} = N$; $\langle N^2 \rangle_{CE} = \langle N \rangle_{CE} \langle N \rangle_{CE} = N^2$, whereas $\langle N^2 \rangle_{GCE} \neq \langle N \rangle_{GCE} \langle N \rangle_{GCE}$ in general)

+ classical systems

* Define two-body density as

$$n_2(\vec{r}, \vec{r}\,') \equiv \left\langle \sum_{i \neq j} \delta(\vec{r}-\vec{r}_i)\, \delta(\vec{r}\,'-\vec{r}_j) \right\rangle$$

$\therefore\ n_2(\vec{r}, \vec{r}\,')\, d^3r\, d^3\vec{r}\,' =$ # of particles in d^3r about $\vec{r}$ $\times$ # of particles in d^3r' about $\vec{r}\,'$

$$\Rightarrow \iint n_2(\vec{r}, \vec{r}\,')\, d^3\vec{r}\, d^3\vec{r}\,' = \left\langle \sum_{i \neq j}^{N} \right\rangle = \langle N^2 - N \rangle$$

$$= N^2 - N \quad CE$$

$$= \langle N^2 \rangle - \langle N \rangle \quad GGE$$

* Limiting behavior for non-interacting system, expect

$$n_2(\vec{r},\vec{r}\,') \longrightarrow n_1(\vec{r})\, n_1(\vec{r}\,') = n^2$$

For uniform translational invariant sys

* Define Pair correlation function

$$\boxed{\begin{aligned} g_N(\vec{R}) &\equiv \frac{V}{N(N-1)} \int d^3r \; n_2(\vec{r}, \vec{r}-\vec{R}) \\ &= \frac{V}{N(N-1)} \int d^3r \left\langle \sum_{i\neq j}^{N} \delta(\vec{r}-\vec{r}_i)\, \delta(\vec{r}-\vec{R}-\vec{r}_j) \right\rangle \\ &= \frac{V}{N(N-1)} \left\langle \sum_{i\neq j}^{N} \delta(\vec{R}+\vec{r}_j-\vec{r}_i) \right\rangle \end{aligned}}$$

$\propto$ prob. a pair of particles is separated by $\vec{R}$

Note: 1) $\int d^3\vec{R}\, g_N(\vec{R}) = \frac{V}{N(N-1)} N(N-1) = V$

2) $\int d^3R\, g(R)\Big|_{GCE} = \frac{V}{\langle N\rangle} \cdot \frac{\langle N^2 - N\rangle}{\langle N\rangle - 1}$

Eg: Non-interacting (non-correlated trans. invariant gas)

$$g_N(\vec{R}) = \frac{V}{N(N-1)} \int d^3r \, n_1^2$$

$$= \frac{V}{N(N-1)} \cdot V \frac{N^2}{V^2}$$

$$= \frac{N}{N-1} \approx 1$$

$\Rightarrow$ deviation of $g_N(\vec{R})$ from 1 gives measure of non-trivial spatial correlations

Evaluation of $g_N(\vec{R})$ (Classical) in Canonical Ensemble

$$g_N(\vec{R}) = \frac{V}{N(N-1)} \left\langle \sum_{i \neq j}^{N} \delta(\vec{R} - (\vec{r}_i - \vec{r}_j)) \right\rangle$$

$$= \frac{V}{N(N-1)} \frac{\cancel{\frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta \sum_i \frac{p_i^2}{2m}}} \int d^{3N}\vec{r} \sum_{i \neq j}^{N} \delta(\vec{R} - (\vec{r}_i - \vec{r}_j)) e^{-\beta U}}{\cancel{\frac{1}{N!} \int \frac{d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta \sum_i \frac{p_i^2}{2m}}} \int d^{3N}r \, e^{-\beta U}}$$

$$= \frac{V}{N(N-1)} \frac{1}{Q_N} \int d^3r_1 \dots d^3\vec{r}_N \sum_{i \neq j}^{N} \delta(\vec{R} - (\vec{r}_i - \vec{r}_j)) \, e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)}$$

Configuration integral $Q_N = \int d\vec{r}_1 \dots d\vec{r}_N \, e^{-\beta U}$

$N^2 - N$ terms that give identical contributions. Just pick 1 pair (say $i\,j = 1,2$) & m. by $N(N-1)$

$$\therefore\ g_N(\vec{R}) = \frac{V}{Q_N}\int d^3\vec{r}_1 \cdots d^3\vec{r}_N\ \delta(\vec{R}-(\vec{r}_1-\vec{r}_2))\ e^{-\beta U(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)}$$

* integrate over $\vec{r}_1$ w/ δ-function

$$= \frac{V}{Q_N}\int d^3\vec{r}_2 \cdots d^3\vec{r}_N\ e^{-\beta U(\vec{R}+\vec{r}_2,\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_N)}$$

$$U = u(\vec{R}) + u(\vec{R}+\vec{r}_2-\vec{r}_3) + \cdots + u(\vec{R}+\vec{r}_2-\vec{r}_N)$$
$$+ u(\vec{r}_2-\vec{r}_3) + \cdots + u(\vec{r}_{N-1}-\vec{r}_N)$$

Claim: Can use trans. inv. to take $\int d\vec{r}_2 \to V$

(let $\vec{\rho}_2 = \vec{r}_2$

$\vec{\rho}_3 = \vec{r}_3 - \vec{r}_2$

$\vec{\rho}_4 = \vec{r}_4 - \vec{r}_3$

$\vdots$

$\vec{\rho}_N = \vec{r}_N - \vec{r}_{N-1}$

$\Rightarrow U = u(\vec{R}) + u(\vec{R}-\vec{\rho}_3) \cdots$

no ρ_2-deps

$\int d\vec{\rho}_2 \to V$

& then transform back to $\vec{r}_i$ $i=3\ldots N$ variables)

$$\Rightarrow \boxed{g_N(R) = \frac{V^2}{Q_N}\int d^3\vec{r}_3 \cdots d^3\vec{r}_N\ e^{-\beta U}} \quad (*)$$

in general, (*) hard to evaluate. But we can simplify in the low n/high T limit

* high T / low n, dominated by pairwise int. of particle 1 & nearest particle $\Rightarrow$ $d^3r_3 \cdots d^3r_N$ in Q_N cancels w/ numerator
call it particle 2

$$g_N(\vec{R}) \simeq \frac{V^2 e^{-\beta u(R)}}{\int d^3r_1 d^3r_2 \, \underline{e^{-\beta u(r_{12})}}} \simeq e^{-\beta u(R)}$$

(Later, we'll obtain this result in a different way by deriving an exact relation between P & $g_N(R)$, & then by matching to the leading virial expansion we get $g_N(R) \simeq e^{-\beta u(R)}$)

Average PE in terms of $g_N(\vec{R})$

* Physically, expect average PE from pairwise $u(\vec{r}_{ij})$ to depend on pair correlations

$$\langle U \rangle = \frac{1}{Q_N} \int d^3r_1 \cdots d^3r_N \, \frac{1}{2}\sum_{i\neq j} u(\vec{r}_i - \vec{r}_j)\, e^{-\beta U}$$

$$= \frac{1}{Q_N} \int d^3r_1 \cdots d^3r_N \int d^3R\, u(R)\, \frac{1}{2}\sum_{i\neq j} \delta(\vec{R} - (\vec{r}_i - \vec{r}_j))\, e^{-\beta U}$$

$$= \frac{1}{2}\int d^3\vec{R}\, u(\vec{R}) \underbrace{\left\langle \sum_{i\neq j} \delta(\vec{R} - (\vec{r}_i - \vec{r}_j)) \right\rangle}_{= \frac{N(N-1)}{V} g_N(\vec{R}) \approx \frac{N^2}{V} g_N(\vec{R})}$$

$$\boxed{\langle U \rangle = \frac{N^2}{2V} \int d^3\vec{R}\, u(\vec{R})\, g_N(\vec{R})}$$

* Likewise, we can express the interacting EOS in terms of $g(\vec{R})$

recall, $$Z_N = \frac{1}{N!}\int \frac{d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta \sum_i \frac{p_i^2}{2m}} \times Q_N$$

$$Z_N = \frac{1}{N!}\int \frac{d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta \sum_i \frac{p_i^2}{2m}} \times Q_N$$

$$= \frac{1}{N!\, l_Q^{3N}} Q_N$$

$$= \underbrace{\frac{V^N}{N!\, l_Q^{3N}}}_{= Z_N^{ideal}} \cdot \frac{Q_N}{V^N}$$

$$\therefore \log Z_N = \underbrace{\log Z_N^{ideal}}_{\text{free particles}} + \underbrace{\log\left(\frac{Q_N}{V^N}\right)}_{\text{interaction effects}}$$

Now, $\log Z_N = -\beta F$ and $P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$

$$\therefore P = \left.\frac{\partial}{\partial V}\left(k_B T \log Z_N\right)\right|_{T,N}$$

$$= \frac{\partial}{\partial V}\left(k_B T \log Z_N^{ideal} + k_B T \log\left(\frac{Q_N}{V^N}\right)\right)$$

$$= \frac{k_B T N}{V} + k_B T \frac{\partial}{\partial V} \log\left(\frac{Q_N}{V^N}\right)$$

$$= \frac{N k_B T}{V} + \frac{k_B T V^N}{Q_N} \cdot \frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right)$$

* To extract the V-dependence of Q_N,

$$\text{let } \vec{r}_i' = \frac{\vec{r}_i}{V^{1/3}} = \frac{\vec{r}_i}{L} \qquad (\text{for } V = L^3)$$

$$\Downarrow$$

$$Q_N = V^N \int d^{3N} r' \, e^{-\frac{\beta}{2} \sum_{i \neq j} u(V^{1/3} \vec{r}_{ij}')}$$

$$\therefore \frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right) = \frac{\partial}{\partial V} \int d^{3N} r' \, e^{-\frac{\beta}{2} \sum_{i \neq j} u(V^{1/3} \vec{r}_{ij}')}$$

$$= \int d^{3N} r' \left(-\frac{\beta}{2} \sum_{i \neq j} \frac{\partial u}{\partial (V^{1/3} r_{ij}')} \frac{\partial (V^{1/3} r_{ij}')}{\partial V} \right) \times e^{-\frac{\beta}{2} \sum_{i \neq j} u(r_{ij}' V^{1/3})}$$

$$= \int d^{3N} r' \left(-\frac{\beta}{6} \sum_{i \neq j} \frac{\partial u}{\partial (V^{1/3} r_{ij}')} \frac{r_{ij}'}{V^{2/3}} \right) \times e^{-\frac{\beta}{2} \sum_{i \neq j} u(V^{1/3} r_{ij}')}$$

$$\boxed{\frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right) = \frac{1}{V^N} \int d^{3N} r \left(-\frac{\beta}{6} \sum_{i \neq j} \frac{\partial u}{\partial r_{ij}} \frac{r_{ij}}{V} \right) e^{-\frac{\beta}{2} \sum_{i \neq j} u(r_{ij})}}$$

$$\therefore \frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right) = \frac{1}{V^N}\int d^{3N}r \left(-\frac{\beta}{6}\sum_{i\neq j}\frac{\partial u}{\partial r_{ij}}\frac{r_{ij}}{V}\right) e^{-\beta U}$$

*Use analogous trick as what we did to write $\langle U\rangle$ in terms of $g_N(\vec{R})$:

$$\frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right) = \frac{1}{V^N}\int d^{3N}r \int d^3R \left(-\frac{\beta}{6}\frac{\partial u(R)}{\partial R}\frac{R}{V}\sum_{i\neq j}\delta(\vec{R}-(\vec{r}_i-\vec{r}_j))\right) e^{-\beta U}$$

$$= \frac{1}{V^N}\int d^3R \left[-\frac{\beta}{6}\frac{\partial u(R)}{\partial R}\frac{R}{V}\right] \underbrace{\int d^3r_1 \cdots d^3r_N \sum_{i\neq j}\delta(\vec{R}-\vec{r}_{ij})\, e^{-\beta U}}_{= \frac{Q_N N^2}{V} g_N(\vec{R})}$$

$$\therefore \boxed{\frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right) = \frac{-N^2}{6k_BTV^2}\cdot\frac{Q_N}{V^N}\int d^3R \frac{du}{d\log R}\, g_N(\vec{R})}$$

Plugging back into

$$P = nk_BT + k_BT\frac{V^N}{Q_N}\frac{\partial}{\partial V}\left(\frac{Q_N}{V^N}\right)$$

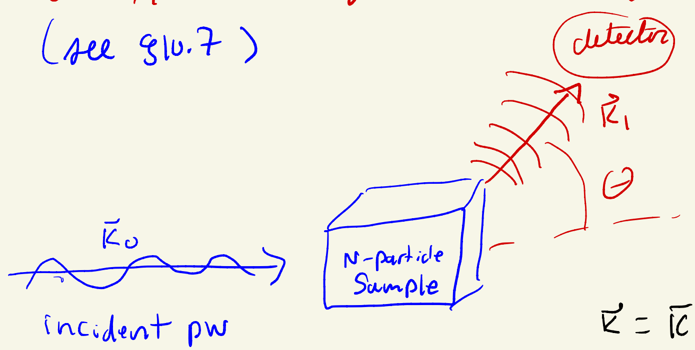
$$= nk_BT - k_BT\frac{\cancel{V^N}}{\cancel{Q_N}}\frac{n^2}{6k_BT}\cdot\frac{\cancel{Q_N}}{\cancel{V^N}}\cdot\int d^3R \frac{du(R)}{d\log R}\, g_N(R)$$

$$\Rightarrow \boxed{P = nk_BT\left[1 - \frac{n}{6k_BT}\int d^3R \, \frac{du}{d\log R}\, g_N(\vec{R})\right]} \quad (\star)$$

Note: ① Plugging in our approximate $g_N(R) \simeq e^{-\beta u(R)}$ valid at high T / low-n, we recover the same leading virial expansion EOS obtained earlier

② Eqn. $(\star)$ is useful as it parameterizes the effects of interactions in $g_N(\vec{R})$, which can either be calculated in some approximation (e.g., high T / low-n virial expansion), or can be "extracted" from scattering measurements,

(see §10.7)



$$\vec{k} = \vec{k}_1 - \vec{k}_0$$

$$I_N(\vec{k}) = N\, I_1(\vec{k})\, S(\vec{k})$$ scattered intensity at detector

$$S(\vec{k}) = \frac{1}{N}\left\langle \sum_{ij} e^{-i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)} \right\rangle$$ "Static Structure Factor"

$$= 1 + n\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\left(g_N(\vec{r}) - 1\right)$$

∴ Can measure $S(\vec{k})$ & extract what $g(\vec{R})$ is.

(3) Correlation function $g(\vec{R})$ related to fluctuations in N (in GCE)

From $$\int d^3R\, g(R)\Big|_{GCE} = \frac{V}{\langle N\rangle} \cdot \frac{\langle N^2 - N\rangle}{\langle N\rangle - 1}$$

$$\Downarrow$$

$$1 + \frac{\langle N\rangle}{V} \int d^3R \left(g(R) - 1 \right)$$

$$= \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}$$

$$= \frac{\langle (N - \langle N\rangle)^2 \rangle}{\langle N\rangle}$$

$$= \frac{\langle (\Delta N)^2 \rangle}{\langle N\rangle}$$

$$= \frac{T}{N} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} = n T \kappa_T$$

where $\kappa_T = -V \left(\frac{\partial P}{\partial V} \right)_{T,N}$ compressibility