Lecture 4: Applications of correlation functions

Recap: $\beta p(\rho, T) = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$

Virial expansion, Mayer expansion, cluster expansion.

We find also expansion of the free energy:

$$\frac{\beta F}{V} = \rho[\log(\rho\Lambda^3) - 1] + B_2(T)\rho^2 + \frac{1}{2}B_3(T)\rho^3 + \dots$$

Approximate resummation of virial expansion gives the Carnahan-Starling (CS) equation of state

$$\frac{\beta P_{CS}}{\rho} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \qquad \frac{\beta F_{CS}}{N} = \log(\rho\Lambda^3) - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$

Widely used equation of state!

- Virial coefficients not easy to compute at high order (slowly converging), sometimes ill-defined (e.g. Coulomb)

$\Rightarrow$ Correlation functions.

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

$$\rho^{(2)}(\vec{r}, \vec{r}\,') = \left\langle \sum_{i \neq j} \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_i)\,\delta(\vec{r}\,' - \vec{r}_j) \right\rangle$$

radial distribution function "conditional probability"

Translational invariant + isotropic $\longrightarrow \rho^{(2)}(\vec{r}, \vec{r}\,') = \rho^2 g(|\vec{r} - \vec{r}\,'|)$

E.g # atoms in first coordination shell: $n(r) = 4\pi\rho \int_0^r dx\, x^2 g(x)$

$n(\text{first coordinate shell}) \simeq 12$ (liquid and solid!)

Tutorials: $g(r; \rho, T) = e^{-\beta v(r)} + \mathcal{O}(\rho)$ (gas is just Boltzmann weight!)

In this week tutorials: $w(r) = -k_B T \log g(r)$

$$\Rightarrow -\frac{\partial}{\partial \vec{r}_1} w(\vec{r}_{12}) = \left\langle -\frac{\partial \Phi}{\partial \vec{r}_1} \right\rangle$$

potential of mean force.

Claim: if we know $g(r)$ $\rightsquigarrow$ entire thermodynamics.

- Caloric route to thermodynamics

Consider internal energy of the system for pair-wise additive interactions.

$$U = \langle H \rangle = \left\langle \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \right\rangle + \left\langle \sum_{i=1}^{N} \sum_{j>i} v(|\vec{r}_i - \vec{r}_j|) \right\rangle$$

$$= \underbrace{\frac{3}{2} N k_B T}_{\text{equipartition}} + \frac{1}{2} \left\langle \sum_{i \neq j} \sum_{j=1}^{N} \int d\vec{r} \int d\vec{r}\,' \, \delta(\vec{r} - \vec{r}_i)\, \delta(\vec{r}\,' - \vec{r}_j)\, v(|\vec{r} - \vec{r}\,'|) \right\rangle$$

$$= \frac{3}{2} N k_B T + \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' \rho^{(2)}(\vec{r}, \vec{r}\,') v(|\vec{r} - \vec{r}\,'|).$$

Homogeneous, isotropic systems:

$$\boxed{\frac{U}{V} = \frac{3}{2} \rho k_B T + \frac{\rho^2}{2} \int d\vec{r}\, g(r) v(r).}$$

- Virial route to thermodynamics

Virial theorem from classical mechanics (see Problem 2.5):

$$p = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j>i} \vec{r}_{ij} \cdot \frac{\partial v(r_{ij})}{\partial \vec{r}_{ij}} \right\rangle$$

$$= \rho k_B T - \frac{1}{6V} \int d\vec{r} \int d\vec{r}\,' \rho^{(2)}(\vec{r}, \vec{r}\,') \, (\vec{r} - \vec{r}\,') \cdot \frac{\partial v(\vec{r} - \vec{r}\,')}{\partial (\vec{r} - \vec{r}\,')}$$

For homogeneous and isotropic system:

$$\boxed{p = \rho k_B T - \frac{\rho^2}{6} \int d\vec{r}\; r g(r) v'(r).}$$

$\rightsquigarrow$ if g.c. $\rho = \frac{\langle N \rangle}{V}$!

Note: no ensemble specified! Only valid for pair potentials.
$\rightsquigarrow$ else higher order correlation functions needed.

Remarks: * We restricted only to pair-wise additive potential. However, the scheme is easily extended to the addition of three-body, four-body etc potentials. The downside is that we then need knowledge of higher-order correlation functions.

* Implicitly we worked in canonical ensemble, but can be gc if

- **Compressibility route to thermodynamics.** $\rho = \frac{\langle N \rangle}{V}$.

Valid for arbitrary $\Phi(\vec{r}^N)$. Most easily derived in grand-canonical ensemble. Some notation:

$$\mathrm{Tr}_{cl}(\ldots) = \sum_{N=0}^{\infty} \frac{1}{N!\,h^{3N}} \int d\vec{p}^N \int d\vec{r}^N (\ldots)$$

$$\Xi(\mu, V, T) = \mathrm{Tr}_{cl}\left[e^{-\beta(H-\mu N)}\right]$$

$$f_N(\vec{p}^N, \vec{r}^N; N) = \frac{1}{\Xi} e^{-\beta(H-\mu N)}$$

Note that $\mathrm{Tr}_{cl} f_N = 1$

and

$$\langle \ldots \rangle = \mathrm{Tr}_{cl}\left[f_N(\ldots)\right]$$ Grand-canonical ensemble average.

Note in grand-canonical ensemble:

$$\int d\vec{r}\, \rho(\vec{r}) = \int d\vec{r} \langle \hat{\rho}(\vec{r}) \rangle = \langle N \rangle.$$

$$\int d\vec{r} \int d\vec{r}'\, \rho^{(2)}(\vec{r}, \vec{r}') = \int d\vec{r} \int d\vec{r}' \langle \hat{\rho}^{(2)}(\vec{r}, \vec{r}') \rangle = \langle N^2 \rangle - \langle N \rangle$$

At this point it is useful to introduce the correlation function:

Density-density correlation function:

$$G(\vec{r},\vec{r}\,') = \langle \delta\hat{\rho}(\vec{r})\,\delta\hat{\rho}(\vec{r}\,')\rangle \qquad \delta\hat{\rho}(\vec{r}) = \hat{\rho}(\vec{r}) - \langle\hat{\rho}(\vec{r})\rangle.$$

Note that: $G(\vec{r},\vec{r}\,') = \rho^{(2)}(\vec{r},\vec{r}\,') - \rho(\vec{r})\rho(\vec{r}\,') + \rho(\vec{r})\,\delta(\vec{r}-\vec{r}\,')$.

With this property it is straightforward to show that:

$$\int d\vec{r}\int d\vec{r}\,'\,G(\vec{r},\vec{r}\,') = \langle N^2\rangle - \langle N\rangle^2.$$

We want to relate number fluctuations to measurable quantities. Let $\alpha\in\mathbb{N}$

$$\langle N^\alpha\rangle = \mathrm{Tr}_{cl}(f_N N) = \frac{1}{\Xi}\,\mathrm{Tr}_{cl}\left[N^\alpha e^{-\beta(H-\mu N)}\right]$$

series uniform convergent

$$= \frac{1}{\Xi}\,\mathrm{Tr}_{cl}\left[\frac{\partial^\alpha}{\partial(\beta\mu)^\alpha}\, e^{-\beta(H-\mu N)}\right]_{V,T} = \frac{1}{\Xi}\,\frac{\partial^\alpha}{\partial(\beta\mu)^\alpha}\,\underbrace{\mathrm{Tr}_{cl}\left[e^{-\beta(H-\mu N)}\right]_{V,T}}_{\Xi}$$

$$= \frac{1}{\Xi}\left(\frac{\partial^\alpha\Xi}{\partial(\beta\mu)^\alpha}\right)_{V,T}.$$

The number fluctuations are therefore:

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\Xi}\left(\frac{\partial^2\Xi}{\partial(\beta\mu)^2}\right)_{V,T} - \frac{1}{\Xi^2}\left(\frac{\partial\Xi}{\partial\beta\mu}\right)^2_{V,T}$$

$$= \left(\frac{\partial^2\ln\Xi}{\partial(\beta\mu)^2}\right)_{V,T} = \left(\frac{\partial}{\partial\beta\mu}\left(-\frac{\partial\Omega}{\partial\mu}\right)_{V,T}\right)_{V,T} = \left(\frac{\partial\langle N\rangle}{\partial(\beta\mu)}\right)_{V,T}.$$

(Recall: $d\Omega = -S\,dT - p\,dV - N\,d\mu$).

Using that $\rho = \frac{\langle N \rangle}{V}$

$$\langle N^2\rangle - \langle N\rangle^2 = V\left(\frac{\partial \rho}{\partial \beta\mu}\right)_T \overset{\text{chain rule}}{=} V\left(\frac{\partial \rho}{\partial p}\right)_T\left(\frac{\partial p}{\partial \beta\mu}\right)_T$$

Recall the Maxwell relation: $\left(\frac{\partial p}{\partial \mu}\right)_T = \rho$ $\Bigg\} \Rightarrow$

$$\langle N^2\rangle - \langle N\rangle^2 = k_B T\langle N\rangle \underbrace{\left(\frac{\partial \rho}{\partial p}\right)_T}_{\rho\kappa_T}$$

$\rho\kappa_T$ with $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$ isothermal compressibility.

So we conclude that: $\langle N^2\rangle - \langle N\rangle^2 = \rho k_B T\langle N\rangle \kappa_T$.

For homogenous isotropic systems:

$$\underbrace{\int d\vec{r}\int d\vec{r}\,'\, G(|\vec{r}-\vec{r}\,'|)}_{\langle N^2\rangle - \langle N\rangle^2} = V\int d\vec{r}\, G(r)$$

Hence, we obtain the so-called compressibility sum rule:

$$\boxed{\int d\vec{r}\, G(r) = \rho^2 k_B T \kappa_T}$$

Exact result for any $\Phi(\vec{r}^{\,N})$!

In terms of radial distribution function:

$$\boxed{1 + \rho\int d\vec{r}\,[g(r)-1] = \rho k_B T \kappa_T}$$

The structure factor

For homogeneous system: $G(\vec{r},\vec{r}') = G(\vec{r}-\vec{r}')$

We introduce the Fourier transform:

$$\tilde{G}(\vec{k}) = \int d\vec{r}\, G(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} \quad ; \quad G(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^3}\, \tilde{G}(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}.$$

When system is also isotropic: $G(\vec{r}-\vec{r}') = G(|\vec{r}-\vec{r}'|)$

$\Rightarrow \tilde{G}(\vec{k}) = \tilde{G}(k)$.

We define the static structure factor as $\tilde{G}(k) = \rho S(k)$

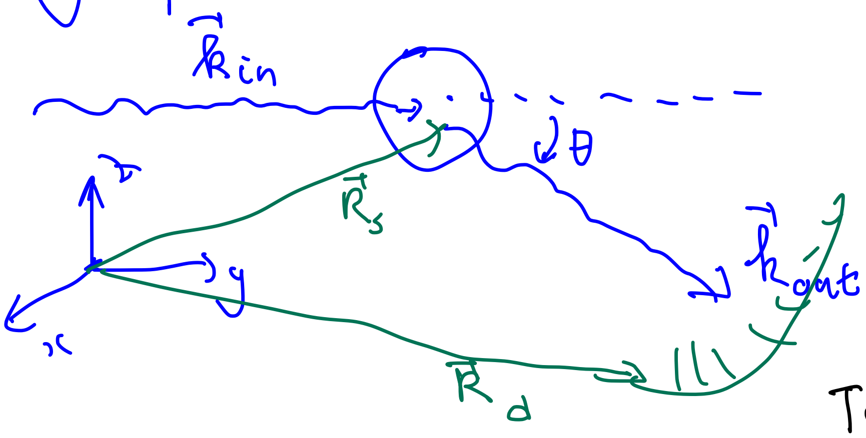
Note that in terms of $g(r)$:

$$S(k) = 1 + \rho \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \left[g(r) - 1\right] + (2\pi)^3 \delta(\vec{k}).$$

Define $\lim_{k\to 0} S(k) = 1 + \rho \int d\vec{r}\, [g(r) - 1]$.

So compressibility sum rule is: $\boxed{\lim_{k\to 0} S(k) = \rho k_B T \kappa_T}$

The static structure factor can be obtained from scattering experiments.



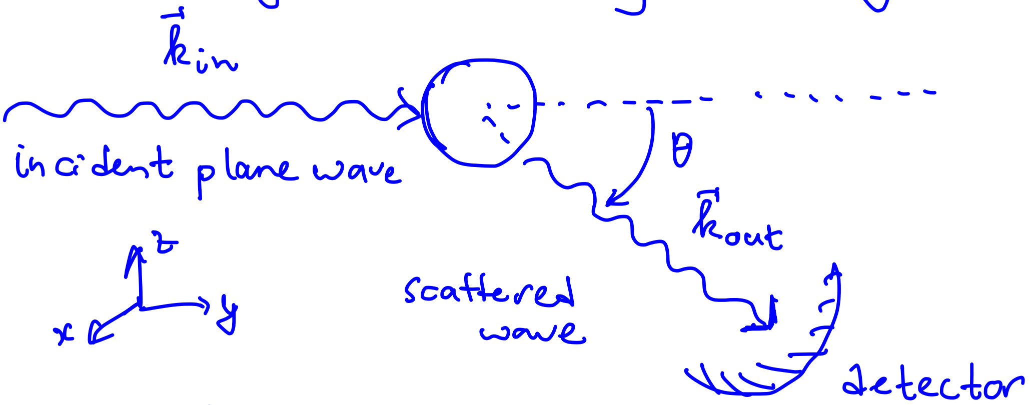
$I(\theta) \propto S(q)$

momentum transferred.

Next lecture.

Tutorial: P2.4C, 2.5

Static structure factor via X-ray scattering



Scattered wave has amplitude at detector:

$$\left[\begin{array}{c}\text{atomic scattering}\\ \text{factor}\end{array}\right] \frac{1}{|\vec{r}_0 - \vec{r}_i|} \exp^{i[\vec{k}_{in}\cdot\vec{r}_i + \vec{k}_{out}\cdot(\vec{r}_D - \vec{r}_i)]}$$

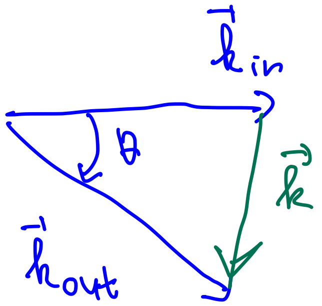
(first Born approximation)

from scattering from an atom at position $\vec{r}_i$ to detector at $\vec{r}_d$.

Assumption: detector far from scattering center of the cell.

$\Rightarrow \vec{r}_i \approx \vec{r}_C$. $\quad f(k)$ atomic scattering factor.

Hence scattered wave: $f(k) \dfrac{1}{|\vec{r}_D - \vec{r}_C|} e^{i\vec{k}_{out}\cdot\vec{r}_d} e^{-i\vec{k}\cdot\vec{r}_i}$



$\vec{k} = \vec{k}_{out} - \vec{k}_{in}$ (momentum transfer).

Elastic scattering: $|\vec{k}_{out}| = |\vec{k}_{in}|$

$$|\vec{k}|^2 = \vec{k}_{out}^{\,2} - 2\vec{k}_{in}\cdot\vec{k}_{out} + \vec{k}_{in}^{\,2}$$

$$= 2|\vec{k}_{in}|^2 - 2|\vec{k}_{in}|^2 \cos\theta. \Rightarrow |\vec{k}|^2 = 2|\vec{k}_{in}|^2(1-\cos\theta)$$

Recall: $\sin^2\frac{\theta}{2} = \frac{1-\cos\theta}{2}$.

$$\Rightarrow |\vec{k}| = 2|\vec{k}_{in}| \sin\frac{\theta}{2}.$$

$$= \frac{4\pi}{\lambda_{in}} \sin\frac{\theta}{2}.$$

Total scattered wave amplitude $= f(k) \dfrac{e^{i\vec{k}_{out}\cdot\vec{r}_d}}{|\vec{r}_c-\vec{r}_d|} \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}$ fixed configuration of scattering centres

$I(\theta)$ = observed intensity at the observer $= \dfrac{N|f(k)|^2}{|\vec{r}_c-\vec{r}_d|^2} \underbrace{\dfrac{1}{N}\left\langle \sum_{i,j} e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle}_{\text{ensemble average.}}$

However: $\dfrac{1}{N}\left\langle \sum_{i,j} e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle$

$$= 1 + \left\langle \frac{1}{N}\sum_{i\neq j} e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle = 1 + \frac{1}{NQ_N}\int d\vec{r}^N e^{-\beta\Phi(\vec{r}^N)} \sum_{i\neq j} e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}$$

$$= 1 + \frac{1}{N}\int d\vec{r}_1 \int d\vec{r}_2\, e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)} \underbrace{\frac{N(N-1)}{Q_N}\int d\vec{r}_3 \cdots \int d\vec{r}_N\, e^{-\beta\Phi(\vec{r}^N)}}_{\rho^{(2)}(\vec{r}_1,\vec{r}_2).}$$

$$= 1 + \rho\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} g(r) = 1 + \rho\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}[g(r)-1] + (2\pi)^3\delta(\vec{k})$$

$$= S(\vec{k})$$

Hence we conclude that: $I(\theta) \propto S(k)$.

FT's are unique: inversion gives $g(r)$.

Properties of static structure factor:

- $S(k) = 1 \;\; \forall k$ (ideal system)
- $S(k) \to 1 \quad k \to \infty$.
- first peak of $S(k)$ is at $k_{max} \approx \dfrac{2\pi}{\sigma}$ (first reciprocal lattice vector of solid)