Lecture 9: Properties of density-density correlation functions

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

(Virial expansion, Mayer expansion, cluster expansion)

Virial coefficients are not easy to compute at higher order, sometimes ill-defined (e.g. Coulomb). So we would like to have methods to describe dense fluids: ⇝ correlation functions.

$$\rho(\vec r) = \left\langle \sum_{i=1}^{N} \delta(\vec r - \vec r_i)\right\rangle \quad \text{(one-body density).}$$

$$\rho^{(2)}(\vec r, \vec r\,') = \left\langle \sum_{i\neq j} \delta(\vec r - \vec r_i)\,\delta(\vec r - \vec r_j)\right\rangle \quad \text{(two-body density)}$$

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

(radial distribution function)
"conditional probability.

E.g. # atoms in first coordination shell:

$$n(r) = 4\pi\rho\int_0^r dx\, x^2 g(x) \qquad n(\text{first coordination shell}) \approx 12 \quad (\text{liquid and solid!})$$

Last tutorial: $$g(r;\rho,T) \approx \underbrace{e^{-\beta v(r)} + O(\rho)}_{\text{virial expansion for } g(r)}$$

For gas conditional probability is just the Boltzmann weight.

This week: $$w(r) = -k_B T \log g(r)$$

$$\Rightarrow \quad -\frac{\partial}{\partial \vec r_1} w(\vec r_{12}) = \left\langle -\frac{\partial \Phi}{\partial \vec r_1}\right\rangle_{\vec r_1, \vec r_2 \text{ fixed}}$$

potential of mean force.

The radial distribution function is useful in more ways.

Claim: If we know $g(r)$ ⇝ entire thermodynamics!

• Caloric route to thermodynamics

Let us consider the internal energy of a system with pairwise additive interactions

$$\mathcal{U} = \langle H\rangle = \left\langle \sum_{i=1}^{N} \frac{\vec p_i^{\,2}}{2m}\right\rangle + \left\langle \sum_{i<j} v(|\vec r_i - \vec r_j|)\right\rangle$$

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

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

Since system is homogeneous + isotropic:

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

- Virial route to thermodynamics

$$p = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i<j} \vec{r}_{ij} \cdot \frac{\partial v}{\partial \vec{r}_{ij}} \right\rangle = \rho k_B T - \frac{1}{6V} \int d\vec{r} \int d\vec{r}\,' \rho^{(2)}(\vec{r},\vec{r}\,')\, (\vec{r}-\vec{r}\,') \cdot \frac{\partial v(|\vec{r}-\vec{r}\,'|)}{\partial(\vec{r}-\vec{r}\,')}$$

$$\Rightarrow \boxed{p = \rho k_B T - \frac{\rho^2}{6} \int d\vec{r}\, r\, g(r)\, v'(r)} \rightsquigarrow \text{if g.c.} \quad \rho = \frac{\langle N \rangle}{V}$$

- For virial and caloric route we did not specify the ensemble.
- Only valid for pair interactions (else higher order correlation functions are needed)

- Compressibility route to thermodynamics

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

We introduce the following notation

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

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

Probability density: $f_N(\vec{p}^N, \vec{r}^N; N) = \frac{1}{\Xi} e^{-\beta(H-\mu N)}$ Note: $\mathrm{Tr}_{cl} f_N = 1$

and in this notation the grand-canonical ensemble average is

$$\langle \ldots \rangle = \mathrm{Tr}_{cl}\left[f_N (\ldots)\right]$$ Furthermore note that in the gce

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

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

At this point it is useful to introduce the 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: $$G(\vec{r},\vec{r}\,') = \rho^{(2)}(\vec{r},\vec{r}\,') - \rho(\vec{r})\rho(\vec{r}\,') + \rho(\vec{r})\delta(\vec{r}-\vec{r}\,')$$

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

But: $$\langle N^\alpha\rangle = \frac{1}{\Xi}\left(\frac{\partial^\alpha \Xi}{\partial(\beta\mu)^\alpha}\right)_{V,T}$$ (convince yourself!)

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

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

$d\Omega = -SdT - pdV - Nd\mu$

$\rho = \langle N\rangle/V$

$$= V\left(\frac{\partial\rho}{\partial(\beta\mu)}\right)_T = V\left(\frac{\partial\rho}{\partial p}\right)_T \underbrace{\left(\frac{\partial p}{\partial\beta\mu}\right)_T}_{=\rho\ \text{(Maxwell)}}$$

$$= k_B T\langle N\rangle\left(\frac{\partial\rho}{\partial p}\right)_T$$

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

$$\Rightarrow \langle N^2\rangle - \langle N\rangle^2 = \rho k_B T\langle N\rangle \kappa_T.$$

For homogeneous + isotropic sysem $\langle N^2\rangle - \langle N\rangle^2 = \int d\vec{r}\int d\vec{r}\,'\, G(|\vec{r}-\vec{r}\,'|) = V\int d\vec{r}\, G(r)$

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

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 <u>define</u> the static structure factor as $\tilde G(k) = \rho S(k)$

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

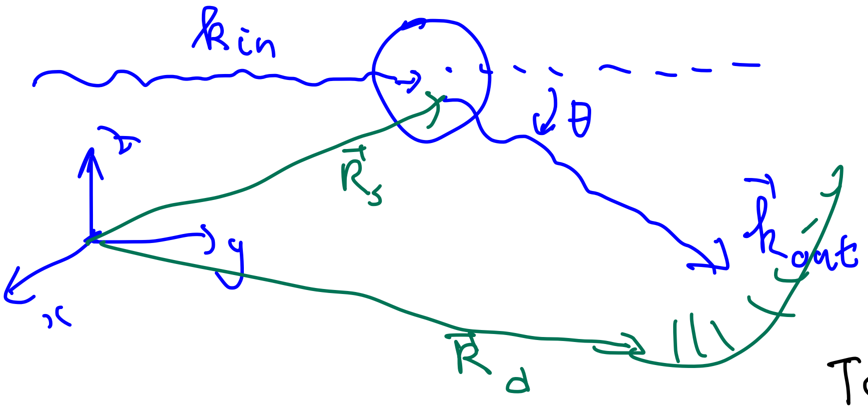
$$S(k) = 1 + \rho \int d\vec r\, e^{-i\vec k\cdot\vec r}\left[g(r) - 1\right] + (2\pi)^3\, \delta(\vec k).$$

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

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

SLIDES

The static structure factor can be obtained from scattering experiments.



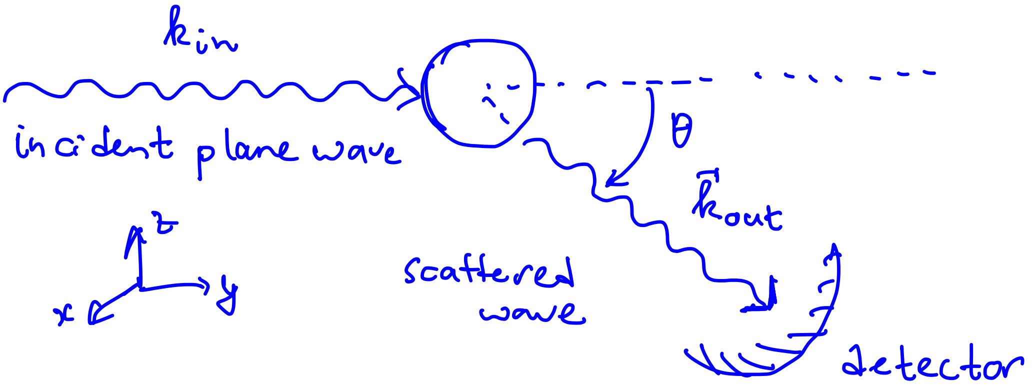
$I(\theta) \propto S(q)$

momentum transferred.

Next lecture.

Tutorial: P2.4C, 2.5

Static structure factor via X-ray scattering



Scattered wave has amplitude at detector:

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

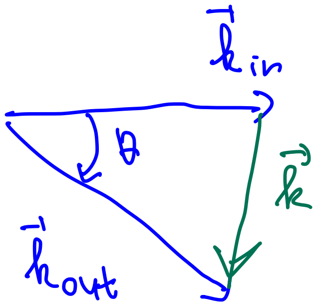
(first Born approximation)

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.

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

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



$\vec{k} = \vec{k}_{out} - \vec{k}_{in}$ (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)
- $S(k)\longrightarrow 1 \quad k\rightarrow\infty$.
- first peak of $S(k)$ is at $k_{max}\approx\frac{2\pi}{\sigma}$ (first reciprocal lattice vector of solid)

Ornstein-Zernike (OZ) integral equation

Define the indirect correlation function: $h(r) = g(r) - 1$

Note that $h(r) \to 0$ for $r \to \infty$ (uncorrelated particles).

The indirect correlation function satisfies the integral equation:

$$h(r) = c(r) + \rho \int d\vec{r}\,' \, c(|\vec{r} - \vec{r}\,'|)\, h(r').$$

(for now this relation <u>defines</u> $c(r)$.)

↳ can be derived using DFT

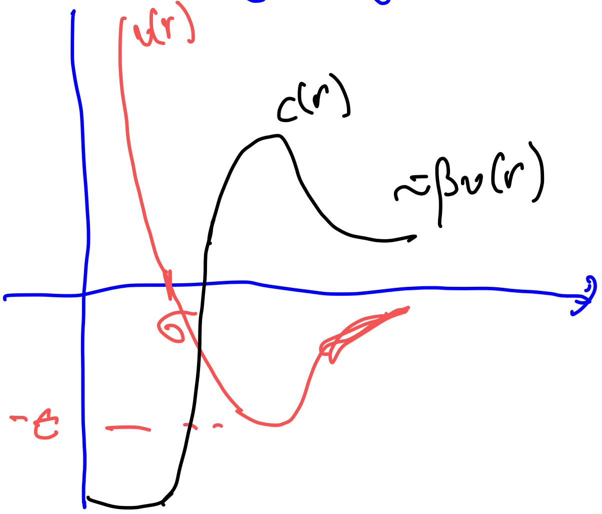
↳ direct correlation function

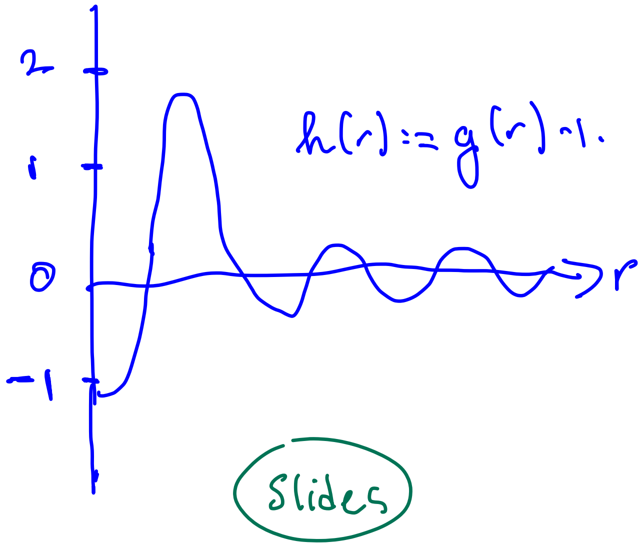
Dyson-like equation.

"More directly related to interaction potential since $c(r) \sim -\beta v(r)$ $(r \to \infty)$.

$c(r)$ does not contain any oscillations unlike $h(r)$.

E.g. Lennard-Jones fluid:



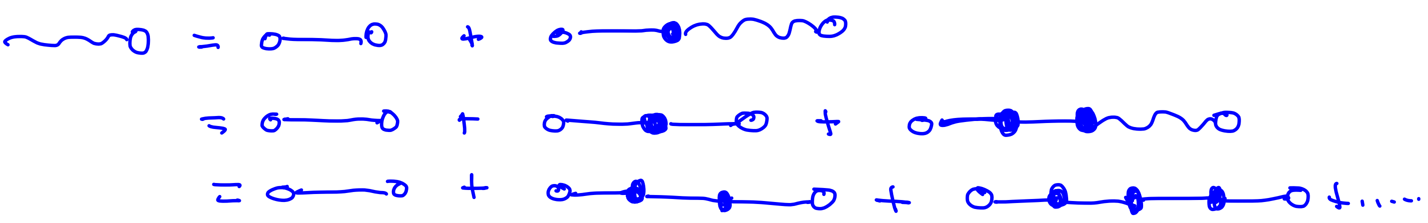


Slides

Iteration of OZ equation:

$$h(r_{12}) = c(r_{12}) + \rho \int d\vec{r}_3 \, c(r_{13}) \left[c(r_{32}) + \rho \int d\vec{r}_4 \, c(r_{34}) c(r_{42}) + \dots \right]$$

Diagrammatically:



Looks easier in Fourier space!

$$\tilde{h}(k) = \tilde{c}(k) + \rho\,\tilde{c}(k)\,\tilde{h}(k) \quad \Rightarrow \quad \tilde{h}(k) = \frac{\tilde{c}(k)}{1-\rho\,\tilde{c}(k)}$$

Or since $S(k) = 1+\rho\,\tilde{h}(k)$ $\qquad S(k) = \dfrac{1}{1-\rho\,\tilde{c}(k)}$ (Interpretation in terms of structure factor)

So from OZ equation, we can determine $g(r)$ if $c(r)$ is known!

random phase approximation

$\Rightarrow$ We need a closure relation. E.g. RPA $c(r) = -\beta v(r)$. (soft core systems).

No exact way to obtain a closure relation $\Rightarrow$ approximative closure relations.

(see lecture notes for some examples)

For now, let's focus on one more approximative closure relation:

$$c_{PY}(r) = \left\{1-e^{\beta v(r)}\right\} g_{PY}(r).$$

Excellent approximation for hard spheres.

For hard spheres, one can determine within PY closure an analytical solution for the direct correlation function:

$$c_{PY}(r) = \begin{cases} \dfrac{-(1+2\eta)^2 + 6\eta\left(1+\frac{1}{2}\eta\right)^2\left(\frac{r}{\sigma}\right) - \frac{1}{2}\eta(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3}{(1-\eta)^4} & (r<\sigma) \\ 0 \quad (r>\sigma) & \end{cases}$$

(follows from OZ equation).

<u>Note:</u> Straightforward to obtain $S(k)$ via Fourier transformation.
However for $g(r)$: numerical calculations.

PY closure approximation is quantitative up until HS freezing, Although $g_{PY}(r)$ is not analytically available we can still obtain analytical results using compressibility or virial route:

$$\frac{\beta p_c}{\rho} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \qquad \frac{\beta p_v}{\rho} = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}.$$

⇒ Consistent up until $\mathcal{O}(\rho^4)$.

⇒ Inconsistency due to PY approximation.

Interestingly : $\boxed{p_{CS} = \frac{2p_c+p_v}{3}}$

Note: $g(r) \approx e^{-\beta v(r)}$ (dilute system).

⇒ Big difference between hard spheres and e.g. L.J system.

However, for dense systems $g_{HS}(r)$ is almost indistinguishable from $g_{PY}(r)$!

⇒ In dense system short-range repulsions dominate the short-range correlations.

(Slides).