

Structure and scattering

Mario G. Del Pópolo

Atomistic Simulation Centre
Queen's University Belfast

e-mail: m.del-popolo@qub.ac.uk

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Outline

- 1 Introduction
- 2 Particle densities and distribution functions
 - Canonical distribution functions
 - Grand canonical distribution functions
- 3 Structure factor and scattering
 - Scattering theory
 - Structure factor
 - Example: Spherical colloidal particles
- 4 Structure and thermodynamics
 - A fluid in an external field
 - Density response function
 - Response and correlation functions
 - Example: Random phase approximation

Structure and correlations in condensed matter

- At **high temperature** kinetic energy dominates over potential energy
 - Equilibrium phases are **isotropic, homogeneous and weakly correlated**
 - Full symmetry of empty space
- As temperature decreases phase transitions lead to more **correlated states**
 - Such transitions can be **continuous or discontinuous**.
- At **sufficiently low temperature** potential energy dominates over kinetic
 - Equilibrium states are **non-isotropic and strongly correlated**
 - Low symmetry phase characterised by rigidity, low frequency modes and topological defects

Structure and correlations in condensed matter

- Condensation can generate a limitless variety of equilibrium structures
- Such structures are characterised by **average atomic positions** and **inter-particle spatial correlations**

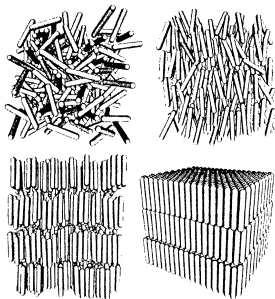


Figure: Different types of mesogenic order: Isotropic, nematic, smectic and crystalline

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The n-particle density (n-PD)

Reduced phase-space distribution function functions $f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n)$ are obtained by integrating $f_0^{[M]}(\mathbf{r}^N, \mathbf{p}^N)$ over $3(N - n)$ positions and $3(N - n)$ momenta.

Canonical n-particle density:

$$\begin{aligned}\rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!} \frac{1}{h^{3N} N! Q_N} \int \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} d\mathbf{p}^N \\ &= \frac{N!}{(N-n)!} \frac{1}{Z_N} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)}\end{aligned}$$

- $\rho_N^{(n)}(\mathbf{r}^n)$ = probability of finding n particles within the volume element $d\mathbf{r}^n$, irrespective of coordinates of other particles and irrespective of all momenta.
- n-PDs **describe the microscopic structure of the fluid**
- For pair-wise potentials $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ allows to calculate equations of state and thermodynamic properties

The n-particle density (n-PD)

The definition of n-PD means that:

$$\int \rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = \frac{N!}{(N-n)!} \quad \text{and} \quad \int \rho_N^{(1)}(\mathbf{r}) d\mathbf{r} = N \quad (1)$$

For a uniform fluids:

$$\rho_N^{(1)}(\mathbf{r}) = N/V\rho \quad \text{uniform fluid} \quad (2)$$

For an ideal gas:

$$\rho_N^{(2)} = \rho^2 \left(1 - \frac{1}{N} \right) \quad \text{ideal gas} \quad (3)$$

δ -function representation

From the definition of δ -function it follows that:

$$\langle \delta(\mathbf{r} - \mathbf{r}_1) \rangle = \frac{1}{Z_N} \int \delta(\mathbf{r} - \mathbf{r}_1) \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2 \cdots, \mathbf{r}_N)] d\mathbf{r}^N \quad (4)$$

$$= \frac{1}{Z_N} \int \exp[-\beta V_N(\mathbf{r}, \mathbf{r}_2 \cdots, \mathbf{r}_N)] d\mathbf{r}_2 \cdots d\mathbf{r}_N \quad (5)$$

where the ensemble average is a function of \mathbf{r} and independent of the particle label.

For a N-particle system the "singlet" density can be written as:

$$\rho_N^{(1)}(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle \text{ ensemble average of } \rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (6)$$

δ -function representation

The average of a product of two delta functions is:

$$\begin{aligned} \langle \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \rangle &= \frac{1}{Z_N} \int \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] d\mathbf{r}^N \\ &= \frac{1}{Z_N} \int \exp[-\beta V_N(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)] d\mathbf{r}_3 \cdots d\mathbf{r}_N \end{aligned}$$

which implies:

$$\rho_N^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \quad (7)$$

The n-particle distribution function (n-DF)

The **n-particle distribution function**, $g_N^{(n)}(\mathbf{r}^n)$ is defined in terms of $\rho_N^{(n)}(\mathbf{r}^n)$:

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)}{\prod_{i=1}^n \rho_N^{(n)}(\mathbf{r}_i)} \quad (8)$$

which for a homogeneous system reduces to:

$$\rho^n g^{(n)}(\mathbf{r}^n) = \rho_N^{(n)}(\mathbf{r}^n) \quad (9)$$

Distribution functions **measure extent of deviation from uniform distribution**

The pair distribution function

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)} \quad (10)$$

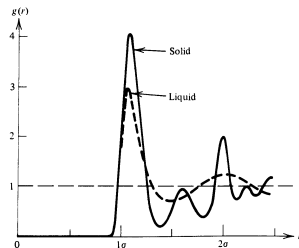
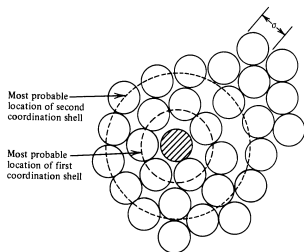
which for a homogenous fluid becomes:

$$g_N^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|) = g(r) = \frac{\rho^{(2)}(|\mathbf{r}_2 - \mathbf{r}_1|)}{\rho^2} \quad (11)$$

with δ -function representation:

$$\left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i) \right\rangle = \frac{\rho^2}{N} \int g^{(2)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \rho g(r) \quad (12)$$

The pair distribution function



- $g(r)$ measured by radiation-scattering experiments
- **coordination number** n_C :

$$n_C(r) = 4\pi\rho \int_0^r g(r')r'^2 dr' \quad (13)$$

- **Note:** for a liquid
 - $g(r) \rightarrow 1$ as $r \rightarrow \infty$. Absence of long-range order
 - $g(r) \rightarrow 0$ as $r \rightarrow 0$. Repulsive forces at small separations

Connection with thermodynamics

For a uniform fluid with total potential energy given by a sum of pair interactions:

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j>i}^N v(r_{ij}) \quad (14)$$

The excess internal energy is:

$$U^{ex} = \frac{N(N-1)}{2} \int \int v(\mathbf{r}_{12}) \left(\frac{1}{Z_N} \int \cdots \int \exp(-\beta V_N) d\mathbf{r}_3 \cdots d\mathbf{r}_N \right) d\mathbf{r}_1 d\mathbf{r}_2 \quad (15)$$

or

Energy equation:

$$U^{ex} / N = 2\pi\rho \int_0^\infty v(r)g(r)r^2 dr \quad (16)$$

Connection with thermodynamics

For pairwise additive forces the internal contribution to the virial function is:

$$\mathcal{V}_{int} = \sum_{i=1}^N \sum_{j>i}^N \mathbf{r}_i \cdot \mathbf{F}_{ij} = - \sum_{i=1}^N \sum_{j>i}^N r_{ij} v'(ij) \quad (17)$$

leading to the following expression for the pressure:

Pressure equation:

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty v'(r)g(r)r^3 dr \quad (18)$$

Reversible work theorem

Reversible work theorem

Under constant (N, V, T) the reversible for work (Helmholtz free energy) necessary to bring two tagged particles from infinite separation to a relative distance r is given by:

$$w(r) = -k_B T \ln(g(r)) \quad (19)$$

Note: $w(r)$ is called the **potential of mean force**, since its gradient gives the force between the two tagged particles averaged over the equilibrium distribution of all the other degrees of freedom

Potential of mean force

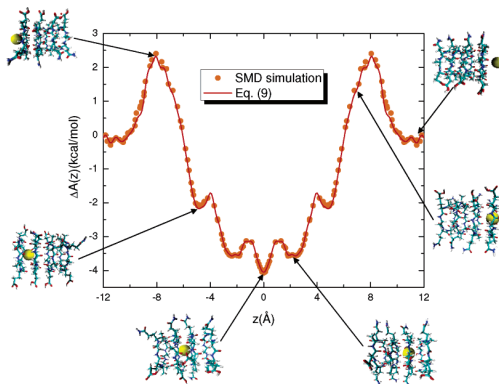


Figure: Potential of mean force, obtained by molecular dynamics simulations, for a sodium ion passing through a cyclic peptide nanotube in water. Hwang et al., J. Phys. Chem. B, 2006, 110, 26448.

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Particle densities in the grand canonical ensemble

Grand canonical ensemble n-particle densities and distributions are constructed from the canonical ones:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N \geq n}^{\infty} \rho(N) \rho^{(n)}(\mathbf{r}^n) \quad (20)$$

$$= \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{z^N}{(N-n)!} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} \quad (21)$$

Normalisation leads to:

$$\int \int [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 \quad (22)$$

which for a homogeneous fluid leads to:

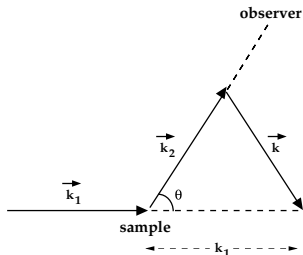
Compressibility equation:

$$1 + \rho \int [g(r) - 1] d\mathbf{r} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \rho k_B T \chi_T \quad (23)$$

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Overview of scattering theory



- Sample bombarded with particles with momentum $\hbar\mathbf{k}_1$. Scattered particles have momentum $\hbar\mathbf{k}_2$.
- Momentum transferred to the sample: $\hbar\mathbf{k} = \hbar\mathbf{k}_1 - \hbar\mathbf{k}_2$
- For elastic scattering $|\mathbf{k}_1| \sim |\mathbf{k}_2|$ and:

$$|\mathbf{k}| = 2|\mathbf{k}_1| \sin(\theta/2) = \frac{4\pi}{\lambda} \sin(\theta/2) \quad (24)$$

Overview of scattering theory

- Particle wave function represented by plane-wave states $|\mathbf{k}_1\rangle \sim \exp(i\mathbf{k}_1 \cdot \mathbf{r})$ and $|\mathbf{k}_2\rangle \sim \exp(i\mathbf{k}_2 \cdot \mathbf{r})$
- Particles interact with the sample via a **weak interaction potential** $\Phi(\mathbf{r})$

$$\Phi(\mathbf{r}) = \sum_{i=1}^N \phi_i(\mathbf{r} - \mathbf{r}_i) \quad (25)$$

as sample is formed by a collection of N scattering centres (particles)

- Transition rate between states \mathbf{k}_1 and \mathbf{k}_2 proportional to the square of

$$\langle \mathbf{k}_1 | \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle = \int d\mathbf{r} \exp(-i\mathbf{k}_1 \cdot \mathbf{r}) \Phi(\mathbf{r}) \exp(i\mathbf{k}_2 \cdot \mathbf{r}) \quad (26)$$

Fermi's golden rule

- The differential cross-section per unit of solid angle Ω is:

$$\frac{d\sigma}{d\Omega} \sim |\langle \mathbf{k}_1 | \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle|^2 \quad (27)$$

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The structure factor

- Using the previous expression for the scattering potential and changing variables to $\mathbf{R}_i = \mathbf{r} - \mathbf{r}_i$

$$\begin{aligned}
 \langle \mathbf{k}_1 | \Phi(\mathbf{r}) | \mathbf{k}_2 \rangle &= \sum_{i=1}^N \int d\mathbf{R}_i \exp(-i\mathbf{k}_1 \cdot (\mathbf{r}_i + \mathbf{R}_i)) \phi_i(\mathbf{R}_i) \exp(i\mathbf{k}_2 \cdot (\mathbf{r}_i + \mathbf{R}_i)) \\
 &= \sum_{i=1}^N \left[\int d\mathbf{R}_i \exp(-i\mathbf{k} \cdot \mathbf{R}_i) \phi_i(\mathbf{R}_i) \right] \exp(i\mathbf{k} \cdot \mathbf{r}_i) \\
 &= \sum_{i=1}^N \phi_i(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_i) \rightarrow \phi(\mathbf{k}) \rho(\mathbf{k})
 \end{aligned}$$

the cross section is

$$\frac{d\sigma}{d\Omega} \sim \sum_{i=1}^N \sum_{j=1}^N \phi_i(\mathbf{k}) \phi_j(\mathbf{k})^* \exp(-i\mathbf{k} \cdot \mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_j) \quad (28)$$

The structure factor

- If all atoms are identical. Taking the ensemble average:

$$\frac{d\sigma}{d\Omega} \sim |\phi(\mathbf{k})|^2 \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp(-i\mathbf{k} \cdot \mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right\rangle \quad (29)$$

$$\sim |\phi(\mathbf{k})|^2 NS(\mathbf{k}) \quad (30)$$

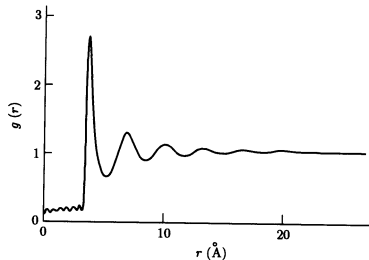
- **Structure factor:**

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp(-i\mathbf{k} \cdot \mathbf{r}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right\rangle = \langle \rho(\mathbf{k})^* \rho(\mathbf{k}) \rangle \quad (31)$$

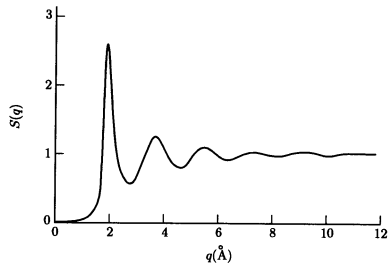
Scattering measures the density-density correlation function, or mean square density fluctuation, at any wave vector \mathbf{k} .

- **Form factor:** $|\phi(\mathbf{k})|^2$

The structure of liquid argon



Experimental, radial distribution function $g(r)$ for liquid argon



Structure factor for liquid argon at the same conditions. Main peak at $k \sim 2\pi/\sigma$

Source: Chaikin & Lubensky

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Application: Suspension of spherical colloidal particles

Consider a suspension of spherical particles.

- Amplitude of radiation scattered by particle i

$$B_i(\mathbf{k}) = \int B_i(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (32)$$

where $B_i(\mathbf{r})$ represents the distribution of scattering centres within the particle

- For **light scattering**, $B_i(\mathbf{r})$ reflects variations of the local index of refraction, and

$$B_i(\mathbf{r}) = n_i(\mathbf{r}) - n_0 \quad (33)$$

with $n_i(\mathbf{r})$ and n_0 the refraction index of the particle and solvent respectively

- For ensemble of N particles the intensity of scattered radiation:

$$I(\mathbf{k}) = \sum_{i=1}^N \sum_{j=1}^N \langle B_i(\mathbf{k}) B_j(\mathbf{k}) \exp(i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \rangle \quad (34)$$

Spherical colloidal particles

- For N identical particles:

$$I(\mathbf{k}) = NB(0)^2 P(\mathbf{k}) S(\mathbf{k}) \quad (35)$$

where $S(\mathbf{k})$ is the centre of mass structure factor, and $P(\mathbf{k}) = (B(\mathbf{k})/B(0))^2$ is called the **form factor**

- For a dilute suspension $S(k) = 1$ for all k
- For homogeneous spherical particles of radius R and refractive index n_c ,

$$B(r) = n_c - n_0 \quad \text{for } |\mathbf{r}| < R \quad (36)$$

and

$$B(k) = 4\pi(n_c - n_0) \int_0^R \frac{\sin(kr)}{kr} r^2 dr = \left(\frac{4\pi R^3}{3}\right)(n_c - n_0) \frac{3J_1(kR)}{kR} \quad (37)$$

with $J_1(x) = (\sin(x) - x \cos(x))/x^2$

- The intensity of scattered light is:

$$I(k) = NB(0)^2 P(k) \quad \text{with} \quad P(k) = \left[\frac{3J_1(kR)}{kR} \right]^2 \quad (38)$$

Spherical colloidal particles

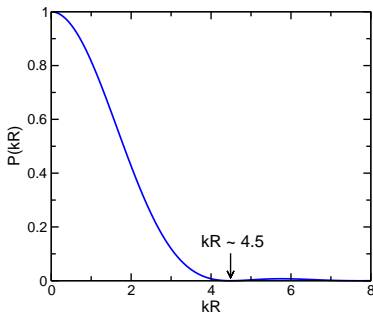


Figure: $S(k)$ for a dilute suspension of spherical particles.

Note: The structure factor, $S(k)$, decays rapidly with k and has a first zero at $kR \sim 4.5$, which allows the experimental determination of the radius of the particles.

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A fluid in an external field

Hamiltonian of a system in presence of external field:

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \quad (39)$$

The external field couples to the density $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (40)$$

The **instantaneous** potential energy due to the field is:

$$\Phi(\mathbf{r}) = \sum_{i=1}^N \phi(\mathbf{r}_i) = \int \rho(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (41)$$

and its **average value** is give by:

$$\langle \rho(\mathbf{r}) \rangle = \rho^{(1)}(\mathbf{r}) \quad \text{and} \quad \langle \Phi(\mathbf{r}) \rangle = \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (42)$$

A fluid in an external field

The **density-density correlation function** describes fluctuations in the local density:

$$H^{(2)}(\mathbf{r}, \mathbf{r}') = \langle [\rho(\mathbf{r}) - \langle \rho(\mathbf{r}) \rangle] [\rho(\mathbf{r}') - \langle \rho(\mathbf{r}') \rangle] \rangle \quad (43)$$

$$= \rho(\mathbf{r}, \mathbf{r}') + \rho^{(1)}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}') \quad (44)$$

$$= \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')h^{(2)}(\mathbf{r}, \mathbf{r}') + \rho^{(1)}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \quad (45)$$

where $h^{(2)}(\mathbf{r}, \mathbf{r}') = g^{(2)}(\mathbf{r}, \mathbf{r}') - 1$

- $H^{(2)}(\mathbf{r}, \mathbf{r}')$ describes correlations between the microscopic density at two points in the space, \mathbf{r} and \mathbf{r}'
- We will see later that $H^{(2)}(\mathbf{r}, \mathbf{r}')$ is the linear **response function** of the system

A fluid in an external field

We seek for a relation between the grand potential, Ω , and $\phi(\mathbf{r})$ or $\rho(\mathbf{r})$

In the presence of external field $\Xi(\mu, V, T)$ is:

$$\Xi = \exp(-\beta\Omega) = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp(-\beta V_N) \left(\prod_{i=1}^N z \exp[-\beta\phi(\mathbf{r}_i)] \right) d\mathbf{r}^N \quad (46)$$

and the corresponding particle densities are:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N=0}^{\infty} \frac{1}{(N-n)!} \int \exp(-\beta V_N) \left(\prod_{i=1}^N z \exp[-\beta\phi(\mathbf{r}_i)] \right) d\mathbf{r}^{(N-n)} \quad (47)$$

defining the **intrinsic chemical potential** as: $\psi(\mathbf{r}) = \mu - \phi(\mathbf{r})$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \exp(-\beta V_N) \left(\prod_{i=1}^N \frac{1}{\Delta^3} \exp[-\beta\psi(\mathbf{r}_i)] \right) d\mathbf{r}^N \quad (48)$$

Thermodynamic potentials as functionals

We suppose the definition of $\phi(\mathbf{r})$ includes the confining potential so we replace the volume, V , by $\phi(\mathbf{r})$. Using the first law

$$\delta U = T\delta S + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N \quad (49)$$

The corresponding change in F is:

$$\delta F = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N \quad (50)$$

Defining the **intrinsic free energy** \mathcal{F} as: $\mathcal{F} = F - \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}$

$$\delta F = -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} + \mu\delta N \quad (51)$$

$$= -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} \quad (52)$$

It becomes clear that $\psi(\mathbf{r})$ is the variable conjugate to $\rho^{(1)}(\mathbf{r})$

Thermodynamic potentials as functionals

The grand potential $\Omega = F - N\mu$ can be expressed in terms of \mathcal{F} :

$$\delta\Omega = \mathcal{F} + \int \rho^{(1)}(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} - N\mu \quad (53)$$

with a differential given by:

$$\delta\Omega = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\phi(\mathbf{r})d\mathbf{r} - N\mu \quad (54)$$

$$= -S\delta T - \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} \quad (55)$$

which shows that \mathcal{F} and Ω are functionals of $\phi(\mathbf{r})$ and $\rho(\mathbf{r})$ respectively:

$$\Omega = \Omega[\psi(\mathbf{r})] \quad \text{and} \quad \mathcal{F} = \mathcal{F}[\rho(\mathbf{r})] \quad (56)$$

and the they are related by a Legendre transformation:

$$\mathcal{F} = \Omega + \int \rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \quad (57)$$

Functional derivatives of the thermodynamic potentials

Aims:

- To derive expressions for density-density correlation functions and response functions by functional differentiation with respect to spatially varying fields
- Obtain relation between density-density correlation functions and energetic of density fluctuations
- Write functional Taylor expansion of the free energy in terms of $\delta\psi(\mathbf{r})$

Consider:

$$\delta\mathcal{F} = -S\delta T + \int \delta\rho^{(1)}(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\mathcal{F}}{\delta\rho^{(1)}(\mathbf{r})} = \psi(\mathbf{r})$$

$$\delta\Omega = -S\delta T + \int \rho^{(1)}(\mathbf{r})\delta\psi(\mathbf{r})d\mathbf{r} \quad \rightarrow \quad \frac{\delta\Omega}{\delta\psi(\mathbf{r})} = -\rho^{(1)}(\mathbf{r})$$

Which shows that:

$$\Omega[\psi] - \int \psi(\mathbf{r})\frac{\delta\Omega}{\delta\psi(\mathbf{r})}d\mathbf{r} \rightarrow \Omega[\psi] + \int \psi(\mathbf{r})\rho^{(1)}(\mathbf{r})d\mathbf{r} = \mathcal{F}[\rho^{(1)}] \quad (58)$$

Higher order derivatives

Higher order derivatives are calculated using standard rules for functional differentiation. Thus

$$\begin{aligned} \frac{\delta^2 \Omega}{\delta \psi(1) \delta \psi(2)} &= \beta \left[\rho^{(1)}(1) \rho^{(1)}(2) - \rho^{(1)}(1) \delta(1, 2) - \rho^{(2)}(1, 2) \right] \\ &= -\beta H^{(2)}(1, 2) \\ &= \frac{\delta \rho^{(1)}(1)}{\delta \psi(2)} \end{aligned}$$

and in general:

$$\frac{\delta^n \beta \Omega}{\delta \beta \psi(1) \cdots \delta \beta \psi(n)} = -H^{(n)}(1, \dots, n) \quad \text{for } n \geq 2 \quad (59)$$

which allow us to write the Taylor expansion:

$$\delta \Omega = - \int \rho^{(1)}(\mathbf{r}) \delta \psi(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \int \int \beta H^2(\mathbf{r}, \mathbf{r}') \delta \psi(\mathbf{r}) \delta \psi(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \quad (60)$$

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The density response function

A uniform fluid of density ρ_0 is perturbed by a weak external field $\delta\phi(\mathbf{r})$. The Hamiltonian of the system is:

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^N \delta\phi(\mathbf{r}_i) \quad (61)$$

and the induced density variation:

$$\delta\rho^{(1)}(\mathbf{r}) = \rho^{(1)}(\mathbf{r}) - \rho_0 \quad (62)$$

For a weak perturbation the response is a linear but non-local function of $\delta\phi(\mathbf{r})$

$$\delta\rho^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta\phi(\mathbf{r}') d\mathbf{r}' \quad (63)$$

where the **linear response function or susceptibility** is give by:

$$\chi(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\phi(\mathbf{r}')} \right|_{\phi=0} = \left. \frac{\delta\rho^{(1)}(\mathbf{r})}{\delta\psi(\mathbf{r}')} \right|_{\phi=0} \quad (64)$$

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Response and correlation functions

As shown before: $\frac{\delta \rho^{(r)}(1)}{\delta \psi(\mathbf{r}')} = -\beta H^{(2)}(\mathbf{r}, \mathbf{r}')$ and,

Linear response function:

$$\chi(\mathbf{r}, \mathbf{r}') = -\beta H^{(2)}(\mathbf{r}, \mathbf{r}') \quad \textit{Fluctuation dissipation theorem}$$

Within linear response: **The pair correlation function of the unperturbed system measures the response to an external field**

For an homogeneous system:

$$\chi(|\mathbf{r} - \mathbf{r}'|) = -\beta [\rho_0^2 h(|\mathbf{r} - \mathbf{r}'|) + \rho_0 \delta(|\mathbf{r} - \mathbf{r}'|)] \quad (65)$$

and the induced density change:

$$\delta \rho^{(1)}(\mathbf{r}) = -\beta \rho_0 \delta \phi(\mathbf{r}) - \beta \rho_0^2 \int h(|\mathbf{r} - \mathbf{r}'|) \delta \phi(\mathbf{r}') d\mathbf{r}' \quad (66)$$

Wave-vector dependent response

Taking Fourier transforms:

$$\delta\hat{\rho}^{(1)}(\mathbf{k}) = \chi(\mathbf{k})\hat{\phi}(\mathbf{k}) = -\beta\rho_0\mathbf{S}(\mathbf{k})\delta\hat{\phi}(\mathbf{k}) \quad (67)$$

and

Susceptibility:

$$\chi(\mathbf{k}) = -\beta\rho_0\mathbf{S}(\mathbf{k}) \quad (68)$$

- $\mathbf{S}(\mathbf{k})$ measures the response of an unperturbed system to an external field of wavelength $2\pi/k$
- At linear order the system responds only at the wave-vector of the perturbation
- For $k \rightarrow 0$:

$$\lim_{k \rightarrow \infty} \mathbf{S}(\mathbf{k}) = \rho k_B T \chi_T \quad (69)$$

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Example: The random phase approximation (RPA)

Aim: To calculate the static susceptibility, $\chi(\mathbf{k})$, of a system of particles interacting via weak or long-range forces

- RPA: approximation based on a combination of linear response and mean field theories
- Separate interaction potential into short and weak/long-range parts

$$\begin{array}{ccccc}
 V_T(\mathbf{r}^N) & = & V^o(\mathbf{r}^N) & + & W(\mathbf{r}^N) \\
 \uparrow & & \uparrow & & \uparrow \\
 \textit{Total} & & \textit{Reference} & & \textit{Perturbation}
 \end{array}$$

- The total potential, $\phi(\mathbf{r})$, felt by a particle at point \mathbf{r} is a sum of an external plus a **mean** internal potential:

$$\phi(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \int w(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}') d\mathbf{r}' \quad (70)$$

The random phase approximation (RPA)

- $\delta\rho(\mathbf{r}')$: deviation of the local density from its mean
- The spatially modulated external potential can be written as:

$$\phi_{ext}(\mathbf{r}) = \frac{1}{V} \delta\phi_{ext}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad (71)$$

- Taking Fourier transform of previous equations:

$$\phi(\mathbf{k}) = \delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k}) \quad (72)$$

- According to linear response:

$$\begin{array}{ccccc}
 \delta\rho(\mathbf{k}) & = & \chi^0(\mathbf{k}) & \times & (\delta\phi_{ext}(\mathbf{k}) + w(\mathbf{k})\delta\rho(\mathbf{k})) \\
 \uparrow & & \uparrow & & \uparrow \\
 \text{Density} & & \text{Susceptibility} & & \text{Selfconsistent} \\
 \text{modulation} & & \text{ref. system} & & \text{potential}
 \end{array}$$

The random phase approximation (RPA)

- Solving for $\delta\rho(\mathbf{k})$:

$$\delta\rho(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1 - \chi^o(\mathbf{k})w(\mathbf{k})} \delta\phi_{ext}(\mathbf{k}) \quad (73)$$

- For the actual system, interacting through the full potential energy, $\delta\rho(\mathbf{k}) = \chi^T(\mathbf{k})\delta\phi_{ext}(\mathbf{k})$, and :

$$\chi^T(\mathbf{k}) = \frac{\chi^o(\mathbf{k})}{1 - \chi^o(\mathbf{k})w(\mathbf{k})} \quad (74)$$

- In terms of the structure factors $S^T(\mathbf{k})$ and $S^o(\mathbf{k})$:

$$\frac{1}{S^T(\mathbf{k})} = \frac{1}{S^o(\mathbf{k})} + \frac{\rho w(\mathbf{k})}{k_B T} \quad (75)$$

- How does the previous expression look like when $V^o = 0$ (ideal gas) ?

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