Lecture 9

Recap:

- $\langle A \rangle_{\Gamma^2} \hat{=} \langle A \rangle_+ = \frac{1}{N} \sum_i^N A_i$
- $\sigma_A^2 = \langle (A - \langle A \rangle)^2 \rangle$
- $c_{AB}(t) = <A(t)B(O)>$

Continue chapter on correlation functions (CF)

Example: density-density time CF

$$G(r, r', t) := \frac{1}{N} \langle \sum_{i=1}^N \delta(r' + r - r_i(t)) \sum_{j=1}^N \delta(r' - r_j(0)) \rangle$$

- $A(t)$: find any particle at time t at position r
- $B(0)$: find any particle at time 0 and position r'

For homogenous systems, simplify by averaging over r' (independent of origin):

$$\Rightarrow G(r, t) := \frac{1}{N} \langle \sum_{i=1}^N \sum_{j=1}^N \int dr' \delta(r' + r - r_i(t)) \delta(r' - r_j(0)) \rangle$$
$$= \frac{1}{N} \langle \sum_{i,j}^{N,N} \delta(r + r_j(0) - r_i(t)) \rangle$$

This is the **van Hove CF**.

Physically: $G(r, t)dr$ is the probability to find particle i if a particle j has been at the origin.

$$G(r, t) = \underbrace{\frac{1}{N} \langle \sum_{i=1}^N \delta(r + r_i(0) - r_i(t)) \rangle}_{G_{self}(r,t)} + \underbrace{\frac{1}{N} \langle \sum_{i=1, j \neq i}^{N,N} \delta(r + r_j(0) - r_i(t)) \rangle}_{G_{distinct}(r,t)}$$

Important special / limiting cases of G

- $G_s(r, 0) = \delta(r)$
- $G_s(r, t > 0) \rightarrow$ self diffusion
- $G_d(r, 0) = \rho \cdot g(r) \leftarrow$ pair distribution function, where ρ is the number density.

$$g(r) = \frac{V}{N^2} \langle \sum_i^N \sum_{j \neq i}^N \delta(r - (r_i - r_j)) \rangle$$

- This describes the structure of matter at the pair correlation level.
- For a homogenous and isotropic system: $g(r) \rightarrow g(r)$, the **radial distribution function (RDF)**.
- $P(r)dr = \frac{N}{V} g(r)dr^3 :=$ probability to find a particle at distance r with respect to a reference particle.

Typical RDFs:

A graph plotting g(r) vs r for different states of matter:

- **Gas:** A single broad peak indicating collisions.
- **Liquid:** A prominent peak for the "1st shell" of neighbors, followed by a smaller "2nd shell" peak, with the peaks broadening at larger distances due to temperature.
- **Solid:** A series of sharp, well-defined peaks indicating a crystal lattice structure.

RDFs for Crystals:

- **Gas:** No structure, only collisions.
- **Liquid:** Some structuring, but no long-range order.
- **Crystal:** Long-range order and periodicity, leading to sharper, delta-like peaks.
  - A simple cubic lattice with side length a=1 would have peaks at r = 1, $\sqrt{2}$, $\sqrt{3}$, 2, etc.
  - A face-centered cubic lattice would show a different pattern of peaks.

Connection of $g(r)$ and $G(r,t)$ to experiments

Static structure factor $S(k)$ (from X-ray, neutron diffraction)

- $S(k) = \frac{1}{N}\langle \rho(k)\rho(-k)\rangle$
- This is the density-density correlation function in k-space (reciprocal space).
- $S(k) = \frac{1}{N}\langle \sum_{i,j} e^{-ik(r_i - r_j)}\rangle = 1 + \frac{N}{V}\int_V d^3 r g(r)e^{-ik\cdot r}$

- $S(k)$ is related to $g(r)$ via a Fourier Transform (FT).
- For homogenous & isotropic systems: $S(k) = S(k)$
  - $S(k) = 1 + 4\pi\frac{N}{V}\int_0^\infty dr r^2 \frac{\sin(kr)}{kr}[g(r) - 1]$
- There is a reciprocal relationship between real and k-space: $k \sim \frac{2\pi}{r}$
  - Short range in real space $\leftrightarrow$ Long range in reciprocal space.
  - **Small Angle X-ray Scattering (SAXS):** small k probes long-range information.
  - **Large Angle X-ray Scattering (LAXS):** large k probes short-range information.

Dynamical structure factor $S(k,\omega)$ (from inelastic neutron scattering)

- $S(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t}\int_V d^3 r e^{-ik\cdot r}G(r,t)$
- This gives access to the full van Hove CF.

Time CF: Green-Kubo / Einstein relations

Structure Factor ("Spectrum")	Correlation Function (CF)
X-ray / neutron scattering	density-density correlation
IR spectra	dipole-dipole correlation
Raman spectra	polarizability autocorrelation

- **IR Spectra:** The photoabsorption cross-section $I(\omega)$ is a spectral density or line shape function.
  - $I(\omega) \approx \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mu(t)\mu(0) \rangle$
  - This is the FT of the autocorrelation function of the total dipole moment (μ) of the system.
- **Velocity-velocity autocorrelation function (VAF)**
  - $C_{VV}(t) = \frac{1}{N} \sum_{j=1}^{N} \langle \dot{r}_j(t_i) \cdot \dot{r}_j(t_i + \Delta t) \rangle$
  - Its Fourier Transform is related to IR, Raman, and NMR spectra.

Transport Processes: Self-Diffusion

Self-diffusion is the process by which an initially non-uniform concentration spreads out in the absence of flow. There are two equivalent definitions for the diffusion constant, D:

1. **Green-Kubo relation (1957):**
   $D_{GK} = \int_{0}^{\infty} dt \frac{1}{3} \langle \dot{r}(t)\dot{r}(0) \rangle$
   - This is the time integral of the velocity autocorrelation function, $C_{vv}(t)$.

2. **Einstein relation (1905):**
   $D_E = \lim_{t \to \infty} \frac{1}{2dt} \langle (r(t) - r(0))^2 \rangle$, where d is the dimensionality (here, d=3).
   - $D_E = \lim_{t \to \infty} \frac{1}{6t} \langle (r(t) - r(0))^2 \rangle$
   - This relates the diffusion constant to the long-time limit of the mean square displacement (MSD).

Mean Square Displacement (MSD)

A plot of MSD vs. time:

- **Liquid:** At short times, particles move freely between collisions (ballistic regime, MSD $\propto t^2$). At long times, particles undergo random walk (diffusive regime, MSD $\propto t$). The curve can be noisy at long times due to statistics.

- **Solid:** Atoms vibrate about their fixed lattice positions, so the MSD plateaus at a value related to the amplitude of these vibrations.

The diffusion constant is calculated from the slope of the linear (diffusive) regime:
$D_E = \frac{1}{6} \frac{\Delta \mathrm{MSD}}{\Delta t}$

Note on plots: It is important to use a continuous trajectory (not wrapped back into the periodic unit cell) when calculating MSD.

General Green-Kubo Relations:

The general form is $K = \int_0^\infty \langle J(t)J(0)\rangle dt$, where K is a transport coefficient and J is the corresponding microscopic flux.

- **Shear Viscosity (η):** J = off-diagonal component of the stress tensor.

- **Thermal Conductivity (λ_T):** J = Energy current.

- **Electrical Conductivity (σ_e):** J = Electrical current.