Dynamical correlations & transport coefficients

Dynamics is why we do molecular dynamics! (vs Monte Carlo)

• Perturbation theory
• Linear-response theory.
• Diffusion constants, velocity-velocity auto correlation function
• Transport coefficients
  – Diffusion: Particle flux
  – Viscosity: Stress tensor
  – Heat transport: energy current
  – Electrical Conductivity: electrical current
Consider a perturbation in potential by $\lambda A(r)$:

$$e^{-\beta F(\lambda)} = \int d^3N r \, e^{-\beta V(r) - \beta \lambda A(r)}$$

$$e^{-\beta F(\lambda)} = \int d^3N r \, e^{-\beta V(r)} \left[ 1 - \beta \lambda A(r) + \frac{1}{2} (\beta \lambda)^2 A^2(r) - \cdots \right]$$

$$= e^{-\beta F(0)} - \beta \lambda \int d^3N r \, A(r) e^{-\beta V(r)} + \frac{1}{2} (\beta \lambda)^2 \int d^3N r \, A^2(r) e^{-\beta V(r)} - \cdots$$

$$= e^{-\beta F(0)} \left[ 1 - \beta \lambda \langle A \rangle_0 + \frac{1}{2} (\beta \lambda)^2 \langle A^2 \rangle_0 - \cdots \right]$$

$$-\beta F(\lambda) = -\beta F(0) + \ln \left[ 1 - \beta \lambda \langle A \rangle_0 + \frac{1}{2} (\beta \lambda)^2 \langle A^2 \rangle_0 - \cdots \right]$$

$$F(\lambda) = F(0) + \lambda \langle A \rangle_0 - \frac{1}{2} \beta \lambda^2 \left[ \langle A^2 \rangle_0 - \langle A \rangle_0^2 \right] + \cdots$$

For an observable $B$: $B(\lambda) = \langle B \rangle_\lambda = B(0) - \beta \lambda \left[ \langle BA \rangle_0 - \langle B \rangle_0 \langle A \rangle_0 \right] + \cdots$

For example let $A=\rho_k$ and $B=\rho_{-k}$, then:

$$\left. \frac{d\rho_{-k}}{d\lambda} \right|_{\lambda=0} = -\beta \left\langle |\rho_k|^2 \right\rangle = -\beta N \langle S_k \rangle$$

The structure factors gives the static response to a "density field" as measured by neutron and X-ray scattering (applied nuclear or electric field).
Dynamical Correlation Functions

\[ C_{AB}(t) = \langle \delta A(t_0) \delta B(t_0 + t) \rangle \]

• If system is ergodic, ensemble average equals time average and we can average over \( t_0 \).

• Decorrelation at large times: \( \lim_{t \to \infty} C_{AB}(t) = 0 \)

• Autocorrelation function \( B = A^\ast \). \( |C_{AA}(t)| \leq C_{AA}(0) \)

Fourier transform:

\[ C_{AB}(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} C_{AB}(t) \]

\[ C_{AA}(\omega) \geq 0 \]
Dynamical Properties

• Fluctuation-Dissipation theorem:

\[ \chi(\omega) = \beta \int_0^\infty dt \ e^{i\omega t} \left\langle B(t) \left. \frac{dA}{dt} \right|_{t=0} \right\rangle \]

• We calculate the average in equilibrium (no external perturbation).
• \([A \ e^{-i\omega t}]\) is a perturbation and \([\chi(\omega) \ e^{-i\omega t}]\) is the response of B.
• Fluctuations we “see” in equilibrium are equivalent to how a non-equilibrium system approaches equilibrium. (Onsager regression hypothesis; 1930 Nobel prize)
• Density-density response function is \(S(k, \omega)\). It can be measured by scattering and is sensitive to collective motions.

\[ S(k, \omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} \ e^{i\omega t} F_k(t) \quad \text{with} \quad F_k(t) = \frac{1}{2} \left\langle \rho_k(t) \rho_{-k}(0) \right\rangle \]
Linear Response in quantum mechanics

\[ \delta B(\omega) = \chi(\omega) \delta A(\omega) \]

\[ \chi(\omega) = \chi'(\omega) + i \chi''(\omega) \]

\[ \chi'(\omega) = \frac{1}{\pi} P \int d\omega' \frac{\chi''(\omega')}{\omega' - \omega} \]

\[ \chi''(\omega) = -\frac{1}{\pi} P \int d\omega' \frac{\chi'(\omega')}{\omega' - \omega} \]

Power dissipation = \[\frac{\omega}{2} \chi''(\omega) A^2(\omega)\]

\[ \chi''(\omega) = \frac{1}{2\hbar} \left( e^{\beta\hbar\omega} - 1 \right) \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \langle \delta B(t) \delta A(0) \rangle \]

\[ (\hbar \to 0) = \frac{1}{2} \beta \omega \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \langle \delta B(t) \delta A(0) \rangle \]
Transport coefficients

- Define as the response of the system to some dynamical or long-term perturbation, e.g., velocity-velocity
- Take zero frequency limit:
- Kubo form: integral of time (auto-) correlation function.

\[ \mu = \int_0^\infty dt \left\langle A(t_0)A(t_0 + t) \right\rangle \]

perturbation

response
Transport Coefficients: examples

- Diffusion: Particle flux
- Viscosity: Stress tensor
- Heat transport: energy current
- Electrical Conductivity: electrical current

\[ \sigma = \int_{0}^{\infty} dt \, \langle J(0)J(t) \rangle \quad J(t) = \text{total electric current} \]

- These can also be evaluated with non-equilibrium simulations.
  - Impose a shear, heat or current flow
  - Initial difference in particle numbers
- Need to use thermostats to have a steady-state simulation, otherwise energy (temperature) is not constant.
Diffusion Constant

- Defined by Fick’s law and controls how systems mix:

\[
\begin{align*}
    j(r, t) &= -D \nabla \rho(r, t) \\
    \frac{d\rho}{dt} &= -\nabla \cdot j(r, t) = D \nabla^2 \rho(r, t)
\end{align*}
\]

Linear response + Conservation of mass

\[
D = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle
\]

Einstein relation (no PBC!)

\[
= \frac{1}{3} \int_0^\infty dt \left\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \right\rangle
\]

Kubo formula

Use “unwound” positions to get equivalence between the 2 forms.
Consider a mixture of identical particles
Fig. 6.5 Calculating the diffusion coefficient in CS$_2$. (a) Mean square displacements at $T = 192$ K, $244$ K, $294$ K. (b) Velocity autocorrelation functions at $T = 192$ K. In each case we show components parallel and perpendicular to the molecular axis system at $t = 0$ [Tildesley and Madden 1983]

Fig. 2.3 (a) The velocity autocorrelation function and (b) its Fourier transform, for Lennard-Jones liquid near the triple point ($\rho^* = 0.85, T^* = 0.76$).
Multiple species diffusion in liquid metal

Simulations have changed perceptions

- Alder-Wainwright discovered long-time tails on the velocity autocorrelation function. The diffusion constant does not exist in 2D because of hydrodynamic effects.

- Results from computer simulation have changed our picture of a liquid. Several types of motion are allowed.

- **Train effect**: one particle pulls other particle along behind it.

- **Vortex effect**: at very long time one needs to solve using hydrodynamics--this dominates the long-time behavior.

- Hard sphere interactions are able to model this aspect of a liquid.
Density-Density response: a sound wave

\[ S(k, \omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} F_k(t) \quad F_k(t) = \frac{1}{2} \langle \rho_k(t) \rho_{-k}(0) \rangle \]

Measured by scattering and is sensitive to collective motions.

Suppose we have a sound wave:

\[ \delta \rho(x, t) = \mathcal{R} \{ e^{iqx-i\omega t} \} = \frac{\mathcal{E}}{2} \left[ e^{iqx-i\omega t} + e^{-iqx+i\omega t} \right] \]

\[ \rho_k(t) = \int d^3r \ \rho(r, t)e^{iqr} = \rho_0 \delta(k) + \varepsilon \left[ \delta(k + q)e^{i\omega t} + \delta(k - q)e^{-i\omega t} \right] \]

Peaks in \( S(k, \omega) \) at \( q \) and \(-q\).

Damping of sound wave broadens the peaks.

Inelastic neutron scattering can measure microscopic collective modes.
Dynamical Structure Factor for Hard Spheres

For $V_0 = N d^3 / \sqrt{2}$, HS fluid for:
(a) $V/V_0 = 1.6$, $kd = 0.38$
(b) $V/V_0 = 1.6$, $kd = 2.28$
(c) $V/V_0 = 3.0$, $kd = 0.44$
(d) $V/V_0 = 10$, $kd = 0.41$

Freq. = $kd / \tau$,  
$\tau$ = mean collision time

Points: MD (Alley et al, 1983) 
Lines: Enskog theory
Some experimental data from neutron scattering

- water
- liquid 3 helium