Dynamical correlations & transport coefficients

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

• Perturbation theory
• Linear-response theory.
• \textit{Diffusion constants, velocity-velocity} auto correlation function
• Transport coefficients
  – Diffusion: Particle flux
  – Viscosity: Stress tensor
  – Heat transport: energy current
  – Electrical Conductivity: electrical current
Static Perturbation theory

Consider a perturbation by $\lambda A(R)$. Change in equilibrium distribution is:

$$e^{-\beta F(\lambda)} = \int dR e^{-\beta V(R) - \beta \lambda A(R)}$$

Expand in powers of $\lambda$:

$$F(\lambda) = F(0) + \lambda <A>_0 - \beta \lambda^2 [<A^2>_0 - <A>_0^2]/2 + \ldots$$

For a property $B(R)$:

$$B(\lambda) = B(0) - \beta \lambda [<AB>_0 - <A>_0 <B>_0] + \ldots$$

Example let $A=B=\rho_k$, then:

$$\frac{d\rho_{-k}}{d\lambda} \bigg|_0 = -\beta <|\rho_k|^2> = -\beta NS_k$$

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 \( B = A^* \):
  \[ |C_{AA}(t)| \leq C_{AA}(0) \]

Fourier transform:

\[ C_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} C_{AB}(t) \quad C_{AA}(\omega) \geq 0 \]
Dynamical Properties

- **Fluctuation-Dissipation theorem:**

\[
\chi(\omega) = \beta \int_0^\infty dt \ e^{i \omega t} < B(t) \frac{dA(0)}{dt} >
\]

We calculate the *lhs* 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.

\[
S_k(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i \omega t} dt \ F_k(t) \quad F_k(t) = \frac{1}{2} < \rho_k(t) \rho_{-k}(0) >
\]
Linear Response in quantum mechanics

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

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

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

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

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

- Reduces to classical formula when \( \hbar=0 \)
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.

\[
\mu = \int_0^\infty dt \, < A(t) A(t+s) >
\]

perturbation

response
Transport Coefficients: examples

- Diffusion: \( \text{Particle flux} \)
- Viscosity: \( \text{Stress tensor} \)
- Heat transport: \( \text{energy current} \)
- Electrical Conductivity: \( \text{electrical current} \)

\[
\sigma = \int_0^\infty dt < J(t)J(0) >
\]

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 \textit{steady-state simulation}, otherwise energy (temperature) is not constant.
Diffusion Constant

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

\[ j(r,t) = -D \nabla \rho(r,t) \]

\[ \frac{d \rho}{dt} = -\nabla j(r,t) = D \nabla^2 \rho(r,t) \]

Linear response

+ Conservation of mass

\[ D = \lim_{t \to \infty} \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle \quad \text{Einstein relation (no PBC!)} \]

\[ D = \frac{1}{3} \int_0^\infty dt \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \quad \text{Kubo formula} \]

- Use “unwound” positions to get equivalence between the 2 forms.
Consider a mixture of identical particles

Initial condition

Later

9/20/16
Fig. 6.5 Calculating the diffusion coefficient in CS₂. (a) Mean square displacements at $T = 192\,\text{K}$, $244\,\text{K}$, $294\,\text{K}$. (b) Velocity autocorrelation functions at $T = 192\,\text{K}$. 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 ($\rho^* = 0.85$, $T^* = 0.76$).
• 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

\[ S_k(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ F_k(t) \quad F_k(t) = \frac{1}{2} < \rho_k(t)\rho_{-k}(0) > \]

- Measured by scattering and is sensitive to collective motions.

- Suppose we have a sound wave:

\[ \delta \rho(x,t) = \epsilon \text{Re}\{e^{iqx-i\omega t}\} = \frac{\epsilon}{2} [e^{iqx-i\omega t} + e^{-iqx+i\omega t}] \]

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

- 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 $^3$He