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

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 λ: $F(\lambda) = F(0) + \lambda \langle A\rangle_0 - \beta\lambda^2[\langle A^2\rangle_0 - \langle A\rangle_0^2\,]/2 + \ldots$

For a property B(R): $B(\lambda) = B(0) - \beta\lambda\,[\langle AB\rangle_0 - \langle A\rangle_0 \langle B\rangle_0\,] + \ldots$

Example let $A=B=\rho_k$, then: $$\left.\frac{d\rho_{-k}}{d\lambda}\right|_0 = -\beta \langle|\rho_k|^2\rangle = -\beta N S_k$$

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

$$C_{AB}(t) = \left\langle \delta A\left(t_0\right) \delta B\left(t_0 + t\right) \right\rangle$$

- If system is ergodic, ensemble average equals time average and we can average over t_0.
- Decorrelation at large times: $\lim_{t \to \infty} C_{AB}\left(t\right) = 0$
- Autocorrelation function B=A*. $\left|C_{AA}(t)\right| \leq C_{AA}\left(0\right)$

Fourier transform: $C_{AB}\left(\omega\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} C_{AB}\left(t\right)$ $\quad C_{AA}\left(\omega\right) \geq 0$

Dynamical Properties

- Fluctuation-Dissipation theorem:

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

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,ω)**. It can be measured by scattering and is sensitive to collective motions.

$$S_k(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t}\, dt\ F_k(t) \qquad F_k(t) = \frac{1}{2} < \rho_k(t) \rho_{-k}(0) >$$

Linear Response in quantum mechanics

$$\delta B(\omega) = \chi(\omega)\delta A(\omega)$$

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

$$\chi'(\omega) = \frac{P}{\pi}\int d\omega' \frac{\chi''(\omega')}{\omega' - \omega} \qquad \chi''(\omega) = -\frac{P}{\pi}\int d\omega' \frac{\chi'(\omega')}{\omega' - \omega}$$

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

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

- Reduces to classical formula when h=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.

perturbation

$$\mu = \int_0^\infty dt < A(t) A(t+s) >$$

response

Transport Coefficients: examples

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

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

J(t)=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

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

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

Linear response
+
Conservation of mass

$$D = \lim_{t\to\infty} \frac{1}{6t} < |\underline{r}_i(t) - \underline{r}_i(0)|^2 >$$

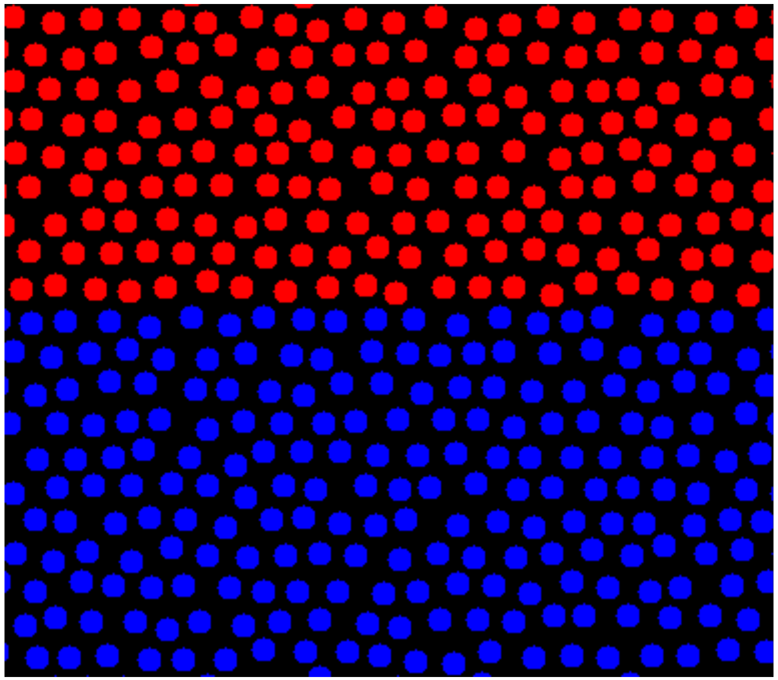
Einstein relation (no PBC!)

$$D = \frac{1}{3}\int_0^\infty dt < \vec{\mathrm{v}}_i(t)\cdot\vec{\mathrm{v}}_i(0) >$$

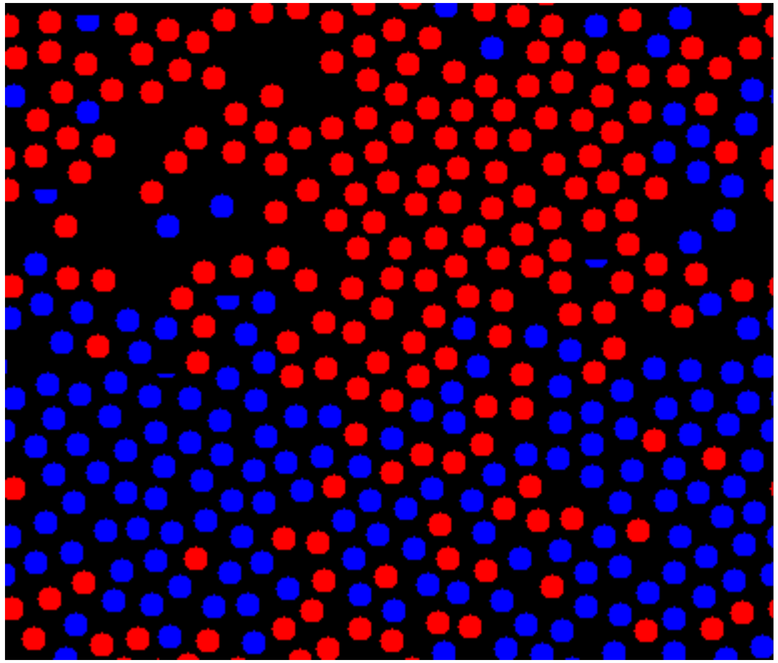
Kubo formula

- Use "unwound" positions to get equivalence between the 2 forms.

Consider a mixture of identical particles



Initial condition



Later

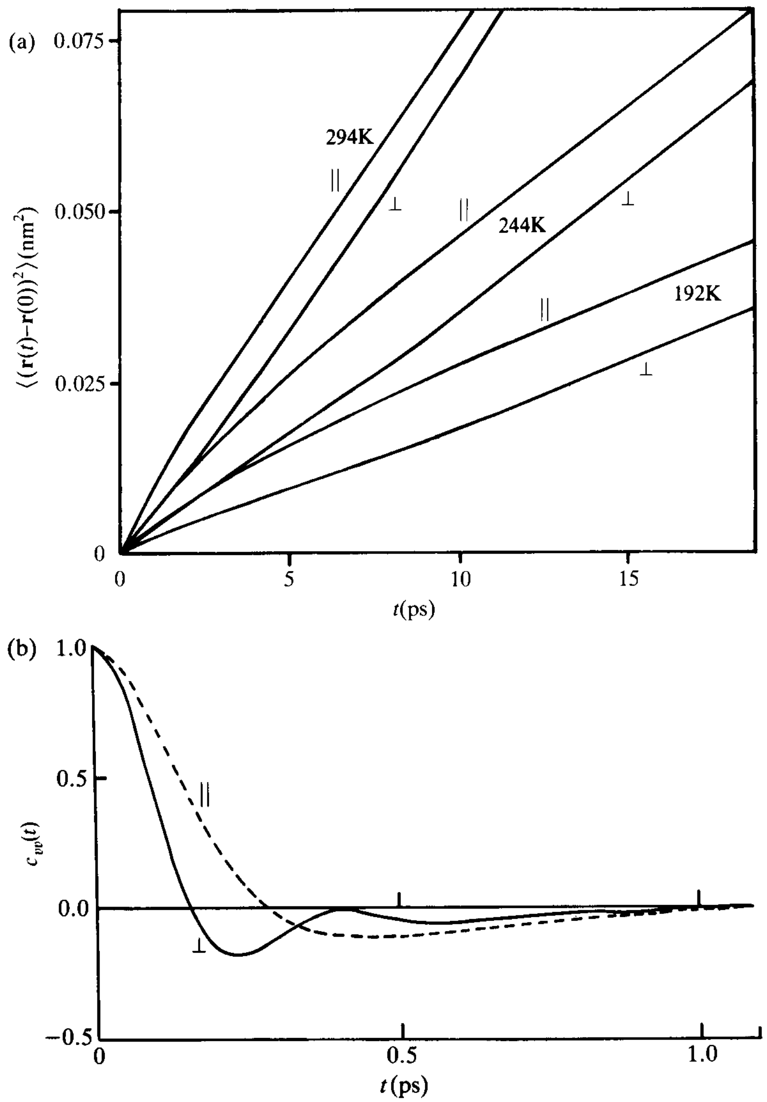


Fig. 6.5 Calculating the diffusion coefficient in CS_2. (a) Mean square displacements at $T = 192\,K, 244\,K, 294\,K$. (b) Velocity autocorrelation functions at $T = 192\,K$. In each case we show components parallel and perpendicular to the molecular axis system at $t = 0$ [Tildesley and Madden 1983]

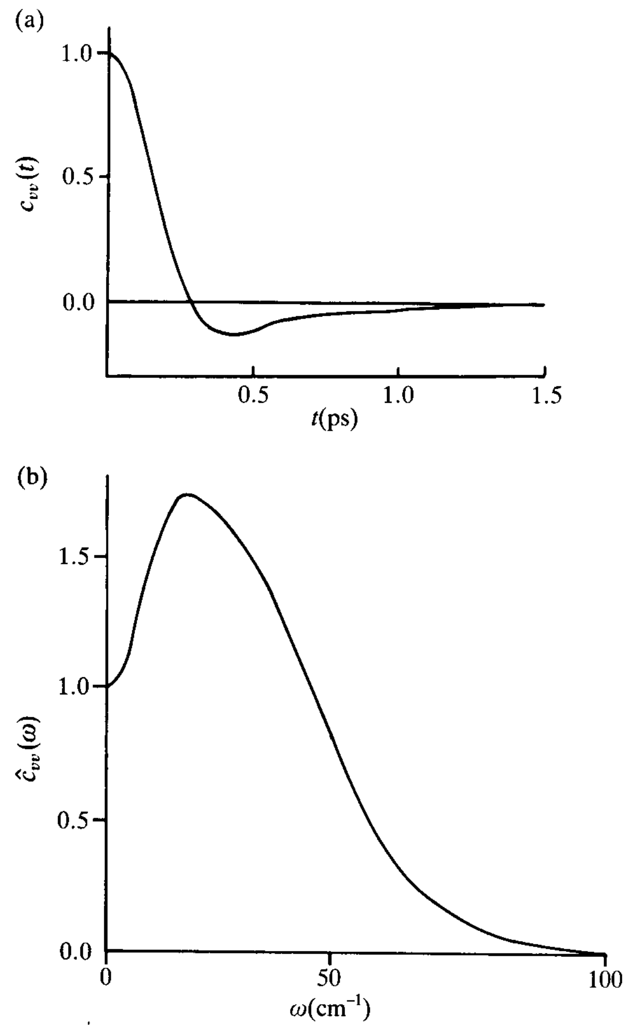


Fig. 2.3 (a) The velocity autocorrelation function and (b) its Fourier transform, for Lennard-Jones liquid near the triple point ($\rho^* = 0.85$, $T^* = 0.76$).

- 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

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

- Measured by scattering and is sensitive to collective motions.
- Suppose we have a sound wave:

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

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

- **Peaks in S(k,ω) at q and -q**.
- ***Damping of sound wave broadens the peaks***.
- Inelastic neutron scattering can measure microscopic collective modes.

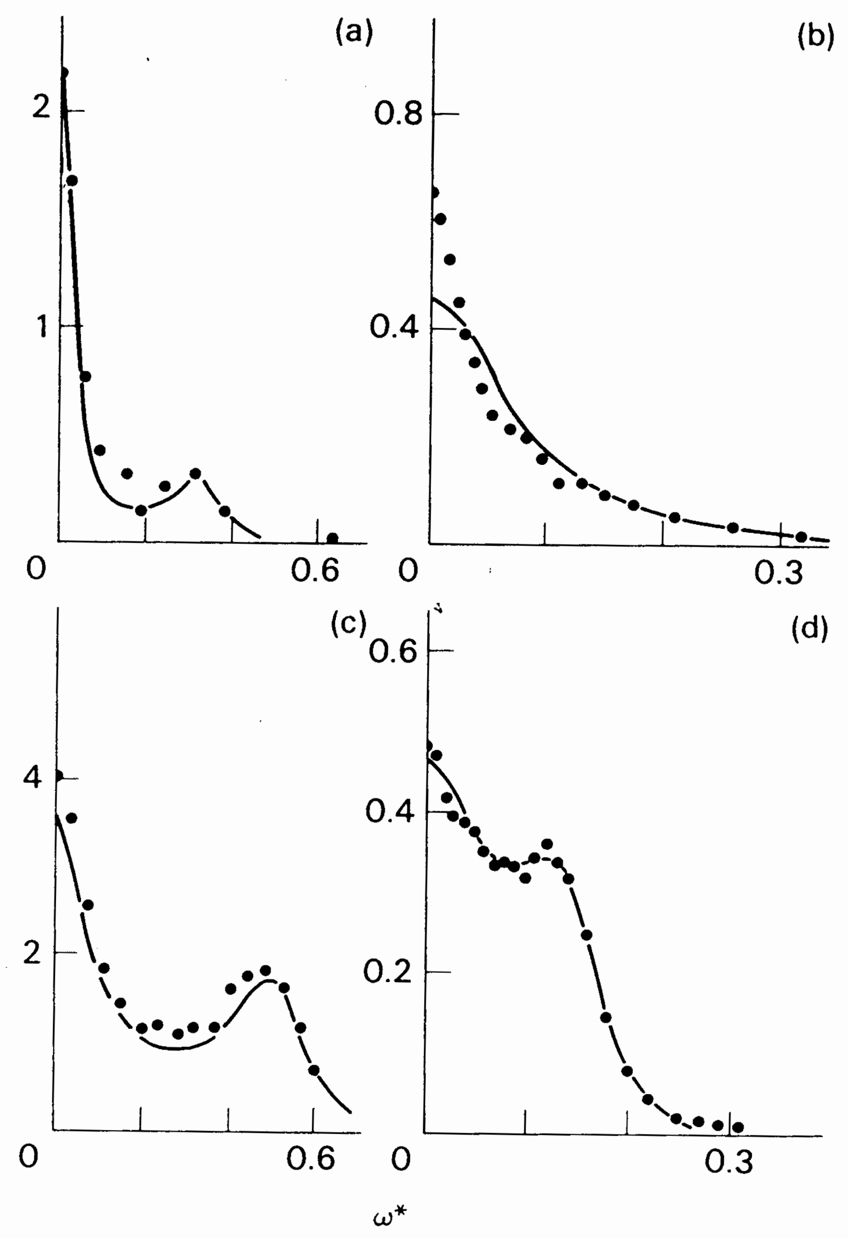
Dynamical Structure Factor for Hard Spheres

For $V_0 = Nd^3/\sqrt{2}$, 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/τ,
τ = mean collision time

Points: MD (Alley et al, 1983)
Lines: Enskog theory



Some experimental data from neutron scattering