Short Course on Molecular Dynamics Simulation

Lecture 9:
Dynamic Properties

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High Level Course Outline

1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

Dynamic Properties

- Time correlation functions
  - Single particle correlations
    - Velocity autocorrelation function
  - Collective correlations
    - Stress autocorrelation function
- Transport coefficients
  - Einstein relations
  - Green-Kubo relations
    - Viscosity
    - Diffusion

Time Correlation Function

- Two time dependent signals A and B; C quantifies the correlation between them

$$C(t) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A(t_0) B(t_0 + t) dt_0 = \langle A(t_0) B(t_0 + t) \rangle$$

- A correlation function is invariant under translations of the time origin

$$C(t) = \langle A(t_0) B(t_0 + t) \rangle = \langle A(t_0 + s) B(t_0 + s + t) \rangle$$

  – A and B different: C is a cross-correlation
  – A and B the same: C is an auto-correlation

Time Correlation Function

- In the limit of no delay time, C(0) is the static correlation function

$$C(0) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A(t_0) B(t_0)\, dt_0$$

$$= \langle A(t_0) B(t_0) \rangle \equiv \langle AB \rangle$$

* Often normalize by this value:

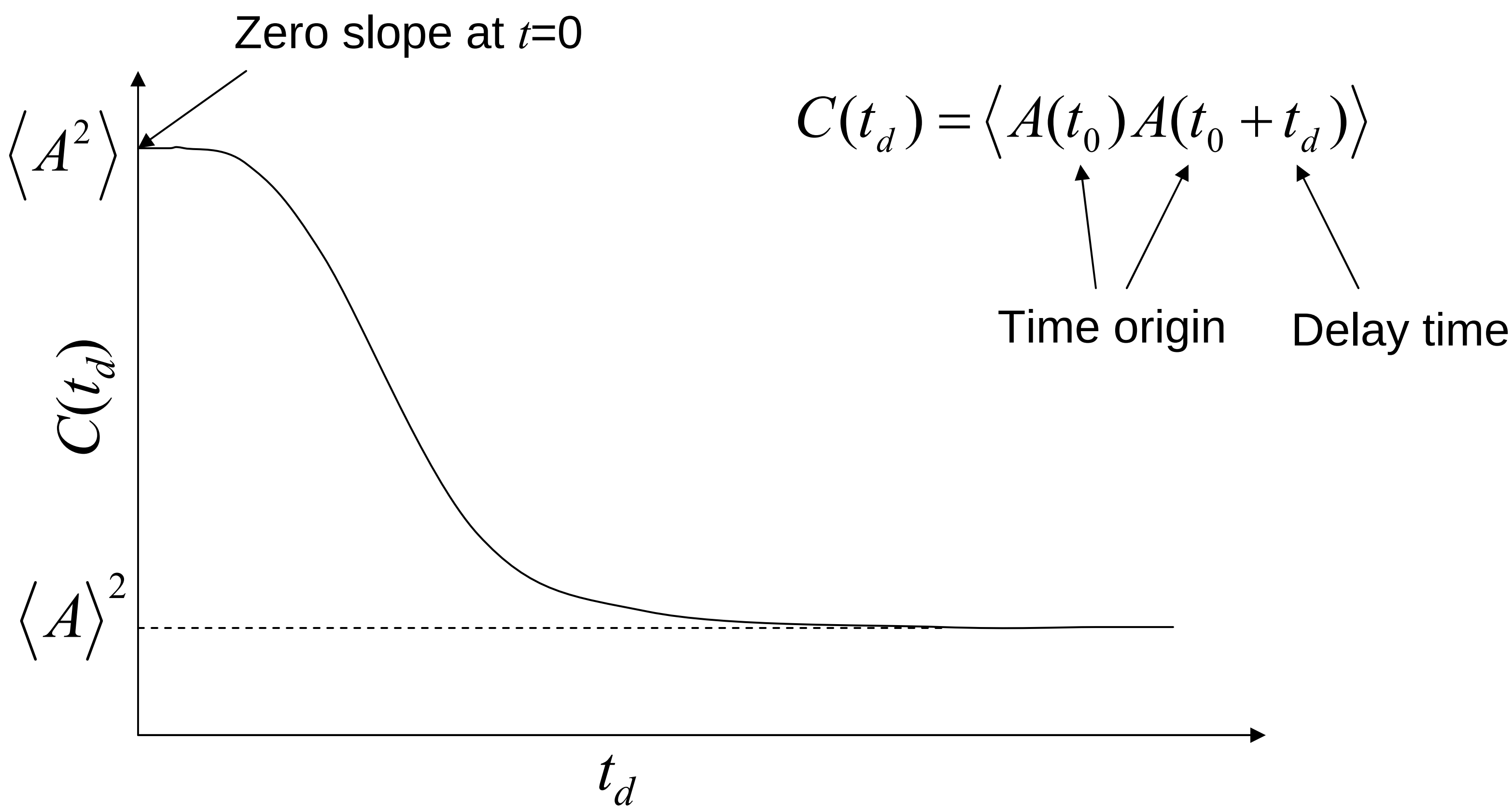
$$\hat{C}(t) = \frac{\langle A(t_0) B(t_0 + t) \rangle}{\langle AB \rangle}$$

- In the long time limit, behavior of C(0) depends on periodicity of A and B
  – If non-periodic (relevant to MD), they will become uncorrelated

$$\lim_{t \to \text{large}} C(t) = \langle A \rangle \langle B \rangle$$

Time Correlation Function

- Characteristic features of an autocorrelation function



Time Correlation Function

- Implementation

$$C(t_d) = \frac{1}{t_{max}} \sum_{t_0}^{t_{max}} A(t_0) A(t_0 + t_d) \qquad t_{max} = L - \frac{t_d}{\Delta t}$$

- Example

index	t	$A(t) = \sin\left(\frac{\pi}{2} t\right)$
1	0	0
2	.2	.31
3	.4	.59
4	.6	.81
5	.8	.95
6	1	1

$$t_{max}(t_d = .4) = 6 - \frac{.4}{.2} = 4$$

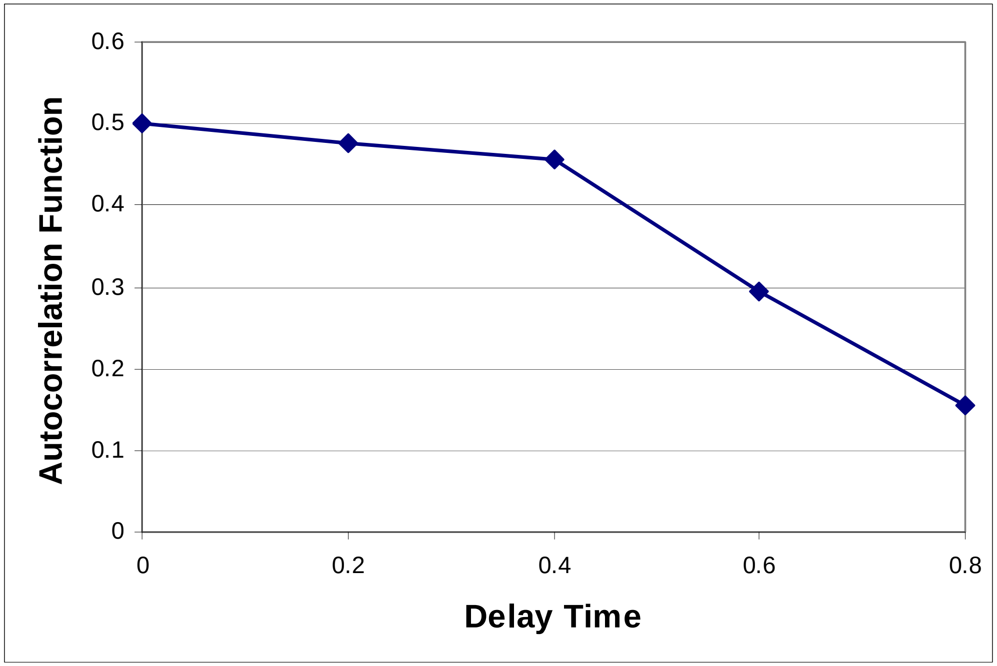
$$C(t_d = .4) = \frac{1}{4}\left[A(0)\cdot A(0+.4) + A(.2)\cdot A(.2+.4) + A(.4)\cdot A(.4+.4) + A(.6)\cdot A(.6+.4)\right]$$

$$C(t_d = .4) = 0.46$$

Time Correlation Function

- Example cont.

t_d	$C(t_d)$
0	0.5
.2	.48
.4	.46
.6	.29
.8	.15

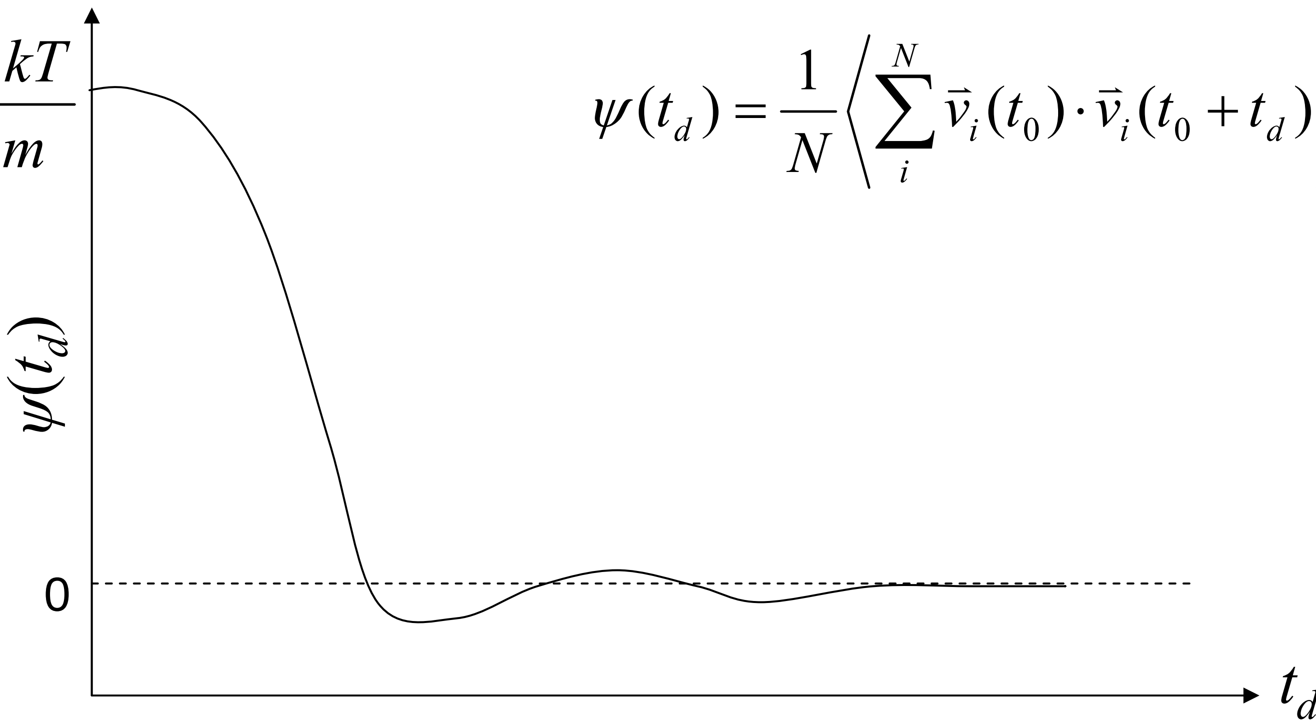


Time Correlation Function

- Single particle correlations
  - Dynamic quantity is a property of individual particles
- Velocity autocorrelation function

$$\psi(0) = \frac{3kT}{m}$$

$$\psi(t_d) = \frac{1}{N}\left\langle \sum_{i}^{N} \vec{v}_i(t_0) \cdot \vec{v}_i(t_0 + t_d) \right\rangle$$



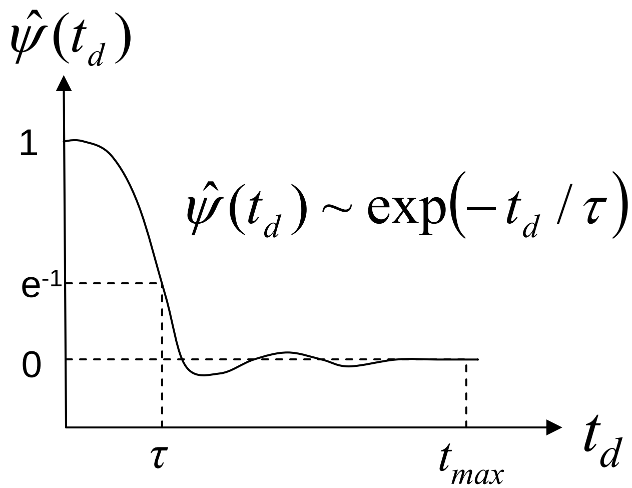
Time Correlation Function

- Uncertainty measurement
  - Equal Cartesian coordinate contributions

$$\left\langle \dot{x}_i(t_0)\dot{x}_i(t_0+t_d)\right\rangle = \left\langle \dot{y}_i(t_0)\dot{y}_i(t_0+t_d)\right\rangle = \left\langle \dot{z}_i(t_0)\dot{z}_i(t_0+t_d)\right\rangle$$

  - Statistical uncertainty

$$\varepsilon(t_d) \approx \pm\sqrt{\frac{2\tau}{t_{\max}}}\left[1-\hat{\psi}(t_d)\right] \qquad \tau = 2\int_0^{\infty}\left[\hat{\psi}(t_d)\right]^2 dt_d$$

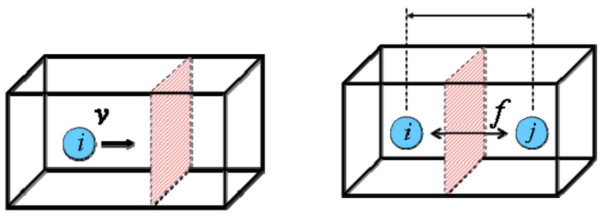


$\hat{\psi}(t_d) \sim \exp(-t_d/\tau)$ ➡ τ = time for $\hat{\psi}(t_d)$ to decrease from 1 to e^{-1}

Time Correlation Function

- Collective correlations
  - Properties of the whole system
    - Easier to compute
    - Less accurate
  - Stress autocorrelation function

$$J = \begin{bmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{bmatrix}$$



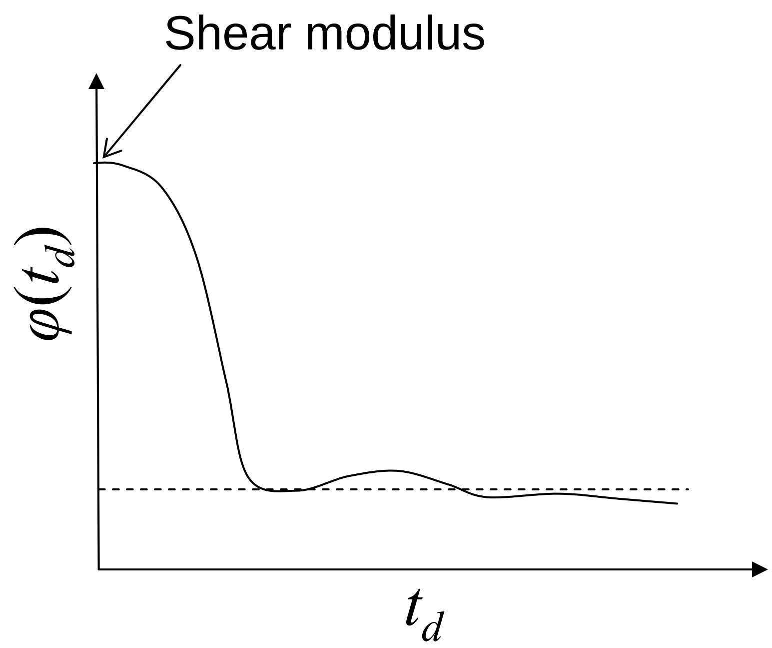
$$J_{\alpha\beta} = m\sum_{i}^{N} v_{i\alpha} v_{i\beta} + \frac{1}{2}\sum_{i \neq j}^{N} r_{ij\beta} F_{ij\alpha}$$

$$\varphi(t_d) = \frac{\rho}{3kT}\frac{1}{N}\sum \left\langle J_{\alpha\beta}(t_0) J_{\alpha\beta}(t_0 + t_d) \right\rangle \qquad \text{for } \alpha \neq \beta$$

Time Correlation Function

- Stress autocorrelation function

$$\varphi(t_d) = \frac{\rho}{3kT}\frac{1}{N}\sum\left\langle J_{\alpha\beta}(t_0)J_{\alpha\beta}(t_0+t_d)\right\rangle \qquad J_{\alpha\beta} = m\sum_{i}^{N} v_{i\alpha}v_{i\beta} + \frac{1}{2}\sum_{i\neq j}^{N} r_{ij\beta}F_{ij\alpha}$$



- Kinetic term: correlation of momentum transport caused by atomic motion
- Potential term: correlation of momentum transport caused by interatomic forces
- Cross term: coupling of the atomic motions and forces

Transport Coefficients

- Einstein relations
  - Transport coefficients from differentiating a correlation function with respect time
- Green-Kubo relations
  - Transport coefficients from integrating a correlation function over time
- General concept
  - Flux = -coefficient x gradient

Transfer per unit area in unit time | Resistance to flow | Driving force for the flux

Transport Coefficients

- Example: 1D diffusion
  - Fick's law and conservation of mass

$$N\dot{x} = -D\frac{\partial N}{\partial x} \qquad \frac{\partial N}{\partial t} + \frac{\partial (N\dot{x})}{\partial x} = 0$$

  - Combine and solve for N

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial x^2} \qquad N(x,t) = \frac{N_0}{2\sqrt{\pi D t}}\exp\left[\frac{-x^2}{4Dt}\right]$$

  - Second moment of the distribution is the mean-square displacement

$$\left\langle [x(t) - x(0)]^2 \right\rangle = \frac{1}{N_0}\int x^2 N(x,t)\,dx$$

Transport Coefficients

- Example: 1D diffusion cont.
  - Combine

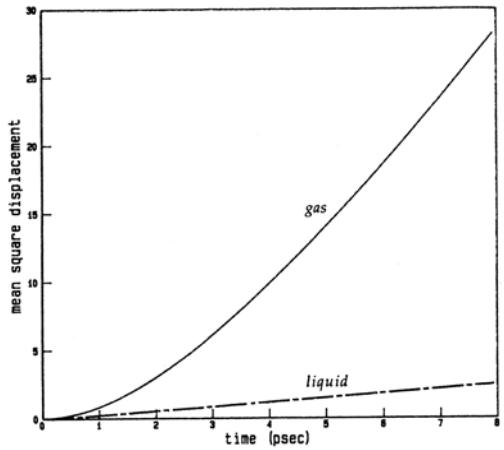
$$\left\langle \left[x(t)-x(0)\right]^2 \right\rangle = 2Dt$$

  - Applicable when the time is large compared to the average time between atomic collisions

  - Finally, Einstein's relation

$$D = \lim_{t\to\infty} \frac{\left\langle \left[x(t)-x(0)\right]^2 \right\rangle}{2t}$$

Mean-squared displacement



Transport Coefficients

- Example: 1D diffusion cont.
  - Time derivative

$$\dot{x}(t) = \frac{dx}{dt} \qquad x(t) - x(0) = \int_0^t \dot{x}(t')dt'$$

  - Square both sides and average over time origins

$$msd = \left\langle [x(t) - x(0)]^2 \right\rangle = \int_0^t dt'' \int_0^t dt' \left\langle \dot{x}(t')\dot{x}(t'') \right\rangle$$

  - Use integrand symmetry, shift the time origin, and change variables

$$msd = 2\int_0^t dt'' \int_0^{t''} d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle$$

τ ← $t'' - t'$

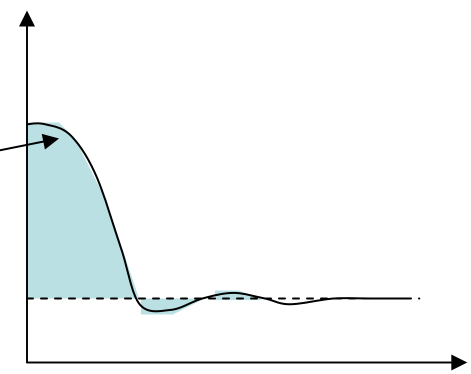
Transport Coefficients

- Example: 1D diffusion cont.
  - Integrate and solve for *msd*

$$\frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t} = \int_0^t d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle \left(1-\frac{\tau}{t}\right)$$

  - Take the long-time limit

VACF



$$\lim_{t\to\infty} \frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t} = \int_0^\infty d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle$$

  - Recall Einstein's relation

$$D = \lim_{t\to\infty} \frac{\left\langle [x(t)-x(0)]^2 \right\rangle}{2t}$$

$$D = \int_0^\infty d\tau \left\langle \dot{x}(\tau)\dot{x}(0) \right\rangle$$

Transport Coefficients

- Green-Kubo relations
  - Diffusion (3D)

$$D = \int_0^\infty \psi(t_d) \qquad \psi(t_d) = \frac{1}{3N}\left\langle \sum_i^N \vec{v}_i(t_0)\cdot\vec{v}_i(t_0+t_d)\right\rangle$$

  - Viscosity

$$\eta = \int_0^\infty \varphi(t_d) \qquad \varphi(t_d) = \frac{\rho}{3kT}\frac{1}{N}\sum\left\langle J_{\alpha\beta}(t_0)J_{\alpha\beta}(t_0+t_d)\right\rangle$$