ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 3: Molecular Dynamics
Section 3.5: Autocorrelation Function and Transport Properties

Xiulin Ruan
School of Mechanical Engineering
Purdue University
Correlation Functions

- Correlation between two time-dependent quantities $A(t)$ and $B(t)$:
  $$C(t) = \langle A(t) \cdot B(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t_0 + t) \cdot B(t_0) dt_0$$
  - For a given time interval $t$, different starting time $t_0$ can be chosen.

- Autocorrelation: $A(t)$ correlates to itself
  $$C(t) = \langle A(t) \cdot A(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t_0 + t) \cdot A(t_0) dt_0$$

- Importance of autocorrelation functions
  - They give a clear picture of the dynamics of the system.
  - Their time integral may often be related directly to macroscopic transport coefficients.
  - Their Fourier transforms may often be related to experimental spectra.
Example: Sinusoidal Function

- Let

\[ A(t) = \sin(\omega t) = \sin\left(2 \times 10^{12} \pi t\right) \]

\[ \omega = 2 \times 10^{12} \pi \text{ rad/s}, \quad \text{period } t_p = \frac{2\pi}{\omega} = 10^{-12} \text{ s} = 1\text{ps} \]
Analytical Solution for Autocorrelation

We have

\[ C(t) = \langle A(t) \cdot A(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t_0 + t) \cdot A(t_0) dt_0 \]

\[ = \frac{1}{10^{-12}} \int_0^{10^{-12}} \sin\left(2 \times 10^{12} \pi (t_0 + t)\right) \cdot \sin\left(2 \times 10^{12} \pi t_0\right) dt_0 \]

\[ = \frac{1}{10^{-12}} \int_0^{10^{-12}} \cos\left(2 \times 10^{12} \pi (t_0 + t) - 2 \times 10^{12} \pi t_0\right) - \cos\left(2 \times 10^{12} \pi (t_0 + t) + 2 \times 10^{12} \pi t_0\right) \frac{dt_0}{2} \]

\[ = \frac{1}{2 \times 10^{-12}} \int_0^{10^{-12}} \left[ \cos\left(2 \times 10^{12} \pi t\right) - \cos\left(4 \times 10^{12} \pi t_0 + 2 \times 10^{12} \pi t\right) \right] dt_0 \]

\[ = \frac{1}{2} \cos\left(2 \times 10^{12} \pi t\right) \]
Implementation in MD

- In MD, we can only obtain $A(t)$ on discrete $\Delta t$ intervals.
- Implementation:

$$C(t) = \langle A(t) \cdot A(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} A(t_0 + t) \cdot A(t_0) dt_0$$

$$= \lim_{N \to \infty} \frac{1}{N \cdot \Delta t} \sum_{j=0}^{N-1} [A(j \Delta t + t) \cdot A(j \Delta t) \cdot \Delta t]$$

$$= \lim_{N \to \infty} \frac{1}{N} \sum_{j=0}^{N-1} [A(j \Delta t + t) \cdot A(j \Delta t)]$$

\[ C(t) = \langle A(t) \cdot A(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} A(t_0 + t) \cdot A(t_0) dt_0 \]

\[ = \lim_{N \to \infty} \frac{1}{N \cdot \Delta t} \sum_{j=0}^{N-1} [A(j \Delta t + t) \cdot A(j \Delta t) \cdot \Delta t] \]

\[ = \lim_{N \to \infty} \frac{1}{N} \sum_{j=0}^{N-1} [A(j \Delta t + t) \cdot A(j \Delta t)] \]
Back to the Sinusoidal Example

- Let
  \[ A(t) = \sin(\omega t) = \sin(2 \times 10^{12} \pi t) \]
  \[ \omega = 2 \times 10^{12} \pi \text{ rad/s}, \quad \text{period } t_p = \frac{2\pi}{\omega} = 10^{-12} \text{ s} = 1 \text{ ps} \]

- Choose
  \[ \Delta t = \frac{t_p}{40} = \frac{1}{40} \text{ ps} \]

We have

\[
C(0) = \frac{1}{40} \left[ A(0) \cdot A(0) + A(\Delta t) \cdot A(\Delta t) + A(2\Delta t) \cdot A(2\Delta t) + \ldots + A(39\Delta t) \cdot A(39\Delta t) \right] = 0.5000
\]

\[
C(\Delta t) = \frac{1}{40} \left[ A(\Delta t) \cdot A(0) + A(2\Delta t) \cdot A(\Delta t) + A(3\Delta t) \cdot A(2\Delta t) + \ldots + A(40\Delta t) \cdot A(39\Delta t) \right] = 0.4938
\]

Discrete data points, but agree with the analytical solution very well.
Green-Kubo Relations for Transport Properties

- Diffusivity for gases and liquids

\[
D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \, dt
\]

- Shear viscosity

\[
\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle \, dt
\]

where \( P_{\alpha\beta} \) is an off-diagonal element of the pressure tensor given by

\[
P_{\alpha\beta} = \frac{1}{V} \left( \sum_i \frac{P_{i\alpha} P_{i\beta}}{m_i} + \sum_i \sum_{j>i} r_{i\alpha} f_{i\beta} \right)
\]
Velocity-Velocity Autocorrelation Function for Solids

- Velocity-velocity autocorrelation in solids can be done on all atoms, on a certain species, or on a certain region

- On a particular species $\beta$:

$$\Gamma_{\beta}(t) = \frac{\left\langle \sum_{i_{\beta}=1}^{N_{\beta}} u_{i_{\beta}}(t) \cdot u_{i_{\beta}}(0) \right\rangle}{\left\langle \sum_{i_{\beta}=1}^{N_{\beta}} u_{i_{\beta}}(0) \cdot u_{i_{\beta}}(0) \right\rangle}$$

- $\beta$: species
Phonon Density of States

- Partial phonon DOS is calculated by Fourier transform of dimensionless velocity-velocity autocorrelation function

\[ D_{p,\beta}(\omega) = \int_{0}^{\infty} \Gamma_{\beta}(t) \cos(\omega t) dt \]

- The partial phonon density of states is useful to analyze the power spectra, especially for nanocrystals.

Ruan, PHD thesis
Heat Current

The heat current vector is given by

\[ S = \frac{d}{dt} \sum_i \mathbf{r}_i E_i = \frac{d}{dt} \sum_i \mathbf{r}_i \left( E_{k,i} + E_{p,i} \right) \]

For a pair potential, such as the LJ potential, the expression can be recast as:

\[ S = \sum_i E_i \mathbf{v}_i + \frac{1}{2} \sum_{i,j} \left( \mathbf{F}_{ij} \cdot \mathbf{v}_i \right) \mathbf{r}_{ij} \]

where \( \mathbf{v} \) is the velocity vector of a particle, and \( \mathbf{r}_{ij} \) and \( \mathbf{F}_{ij} \) are the inter-particle separation vector and force vector between particles \( i \) and \( j \).

For multi-body potentials, see: Zheyong Fan et al., PRB 92, 094301 (2015).
In general, for anisotropic systems:

\[
 k_x = \frac{1}{k_B T^2 V} \int_0^\infty \langle S_x(t) \cdot S_x(0) \rangle \, dt
\]

\[
 k_y = \frac{1}{k_B T^2 V} \int_0^\infty \langle S_y(t) \cdot S_y(0) \rangle \, dt
\]

\[
 k_z = \frac{1}{k_B T^2 V} \int_0^\infty \langle S_z(t) \cdot S_z(0) \rangle \, dt
\]

For isotropic system,

\[
 k = \frac{k_x + k_y + k_z}{3} = \frac{1}{k_B T^2 V} \int_0^\infty \frac{\langle S(t) \cdot S(0) \rangle}{3} \, dt
\]

\[
 = \frac{1}{k_B T^2 V} \int_0^\infty \frac{\langle S_x(t) \cdot S_x(0) + S_y(t) \cdot S_y(0) + S_z(t) \cdot S_z(0) \rangle}{3} \, dt
\]
Ensemble Average

The heat current autocorrelation function is

\[ AC(t) = \frac{\langle S(t) \cdot S(0) \rangle}{3} \]

- Where \( \langle S(t) \cdot S(0) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} S(t_0 + t) \cdot S(t_0) dt_0 \)

Implementation:

\[ \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} S(t_0 + t) \cdot S(t_0) dt_0 = \frac{1}{N} \sum_{j=0}^{N-1} S(j \Delta t + t) \cdot S(j \Delta t) \]
EMD on Solid Argon

- **Settings:**
  - Lennard-Jones potential
  - $T = 40$ K
  - Domain size: 6x6x6 unit cells
  - Time step: 4 fs
  - $NPT$: 0.4 ns; $NVE$: 4 ns
  - Max. correlation time: 40 ps

- **Thermal conductivity:**
  - $k_x = 0.398$ W/m-K
  - $k_y = 0.575$ W/m-K
  - $k_z = 0.642$ W/m-K
  - $k_{ave} = 0.538$ W/m-K
  - ($k_{exp} = 0.56$ W/m-K)
    (Touloukian *et al.*, 1970)

- **Repeat multiple times to reduce statistical errors**

Truncation Errors and Averaging Uncertainty

- In principle, the integration should go infinite long, but practically we can only run MD for a finite time.
- We will need to truncate $t$ at an upper limit $t_{corre,UL}$, which will result in truncation errors.
- For a given $t_{corre}$, the length we can use for ensemble average (or the different starting point) is $t_{total} - t_{corre}$. For long $t_{corre}$, we will see less ensembles to calculate the ACF and hence higher uncertainty in the ACF.
- The eventual calculation becomes:

$$k = \frac{k_x + k_y + k_z}{3} = \frac{1}{k_B T^2 V} \int_{t_{corre,UL}}^{t_{total}} \frac{\langle S(t_{corre}) \cdot S(0) \rangle}{3} dt_{corre}$$
Exponential fitting of the HCACF

- **Double exponential fitting:**
  \[
  k = \frac{1}{k_B VT^2} \left( AC_1 \tau_1 + AC_2 \tau_2 \right)
  \]
  \[
  = 0.482 \text{ W/m-K}
  \]

- **Single exponential fitting:**
  \[
  k = \frac{1}{k_B VT^2} \int_0^\infty AC(t) dt
  \]
  \[
  = \frac{1}{k_B VT^2} \int_0^\infty AC(t=0) \exp \left( -\frac{t}{\tau} \right) dt
  \]
  \[
  = \frac{1}{k_B VT^2} AC(t=0) \tau
  \]
  \[
  = 0.385 \text{ W/m-K}
  \]

- An effective way to remove truncation error.

- **Here \( \tau \)'s are the vibrational coherence times, or the effective phonon relaxation times.**
Applications of GK-MD in calculating $k$

Simulation Domain Size Effect

- The equilibrium (Green-Kubo) method do not usually show significant size effect – periodic boundary conditions helps.

![Graph showing thermal conductivity vs number of atoms for different temperatures]

LJ Argon

![Graph showing thermal conductivity for different temperatures and numbers of atoms]

Silicon
Uncertainty: HCACF and $k$ Distributions of Ar

- $t_{\text{corre, UL}} >> \tau_{p, \text{eff}}$ for a good integration. Here 40 ps is sufficient.
- As $t_{\text{total}}$ increases, the HCACF and $k$ profiles start to converge.

A universal relation of the relative uncertainty

- A long $t_{\text{total}}$ and short $t_{\text{corre, UL}}$ will decrease $\sigma_k / k_{\text{ave}}$. However, a physical constrain is that $t_{\text{corre, UL}} \gg \tau_{p, \text{eff}}$