CE 530 Molecular Simulation

Lecture 12
Dynamical Properties

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Review

- Several equivalent ways to formulate classical mechanics
  - *Newtonian, Lagrangian, Hamiltonian*
  - *Lagrangian and Hamiltonian independent of coordinates*
  - *Hamiltonian preferred because of central role of phase space to development*

- Molecular dynamics
  - *numerical integration of equations of motion for multibody system*
  - *Verlet algorithms simple and popular*
Dynamical Properties

- How does the system respond collectively when put in a state of non-equilibrium?

- Conserved quantities
  - mass, momentum, energy
  - where does it go, and how quickly?
  - relate to macroscopic transport coefficients

- Non-conserved quantities
  - how quickly do they appear and vanish?
  - relate to spectroscopic measurements

- What do we compute in simulation to measure the macroscopic property?
Macroscopic Transport Phenomena

- Dynamical behavior of conserved quantities
  - densities change only by redistribution on macroscopic time scale

- Differential balance

\[
\begin{align*}
\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \mathbf{j} &= 0 \\
\c_p \frac{\partial T(r,t)}{\partial t} + \nabla \cdot \mathbf{q} &= 0 \\
\rho \frac{D\mathbf{v}(r,t)}{Dt} + \nabla \cdot \mathbf{\tau} &= 0
\end{align*}
\]

- Constitutive equation

  - Fick’s law: \( \mathbf{j} = -D \nabla c \)
  - Fourier’s law: \( \mathbf{q} = -k \nabla T \)
  - Newton’s law: \( \mathbf{\tau}_{xy} = -\nabla_y (\rho \mathbf{v}_x) \)

- Our aim is to obtain the phenomenological transport coefficients by molecular simulation
  - note that the “laws” are (often very good) approximations that apply to not-too-large gradients
  - in principle coefficients depend on \( c, T, \) and \( \mathbf{v} \)
Approaches to Evaluating Transport Properties

- Need a non-equilibrium condition

- **Method 1:** Establish a non-equilibrium steady state
  - “Non-equilibrium molecular dynamics” NEMD
  - Requires continuous addition and removal of conserved quantities
  - Usually involves application of work, so must apply thermostat
  - Only one transport property measured at a time
  - Gives good statistics (high “signal-to-noise ratio”)
  - Requires extrapolation to “linear regime”

- **Method 2:** Rely on natural fluctuations
  - Any given configuration has natural inhomogeneity of mass, momentum, energy (have a look)
  - Observe how these natural fluctuations dissipate
  - All transport properties measurable at once
  - Poor signal-to-noise ratio
Mass Transfer

- **Self-diffusion**
  - *diffusion in a pure substance*
  - *consider tagging molecules and watching how they migrate*

- **Diffusion equations**
  - *Combine mass balance with Fick’s law*
    \[
    \frac{\partial c}{\partial t} - D \nabla^2 c(\mathbf{r}, t) = 0
    \]
  - *Take as boundary condition a point concentration at the origin*
    \[
    c(\mathbf{r}, t) = \delta(\mathbf{r})
    \]

- **Solution**
  \[
  c(\mathbf{r}, t) = (2\pi D t)^{-d/2} \exp \left( -\frac{r^2}{2Dt} \right)
  \]

- **Second moment**
  \[
  \langle r^2(t) \rangle = \int r^2 c(\mathbf{r}, t) d\mathbf{r}
  \]
  \[
  = 2dDt
  \]

  *RMS displacement increases as \( t^{1/2} \)*
  *Compare to ballistic \( r \sim t \)*
Interpretation

- Right-hand side is macroscopic property
  - applicable at macroscopic time scales

- For any given configuration, each atom represents a point of high concentration (a weak fluctuation)

- View left-hand side of formula as the movement of this atom
  - ensemble average over all initial conditions
    \[
    \langle r^2(t) \rangle = \int d\mathbf{p}^N \int d\mathbf{r}^N r_1^2(t) \left[ \delta(r_1)\pi(r^N,\mathbf{p}^N) \right]_{t=0}
    \]
  - asymptotic linear behavior of mean-square displacement gives diffusion constant
  - independent data can be collected for each molecule
    \[
    \langle r^2(t) \rangle = \frac{1}{N} \sum \langle r_i^2(t) \rangle
    \]

Einstein equation

\[
\langle r^2(t) \rangle = 2dD t
\]
Time Correlation Function

- Alternative but equivalent formulation is possible
- Write position $\mathbf{r}$ at time $t$ as sum of displacements
  \[ \mathbf{r}(t) = \int_0^t \frac{d\mathbf{r}}{dt} d\tau = \int_0^t \mathbf{v}(\tau) d\tau \]
Time Correlation Function

Alternative but equivalent formulation is possible

Write position \( r \) at time \( t \) as sum of displacements

\[
r(t) = \int_0^t \frac{dr}{dt} d\tau = \int_0^t v(\tau) d\tau
\]

Then

\[
\langle r^2(t) \rangle = \left\langle \int_0^t v(\tau_1) d\tau_1 \cdot \int_0^t v(\tau_2) d\tau_2 \right\rangle
\]

\[= \int_0^t dt_1 \int_0^t dt_2 \left\langle v(\tau_2) \cdot v(\tau_1) \right\rangle\]

r\(^2\) in terms of displacement integrals

rearrange order of averages

\[
= 2 \int_0^t dt_1 \int_0^{\tau_1} dt_2 \left\langle v(\tau_2) \cdot v(\tau_1) \right\rangle
\]

\[
= 2 \int_0^t dt_1 \int_0^{\tau_1} dt_2 \left\langle v(0) \cdot v(\tau_1 - \tau_2) \right\rangle
\]

correlation depends only on time difference, not time origin

\[
= 2 \int_0^t dt_1 \int_0^t dt \left\langle v(0) \cdot v(\tau) \right\rangle
\]

substitute \( \tau = \tau_1 - \tau_2 \)

\[
2dDt = 2t \int_0^t d\tau \left\langle v(0) \cdot v(\tau) \right\rangle
\]

\[
t \to \infty \quad D = \frac{1}{d} \int_0^\infty d\tau \left\langle v(0) \cdot v(\tau) \right\rangle
\]

Green-Kubo equation
Velocity Autocorrelation Function

- **Definition**
  \[ C(t) \equiv \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \quad C(0) = \langle v^2 \rangle = dkT / m \]

- **Typical behavior**
  - Zero slope (soft potentials)
  - Backscattering
  - Diffusion constant is area under the curve
    \[ D = \frac{1}{d} \int_0^\infty d\tau \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle \]
  - Asymptotic behavior (\( t \to \infty \)) is nontrivial (depends on \( d \))
Other Transport Properties

- **Diffusivity**
  \[ D = \frac{1}{Vd\rho} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \]

- **Shear viscosity**
  \[ \eta = \frac{1}{VkT} \int_0^\infty dt \langle \sigma^{xy}(t)\sigma^{xy}(0) \rangle \]

- **Thermal conductivity**
  \[ \lambda_T = \frac{1}{VkT^2} \int_0^\infty dt \langle q(t)q(0) \rangle \]
Evaluating Time Correlation Functions

- Measure phase-space property $A(r^N, p^N)$ for a sequence of time intervals

$$A(t_0) \quad A(t_1) \quad A(t_2) \quad A(t_3) \quad A(t_4) \quad A(t_5) \quad A(t_6) \quad A(t_7) \quad A(t_8) \quad A(t_9)$$

- Tabulate the TCF for the same intervals
  - *each time in simulation serves as a new time origin for the TCF*

<table>
<thead>
<tr>
<th>$\langle A(\Delta t)A(0) \rangle$</th>
<th>$A_0A_1 + A_1A_2^+ + A_2A_3^+ + A_3A_4^+ + A_4A_5^+ + A_5A_6^+ + A_6A_7^+ + A_7A_8^+ + A_8A_9^+ + ...$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle A(2\Delta t)A(0) \rangle$</td>
<td>$A_0A_2 + A_1A_3^+ + A_2A_4^+ + A_3A_5^+ + A_4A_6^+ + A_5A_7^+ + A_6A_8^+ + A_7A_9^+ + ...$</td>
</tr>
<tr>
<td>$\langle A(5\Delta t)A(0) \rangle$</td>
<td>$A_0A_5 + A_1A_6 + A_2A_7 + A_3A_8 + A_4A_9 + ...$</td>
</tr>
</tbody>
</table>
Direct Approach to TCF

- Decide beforehand the time range \((0, t_{\text{max}})\) for evaluation of \(C(t)\)
  - let \(n\) be the number of time steps in \(t_{\text{max}}\)

- At each simulation time step, update sums for all times in \((0, t_{\text{max}})\)
  - \(n\) sums to update
  - store values of \(A(t)\) for past \(n\) time steps
  - at time step \(k\):
    \[
    c_{i+} = A_k - i A_k \quad i = 1, \ldots, n
    \]

- Considerations
  - trade off range of \(C(t)\) against storage of history of \(A(t)\)
  - requires \(n^2\) operations to evaluate TCF
Fourier Transform Approach to TCF

- Fourier transform
  \[ \hat{f}(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} \, dt \quad f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{f}(\omega) e^{+i\omega t} \, d\omega \]

- Convolution
  \[ C(t) = \int_{-\infty}^{\infty} A(\tau) B(\tau + t) \, d\tau \]

- Fourier convolution theorem
  \[ \tilde{C}(\omega) = \tilde{A}(\omega) \tilde{B}(\omega) \]

- Application to TCF
  \[ C(t) = \sum_{t_0} v(t_0) \cdot v(t_0 + t) \quad \text{Sum over time origins} \]
  \[ \hat{C}(\omega) = [\hat{v}(\omega)]^2 \quad \text{With FFT, operation scales as } n \ln(n) \]
Coarse-Graining Approach to TCF 1.

- Evaluating long-time behavior can be expensive
  - *for time interval* $T$, *need to store* $T/\delta t$ *values (perhaps for each atom)*
- But long-time behavior does not (usually) depend on details of short time motions resolved at simulation time step
- Short time behaviors can be coarse-grained to retain information needed to compute long-time properties
  - *TCF is given approximately*
  - *mean-square displacement can be computed without loss*

Method due to Frenkel and Smit
Coarse-Graining Approach to TCF 2.
Coarse-Graining Approach to TCF 2.
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Coarse-Graining Approach to TCF 2.

\[ \nu^{(2)}(1) \]

\[ \nu^{(1)}(1) \nu^{(1)}(2) \nu^{(1)}(3) \nu^{(1)}(4) \nu^{(1)}(5) \]

\[ \sum_{i=0}^{n} \]
Coarse-Graining Approach to TCF 2.
Coarse-Graining Approach to TCF 2.

\[ \nu^{(2)}(1) \quad \nu^{(2)}(2) \]

\[ \nu^{(1)}(1) \nu^{(1)}(2) \nu^{(1)}(3) \nu^{(1)}(4) \nu^{(1)}(5) \nu^{(1)}(6) \nu^{(1)}(7) \]

\[ 0 \sum_{i}^{n} \]
Coarse-Graining Approach to TCF 2.
Coarse-Graining Approach to TCF 2.

\[ V_{n0} \sum v^{(1)}(1) v^{(1)}(2) v^{(1)}(3) v^{(1)}(4) v^{(1)}(5) v^{(1)}(6) v^{(1)}(7) v^{(1)}(8) v^{(1)}(9) \]
Coarse-Graining Approach to TCF 2.

\[ \nu^{(3)}(1) \]

\[ \nu^{(2)}(1) \quad \nu^{(2)}(2) \quad \nu^{(2)}(3) \]

\[ \nu^{(1)}(1) \quad \nu^{(1)}(2) \quad \nu^{(1)}(3) \quad \nu^{(1)}(4) \quad \nu^{(1)}(5) \quad \nu^{(1)}(6) \quad \nu^{(1)}(7) \quad \nu^{(1)}(8) \quad \nu^{(1)}(9) \quad \nu^{(1)}(10) \]

\[ \sum_{i=1}^{n} \]

et cetera
Coarse-Graining Approach to TCF 2.

This term gives the net velocity over this interval $v^{(3)}(1)$.

### Approximate TCF

$$\langle v(0) \cdot v(n^3 \Delta t) \rangle \approx \langle v^{(3)}(0) \cdot v^{(3)}(1) \rangle$$
Coarse-Graining Approach: Resource Requirements

○ Memory
  • for each level, store $n$ sub-blocks
  • for simulation of length $T = n^k \Delta t$ requires $k \times n$ stored values
    compare to $n^k$ values for direct method

○ Computation
  • each level $j$ requires update (summing $n$ terms) every $1/n^j$ steps
  • total
    $$T \times \frac{n}{\Delta t} \left( 1 + \frac{1}{n} + \frac{1}{n^2} + \ldots + \frac{1}{n^k} \right) = T \times \frac{n - n^{-k}}{\Delta t (n - 1)}$$
    $$\approx T \times \frac{n}{\Delta t}$$
  • scales linearly with length of total correlation time
    compare to $T^2$ or $T \ln(T)$ for other methods
Summary

- Dynamical properties describe the way collective behaviors cause macroscopic observables to redistribute or decay

- Evaluation of transport coefficients requires non-equilibrium condition
  - NEMD imposes macroscopic non-equilibrium steady state
  - EMD approach uses natural fluctuations from equilibrium

- Two formulations to connect macroscopic to microscopic properties
  - Einstein relation describes long-time asymptotic behavior
  - Green-Kubo relation connects to time correlation function

- Several approaches to evaluation of correlation functions
  - direct: simple but inefficient
  - Fourier transform: less simple, more efficient
  - coarse graining: least simple, most efficient, approximate